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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Mercury deposition in southern New Hampshire, 2006–2009" *by* M. A. S. Lombard et al.

M. A. S. Lombard et al.

mas3@cisunix.unh.edu

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General response to reviewers' comments.

We are grateful to the reviewers for many helpful comments and suggestions. The purpose of this paper was to provide an overview of the multi-year Hg wet deposition dataset from Thompson Farm, examine possible relationships with concurrent meteorological and gas phase measurements, and compare the RGM measurements and dry deposition estimates to Hg wet deposition. We have emphasized these points more in the revised text while taking the reviewers' comments into consideration. The evidence our data provide for a lack of RGM scavenging by winter snow is also emphasized more in the revised manuscript. Our use of the word trends instead of patterns was an oversight. Statistical comparisons between seasonal wet deposition data were

non-parametric. The data were tested for normality and do not follow a normal distribution. Some of the data are not log-normal therefore non-parametric correlations were calculated. As stated in several review papers, confirmed in our review of the literature, there are very few studies that measure both RGM and wet deposition concurrently and over extended time periods. The studies that are included have data relevant to the region and certainly provide enough information to calculate annual ratios of wet to RGM dry deposition.

Specific comments from each reviewer are addressed below. The reviewers' comments are italicized followed by our response in standard type.

REVIEWER #2 Comments

Specific Comments: It is suggested that the authors eliminate the first two sentences of the abstract and please rewrite the third sentence as a simple declarative statement.

Response: The opening sentences have been revised to discuss all types of Hg deposition as suggested by Reviewer #1 (see lines 22-23).

Page 4570, line 9: change the word occurred to was measured.

Response: Changed. See line 28.

Page 4570, line 11: Inter-annual differences of what? Please specify. Be careful of conclusions drawn in this abstract based on potential auto-correlations. Eliminate the last sentence of the abstract or develop that line of discussion better in the main body of the manuscript.

Response: Specified the inter-annual differences in total wet deposition (line 29). The last sentence is eliminated.

Page 4571, line 3-5: Please re-write to clarify statement.

Response: Sentence is re-written (see lines 53-54).

Page 4571, line 12: Other explanations include differences in weather patterns/storms, oxidative potential of the atmosphere, proximity to various emission sources, etc, etc. Please include a more full discussion. The patterns of the various species of mercury in ambient air depend on many variables.

Response: While the authors agree these are all explanations for differences in ambient mercury this paragraph is about wet deposition.

Page 4571, line 25: The sentence starting "Contradictory. . ." is confusing. Please rewrite.

Response: Contradictory is changed to inconsistent (see line 72).

Page 4572, line 2: needs a reference.

Response: Mason and Sheu, 2002 reference added (see line 78-79).

Page 4572, line 5: This paragraph needs to provide better information. The Bow Power Plant, locate NW of the monitoring site has SCR for NOx control. This results in substantial RGM emissions. Once the plant undergoes additional pollution controls the RGM emissions will be significantly reduced. The Bow plant is an important emission source that may influence deposition.

Response: While the authors agree with the reviewer that the Bow power plant may influence Hg deposition at TF, the determination of Hg emission sources influencing deposition at TF is not the focus of this study.

Page 4572, line 12: Please include in the main discussion comparative information from these MDN sites. Historical data provide windows to understanding current patterns.

Response: A paragraph is added that compares the available historical data to the current data. See lines 254-266.

Page 4572, line 20: Neither the NADP/NTN nor the MDN networks provide weekly

integrated samples.

Response: This sentence is re-written. Integrated was a poor word choice and we did not mean to imply wet + dry deposition. See lines 101-102.

Page 4572, line 23: I believe that the Underhill site also measured (and still measures) ambient air mercury species. Contact Eric Miller. There are other similar sites located in NJ (operated by Rutgers). I also believe that additional sites exist in Canada and elsewhere in the United States.

Response: In the literature there are Canadian sites that measure Hg(0) and wet deposition concurrently but we have not seen any additional studies that report RGM with wet deposition. We were looking specifically for sites measuring RGM and Hg wet deposition. We do not discuss Hg(0) measurements in this manuscript. Similarly a Burke et al. (1995, Water, Air, and Soil Pollution) discuss ambient measurements of Hg(0) at Underhill. Eric Miller did not respond to my e-mail. No published information was found about sites in NJ.

Page 4573, line 1: Why did you pick the Maine sites only? Please explain.

Response: The Maine locations were chosen because they are the sites nearest to TF. ME96 and ME98 are also similar to TF in their proximity to the coast. The Maine sites and TF are also located north-northeast of the major east coast cities. We have further justified our choice in lines 234-236.

Page 4573, line 24-25: How do you define an event. You use a 12 hour no precipitation period to define two separate events. Does a warm front followed by a cold front six hours later comprise one event? Are they two events with two separate meteorological characteristics? This needs to be clarified in the text since you may be sampling two separate events, but reporting only one event. [see Page 4575.]

