Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Potential sources and processes affecting speciated atmospheric mercury at Kejimkujik National Park, Canada

Xiaohong Xu[1*], Yanying Liao[1], Irene Cheng[2], Leiming Zhang[2*]

[1] Department of Civil and Environmental Engineering, University of Windsor, 401 Sunset Avenue, Windsor, Ontario, N9B 3P4, Canada

[2]Air Quality Research Division, Science and Technology Branch, Environment and Climate Change Canada, 4905 Dufferin Street, Toronto, Ontario, M3H 5T4, Canada

Corresponds to Xiaohong Xu (xxu@uwindsor.ca) or Leiming Zhang (leiming.zhang@canada.ca)

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Abstract: Source apportionment analysis was conducted with Positive Matrix Factorization (PMF) and Principal Component Analysis (PCA) methods using concentrations of speciated mercury (Hg), i.e., gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate-bound mercury (PBM), and other air pollutants collected at Kejimkujik National Park, Nova Scotia, Canada in 2009 and 2010. The results were largely consistent between the two years for both methods. The same four source factors were identified in each year using PMF method. In both years, factor Photochemistry and Re-emission had the largest contributions to atmospheric Hg, while the contributions of Combustion Emission and Industrial Sulfur varied slightly between the two years. Four components were extracted with air pollutants only in each year using PCA method. Consistency between the results of PMF and PCA include, 1) most or all PMF factors overlapped with PCA components, 2) both methods suggest strong impact of photochemistry, but little association between ambient Hg and sea salt, 3) shifting of PMF source profiles and source contributions from one year to another was echoed in PCA. Inclusion of meteorological parameters led to identification of an additional component - Hg Wet Deposition in PCA, while it did not affect the identification of other components.

The PMF model performance was comparable in 2009 and 2010. Among the three Hg forms, the agreement between predicted and observed annual mean concentrations were excellent for GEM, very good for PBM and acceptable for GOM. However, on daily basis, the agreement was very good for GEM, but poor for GOM and PBM. Sensitivity tests suggest that increasing sample size by imputation is not effective in improving model performance, while reducing the fraction of concentrations below method detection limit, by either scaling GOM and PBM to higher concentrations or combining them to reactive mercury, is effective. Most of the data treatment options considered had little impact on the source identification/contribution.

1. Introduction

Atmospheric mercury (Hg) exists in the form of gaseous elemental Hg (GEM) and oxidized Hg, the latter can be in gaseous phase (gaseous oxidized Hg - GOM) or associated with particulate matter (particulate - bound Hg - PBM). Identification of major sources and processes affecting ambient levels of different Hg forms will help

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

mitigate the risks of Hg pollution. Atmospheric Hg can be produced from anthropogenic activities, natural events and re-emission of previously deposited Hg, the latter two are sometimes grouped together as natural emission sources (Gustin et al., 2008; Pirrone et al., 2010; UNEP, 2013; Gaffney and Marley, 2014; Zhang et al., 2016). Natural events consist of volatilization from the ocean, volcanic eruption, geothermal activities, and weathering of Hg-containing minerals (Pirrone et al., 2010; Gaffney and Marley, 2014). Small scale or artisanal gold mining, mining and smelting, and coal combustion are the three major anthropogenic sources (UNEP, 2013; Zhang et al., 2016). Some of the dry and wet deposited PBM and GOM will be reduced to GEM in soil, water, and vegetation surfaces where Hg will be re-emitted in the form of GEM to the atmosphere (Gaffney and Marley, 2014). However, the contributions of each source and process to a given receptor site are affected by many factors including proximity to sources and weather conditions.

Various receptor-based models have been used to identify the sources and processes affecting ambient Hg levels (Cheng et al., 2015). Among these, Positive Matrix Factorization (PMF) and Principal Component Analysis (PCA) are two commonly used methods. PMF method provides quantitative source profiles and source contributions. The resultant source profiles could aid future studies in factor interpretation. Another strength of PMF is input variable screening and provision of model performance measures. The users could specify uncertainty values for each variable in each sample to reduce the impact of measurements with high uncertainties on the final results (US EPA, 2014a; Hopke, 2016). However, in order to derive profiles, PMF requires a large number of air pollutants which are often unavailable. In contrast, PCA can only provide qualitative assessment of sources/processes. One advantage of PCA over PMF is its capability of allowing inclusion of meteorological parameters as input, enabling the assessment of the effects of weather conditions on ambient Hg concentrations (Cheng et al., 2015). Therefore, it is beneficial to conduct source apportionment of atmospheric Hg using both PMF and PCA. To date, only one study used this combined approach (Cheng et al., 2009), yet it lacked a thorough comparison of the results. Furthermore, the ability of receptor models to reproduce the observed concentrations should be assessed in order to gauge the model performance (Henry, 1991; Viana et al., 2008), which has been rarely reported in the literature.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

The overall objective of this study is to identify the factors affecting ambient Hg concentrations at a receptor site using PMF and PCA approaches. The specific objectives are to, (1) identify the factors affecting ambient Hg concentrations using PCA and PMF model; (2) summarize the similarity and differences in PMF factors and PCA components; (3) evaluate the PMF model performances by Hg forms; (4) investigate the impact of including meteorological parameters on PCA results, and (5) assess the sensitivity of PMF results and performance to different treatment of missing data and low concentration values of speciated Hg.

2. Method

2.1 Study site

The study site is located in Kejimkujik (KEJ) National Park (44.32°N; 65.2°W; elevation: 170 m), Nova Scotia, Canada. The KEJ site is one of the first speciated Hg sites operated by Environment Canada outside the Arctic. This site was selected primarily because of the bioaccumulation issues at this area. Studies have found that common loons in Kejimkujik National Park had the highest mean blood Hg concentrations in northeastern United States and Southeastern Canada (Evers et al., 2007). Similarly, a 1996/97 survey found that yellow perch and common loons from Kejimkujik National Park and National Historic Site (Nova Scotia) had the highest blood Hg concentrations across North America. A 2006/07 follow up study on yellow perch observed on average a 29% increase in 10 out of 16 lakes, although anthropogenic emission from North America decreased between the mid-90s to the mid-2000s (Wyn, 2010).

The sampling site was surrounded by forests on a flat terrain. It was approximately 50 km away from the nearest coast, 120 km southwest of Halifax, and relatively remote from anthropogenic air emissions. A search of the National Pollutant Release Inventory (NPRI, Environment Canada, 2016) yielded seven Nova Scotia facilities reporting Hg air releases in both 2009 and 2010. Four of them were electric power generation stations, the other three were a refinery, a cement plant, and a university. The provincial annual air emission of Hg were 147.5 kg and 90.3 kg in 2009 and 2010, respectively (Table S1). The two largest Hg emitters were Lingan Power Generating Station (2009-2010 average: 71 kg/yr) and Trenton Power

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Generating Station (26 kg/yr), located 450 km and 250 km from the sampling site, respectively. The nearest anthropogenic Hg sources (Dalhousie University, Halifax: 0.17 kg/yr, Imperial oil, Dartmouth Refinery: 2.8 kg/yr) were 140 km northeast of the sampling site. In addition to Hg sources, the nearby NPRI (Environment Canada, 2016) combustion/industrial sources were a biomass-fueled power station and tire production factory located approximately 50 km east/southeast of the KEJ site (Table S1).

2.2 Data collection

GEM, GOM and PBM concentrations were collected from 2009 to 2010 using Tekran® instruments (Models 1130/1135/2537) at 3-hour intervals. Hourly concentrations of ground level ozone (O_3) and meteorological parameters (temperature, relative humidity, wind speed, and precipitation amount), as well as daily concentrations of SO_2 and HNO_3, $PM_{2.5}$ (2009 only), and particulate SO_4^{2-}, NO_3^-, Mg^{2+}, Cl^-, K^+, Ca^{2+}, NH_4^+, and Na^+ were also collected at KEJ site. Detailed information of data collection can be found in Cheng et al. (2013).

Hourly or 3-hr concentrations of GEM, GOM, PBM, O_3 and meteorological data were averaged into daily values because PMF and PCA require the same interval for all input variables. All daily values were the same as those used in a PCA study by Cheng et al. (2013). The general statistics of the daily concentrations are listed in Table 1 and Table 2 for year 2009 and year 2010, respectively. The number of missing daily concentrations ranged from 0% (ozone, 2010) to 41% (PBM, 2009), which are excluded from PMF or PCA. Among the three Hg forms, GEM had the fewest values below the Method Detection Limit (MDL), while GOM had the largest percentages of concentrations below MDL, followed by PBM, in both years. The variability, as indicated by coefficient of variability, was low for GEM but much higher for GOM and PBM.

2.3 Model setup and case design

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Detailed description of the theory of PMF and PCA methods can be found in Cheng et al. (2015). Model set up and case design are described below.

PMF

EPA PMF5.0 (US EPA, 2014b) was used in this study. The 12 cases investigated are listed in Table 3. Two approaches were employed in PMF modeling to handle missing values. The first approach is listwise deletion. Listwise deletion excludes all the records having one or more missing values, resulting in a complete data matrix as required in PMF. However, it may cause a large reduction of the dataset when one of the pollutants has many missing values or several pollutants have missing values at different time periods. In environmental studies, this approach may lead to biased results because listwise deletion benefits the records with high concentrations when below MDL values are flagged as missing (Huang et al., 1999). The second method is imputation, which increases the sample size in PMF. Hedberg et al. (2005) found that the relative error of factor profiles deceased as the sample size increased. In this study, geometric mean and median imputation were used to minimize the undue influence of extreme values as in Pekey et al. (2004). The effects of imputation was investigated in Cases 09+Mean, 10+Mean, 09+Median, and 10+Median.

Cases 09+RM, 10+RM, 09-RM, and 10-RM were devised to investigate the effects of excluding or combining GOM and PBM into reactive mercury (RM) on the resultant PMF results compared with the full dataset. Uncertainties of GOM and PBM measurements are considered high (Gustin et al., 2015). It has been reported that GOM may be collected on the PBM filter thus GOM concentrations could be biased low (Lynam and Keeler, 2005). Therefore, combining GOM and PBM to RM may reduce the uncertainties (Cheng et al., 2016). RM was calculated by summing GOM and PBM when both forms of Hg are detected.

In Case 09ScaleRM and Case 10ScaleRM, a variable scaling factor was used to increase the GOM and PBM concentrations:

$$\text{scaling factor} = \sqrt{\frac{\max(x)}{x_i}} \qquad (1)$$

where x_i is the concentration of GOM or PBM in the i^{th} sample. The scaling factor is large when the concentration is low, and vice versa, but the maximum concentration is

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

unchanged.

