Anonymous Referee #1
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General Comments

This manuscript details the seasonal and annual variation in gaseous elemental mercury (Hg0), reactive gaseous mercury (RGM), and particulate mercury (HgP) at 3 sites in New England. Initially I thought this was very new and innovative work. However, upon closer examination I am a little concerned that this may be a "data mining" expedition, presenting little if any new valid information. The "data mining" will likely result in another similar paper in the near future since the study is ongoing. There is a distinct lack of differentiation between this and their 2008 study. I am not sure that anywhere in the paper does it say "unlike in our 2008 study" (or anything similar), if there is I am sorry it just didn't stand out. I am also concerned that the trends may not be as significant as the authors point out due to reasons discussed below. Unfortunately based on the criteria set forth by ACP I am not sure this paper is publishable as a standalone article.

All in all I think the relevant data from this article could be distilled and presented in one of the other manuscripts currently being published in this series (Part 2 or 3). If it is to remain as a standalone article major revisions are needed in order to prove that new, novel information is being presented here and the trends are real, and not just a data mining expedition. Also the presentation needs to streamlined and the number of figures reduced to less than 13.

We acknowledge the presentation of the datasets may not have successfully drawn the reviewer's attention to the difference in this study compared to Mao et al. (2008). We have made major revisions to the paper based on the reviewer's suggestions and comments and to underscore the distinction between our previous work and this study. The major difference between this paper and Mao et al. (2008) is summarized as follows:

1. New datasets. Our 2008 paper presented Hg° data only at the three sites. In this paper, we presented datasets of Hg°, RGM, and Hg^P at the three sites.

2. The length of the datasets. Our 2008 paper presented 3.5 years of Hg° at Thompson Farm, ~ 2 years at Pac Monadnock, and 2 months at Appledore Island. This paper covered Hg° data spanning over 7.5 years at Thompson Farm, ~ 5.5 years at Pac Monadnock, and over 3 years at Appledore Island. These extended datasets allowed us to obtain trends in background Hg° at two of the sites.

   In addition, we covered new data including ~ 4, 2, and 3 years of RGM data at Thompson Farm, Pac Monadnock, and AI, respectively, and 1.5 years of Hg^P data at Thompson Farm and Appledore Island.

3. Findings. In Mao et al. (2008), with Hg° data only over a much shorter study period at mainly two sites (only 2 months data at AI), we presented variabilities in Hg° at the three sites, and with less data we were able to study the variabilities in-depth by examining the relationships between Hg° and other chemical compounds such as CO, CO_2, NO_y, SO_2 etc. and impact of change in winter climate, and estimating the Hg° dry deposition. In this study, much longer datasets of Hg° at the three sites suggested some features in their variabilities that are similar to those in the previous work such as the seasonal average diurnal cycles and annual cycles at two sites Thompson Farm and Appledore Island. What is new is:

    1.) Diurnal to interannual variabilities in Hg° in the marine environment (Appledore Island),

    2.) A hypothesis that the nighttime low level of Hg° at the coastal site was largely attributed to Hg° dissolved in dew water,

    3.) Decline trends in background Hg° at the coastal and inland sites,

    4.) Diurnal to interannual variabilities in RGM and Hg^P in three different environments, and

    5.) Interannual variability in the warm season decline and cool season rise of Hg°.

In this study we were dealing with much more massive datasets than we did in Mao et al. (2008). To be honest, we set out to write one paper on the temporal variabilities in speciated mercury at the three sites and their relationships with physical (climate) variables and chemical compounds. This was reflected in our poster at the 2010 Fall AGU meeting. However, as the work progressed, we felt it was not realistic to pack all that amount of information into one single paper and hence we decided to write three papers, Part I on the key characteristics of spatial and temporal variabilities in speciated mercury, Part II on the relationships between speciated mercury and physical parameters, and Part III on the relationships between speciated mercury and other trace gases. Even with this plan of work Part II has already been commented by both reviewers as being too complex; should we combine Parts I and II, it would make the publication of this work very difficult.

Lastly, measurements at all three sites are no longer ongoing, and the authors have moved on to different universities.

Specific Comments

1) There are very few differences between this paper and their 2008 paper. Also, if monitoring is continuing at these sites, what is the real point of this paper? Would it not be more advantageous to wait until more data is collected to actually identify trends at all sites?

Please see our response above.

