**Atmospheric
Chemistry
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Discussions**

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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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Received and published: 17 January 2012

We greatly appreciate all the comments, which improved the paper. We have revised the paper by addressing all the comments.

RC- Review Comments; AC – Authors' Comments

RC: Page 31435 Line 8 – 20, the author should add some discussions on advantages and disadvantages of source-based and receptor-based models.

AC: A brief discussion on the advantages and disadvantages of these two modeling methods was added in the revised paper. For example, source-based models can pre-

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dict three-dimensional fields of concentration and two-dimensional fields of deposition (and thus regional-scale distribution), can be used for conducting various sensitivity tests, e.g., predict the effects of future emission scenarios, identify contributions from different pollution sources and from individual chemical and physical processes. But this approach requires extensive input data (e.g., reasonable emission inventory over the whole model domain) and requires substantial computer resources. Receptor-based models, on the other hand, require little computer time, but is only for the purpose of identifying potential sources affecting a particular site(s) of interest.

RC: Page 31436 Line 5-11, please read and cite relevant references Kabashnikov et al., 2011 Atom env. 5425-5430; Line 27, suggest to add "processes" before the sources

AC: The following references on trajectory statistical methods were added: "These methods have been employed to investigate source-receptor relationships for various atmospheric pollutants (Rua et al., 1998; Wang et al., 2006; Du and Rodenburg, 2007) and validated through model intercomparisons (Lee and Ashbaugh, 2007; Scheifinger and Kaiser, 2007; Kabashnikov et al., 2011)."

Line 27 was revised according to your suggestions.

RC: Page 31437 site description, suggest to add a map of the site with Hg related emission sources, this would help the readers to understand the location of the site.

AC: We have added a map showing the location of the ELA sampling site and Hg point sources (see the new Fig. 1 in the revised paper).

RC: Page 31439, Line 1, what is the external calibration frequency? Line 9-12, it will be good to include the uncertainties of GEM, RGM, and PHg are 10-20, 30, and up to 70%, respectively. See Gustin and Jaffe, 2010, EST.

AC: The following was added: "Manual calibrations were also carried out by injecting a known quantity of GEM into the 2537A Tekran approximately every 6 months of use." We also added uncertainty discuss based on the reference provided and other

references.

RC: Page 31440, Principal components analysis, does the authors normalize the data before the analysis? Previous studies usually used normalized data for PCA. This is not clear in the text. If select eigenvalue as 1, some factors cannot be separated, as discussed later.

AC: The data should be normalized before the analysis. Normalization of variables is performed automatically in SPSS software before running PCA. In addition to examining factors with eigenvalues>1, we also looked at the scree plot and performed monte carlo parallel analysis to determine the number of factors to retain.

The following explanation was added: "The variables were normalized prior to running PCA."

RC: Page 31441, HYSPLIT, the uncertainty of HYSPLIT should be discussed, please see Weiss-Penzias et al., 2009 JGR.

AC: The following was added to address uncertainty of HYSPLIT: "Uncertainties in trajectories are typically 15-20% of the distance traveled. Stohl (1998) and Stohl et al. (2002) suggested the uncertainties may be due to errors in modeled wind fields, interpolating wind fields, truncating trajectory equations, turbulent mixing in the PBL and starting height of trajectories."

RC: Page 31442, Line 12, suggest to add "concentrations" after RGM

AC: Revised according to your suggestion.

RC: Page 31443, higher PHg in winter has the change from wood combustion; please see Choi et al., 2008 ES&T; Huang et al., 2010 ES&T; Huang et al., 2011 Chemosphere.

AC: The following explanation was revised to include wood combustion source: "The higher PHg concentrations in the winter at the ELA site were consistent with other re-

mote and rural studies, which suggested that this observation was related to increase emissions from coal and wood combustion in winter, condensation of gases on atmospheric particles at lower temperatures, and re-suspension of particles during windy conditions (Choi et al., 2008; Huang et al., 2010; Huang et al., 2011)."

RC: Page 31444, Line 9-12, how was the statistical analysis for diel pattern done? Please be clear.

AC: One-way ANOVA (Analysis of Variance) with post-hoc tests was used to compare the mean concentrations between each of the hours (e.g., compares hour 0 with hour 1, 2, 3, ...23; compares hour 1 with 0, 2, 3, ...23; etc.) to determine whether each hour was statistically different from the other hours.

The following explanation was added: "One-way ANOVA (Analysis of Variance) with post-hoc tests was used to compare the mean GEM and RGM concentrations between each of the hours and assess whether each hour was statistically different from other hours."

RC: Page 31445, Line 1, nighttime dry deposition might be not a good explanation for GEM. Could the authors explain the reason Ca^{2+} (sea-salt and soil), K^+ (wood combustion), and Mg^{2+} sea-salt and soil) grouped together by wind direction (they should be from different processes or sources)?

AC: We have removed, "nighttime dry deposition". Ca^{2+}, K^+ and Mg^{2+} may be associated with different sources/processes, but they can still be grouped in the same wind direction because Hg emissions from soil and wood combustion could both be occurring south of the ELA site at the same time.

RC: Page 31446, Correlation analysis, why did the authors choose PHg as the most important species?

AC: The following explanation was added: "In Table 3a, correlation analyses are conducted with fine particulate mercury because the ions are associated with particu-

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late matter. Using PHg would be more appropriate for identifying Hg from crustal/soil dust and sea-salt or road-salt, which are in the particulate phase as well. For industrial/combustion sources and photochemical/gas-phase oxidation, correlations between gaseous Hg species, i.e. GEM and RGM, were examined (see Table 3b)."

RC: Page 31448, Line 22, PCA-1, is this possible from wood combustion? K+ is an important indicator for wood combustion, and the other species are also related to this source. Based on PCA, could the authors look at the time as the PCA-1 factor loadings were high? This might help to identify the source.