Equation-based uncertainties (US EPA, 2014a) were used in this study, expressed as:

$$\begin{aligned} \text{Uncertainty} &= \frac{5}{6} \times MDL, when\ concentration \le MDL \\ \text{Uncertainty} &= \sqrt{(Error\ Fraction \times concentration)^2 + (0.5 \times MDL)^2}, \\ & when\ concentration\ > MDL \end{aligned} \quad (2)$$

The MDLs used in this study are 0.1 ng/m^3, 2 pg/m^3, and 2 pg/m^3 for GEM, GOM and PBM, respectively (Tekran Inc., 2010). For RM, the MDL was assumed to be 4 pg/m^3. The error fractions were assumed to be 15% of concentrations for Hg forms and 10% of concentrations for other compounds. This is because most of the measured GOM and PBM concentrations have low concentrations near or below MDL as seen in Tables 1-2; thus have large uncertainties as pointed out by Croghan and Egeghy (2003). Following Polissar et al. (1998), constant uncertainties (100%, 200% and 1000% of the mean/median for GEM, PBM and GOM, respectively) were used for imputed Hg concentrations, based on the uncertainty distributions of the below MDL values in the two base cases. This is to down weight the imputed values.

No variables or samples were excluded after input data screening to reflect all observations. No variables were down-weighted, with the exception of imputed values, because runs with and without GOM and PBM categorized as "weak" led to similar results. Other PMF input parameters include: the number of runs was set to 20 to enable stability evaluation, and the best run was used; the number of the starting seed was set to 25.

PMF outputs used in this study include source profiles, model performances and factor contributions. Four factors were retained in each case. The factors were interpreted based on the comparison of the major variables (>=25%) in each of the four factors to markers and source profiles in the literature, taking into consideration NPRI emission sources. Stability indexes of model runs, scaled residual plot, Obs/Pred scatter plot and Obs/Pred time series were used to evaluate the model performances for speciated Hg. The impact of each data treatment method on PMF results was assessed, taking into consideration interpretability of the factors and

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

model performance of the three Hg forms.

PCA

The PCA source apportionment analysis using speciated Hg in 2009 and 2010 was already conducted in another study (Cheng et al., 2013). In this study, different cases were investigated, as listed in Table 4. Briefly, all compounds were included to enable comparison with PMF results (Case 2009 and Case 2010), instead of removing some air pollutants as in Cheng et al. (2013) due to a lack of correlation between those air pollutants and atmospheric Hg. Pairwise deletion of missing values in Cheng et al. (2013) was replaced with listwise deletion to be consistent with the PMF model input which must be a complete data matrix. The PCA runs were conducted using SPSS 22.0 (IBM Corp., USA). Cases 09-C&M and Case 10-C&M were included to evaluate the effects of weather conditions on factor identification. The components with eigenvalues greater than 1 were retained for further analysis, following the Kaiser Criterion (Kaiser, 1960). Principal components after Varimax rotation were interpreted by comparing the major variables (loadings > 0.25) of the component with the outcomes of other studies, and by checking NPRI sources in the region (Table S1).

3. Results and discussion

3.1 PMF - base cases

In this section, only the two base cases, Case 2009 and Case 2010 are considered.

PMF sources

Table 5 and Figures 1-2 present percent concentration of each pollutant apportioned to each of the four factors. Factor 1 was named Combustion Emission due to large contributions of SO_4^{2-} (64%) and HNO_3 (54%) and a moderate contribution of GOM (31%). SO_2 and NO_x are precursors of SO_4^{2-} and HNO_3, respectively. These precursors are from combustion sources and probably oxidized during the transport from sources to receptor sites (Liu et al., 2007). The presence of GOM is consistent with the combustion emission which is one of the GOM sources (Carpi, 1997). There was little NH_3 emissions from point sources near the study site (Table S1). Thus, the presence of NH_4^+ (71%) should be related to the transport and transformation of NH_3 from agriculture emissions as well as other physical and

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

chemical processes (e.g., aqueous phase chemistry, condensational growth, droplet evaporation) producing NH_4^+ (Zhang et al, 2008; Pitchford et al., 2009). In this factor, the molar ratio of NH_4^+ to SO_4^{2-} is 1.7, although some observed profiles having ratios greater than 2 (Lee et al, 1999). Ratios less than 2 suggest insufficient amount of NH_3 to neutralize H_2SO_4 thus H_2SO_4 will react with other compounds to form sulfate (Pavlovic et al., 2006; Zhang et al., 2008). The moderate contribution of PM (42%) is consistent with the presence of particulate SO_4^{2-} and NH_4^+. Also, SO_4^{2-} accounted for over 50% of PM mass (Table 1). In addition to a lack of major combustion facilities nearby (Table S1), a strong correlation between SO_4^{2-} and NH_4^+ (Tables S2-S3) also suggest formation of secondary aerosols. Therefore, this factor suggests transported plumes instead of fresh emissions.

Factor 2 was assigned to Industrial Sulfur. The major variables PBM and SO_2 are indicators of coal combustion (Huang et al., 2010). The minor contributions of HNO_3 and NO_3^- also suggest combustion sources because their precursor, NO_x, is mainly released by combustion sources (Liu et al., 2007). However, there were no combustion sources emitting Hg compounds near the KEJ site in 2009 (Table S1). Therefore, this factor is more likely related to industrial sources in the region.

Factor 3 was named Photochemical Process and Re-emission of Hg due to the high contributions of ozone (72%), GEM (76%), GOM (69%), PBM (63%), and moderate contributions of Ca^{2+} (45%) and K^+ (37%). The high contribution of ozone indicates an ozone rich environment, resulting in oxidation of GEM to GOM and the sequential formation of PBM (Pal and Ariva, 2004; Liu et al., 2007). Although results of recent studies show that the reaction rate of Hg and ozone has large uncertainties, the oxidation of Hg by bromine is very fast (Goodsite et al., 2004). The KEJ site is near the Atlantic, making the oxidation of Hg by bromine applicable. The presence of K^+ is related to soil emission or biomass burning (Andersen et al., 2007), while Ca^{2+} is related to soil/crustal. The site is located in Kejimkujik National Park. Therefore, it is under the impact of soil emission, emission from the nearby biomass-fired power station (Table S1), and transported biomass combustion. It was estimated that re-emission of Hg from biomass burning and land surfaces contributed 13% and 34% of the global re-emission budget, respectively (Pirrone et al., 2010). Thus, the high contribution of GEM may be attributable to the re-emission of GEM. The emission

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

253 from soil and biomass combustion was also identified in the PCA study at this site
254 (Cheng et al., 2013).

255 Factor 4 has high contributions of Cl^- (100%), Mg^{2+} (82%) and Na^+ (86%) and
256 moderate contributions of Ca^{2+} (31%), K^+ (39%) and NO_3^- (40%). The presence of
257 Na^+, Mg^{2+}, and Cl^- indicates marine aerosols because these elements are rich in sea
258 water (Huang et al., 1999). The strong correlations among these three compounds
259 ($\geq$0.89, Tables S2-S3) also suggest a common source. As the sampling site is located
260 near the Atlantic, the presence of marine aerosols is reasonable. Major production
261 pathways of NO_3^- include reaction of HNO_3 with NH_3, sea salt and soil dust
262 (Pakkanen, 1996). In this factor, the NO_3^- is probably related to the reaction of HNO_3
263 and sea salt. Thus, this factor was named Sea Salt.

264 As seen in Table 5 and Figures 1-2, the same four factors were identified in year
265 2009 and 2010. The profiles of each factor were also largely consistent between the
266 two years. Factor 1 in 2010 is similar to the factor named Combustion Emission in
267 Case 2009. However, this factor lacks PM (not available in 2010) and has a higher
268 contribution from K^+, which may relate to biomass burning. This factor is assigned to
269 the same name as in 2009 because the presence of SO_4^{2-} and HNO_3 is enough to
270 identify combustion process (Liu et al., 2007). It should be noted that this factor has a
271 much smaller constitution of GOM than in 2009. This may be due to a large reduction
272 in SO_2 emissions (2.42 million tons or 32% reduction) from coal-fired power plants
273 across the United States between 2008 and 2010 (US EPA, 2011). Large reductions in
274 Hg (-39%) and SO_2 (-35%) emissions also occurred in Nova Scotia between 2009 and
275 2010, as seen in Table S1. However, reduction in Hg emissions is only reflected on
276 GOM (-75%), while GEM decreased a little and PBM increased slightly.

277 The major variables of factor 2 are also similar to those of the factor Industrial
278 Sulfur in Case 2009. However, this factor has a moderate contribution of GOM
279 instead of PBM in 2009. Factor 3 has similar major variables as the factor named
280 Photochemistry and Re-emission in Case 2009. Factor 4 is dominated by Cl^- (100%),
281 Na^+ (83%) and Mg^{2+} (75%). This factor was named Sea Salt as in Case 2009.

282 ***PMF source contributions***

283 The PMF factor contributions of the two base cases are presented in Table S4
284 (Case 2009) and Table S5 (Case 2010). In both years, factor Photochemistry and

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Re-emission had the largest contributions to GEM (averaging 77% and 79% in 2009 and 2010, respectively), GOM (70% and 67%), and PBM (69% and 80%) among all four factors. In other words, ambient Hg concentrations at the KEJ site were dominated by photochemistry and re-emission of Hg. Industrial Sulfur had moderate contributions to GOM (average, 29%) in 2010 instead of PBM in 2009 (21%). Combustion Emission contributed 25% of GOM in 2009 but 11% each of GEM and PBM in 2010. The factor Sea Salt only had minor contribution to GEM (14% in 2009 and 9% in 2010) and PBM (<10% in both years). This is not unexpected because GEM is likely to be oxidized to GOM by the *in situ* photochemical process under the bromine-rich environment (Obrist et al., 2011). However, this factor has no contribution to GOM because it was estimated that >80% of GOM in the marine boundary layer is absorbed by sea salt aerosols and it is sequentially deposited onto the earth's surface where evasion occurs (Holmes et al., 2009).

PMF model performance

Among the three Hg forms, GEM had the best performances in terms of scaled (i.e. standardized) residual because it had normal distribution and fewer absolute values of scaled residual greater than 3 in both years (Case 2009 and Case 2010, Table 6). Table 6 also lists the coefficient of determination (R^2) and the slope of the regression line for speciated Hg in Obs/Pred scatter plot (Figures S1-S2), to evaluate the overall model-measurement agreement. Between the two years, the agreement was better with GEM in 2010 and PBM in 2009 because of higher R^2 values and slope closer to 1. The low values of R^2 and slope in both years indicate the agreement was poor for GOM.