2) The authors report a significant negative trend in Hg0 concentrations that is below the detection limit of their analyzer (10 ppqv). This is potentially the most significant result of the study, but no indications of the statistical significance of this relationship are given. Therefore, I am not convinced that this trend is real. Much more explanation needs to be given on the possible factors (i.e. climatology, emission inventories, etc.) that may be influencing these trends. See Steffen, A., W. Schroeder, et al. (2005). "Mercury in the Arctic atmosphere: An analysis of eight years of measurements of GEM at Alert (Canada) and a comparison with observations at Amderma (Russia) and Kuujjuarapik (Canada)." Science of the Total Environment 342(1-3): 185-198.

The total change of the background Hg° level at Thompson Farm from 2003 to 2010 was around -22 ppbv and was estimated from the slope value of the regression line in Figure 3.

We agree with the reviewer that this negative trend in background Hg° levels can potentially be the most significant result of the study. We have added the statistical significance test of the trend. We used the Student's t-test (Wilks, 1995) to test the statistical significance of the trend. For the 79 monthly median background Hg° mixing ratios at Thompson Farm, the calculated t-value is -3.051, exceeding the critical t-value 1.664 for one-sided t-distribution at the 95% confidence interval. For the 64 monthly median background Hg° mixing ratios at Pack Monadnock, the calculated t-value is 4.344, exceeding the critical t-value 1.671 for one-sided t-distribution at the 95% confidence interval. Therefore, the decline trends at the two sites are statistically significant. Results of these tests have been added into the text now. See lines 262 – 267 on pages 11-12.

Currently we are working to unravel the potential causal factors for these decline trends. It is a challenging study, as demonstrated in Steffen et al. (2005), the reference provided by the reviewer and Slemr et al. (2011, ACP). These trends most definitely need to be examined for possible influences from climate, emissions, and chemistry, as the reviewer keenly pointed out. Slmer et al. (2001, ACP) dedicated the entire study to unravel the potential causal mechanisms for the decline trend. Since this paper is the first part of a three part series, we intended for it to serve to provide the important characteristics in the time series of speciated mercury at the three sites, and thus we strived to cover the breadth, admittedly not the depth. Therefore we would like to point out that we did not intend to gloss over such an important result, which was stated in lines 4-5 on page 32310 that “we will investigate the possible factors that might have contributed to these trends in a separate paper (Mao et al., 2011b)”.

3) I have problems with the discussion of Hg0 increase or decrease rates in “warm” and “cold” seasons (p. 32308 line 1). This discussion is confusing and vague. How were the rates calculated? Were they simply calculated with the single maximum and minimum concentrations then “scaled” to a daily rate? Were they calculated from single data points, daily means on single days, points from a moving average, etc.? The calculation of these rates was also not discussed in the 2008 paper. Depending on the values used these rates may be misleading. Does a single 5 minute point “high” or “low” point influence the “rate”? If daily means (or medians) are used how does this affect the rate. Before I can believe conclusions drawn from these “rates” I need to be convinced of exactly what they are representing. There are also no statistics presented to show whether the differences in these “rates” are actually statistically different by site. Significant further explanation is needed. Also if only two points in the calculation of this rate, the entire discussion of this rate is focusing on only two points in a very large dataset collected each year at each site, therefore may not be an actual representation of the temporal variability at the sites.

The “warm” and “cool” seasons were defined in lines 2-6 on page 32308: “The warm season spans the time period between the times of the annual maximum and minimum, approximately 1April to 30 September at TF, 1 March to 31 October at AI, and 1 March to 31 October at PM. The cool season extends from the time of the annual minimum to that of the following annual maximum.” In another word, the warm and cool seasons represent the growth and senescence seasons, respectively.

The rates were calculated based on the slope values of the linear trend that was fitted through all the data points, in 5-minute average, from the warm and cold seasons as defined above for every year. Therefore, the calculation of these trends did not involve only one or two single maximum and minimum points, daily means on single days, or points from a moving average etc., and a single 5 minute “high” or “low” point would not be able to influence the “rate”.

These rates were quantitatively determined to describe the annual cycle of Hg°, and they were used to describe interannual variability and site difference of the annual cycle of Hg°.

4) Is there a precedent for removing mercury data at “CO below its 25th percentile?” How much data is removed by doing this? What happens if this data is left in? The decreasing “trend” in Hg0 concentrations is probably the most significant finding of the article but very little time is devoted to proving that this trend is real. No statistics, etc. It is completely buried and “glossed over.”