AC: Given the data available for this study, we were only able to identify major classes of sources instead of specific types of combustion or industrial sources. K+ is one of the indicators for wood combustion and wildfires; however other studies are also using other markers to characterize wood combustion and biomass burning, such as organic carbon (Choi et al., 2008; Watson et al., 2008), Delta-C (difference between two wavelengths of black carbon, Huang et al., 2010, 2011) and levoglucosan (Brinkman et al., 2006; Rutter et al., 2008; Watson et al., 2008).

We have included the possibility of wood combustion and wildfire sources in the revised paper: "The presence of K+ in PCA-1 indicates wood combustion and biomass burning (e.g., wildfires) are potential sources, but this needs to be confirmed with other pollutant markers, such as carbon measurements (Choi et al. 2008; Huang et al., 2010; 2011) or levoglucosan (Watson et al., 2008)."

The factor loadings provide information on the correlation coefficients between each variable and factor; therefore we would not be able to look at the time when PCA-1 factor loadings were high. We have included temperature in PCA to give us an idea on the time period of PCA-1. As shown in Table 4, temperature was not an important variable in PCA-1.

RC: Page 31449, Line 1, PCA-2, this looks like two or more factors combined in PCA-2, could the authors separate them? Line 10-13, halogens can be emitted from coal-fired

power plants, so the reactions in the inland sites are still possible. Line 22, PCA-4 is still correlated to SO2, could the authors explain this? Two factors (PCA-2 and 4) seem to contain two or more factors together, the authors should discuss this.

AC: The following was added to address the two factors, PCA-2 and PCA-4: "PCA-2 contained several sources/processes that could not be separated into individual factors. This suggests that these sources/processes may be occurring simultaneously.".... "The factor loading on SO2 is relatively weak compared to Na+ and Cl-; therefore, it is not closely related to this factor."

We pointed out in the revised paper that halogens can be emitted from coal-fired power plants and cited global modeling studies to support this hypothesis (Seigneur and Lohman, 2008; Holmes et al., 2010)."

RC: Page 31450, Line 10-12, this is not clear. Line 12, KCA-3, the wood combustion should be considered as discussed above (same for HCA).

AC: The sentence in line 10 was removed. We added a sentence that considers wood combustion and wildfires as a potential source of Hg based on mean values in KCA-3: "The transport of industrial emissions as previously described was also apparent in KCA-3, which had high mean values for GEM, HNO3, K+, NH4+, NO-3 , and SO2-4 .The elevated K+ and GEM concentrations may be attributed to wildfires and wood combustion (Watson et al., 2008; Huang et al. 2011)."

We also included the possibility of wood combustion source for HCA-2: "In addition to transport of industrial emissions, HCA-2 is attributed to transportation and coal and wood combustion emissions, which frequently emit volatile organic compounds, CO and NO2 that can lead to O3 formation."

RC: Page 31452, Line 5-7, What is the percentage of trajectories coming from fossil fuel power plants? Line 11, KCA-2 is associated with PHg and RGM, the authors should mention the uncertainty of precipitation during transport using HYSPLIT. Line

26, please read and cite Holmes et al., 2009; 2010. Line 26, what is the percentage corresponding to "mainly"?

AC: The percentage of trajectories coming from fossil fuel power plants is ∼25%

The following explanation was added to address the uncertainty of precipitation during transport of RGM using HYSPLIT: "The transport of PHg and RGM to the ELA site by the modeled air trajectory path may not be fully accurate due to the possibility of wet deposition."

The following was also added: "Reactive halogen species are more likely to be responsible for the depletion and conversion of GEM to RGM based on measurements of atmospheric Hg, O3 and BrO in marine environments (Peleg et al., 2007; Obrist et al., 2011), and models suggest that similar reactions with Br might also be occurring on a global scale (Seigneur and Lohman, 2008; Holmes et al. 2009, 2010). Seigneur and Lohman (2008) conducted interhemispheric simulations with different sets of Br reaction kinetics and found 20-40% difference in the mean GEM concentrations using different reaction kinetics. The global atmospheric Hg model with Br chemistry by Holmes et al. (2010) was capable of producing averaged TGM measurements at polar regions and some MBL and land-based sites. Agreement between modeled and measured TGM concentrations at land-based sites in the northern hemisphere was found for both Hg+Br and Hg+O3/OH models (Holmes et al., 2010)."

The percentage corresponding to "mainly" is ∼83%.

RC: Page 31454, Line 1-3, wood combustion will show the similar result.

AC: The sentence was revised to include wildfire/wood combustion locations: "The elevated O3 concentration was likely because the trajectories passed over major Hg point sources, urban areas and wildfire/wood combustion locations that may have contributed to CO, NOx, and volatile organic compound emissions."

RC: Overall, this study compared Hg sources/processes using three different receptor

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models and came out a very good agreement. However, some factors were still mixed together and confused the readers.

AC: The following explanation was added before the conclusion (note the changes to figure numbers): "The trajectories shown for the hierarchical clusters in Fig. 4 were similar to some of the trajectories belonging to several k-means clusters in Fig. 3. This led to some differences in the trajectory plots for the two cluster methods even though they represented the same cluster based on the mean cluster centres in Tables 5 and 6. The clusters generated from both methods often represented several sources and processes (e.g., industrial/combustion emissions, photochemical production of RGM, and/or crustal/soil emissions). One possible reason for the discrepancy can be attributed to differences in the theoretical approaches of the two cluster analysis techniques (Viana et al., 2008), e.g. different clustering algorithm and distance/linkage measures. Another reason might be because these sources and processes are occurring simultaneously and could not be separated out in the data and hence, in the trajectory plots as well."

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