The Obs/Pred time series of the three Hg forms reveal the model's ability to reproduce the observational concentrations on a day-to-day basis. In Case 2009, the Obs/Pred time series (Figure S3) were split into three time periods by the data gaps, January to February (period 1), March to July (period 2), and October to December (period 3). GEM had better performances than the other two forms because the peak values were reproduced by the model in all three periods. However, the modeled values in period 3 are too low compared to observed concentrations, leading to a lower R^2 (Table 6). The performance for PBM is better than GOM because the predicted concentrations tracked the observed concentrations well in period 2.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

317 However, PBM concentrations were underestimated and overestimated by the model
318 in period 1 and period 3, respectively. The GOM concentrations were not reproduced
319 well with unmatched peak values in period 2, and there was a clear separation of
320 observed and predicted trend lines in periods 1 and 3, leading to over prediction.

321 In Case 2010, the time series (Figure S4) were split into two periods,
322 January-June (period 1) and July-December (period 2), based on a clearly visible
323 overestimation of GOM concentrations in the second period. The predicted GEM
324 concentrations tracked the trend of observations well in both periods but with more
325 fluctuations. The model was unable to reproduce high GOM concentrations in period
326 1. For PBM, the predicted concentration was rather flat, missing completely the high
327 concentration episode in spring 2010.

328 The model-measurement agreement was further quantified with the ratios of
329 predicted to observed concentrations (Pred/Obs ratio, Figure 3). In both years, the
330 predicted GEM agreed well with the observed concentrations as supported by the
331 small range of Pred/Obs ratios (0.56-1.32 in 2009, 0.42-1.43 in 2010) and mean ratios
332 approaching 1 (0.97 and 0.98). On an annual basis, the observed GEM concentrations
333 were also well reproduced because the ratios of predicted to observed annual means
334 (annual Predmean/Obsmean) were almost 1 (0.97 and 0.98) (Tables S4-S5).
335 Compared with GOM, PBM had better agreement between the predicted and observed
336 concentrations with a smaller range of Pred/Obs ratios (0.40-13.4 and 0.14-18.3 vs.
337 0.13-53 and 0-193) and mean ratios closer to 1 (2.09 and 1.98 vs. 5.89 and 4.44). In
338 spite of large sample to sample variability in the Pred/Obs ratios, the model
339 performance was very good for PBM (annual Predmean/Obsmean ratio of 1.03 and 1)
340 and reasonable for GOM (0.86 and 1.34) in reproducing annual means.

341 ***Comparison between PMF in year 2009 and 2010***

342 Overall, the interpretability of the factors was similar in the two years. The same
343 factors were observed in 2009 and 2010, and most factor contributions were highly
344 consistent between the two years. Among the three Hg forms, PMF reproduced GEM
345 concentrations well in both years. Possible reasons of poor performance on PBM and
346 GOM include lower concentration levels and much higher percentages of readings
347 below MDL (Tables 1-2) leading to large uncertainties. However, the differences in

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

sample size (161 in 2009 vs. 290 in 2010) and fractions of below MDL values (Tables 1-2) alone could not explain the mixed results of poor performance on GOM in 2009 and PBM in 2010. Further examination of time series (Figures S3 and S4) suggests that the reduced performance could also be attributable to high concentration episodes in GOM in 2009 and PBM in 2010. The impact of Hg data treatment on PMF results was investigated and the results are presented in section 3.4.

3.2 PCA components

Case 09-C

The component loadings of Case 09-C are presented in Table 7. PC1 was named Combustion/industrial Emission due to positive loadings of PBM, PM, O_3, SO_2, HNO_3, Ca^{2+}, K^+, NO_3^-, NH_4^+, and SO_4^{2-}. Most major compounds except O_3 were also found in a component named "transport of combustion and industrial emissions" in another PCA study using the same dataset (Cheng et al., 2013). The high loadings of secondary pollutants HNO_3, NO_3^-, and SO_4^{2-} indicate the factor represents transport of combustion/industrial emission because their precursors (NO_x and SO_2) are mainly emitted by combustion/industrial sources (Liu et al., 2007). The precusors may be oxidized during the transport process. The moderate loading of O_3 is also related to the transport of combustion emission because the precursors of O_3 (NO_x and VOC) are emitted from mobile and stationary combustion sources. Ammonia is likely related to the transport of agriculture emissions and reaction of NH_3 and H_2SO_4 or HNO_3 (Pichford et al., 2009).

PC2 has high loadings of Na^+, Mg^{2+}, Cl^-, and K^+ and and moderate loadings of Ca^{2+}. Those compounds indicate marine aerosols (Huang et al., 1999). The moderate loading of NO_3^- is likely due to the reaction of HNO_3 and sea salt (Pakkanen, 1996). As in the PMF factor interpretation, the identification of component Sea Salt is relevant because the monitoring site is near the Atlantic.

PC3 has positive loadings of GEM, GOM, PBM and O_3. The positive loadings on O_3 and GOM indicate the photochemical production of GOM (Huang et al., 2010). The positive loading of GEM is somewhat unexpected because the photochemical production of GOM consumes GEM thus leading to opposite signs of GEM and GOM (e.g. Huang et al., 2010). However, daily average concentrations were used in this

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

study instead of two-hour means in Huang et al. (2010). The daily GEM and GOM were indeed positively correlated (r=0.37 in 2009, Table S2; 0.31 in 2010, Table S3). Using the same dataset, Cheng at al. (2013) conducted further analysis on O_3 concentrations and %GOM/TGM (TGM=GEM+GOM) ratios. The ratio is indicative of the degree of oxidation. The results showed that the %GOM/TGM ratio increased with O_3 when O_3 concentrations were greater than 40 ppb, suggesting gas phase oxidation of Hg at this coastal site. Therefore, this factor was named Photochemical Production of GOM.

PC4 represents Gas-particle Partitioning of Hg. The negative loading of PBM and the positive loading of GOM indicate the partition process. The positive loadings of Ca^{2+} and K^{+} suggest soil aerosols (Cheng et al., 2012) which could be abundant at the Kejimkujik National Park.

Three out of four components (Combustion/industrial Emission, Photochemical Production of GOM and Gas-particle Partitioning of Hg) have significant association with ambient Hg concentrations at the site, while Sea Salt has little.

Case 09-C&M

Five principal components are extracted when meteorological data were included in PCA (Case 09-C&M, Table 7). The loadings in PC1-PC4 are similar with the loadings of PC1, PC2, PC4, PC3 in Case 09-C, respectively. Thus the names of those four components were retained. The inclusion of meteorological parameters resulted in small loadings of relative humidity (-0.26) in PC1 and wind speed (0.32) in PC2, as well as a moderate loading of wind speed (0.52) in PC4. A large loading of temperature (0.94) was observed in PC3. The opposite signs of temperature and PBM are consistent with the gas-particle partitioning process because low temperatures favor the formation of PBM (Rutter and Schauer, 2007). The lack of GEM in PC3 (Case 09-C&M) did not affect the identification of this factor, because the partitioning of GEM onto particles is much weaker than that of GOM (Liu et al., 2007).

PC5 was derived mostly from meteorological variables. The negative loading of GOM and positive loadings of relative humidity and precipitation suggest removal of GOM by dew, cloud and precipitation (Cheng et al., 2013). The loading of GOM is small, nonetheless consistent with the wet deposition process because GOM is more easily removed compared to GEM due to its higher water solubility (Gaffney and

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

412 Marley, 2014). Therefore, this component was named Hg Wet Deposition.

413 Similar to Case 09-C, all components except Sea Salt are associated with ambient
414 Hg concentrations. After the inclusion of meteorological data, each factor contains at
415 least one meteorological parameter. The presence of meteorological variables did not
416 contribute to the determination of the components except a new component Hg wet
417 deposition was identified.

418 ***Case 10-C***

419 The component loadings of Case 10-C are listed in Table 8. PC1 was named
420 Combustion Emission. The positive loadings of HNO_3, NO_3^- and SO_4^{2-} are indicative
421 of transport of combustion emission because their precursors (NO_2 and SO_2) are
422 mainly released by combustion emissions (Liu et al., 2007). The high positive loading
423 of NH_4^+ represents transport of agriculture emissions of ammonia which may react
424 with H_2SO_4 and HNO_3 during the transport process (Pitchford et al., 2009). The
425 positive loadings of Ca^{2+} and K^+ indicates biomass burning from wildfires or
426 biomass-fueled power station (Andersen et al., 2007).

427 PC2 was named Sea Salt due to high loadings of Na^+, Mg^{2+}, and Cl^-, because
428 these three compounds are rich in sea water (Huang et al., 1999). PC3 has the same
429 major variables as the component Photochemical Production of GOM in 2009.
430 Therefore, PC3 was also named as such.

431 PC4 was assigned to Industrial Source. The positive loadings of GOM and SO_2
432 indicate coal combustion (Lynam and Keeler, 2006), although no combustion facilities
433 were reported near the KEJ site in 2010 (Table S1). The positive loadings of SO_4^{2-} and
434 HNO_3 are consistent with the transport of industrial emissions which release their
435 precursors, SO_2 and NOx (Liu et al., 2007). Therefore, this factor was named
436 Industrial Source. Two out of four factors (i.e. Photochemical Production of GOM and
437 Industrial source) have significant association with Hg compounds.

438 ***Case 10-C&M***

439 As shown in Table 8, five principal components are extracted in Case 10-C&M.
440 The loadings in PC1-PC3 and PC5 are similar with the loadings of PC1-PC4 in Case
441 10-C, respectively. Thus the name of those four components were retained. PC4 in
442 Case 10-C&M was named Hg Wet Deposition due to negative loadings of GOM and
443 PBM and positive loadings of relative humidity, wind speed and precipitation, similar

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

with PC5 in Case 09-C&M (Table 7). Three out of five components (i.e. Photochemical Production of GOM, Industrial Source, and Hg Wet Deposition) were associated with Hg concentrations. The influence of meteorological data on identification of components were also similar to in 2009.

Comparison between PCA in year 2009 and 2010

In each year, four components were extracted in PCA with air pollutants only. The two common factors between the two years are Photochemical Production of GOM and Sea Salt. The former has a strong association with Hg compounds, while the latter has little. Component Gas-particle Partitioning of Hg was only identified in 2009, likely due to a lower percentage of PBM readings <MDL than those in 2010 (Table 9, Case 2009 and 2010). It is also consistent with strong correlations between temperature as well as GOM and PBM (r=0.46 and -0.43, Table S2) in 2009 but non-significant or weak correlations (r=-0.04, and -0.16, Table S3) in 2010.