Mercury data at “CO below its 25th percentile” value were not removed; instead, they were considered to represent “background air”. This is the subset of data that was used to study the trend in the background Hg° level.

CO is an excellent anthropogenic tracer because it mostly comes from mobile combustion. Using low percentile values of CO is a common practice in literature to pick out background air masses, such as Lin, Jacob, Munger, and Fiore’s 2000 GRL paper. Slemr et al. (2011) and Ebinghaus et al. (2011) used wind direction to pick out background air masses. At our sites, since we have concurrent measurements of CO, we used the CO data to gauge anthropogenic influence on our sites.

In doing so, we used 5-minute average data of CO and Hg° without missing values. Therefore the Hg° data that were selected to represent background air masses were 25% of the total data set. We included these details for clarification. See lines 168 – 174 on pages 7-8.

As we stated above, in our response to Specific Comment #2, we did not gloss over this result; we intend to address it in-depth in a separate study (See lines 4-5, page 32310).

Technical Suggestions:

I suggest the authors give the manuscript a significant editing. Possibly having an outside person read the document. Here are my suggestions but there may be more needed:

1) P. 32302 line 2. Should be “reactive gaseous mercury” not reactive mercury.

Corrected.

2) p. 32302 line 5. What is meant by elevated? Elevated concentrations? Elevation?

The site is 700 m above ground level as stated on p. 32305, line 7. Hence it was referred to as an elevated site in this paper.

3) P. 32308 line 1. The choice of the authors to refer to a “warm” and “cold” season is very ambiguous and confusing, since the “warm” and “cold” seasons are defined by mercury concentrations. I think. This needs more clearly explained.

The warm and cool seasons were defined in lines 2-6 on page 32308: “The warm season spans the time period between the times of the annual maximum and minimum, approximately 1April to 30 September at TF, 1 March to 31 October at AI, and 1 March to 31 October at PM. The cool season extends from the time of the annual minimum to that of the following annual maximum". In another word, the "warm" and "cool" seasons correspond to the growth and senescence seasons.

An annual cycle of Hg° consists of the decreasing trend in the growth period describing how fast the Hg° mixing ratio decreases from the annual maximum to the minimum, and the increasing trend in the senescence period showing how fast the Hg° mixing ratio increases from the annual minimum to the maximum. The magnitude of these two trends is determined by source and sink strengths, and the interannual variability in these trends can shed light on how these source and sink strengths might have changed from year to year. Revisions have been made to reflect these points. See lines 206 – 211 on page 9.

4) P. 32308 line 27: Add "of" between "decline rate" and "0.6" 5) P. 32308 line 28: Add "rate of" between "minimum" and "0.1"

Added.

6) P. 32308 line 28: Add "in" between "resulting" and "a total"

Added.

7) P. 32309 line 20-21: How much of the data was "parsed out"? Were there significant differences between the entire dataset and parsed set? More discussion and justification is needed here.

See our response to Specific Comment #4.

8) P. 32310 line 6-7: Upper range of mixing ratios for where? Global? Regional?

This sentence has been revised as follows:

"The complete time series of RGM exhibited distinct annual cycles in the occurrence of higher mixing ratios at TF and AI."

See lines 279 – 280 on page 12.

9) P.32310: no statistics are presented on the differences among the sites. So discussions of the differences among sites and their causes may not be valid.

The LOD of our RGM measurement is 0.1 ppqv. It is fair to state that the median or 90th percentile values at the sites are different when their difference is several times to an order of magnitude larger than the LOD. This paragraph has been revised. See lines 279 – 290 on pages 12 – 13.

10) P. 32311 line 5: “Hg0:” – bad form and does not fit with the style of the Seasonal and annual variations section

A subsection for Hg° was made as “3.2.1 Hg°”.

11) P. 323313 line 18: “RGM:” see above

A subsection for RGM was made as “3.2.2 RGM”.

12) P. 32314 line 13: “HgP:” see above

A subsection for Hg^P was made as “3.2.3 Hg^P”.

13) Figures 6 through 13 could be streamlined by only including the panels that are worthy of discussion.

Per the reviewer’s suggestion, we removed previous Figures 6, 7, and 8, and combined the seasonal average diurnal cycles of Hg° for summers at TF and AI into the new Figure 7. The previous Figure 11 for the seasonal diurnal cycles of RGM at PM was removed. We combined previous Figures 11 and 12 into the new Figure 10. We moved Table 1 into the Supplementary Material section and made the new Figure 3 of the values from that table.