The component Combustion/industrial Emission in 2009 affected PBM and SO_2 levels. It was split into two components in 2010, Combustion Emission and Industrial Source. The former was no longer strongly associated with any of the three Hg forms, while the latter was associated with GOM and SO_2. This is probably due to the reduction of coal combustion in Canada and the USA, evident by lower provincial Hg (reduction of 39%) and SO_2 emissions (-35%) in 2010 (Table S1). The reductions in GEM, GOM, and SO_2 concentrations at the KEJ site were 3%, 75%, and 43% respectively in 2010 (Tables 1-2). The shifting of PBM & SO_2 relation in 2009 to GOM & SO_2 in 2010 is sustained by a strong correlation between PBM and SO_2 (r=0.63, Table S2) in 2009, but little correlation (r=0.06) accompanied by a moderate correlation between GOM and SO_2 (r=0.30) (Table S3) in 2010. The shift is also consistent with the PMF results where Industrial Sulfur accounted for 21% of PBM in 2009 (Table S4) but 29% of GOM in 2010 (Table S5).

In both years, inclusion of meteorological parameters did not affect the identification of the four factors from air concentrations. However, relative humidity and precipitation yielded an additional component named Hg Wet Deposition.

Overall, the PCA results were largely consistent between the two years, in terms of the number of components, impact of meteorological parameters, and major processes associated with ambient Hg. The changing emissions/concentrations and the

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

476 resultant correlations among monitored air pollutants from one year to another are
477 reflected in the limited shifting of variable loadings. .
478
479 **3.3 Comparison of PMF and PCA results**
480 The PCA loadings and the factor profiles as well as factor contributions in PMF
481 model have very different meanings. In PCA, variables with large loading indicate
482 their correlation or association with that component derived from all samples. In PMF,
483 presence of variables in profiles indicates their contribution to that source/process
484 derived from all samples, while the contribution values are further quantified in
485 source contribution tables of each sample. Therefore, a direct comparison between the
486 PMF and PCA results is not feasible. However, the similarities and differences in the
487 major sources/processes identified by each approach, chemical markers in each factor
488 profile or component, and the impact/association of factors/components on Hg could
489 reveal strength and weakness of each method.
490 A comparison of Table 5 and Tables 7-8 (cases with air concentrations only)
491 shows that Na^+, Cl^-, and Mg^{2+} are markers of Sea Salt in both PMF and PCA.
492 Similarly, GEM, GOM, PBM and O_3 indicate Photochemistry. Both methods suggest
493 strong contribution to or association between Hg compounds and photochemistry, but
494 weak with Sea Salt. Both methods identified combustion and industrial sources, while
495 the variables in factors/components differed to some extent. Furthermore, combustion
496 and industrial were separate sources in PMF in both years and in PCA in 2010, but
497 combined as one component in PCA in 2009. Overall, PMF profiles are more
498 consistent between the two years, while the PCA loadings are more sensitive to
499 correlation among variables. However, the shift of PBM & SO_2 to GOM & SO_2
500 loadings in PCA between the two years is consistent with the shift of those two pairs
501 in Combustion & Industrial Sulfur profiles/contributions in PMF. On the other hand,
502 Gas-particle Partitioning of Hg was only recognized in PCA. This is because the
503 identification of this factor relies on negative association between PBM and GOM
504 (Table 7), but such association is not reflected in PMF due to its non-negative nature.
505 This is one of the limitations of PMF. Furthermore, the inclusion of meteorological
506 conditions in PCA enables identification of a new component related with weather
507 conditions. The good agreement between PMF and PCA outputs is consistent with a

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

comparison of receptor models in PM source appointment (Viana et al., 2007). A common weakness of PCA and PMF is the suggestiveness of factors/components. Other techniques, such as back trajectories, have been used in previous studies to verify some factors (Cheng et al. 2015). Overall, when accompanied by model performance evaluation, PMF results are with more confidence.

3.4 Sensitivity of PMF results to data treatment

3.4.1 Year 2009

Case 09+mean & Case 09+median

The factor profiles of the six PMF cases in 2009 are displayed in Figure 1. In Case 09+mean and Case 09+median, all four factors have similar profiles as in Case 2009. Compare with the base case, factor 3 (Photochemistry and Re-emission of Hg) has a higher contribution by NO_3^-, however it is common to observe NO_3^- from soil emissions (Parmar et al., 2001). GOM has a much smaller contribution in factor 1 (Combustion Emission) (Figure 1, Table S4). This is likely because the correlation coefficients between GOM, NH_4^+ and SO_4^{2-} become insignificant after imputation (Table S6). Consequently, GOM is not strongly related to that factor which is dominated by NH_4^+ and SO_4^{2-}. Changing correlation among variables is a shortcoming of imputation (Huang et al., 1999).

Case 09+RM & Case 09-RM

As shown in Figure 1 and Table S4, by combining GOM and PBM into RM, RM replaced PBM instead of GOM in related factors as major variables with similar contributions. This is because the median concentration of PBM is approximately 5 time of the median concentration of GOM (Table 9). Once these two forms are combined to RM, the variance of RM is dominated by PBM. The presence of other compounds including GEM in factor profiles/contributions in these two cases are similar to those in Case 2009.

Case 09ScaleRM

The factor profiles were similar to those in Case 2009 (Figure 1). The same can be said about factor contributions to speciated Hg (Table S4).

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Performance

Case 09-RM, Case 09+RM and Case 09ScaleRM have similar performances with Case 2009, on distribution of scaled residuals (Table 6). Imputation (Case 09+mean and Case 09-median) worsened the performance because the scaled residuals are concentrated near zero for gaseous Hg.

In terms of the coefficients of determination (R^2) and the slopes of the regression line for speciated Hg in Obs/Pred scatter plot (Table 6, Figure S1), imputation (Case 09+mean and Case 09+median) deteriorated PMF performance compared to the base case. This is not unexpected because the use of a constant imputation value reduced the variance in observed concentrations (Table 9). The similar performances on GEM in Case 2009, Case 09+RM, Case 09-RM, and Case 09ScaleRM indicate combining, excluding, or scaling GOM and PBM, respectively, did not affect the performance on GEM. The performances on RM are similar to that of PBM in Case 2009 because the RM concentrations are dominated by PBM. Using scaling factors to increase GOM and PBM concentrations resulted in better performances on those two forms than in the base case. This is attributable to a significant reduction in percent of concentrations below MDL (Table 9).

The changes in model performance are more evident in the observed and predicted time series (Figure S3). Compared with the base case, imputation led to more fluctuation in the predicted GEM values, thus slightly worse. RM had better model-measurement agreement than GOM or PBM as individual compound. The agreement was also improved by scaling GOM or PBM. The peak values (PBM in period 1 and both forms in period 2) were better reproduced and the over prediction in period 3 with low concentrations was greatly corrected.

Compared with the base case, the distributions of the ratios of predicted to observed Hg concentrations and the ratio of predicted to observe annual means changed little for GEM among the six cases (Figure 3, Table S4). Scaling GOM and PBM improved model-measurement agreement of those two forms, evident by a much narrower range and a shift toward smaller values in the distribution of ratios.

3.4.2 Year 2010

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Case 10+mean & Case 10+median

Factor profiles (Figure 2) and contributions (Table S5) after imputation have minor changes compared to those in Case 2010. However, less changes were observed with the use of median imputation. The small deviations after imputations is probably because only a small fraction (4%) of Hg concentrations were missing in 2010 than in 2009 (31-41%). Although HNO_3, SO_2, and inorganic ions have up to 19% missing values (Table 2), the correlations between each of the three Hg forms and other compounds changed little (Table S7).

Case 10+RM & Case 10-RM

The impact of combining or removing GOM and PBM (Figure 2, Table S5) is the same as in 2009. The dominance of PBM in RM is stronger in 2010 with the ratio of median PBM to median GOM concentration being approximately 10 (Table 9).

Overall, excluding or combining GOM and PBM did not affect the source identification in PMF model in both years (Figures 1 and 2). However, the identification of the factors relying on GOM or PBM only (e.g. gas-particle partitioning of Hg) may be affected after combining or excluding GOM and PBM. In this study, such factors were not encountered in PMF. Nonetheless, excluding or combining GOM and PBM did affect the source contributions. After combining GOM and PBM, factors contributing to GOM only (Combustion Emission, 2009; Industrial Sulfur, 2010, Table 10) did not contribute to any Hg forms, and the factor contributing to PBM only (Industrial Sulfur, 2009) was contributing to RM, due to dominance of PBM in RM. In both years, using three Hg forms instead of GEM only led to more Hg sources/processes identified. Therefore, monitoring speciated Hg could help us better understand Hg cycling.

Case 10ScaleRM

The factor profiles and contributions of Case 10ScaleRM are similar to those in Case 2010 (Figure 2, Table S5). A noticeable deviation is the much smaller contribution by GOM in factor 2 compared to Case 2010. However, factor 2 was still assigned to Industrial Sulfur because of the presence of SO_2 and NO_3^-.

Performance

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

599 Firstly, the distribution of scaled residuals as well as R^2 value and the slope of the
600 regression line for speciated Hg in Obs/Pred scatter plot was evaluated for the six
601 cases (Table 6, Figure S2). Similar to 2009, the comparable performances observed in
602 Case 2010, Case 10-RM, Case 10+RM, and Case 10ScaleRM indicate that the model
603 performance on GEM is insensitive to excluding, scaling, or combining GOM and
604 PBM to RM. Case 10ScaleRM also has the best performances on GOM and PBM
605 among all the cases in 2010. Unlike in 2009, the negative impact of imputation was
606 smaller when median value was used, compared with the mean imputation.

607 Secondly, in the observed and predicted time series (Figure S4), imputation
608 resulted in more severe fluctuation in predicted GEM concentration as in 2009, but
609 less so when median values were used. Scaling of GOM or PBM also improved the
610 reproducibility of day-to-day variability in the observed values, owing to a large
611 reduction in concentrations below MDL (Table 9). Among the 6 cases, the most
612 significant change is in PBM with imputation. There were additional high
613 concentration episodes in early 2010 when imputation of non-Hg compounds brought
614 back Hg concentrations otherwise removed by listwise deletion in the base case,
615 leading to increased standard deviation (Table 9). Those peaks were completely
616 missed by the model, leading to deteriorated agreement.

617 Finally, the distributions of the ratios of predicted to observe Hg concentrations
618 and the ratio of predicted to observe annual means changed little among the first five
619 cases in 2010 (Figure 3 and Table S5). The exceptions are under prediction of the
620 annual mean of PBM in the two imputation cases and over prediction for RM.
621 Compared with the base case, the distribution of ratios for GOM and PBM became
622 narrower and shifted toward smaller values, but leading to under prediction of PBM.

623 **3.4.3 Comparison of 2009 and 2010 among different data treatments**

624 The different characteristics of Hg forms led to different impact of data treatment
625 on model results and performances in the two years. Imputation using geometric
626 mean and median values led to minor changes in factor profiles in both years, with
627 more variations in contributions of Hg forms in 2009 but non-mercury compounds in
628 2010. This is likely because the Hg and non-Hg compounds were missing at a larger
629 percentage in 2009 and 2010, respectively. The lack of significant impact is likely due

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

630 to already high sample to compound ratios (161 samples/15 compounds in 2009, 290
631 samples/14 compounds in 2010, Tables 1-3). Huang et al. (1999) have reported that
632 mean imputation generally yielded better PMF results than listwise deletion,
633 especially with higher percentage of missing values. Particularly, composition of
634 crustal and marine factors were closer to those of crust and sea water. Imputation
635 resulted in degraded performance on all three Hg forms, but for different reasons. For
636 GEM, it is largely due to more fluctuation than the already over predicted one in the
637 base case in both years. For PBM in 2010, the peak values otherwise removed in
638 listwise deletion (base case) are beyond the model's ability to match. This seems to be
639 a random occurrence and is an uncertainty of imputation. Between geometric mean
640 and median imputations, the impact was similar in both years for each of the three Hg
641 forms. The exception is with median imputation in 2010, there was less deviation in
642 factor profile/contribution from the base case. The reason is unclear because the
643 difference in geometric mean and median was very small for GEM in both years and
644 slightly greater in 2009 for GOM and PBM (Tables 1-2).

645 In both years, some changes in the factor profiles and factor contributions but
646 little changes in model performances were observed in the cases excluding GOM and
647 PBM. Scaling GOM and PBM or combining them into RM improved
648 model-measurement agreement, suggesting the approach is effective in both year in
649 spite of large percentages of below MDL values (GOM, 78% in 2009 vs. 96% in 2010;
650 PBM, 48% in 2009 vs. 46% in 2010, Tables 1-2). The improvement is largely
651 attributable to reduction in concentrations below MDL (Table 9) which in turn
652 reduced PMF uncertainty expressed in equation (2). Another benefit of using a
653 variable scaling factor is reduced data variability as indicated by smaller coefficients
654 of variation in Table 9. PMF is more likely reproducing well compounds with less
655 variability. However, there is little evidence that the scientific uncertainties of scaled
656 GOM and PBM concentrations are indeed reduced from that of the original dataset.

657

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

4. Conclusions

Source apportionment analysis was conducted with PMF and PCA using concentrations of speciated Hg and other air pollutants collected at KEJ site in 2009 and 2010. Year 2010 was characterized by reduced Hg and SO_2 emissions compared with 2009. However, GOM is more sensitive to the decrease in Hg emissions while GEM and PBM are not, underscoring the benefits of speciated Hg measurements. It was found that consideration of emission inventories and correlation among air pollutants is useful in factor/component interpretation.

Using PMF, the nature of each of the four factors identified was the same in 2009 and 2010. In both years, ambient concentration of all three Hg forms at the KEJ site were dominated by contributions from factor Photochemistry and Re-emission, and the contribution by Sea Salt was the smallest. However, slight variations between the two years were observed in the contributions by the other two factors (Combustion Emission, Industrial Sulfur).

Good agreement was found between PMF and PCA results. In each year, four components were extracted in PCA with air pollutants only. Three or four of them overlapped with factors obtained in PMF. PCA results suggest little association between Hg and Sea Salt, consistent with PMF. Furthermore, PMF and PCA had similar shift of source profile/contribution from one year to another, suggesting both methods were able to respond to changing concentration levels, and interrelationships among the air pollutants. In both years, inclusion of meteorological parameters in PCA led to extraction of an additional component Hg Wet Deposition while the identification of other components was not affected. Therefore, PCA is superb to PMF in terms of identifying factors related to atmospheric processes. With regards to atmospheric processes represented by negative correlation among variables, such as Gas-particle Partitioning of Hg (Table 8), PCA is more likely to identify them because component loadings reflect correlations, while it is difficult for PMF because its variable contributions in source profile are all positive.

A comprehensive PMF model performance evaluation was conducted for each of the three Hg forms. Between the two years, the model performance was comparable. In both years, the observed daily GEM concentrations were well reproduced, but

relatively poor for GOM and PBM. On an annual basis, the model-measurement agreement of annual mean concentrations were excellent for GEM, very good for PBM and acceptable for GOM.

The sensitivity of PMF results and model performance to different approaches of dealing with missing values and concentrations with large uncertainties was investigated. In our study of more than 160 samples with 15 or 14 air pollutants, increasing the sample size by geometric mean or median imputation of missing values is not effective in improving the model performance. With over 70% GOM and over 40% PBM concentrations below MDL in our dataset, the impact of large measurement uncertainties in GOM and PBM is much more significant. Scaling GOM and PBM to increase their concentrations or combining them to reactive mercury is effective in improving the model-measurement agreement. The identification of sources/processes and their contributions to speciated Hg are relatively insensitive to any of the data treatment options considered. The exception is that less sources/processes affecting ambient Hg were identified when GOM and PBM were excluded, further underlining the importance of monitoring speciated Hg.

The good agreement between PCA and PMF results in both years is encouraging although these two methods bear little resemblance. PMF partitions observed concentrations by solving mass balance equations, while PCA is a data reduction tool to explain majority of variances in the entire dataset with a small number of components. Our observation was made possible by the use of multiple-year dataset. Future studies should conduct more PMF and PCA comparisons to validate our findings.

Overall, PMF results are quantitative and with more confidence with model performance evaluation. However, when ancillary air pollutant data are available, it is recommended to carry out both PCA and PMF simulations to verify the sources/processes identified.

Our PMF results suggest that PMF has difficulties reproducing daily concentrations of GOM and PBM, because of high concentration episodes and large uncertainties due to low concentrations and large percentage of below MDL values. More attention should be devoted to those issues in future studies.

Acknowledgements: Funding of this project was provided by Environment Canada and National Sciences and Engineering Research Council of Canada. The authors acknowledge John Dalziel and Rob Tordon of Environment Canada for providing mercury data and US EPA for the PMF model used in this study.

References

Andersen, Z. J., Wahlin, P., Raaschou-Nielsen, O., Scheike, T., and Loft, S.: Ambient particle source apportionment and daily hospital admissions among children and elderly in Copenhagen, Journal of Exposure Science and Environmental Epidemiology, 17, 625-636, 10.1038/sj.jes.7500546, 2007.

Carpi, A.: Mercury from combustion sources: a review of the chemical species emitted and their transport in the atmosphere, Water, Air, Soil Pollut., 98, 241-254, 10.1023/A:1026429911010, 1997.

Croghan, C. W., and Egeghy, P. P.: Methods of dealing with values below the limit of detection using SAS, available at: http://analytics.ncsu.edu/sesug/2003/SD08-Croghan.pdf (last access: May 30, 2016), 2003.

Cheng, I., Lu, J., and Song, X.: Studies of potential sources that contributed to atmospheric mercury in Toronto, Canada., Atmos. Environ., 43, 6145-6158, 10.1016/j.atmosenv.2009.09.008, 2009.

Cheng, I., Zhang, L., Blanchard, P., Graydon, J. A., and Louis, V. L. S.: Source-receptor relationships for speciated atmospheric mercury at the Remote Experimental Lakes Area, Northwestern Ontario, Canada, Atmos. Chem. Phys., 12, 1903-1922, 10.5194/acp-12-1903-2012, 2012.

Cheng, I., Zhang, L., Blanchard, P., Dalziel, J., Tordon, R., Huang, J., and Holsen, T. M.: Comparisons of mercury sources and atmospheric mercury processes between a coastal and inland site, J, Geophys. Res-Atmos., 118, 2434-2443, 10.1002/jgrd.50169, 2013.

Cheng, I., Xu, X., and Zhang, L.: Overview of receptor-based source apportionment studies for speciated atmospheric mercury, Atmos. Chem. Phys., 15, 7877-7895, 10.5194/acp-15-7877-2015, 2015.

Cheng, I., Zhang, L., and Xu, X.: Impact of measurement uncertainties on receptor modeling of speciated atmospheric mercury, Scientific Reports, 6, 20676, 10.1038/srep20676, 2016.

Environment Canada (EC): National Pollutants Release Inventory (NPRI) Datasets, available at: https://www.ec.gc.ca/inrp-npri/default.asp?lang=en&n=0EC58C98-1 (last access: May 29, 2016), 2016.

Evers, D. C., Han, Y.-J., Driscoll, C. T., Kamman, N. C., Goodale, M. W., Lambert, K. F., Holsen, T. M., Chen, C. Y., Clair, T. A., and Butler, T.: Biological mercury hotspots in the Northeastern United States and Southeastern Canada, BioScience, 57, 29-43, 10.1641/B570107, 2007.

763 Gaffney, J. S., and Marley, N. A.: In-depth review of atmospheric mercury: sources,
764 transformations, and potential sinks, Energy and Emission Control
765 Technologies, 2, 1-21, 10.2147/EECT.S37038, 2014.
766 Goodsite, M. E., Plane, J. M. C., and Skov, H.: A theoretical study of the oxidation of
767 Hg0 to HgBr2 in the troposphere, Environ. Sci. Technol., 38, 1772-1776,
768 10.1021/es034680s, 2004.
769 Gustin, M. S., Lindberg, S. E., and Weisberg, P.J.: An update on the natural sources
770 and sinks of atmospheric mercury, Applied Geochemistry, 23, 482-493, 2008.
771 Gustin, M. S., Amos, H. M., Huang, J., Miller, M. B., & Heidecorn, K.: Measuring
772 and modeling mercury in the atmosphere: a critical review, Atmos. Chem.
773 Phys., 15(10), 5697-5713. 10.5194/acp-15-5697-2015, 2015.
774 Hedberg, E., Gidhagen, L., and Johansson, C.: Source contributions to PM_{10} and
775 arsenic concentrations in Central Chile using positive matrix factorization,
776 Atmos. Environ., 39, 549-561, 10.1016/j.atmosenv.2004.11.001, 2005.
777 Henry, R. C.: Multivariate receptor models, in: Receptor modeling for air quality
778 management, 1st ed., edited by: Hopke, P. K., Elsevier Science Publishers,
779 Amsterdam, 1991.
780 Holmes, C. D., Jacob, D. J., Mason, R. P., & Jaffe, D. A.: Sources and deposition of
781 reactive gaseous mercury in the marine atmosphere. Atmos. Environ., 43(14),
782 2278-2285, 10.1016/j.atmosenv.2009.01.051, 2009.
783 Hopke, P. K.: Review of receptor modeling methods for source apportionment, J. Air.
784 Waste. Manage., 66, 237-259, 10.1080/10962247.2016.1140693, 2016.
785 Huang, S., Rahn, K. A., and Arimoto, R.: Testing and optimizing two factor-analysis
786 techniques on aerosol at Narragansett, Rhode Island, Atmos. Environ., 33,
787 2169-2185, 10.1016/S1352-2310(98)00324-0, 1999.
788 Huang, J., Choi, H.-D., Hopke, P. K., and Holsen, T. M.: Ambient Hg sources in
789 Rochester, NY: results from principle components analysis (PCA) of Hg
790 monitoring network data, Environ. Sci. Technol., 44, 8441-8445,
791 10.1021/es102744j, 2010.
792 Kaiser, H. F.: The Application of Electronic Computers to Factor Analysis, Educ.
793 Psychol. Meas., 20, 141-151, 10.1177/001316446002000116, 1960.
794 Lee, E., Chan, C. K., & Paatero, P.: Application of positive matrix factorization in
795 source apportionment of particulate pollutants in Hong Kong. Atmos. Environ.,
796 33(19), 3201-3212, 10.1016/S1352-2310(99)00113-2, 1999.
797 Liu, B., Keeler, G. J., Dvonch, J. T., Barres, J. A., Lynam, M. M., Marsik, F. J., and
798 Morgan, J. T.: Temporal variability of mercury speciation in urban air, Atmos.
799 Environ., 41, 1911-1923, 10.1016/j.atmosenv.2006.10.063, 2007.
800 Lynam, M. M., and Keeler, G. J.: Artifacts associated with the measurement of
801 particulate mercury in an urban environment: the influence of elevated ozone
802 concentrations, Atmos. Environ., 39, 3081-3088,
803 10.1016/j.atmosenv.2005.01.036, 2005.
804 Lynam, M. M., and Keeler, G. J.: Source-receptor relationships for atmospheric
805 mercury in urban Detroit, Michigan, Atmos. Environ., 40, 3144-3155,
806 10.1016/j.atmosenv.2006.01.026, 2006.
807 Obrist, D., Tas, E., Peleg, M., Matveev, V., Faïn, X., Asaf, D., and Luria, M.:
808 Bromine-induced oxidation of mercury in the mid-latitude atmosphere, Nat.
809 Geosci., 4, 22-26, 10.1038/ngeo1018, 2011.

Pakkanen, T. A.: Study of formation of coarse particle nitrate aerosol, Atmos. Environ., 30, 2475-2482, 10.1016/1352-2310(95)00492-0, 1996.

Pal, B., and Ariya, P. A.: Studies of ozone initiated reactions of gaseous mercury: kinetics, product studies, and atmospheric implications, Phys. Chem. Chem. Phys., 6, 572-579, 10.1039/B311150D, 2004.

Parmar, R. S., Satsangi, G. S., Kumari, M., Lakhani, A., Srivastava, S. S., and Prakash, S.: Study of size distribution of atmospheric aerosol at Agra, Atmos. Environ., 35, 693-702, 10.1016/S1352-2310(00)00317-4, 2001.

Pavlovic, R. T., Nopmongcol, U., Kimura, Y., and Allen, D. T.: Ammonia emissions, concentrations and implications for particulate matter formation in Houston, TX, Atmos. Environ., 40, 538-551, 10.1016/j.atmosenv.2006.04.071, 2006.

Pekey, H., Karakaş, D., & Bakoglu, M.: Source apportionment of trace metals in surface waters of a polluted stream using multivariate statistical analyses. Marine Pollution Bulletin, 49(9), 809-818, 2004.

Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R.B., Friedli, H.R., Leaner, J., Mason, R., (...), Telmer, K.: Global mercury emissions to the atmosphere from anthropogenic and natural sources. Atmos. Chem. Phys., 10, 5951-5964, 2010.

Pitchford, M. L., Poirot, R. L., Schichtel, B. A., and Malm, W. C.: Characterization of the winter midwestern particulate nitrate bulge, J. Air Waste Manage., 59, 1061-1069, 10.3155/1047-3289.59.9.1061, 2009.

Polissar, A. V., Hopke, P. K., Paatero, P., Malm, W. C., and Sisler, J. F.: Atmospheric aerosol over Alaska: 2. Elemental composition and sources, J, Geophys. Res-Atmos., 103, 19045-19057, 10.1029/98JD01212, 1998.

Rutter, A. P., and Schauer, J. J.: The effect of temperature on the gas-particle partitioning of reactive mercury in atmospheric aerosols, Atmos. Environ., 41, 8647-8657, 10.1016/j.atmosenv.2007.07.024, 2007.

Tekran Inc.: Products. Ambient Air, available at: http://www.tekran.com/products/ambient-air/overview/ (last access: May 29, 2016), 2010.

United Nations Environmental Programme (UNEP): Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport. UNEP Chemicals Branch, Geneva, Switzerland, available at: http://www.unep.org/PDF/PressReleases/GlobalMercuryAssessment2013.pdf (last access: May 30, 2016), 2013.

US Environmental Protection Agency (US EPA): Clean Air Markets: 2010 Progress Report Emission, Compliance, and Market Analyses, available at: https://www.epa.gov/airmarkets/acid-rain-program-historical-reports (last access June 9, 2016), 2011

US Environmental Protection Agency (US EPA): EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide, available at: https://www.epa.gov/sites/production/files/2015-02/documents/pmf_5.0_user_guide.pdf (last access: May 30, 2016), 2014a.

US Environmental Protection Agency (US EPA): Positive Matrix Factorization Model (version 5.0), available at: https://www.epa.gov/sites/production/files/2015-03/epa_pmf_5.0_setup.exe (last access: June 6, 2015), 2014b.

857 Viana, M., Pandolfi, M., Minguillón, M. C., Querol, X., Alastuey, A., Monfort, E.,
858 and Celades, I.: Inter-comparison of receptor models for PM source
859 apportionment: case study in an industrial area, Atmos. Environ., 42,
860 3820-3832, 10.1016/j.atmosenv.2007.12.056, 2008.
861 Wyn, B., Kidd, K. A., Burgess, N. M., Curry, R. A., and Munkittrick, K. R.:
862 Increasing mercury in yellow perch at a hotspot in Atlantic Canada,
863 Kejimkujik National Park, Environ. Sci. Technol., 44, 9176–9181,
864 10.1021/es1018114, 2010.
865 Zhang L., Vet R., Wiebe A., Mihele C., Sukloff B., Chan E., Moran M., and Iqbal S.:
866 Characterization of the size-segregated water-soluble inorganic ions at eight
867 Canadian rural sites, Atmos. Chem. Phys., 8, 7133-7151, 2008.
868 Zhang L., Wang S., Wu Q., Wang F., Lin C.-J., Zhang L., Hui M., and Hao J.:
869 Mercury transformation and speciation in flue gases from anthropogenic
870 emission sources: A critical review, Atmos. Chem. Phys., 16, 2417-2433,
871 2016.
872

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

873 **List of Tables**

888

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

889 **List of Figures**

896

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Table 1. General statistics of air pollutant concentrations (in μg/m^3 unless otherwise noted) in 2009.

Compound	Percent of missing values	Method detection limit (MDL)	Percent of values <MDL	Geometric Mean	Median	Mean	Standard deviation	Coefficient of variability (%)
GEM (ng/m^3)	31%	0.1	0%	1.37	1.41	1.39	0.26	18.7
GOM (pg/m^3)	32%	2	78%	0.57	0.42	1.77	3.70	209
PBM (pg/m^3)	41%	2	48%	1.78	2.15	2.81	2.72	96.8
PM	20%	1	9%	2.71	2.91	3.44	2.49	72.4
O_3	0%	4.3	0%	59.4	62.1	62.4	19.1	30.6
SO_2	3%	0.002	0%	0.20	0.22	0.40	0.51	128
HNO_3	3%	0.05	12%	0.13	0.12	0.19	0.22	116
Ca^{2+}	1%	0.002	0%	0.05	0.05	0.06	0.04	66.7
K^+	1%	0.029	17%	0.04	0.03	0.04	0.03	75.0
Na^+	1%	0.05	9%	0.25	0.30	0.43	0.47	109
Mg^{2+}	1%	0.0004	2%	0.04	0.04	0.06	0.06	100
Cl^-	1%	0.046	23%	0.19	0.23	0.46	0.64	139
NO_3^-	1%	0.06	9%	0.18	0.17	0.28	0.39	139
NH_4^+	1%	0.001	0%	0.19	0.17	0.28	0.32	114
SO_4^{2-}	1%	0.05	0%	0.78	0.76	1.14	1.27	111

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Table 2. General statistics of air pollutant concentrations (in μg/m^3 unless otherwise noted) in 2010, MDL same as in Table 1.

Compound	Percent of missing values	Percent of values <MDL	Geometric Mean	Median	Mean	Standard deviation	Coefficient of variability (%)
GEM (ng/m^3)	4%	0%	1.34	1.38	1.35	0.17	12.6
GOM (pg/m^3)	4%	96%	0.27	0.21	0.44	0.64	145
PBM (pg/m^3)	4%	46%	2.08	2.20	3.40	4.13	121
O_3	1%	0%	62.2	63.4	64.5	16.6	25.7
SO_2	19%	1%	0.10	0.13	0.23	0.31	135
HNO_3	19%	25%	0.10	0.10	0.18	0.22	122
Ca^{2+}	19%	0%	0.04	0.04	0.07	0.13	186
K^+	19%	46%	0.04	0.03	0.06	0.07	117
Na^+	19%	16%	0.20	0.24	0.40	0.53	133
Mg^{2+}	19%	0 %	0.03	0.04	0.05	0.06	120
Cl^-	19%	27%	0.14	0.15	0.46	0.83	180
NO_3^-	19%	21%	0.14	0.13	0.25	0.36	144
NH_4^+	19%	0%	0.16	0.15	0.30	0.57	190
SO_4^{2-}	19%	0%	0.69	0.64	1.11	1.65	149

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Table 3. PMF case design with different treatments of speciated Hg data.

Case		Input variables	Treatment of missing value	Sample size	
2009	2010			2009	2010
2009 (base case)	2010 (base case)	All compounds	Excluding listwise	161	290
09+Mean	10+Mean	All compounds	Geometric mean imputation	365	365
09+Median	10+Median	All compounds	Median imputation	365	365
09+RM	10+RM	All compounds, but combining GOM & PBM to RM	Excluding listwise	161	290
09-RM	10-RM	All compounds, except GOM & PBM	Excluding listwise	201	290
09ScaleRM	10ScaleRM	All compounds, GOM & PBM scaled	Excluding listwise	161	290

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Table 4. PCA input and set-up.

Case	Year	Input variables	Sample size	Other settings
09-C	2009	All compounds	161	1) Missing value: Listwise deletion
09-C&M	2009	All compounds and meteorological parameters	159	2) Components to keep: eigenvalues >1)
10-C	2010	All compounds	290	3) Rotation: Varimax
10-C&M	2010	All compounds and meteorological parameters	285	4) Cut-off value for major loadings: 0.25

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Table 5. Factor profiles (concentration >25%, between 20% and 25% in parenthesis) of Case 2009 and Case 2010.

	2009				2010			
Compound	F1	F2	F3	F4	F1	F2	F3	F4
GEM			76				79	
GOM	31		69			37	59	
PBM		29	63				81	
PM	42		34		-	-	-	-
O_3			72				80	
SO_2		82				93		
HNO_3	54	(21)	(25)		64	26		
Ca^{2+}	(19)		45	31		29	36	(21)
K^+	(22)		37	39	51		27	(23)
Na^+				86				83
Mg^{2+}				83				75
Cl^-				100				100
NO_3	(25)	(23)		40		41	(23)	
NH_4^+	71				87			
SO_4^{2-}	64				79			
Factor	Combustion emission	Industrial sulfur	Photochemistry & re-emission of Hg	Sea salt	Combustion emission	Industrial sulfur	Photochemistry & re-emission of Hg	Sea salt

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Table 6. PMF model performances on speciated mercury in 2009 and 2010.

Hg form	Case	Distribution	Number of scaled residuals greater than 3	Coefficient of determination (R^2)	Slope of regression line
GEM	09	Normal	0	0.28	0.59
	09+mean	Concentrated near zero	5	0.17	0.57
	09+median	Concentrated near zero	5	0.15	0.54
	09+RM	Normal	0	0.29	0.59
	09-RM	Normal	1	0.25	0.59
	09ScaleRM	Normal	0	0.28	0.58
	10	Normal	2	0.46	1.29
	10+mean	Normal	19	0.32	1.26
	10+median	Normal	2	0.41	1.26
	10+RM	Normal	2	0.46	1.31
	10-RM	Normal	2	0.47	1.31
	10ScaleRM	Normal	1	0.44	1.19
GOM	09	Right skewed	17	0.23	0.09
	09+mean	Concentrated near zero, right skewed	17	0.08	0.05
	09+median	Concentrated near zero, right skewed	19	0.09	0.05
	09+RM	-	-	-	-
	09-RM	-	-	-	-
	09ScaleRM	Right skewed	26	0.33	0.18
	10	Narrower	0	0.31	0.29
	10+mean	Narrower	0	0.23	0.22
	10+median	Narrower	0	0.28	0.28
	10+RM	-	-	-	-
	10-RM	-	-	-	-
	10ScaleRM	Narrower	0	0.42	0.33
PBM	09	Normal	5	0.57	0.39
	09+mean	Right skewed	6	0.33	0.32
	09+median	Right skewed	6	0.34	0.34
	09+RM	Right skewed (RM)	8 (RM)	0.48(RM)	0.31(RM)
	09-RM	-	-	-	-
	09ScaleRM	Left skewed	2	0.59	0.48
	10	Right skewed	14	0.13	0.09
	10+mean	Right skewed	28	0.15	0.09
	10+median	Right skewed	29	0.16	0.08
	10+RM	Right skewed (RM)	5	0.19	0.15
	10-RM	-	-	-	-
	10ScaleRM	Normal	18	0.25	0.24

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Table 7. PCA component loadings (>0.25) of Case 09-C and Case 09-C&M.

Variable	Case 10-C				Case 10-C&M				
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4	PC5
GEM			0.86	0.27				0.80	
GOM			0.26	0.84			0.64	0.41	-0.29
PBM	0.63		0.50	-0.33	0.59		-0.47	0.34	
PM	0.80				0.81				
O_3	0.50		0.70		0.47			0.72	-0.27
SO_2	0.88				0.86				
HNO_3	0.86			0.34	0.88				
Ca^{2+}	0.59	0.39		0.45	0.60	0.38	0.33		
K^+	0.29	0.70		0.33	0.36	0.66	0.39		
Na^+		0.97				0.96			
Mg^{2+}		0.95			0.28	0.95			
Cl^-		0.97				0.98			
NO_3^-	0.73	0.48			0.76	0.45			
NH_4^+	0.92				0.94				
SO_4^{2-}	0.86				0.88				
Temperature	-	-	-	-			0.94		
Relative humidity	-	-	-	-	-0.26				0.79
Wind speed	-	-	-	-		0.32		0.52	0.49
Precipitation	-	-	-	-					0.79
Component	Combustion/ industrial emission	Sea salt	Photochemical production of GOM	Gas-particle partition of Hg	Combustion/industrial emission	Sea salt	Gas-particle partition of Hg	Photochemical production of GOM	Hg wet deposition
Variance explained	37%	25%	11%	9%	30%	20%	10%	10%	9%

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Table 8. PCA component loadings (>0.25) of Case 10-C and Case 10-C&M.

Variable	Case 10-C				Case 10-C&M				
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4	PC5
GEM			0.79				0.87		
GOM			0.71	0.33			0.51	-0.51	0.38
PBM			0.48				0.29	-0.62	
O_3			0.91				0.87		
SO_2				0.89					0.84
HNO_3	0.34			0.83	0.33				0.82
Ca^{2+}	0.89				0.89				
K^+	0.77				0.77				
Na^+		0.99				0.99			
Mg^{2+}	0.34	0.93			0.34	0.92			
Cl^-		0.98				0.97			
NO_3^-	0.79				0.80				
NH_4^+	0.94				0.94				
SO_4^{2-}	0.90			0.26	0.89				0.26
Temperature	-	-	-	-	0.27		-0.52		0.27
Relative humidity	-	-	-	-				0.74	-0.33
Wind speed	-	-	-	-		0.26	0.52	0.57	
Precipitation	-	-	-	-				0.76	
Component	Combustion emission	Sea salt	Photochemical production of GOM	Industrial source	Combustion emission	Sea salt	Photochemical production of GOM	Hg wet deposition	Industrial source
Variance explained	28%	21%	16%	13%	22%	17%	14%	12%	10%

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Table 9. General statistics of speciated Hg with different data treatment options.

a) 2009

Hg form	Case	Percent of missing values	MDL	Percent of values <MDL	Geometric Mean	Median	Mean	Standard deviation
GEM (ng/m^3)	09	31%	0.1	0%	1.37	1.41	1.39	0.28
	09+mean	0%		0%	1.37	1.37	1.38	0.22
	09+median	0%		0%	1.38	1.41	1.39	0.22
GOM (pg/m^3)	09	32%	2	73%	0.57	0.42	1.77	3.98
	09+mean	0%		86%	0.57	0.57	1.39	3.11
	09+median	0%		86%	0.51	0.42	1.34	3.12
	09+RM	-		-	-	-	-	-
	09Scale RM	32%		16%	3.91	3.35	5.02	5.49
PBM (pg/m^3)	09	41%	2	37%	1.79	2.15	2.81	2.71
	09+mean	0%	2	70%	1.79	1.79	2.39	2.14
	09+median	0%	2	28%	1.93	2.15	2.53	2.11
	09+RM	42%	4 (RM)	52%	2.73	3.02	4.69	5.56
	09Scale RM	41%	2	4%	5.52	6.05	6.19	3.15

b) 2010, MDL same as in a)

Hg form	Case	Percent of missing values	Percent of values <MDL	Geometric Mean	Median	Mean	Standard deviation
GEM (ng/m^3)	10	4%	0%	1.33	1.37	1.34	0.17
	10+mean	0%	0%	1.34	1.37	1.35	0.16
	10+median	0%	0%	1.34	1.38	1.35	0.17
	10+RM	4%	0%	1.33	1.37	1.34	0.17
	10ScaleRM	4%	0%	1.33	1.38	1.34	0.17
GOM (pg/m^3)	10	4%	96%	0.29	0.26	0.49	0.69
	10+mean	0%	96%	0.27	0.24	0.43	0.63
	10+median	0%	96%	0.27	0.21	0.43	0.63
	10+RM	-	-	-	-	-	-
	10ScaleRM	4%	67%	1.15	1.12	1.40	0.86
PBM (pg/m^3)	10	4%	51%	1.79	1.92	2.59	2.67
	10+mean	0%	44%	2.08	2.12	3.35	4.04
	10+median	0%	44%	2.08	2.20	3.35	4.04
	10+RM	4%	75%	2.16	2.31	3.08	2.95
	10ScaleRM	4%	1%	6.15	6.38	6.75	3.01

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

Atmospheric Chemistry and Physics Discussions

Table 10. Impact of combining or excluding GOM and PBM on PMF factor contributions (>15%) to Hg compounds.

Case	Combustion emission	Industrial sulfur	Photochemistry and re-emission	Sea salt
Case 2009	GOM	PBM	GEM, GOM, and PBM	
Case 09+RM		RM	GEM and RM	
Case 09-RM			GEM	
Case 2010		GOM	GEM, GOM, and PBM	
Case 10+RM			GEM and RM	
Case 10-RM			GEM	

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

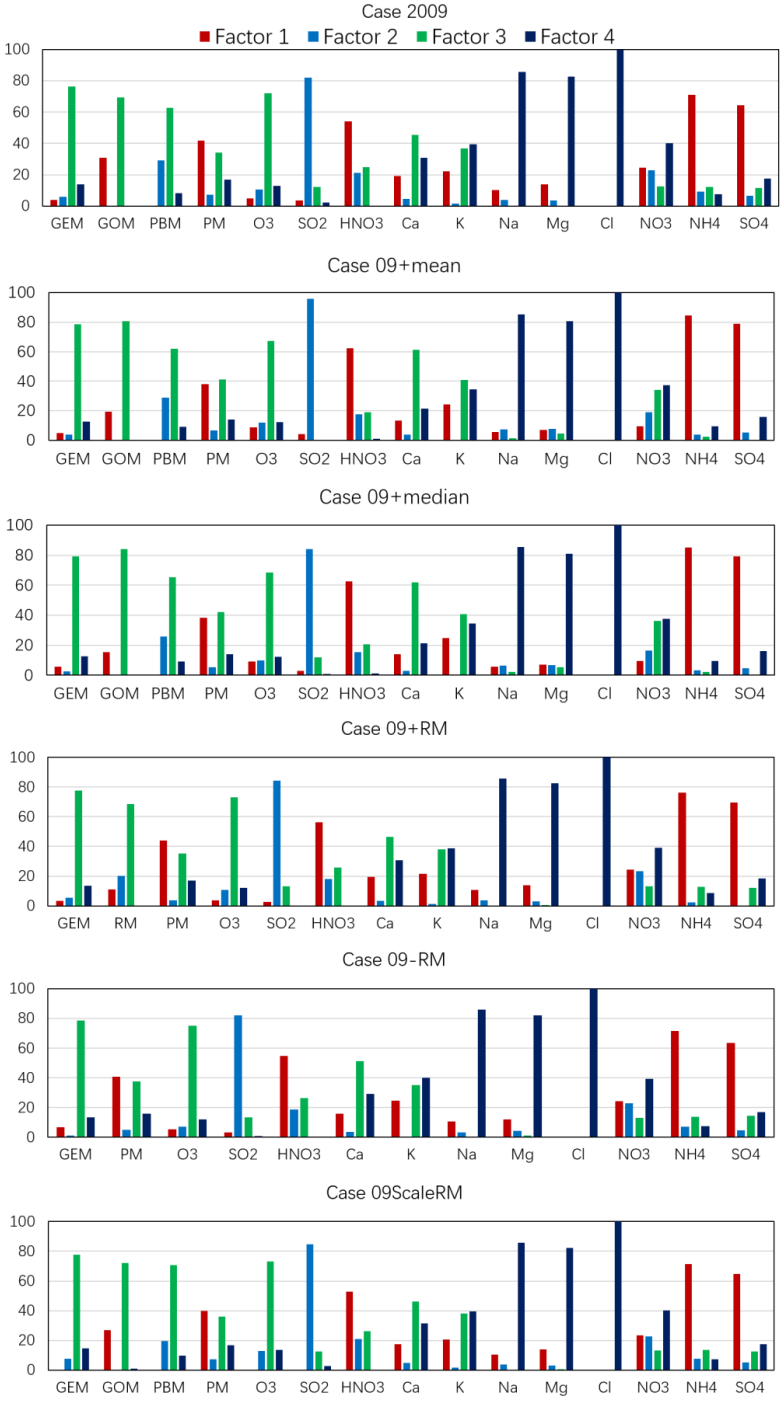

Figure 1. PMF source profiles in percent of concentration, 2009.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

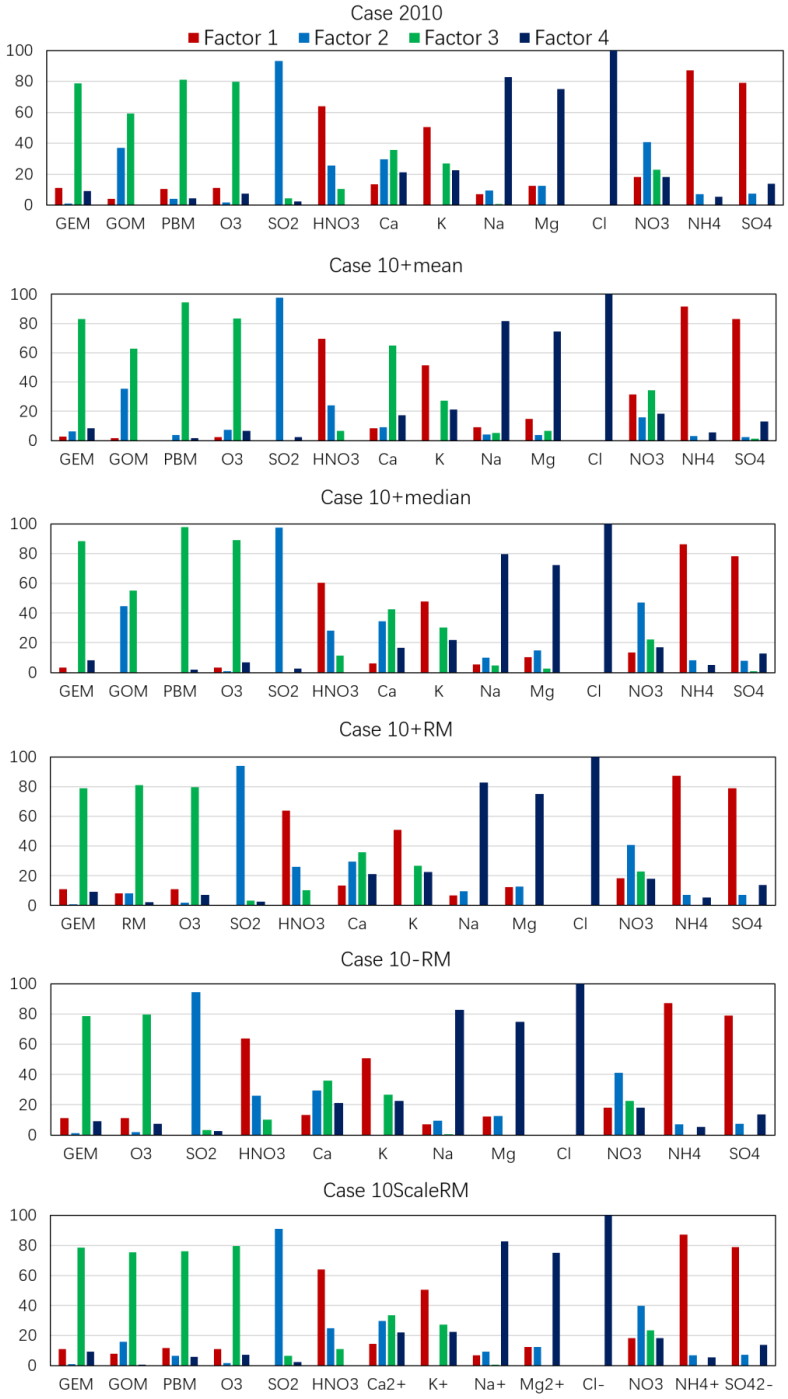

Figure 2. PMF source profiles in percent of concentration, 2010.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-516, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 29 June 2016

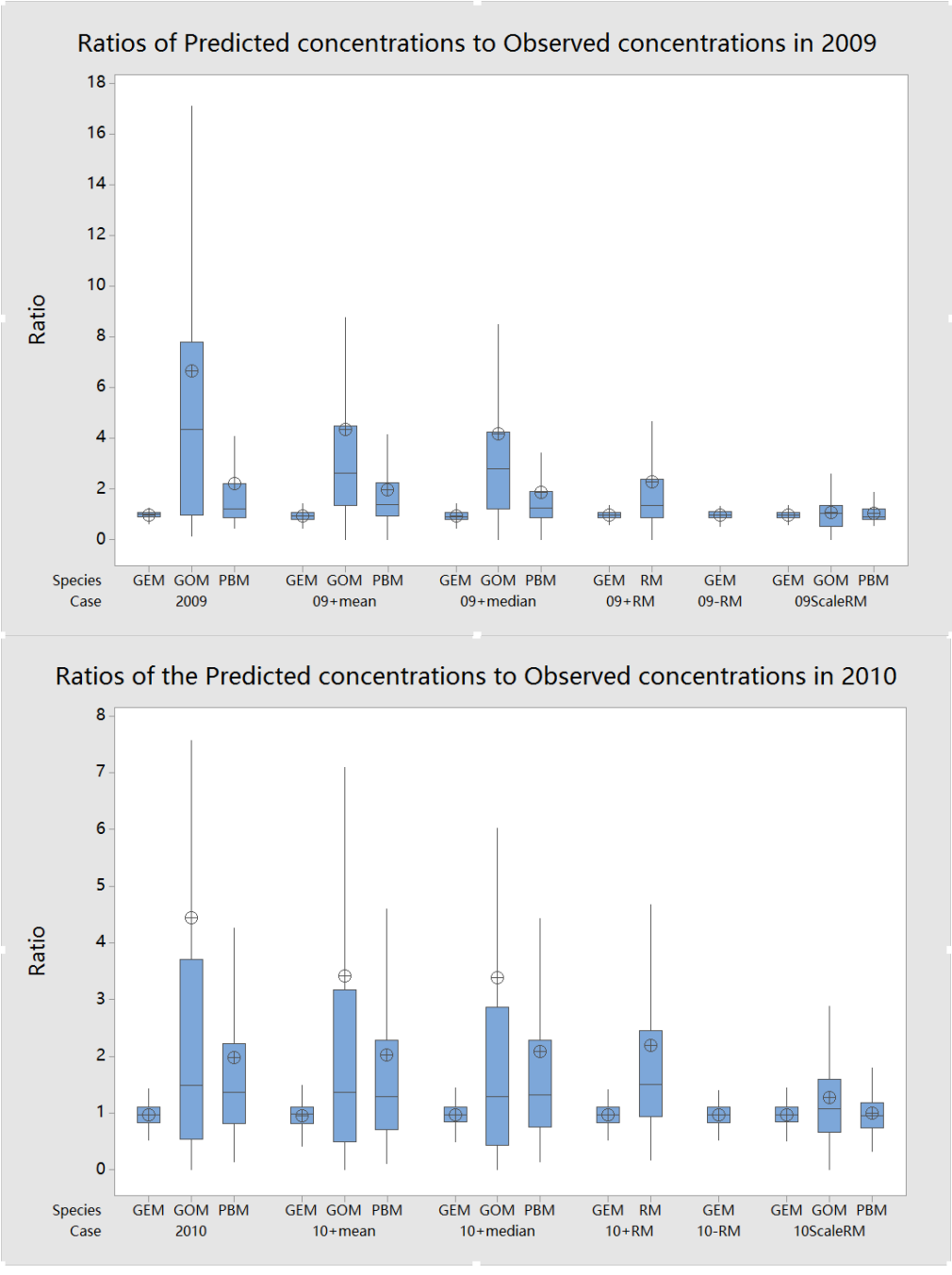

Figure 3. Box plot of predicted to observed concentration ratios (upper whisker- upper 25% of the distribution excluding outliers; interquartile range box - middle 50% of the data; horizontal line in the box - median; lower whisker- lower 25% of the distribution excluding outliers;⊕ - mean).