Response: Yes according to our definition, a warm front followed by a cold front six hours later would comprise one event. We did not do a detailed meteorological analy-

sis of the cause of precipitation events (warm front, cold front, convective, hurricane). Explanation in text added (see lines 170-174).

Page 4573: How efficient were the ppt samplers during the winter snows? Sample bottle preparation appears to be different from those used by MDN. How likely are these differences to cause bias? What method was followed by bench chemists when analyzing precipitation for mercury? Was the protocol used by Frontier Geochemical used and if so were there differences in methods?

Response: Sampling collection efficiency during the winter months was more variable than during the other seasons of the year and a brief discussion of is added (see lines 320-332). The authors believe that improvements in the collection techniques for snow are needed and the publication of Nelson et al. (2008, Applied Geochemistry) contains important contributions to this area of research.

Sample bottle preparation and cleaning are modifications of EPA method 1631. The cleaning methods used in this study are more rigorous than those used by the MDN. In addition, we collected bottle blanks prior to every sample deployment to ensure no contamination from the bottles. Based on marine mercury studies and the fact that our water had very low mercury blanks (due in part to treatment with a UV source), we used a lower quantity (1.25 ml) of a higher concentration (6N) HCl in the preservation pre-charge solution than the MDN network which reports using 20ml of 0.12M HCl. These approaches are nearly equivalent when the final pre-charge solutions are brought up in 1 L of water, but we found that using a slightly stronger acidic solution helped reduce our blanks. These slight modifications of EPA method 1631 are unlikely to introduce bias and if anything have improved our capability to measure low-volume deposition events precisely and accurately. The authors followed modifications of EPA method 1631 as recommended in the Tekran 2600 user manual when analyzing samples.

Page 4575: Sigler et al., 2009 indicate that RGM measurements began in the winter of 2006. The manuscript indicates that RGM measurements began in November 2006.

Does the change in sampling time (120 minutes to 175 minutes) for Hg(p) introduce any bias to the data?

Response: Sigler et al., 2009 indicates that RGM measurements began in November 2006 (same as this manuscript). See page 1930 section 2.2 second sentence of Sigler et al., 2009. Sigler et al., 2009 indicates that total gaseous mercury (TGM) measurements began at TF in November 2003. The authors incorrectly stated that there was a change in sampling times. There was a change in the desorption times after the addition of Hg(p). After the addition of Hg(p) the zero flushes were generally very good providing no clear evidence of contamination, and we also observed no significant differences in GEM and RGM levels before and after we added the Hg(p) measurement. This is edited in the manuscript (see lines 161-167).

Page 4575: The NOy and CO measurements could be used more extensively to help explain changes in boundary conditions and dry deposition of RGM. Pleases explain why these were not used.

Response: We did examine the relationships of CO, NOy, and SO with Hg wet deposition and did not find any statistically significant correlations (See Section 6 on page 4580). The reviewers is right that NOy and CO are potentially good indicators for boundary conditions and dry deposition of RGM and will be very useful to quantify the budget of RGM. However, this study is an overview paper on the three year data of Hg wet deposition, we feel in-depth analysis of RGM dry depositional loss using multi-tracer relationships is beyond the overview scope of this study.

Page 4575: Please compare the single precipitation event data with the two precipitation event data to determine how this may change your statistics.

Response: This was done during the initial analysis with little difference in the results. The results reported are for single precipitation event collections only. This clarification is added to the manuscript. See lines 270-271.

Page 4575: You may wish to discuss the high deposition storms more. The MDN site at Casco Bay did not receive this amount of deposition during the week July 22- July 29. It recorded 0.27 ug/m2 and a concentration of 7-8 ng/l. This would argue the potential for a very isolated precipitation event (convective storm?). You may wish to look at the wind vectors (wind roses) for this event (and similar events) and run the HYSPLIT back trajectories.

Response: We have carried out some of these suggested analyses and plan to cover these topics in a separate in-depth study. The primary purpose of our current manuscript is to provide an overview of our multi-year dataset.

Page 4576-4577: Please let the reader know how you define your seasons. The variability in the recorded seasonal average concentration of mercury in precipitation among the MDN and TF sites (for the limited number of summers that were compared) do not indicate that the TF concentration for summer 2008 was particularly out of the ordinary. One should expect such inter-annual and seasonal differences. If you compared inter-annual season differences for precipitation, you might find a similar pattern (statistical differences). Please define “the northeastern United States”. What geographic area does this cover? You may want to clarify what you mean by “numerous conditions affecting deposition”.

Response: We define our seasons according to the calendar and have added our definition to the text. The Hg concentration at TF for summer 2008 was not out of the ordinary but the Hg deposition was very high. The sentence is changed to and now excludes Hg concentration. The northeastern United States is revised to Northeastern North America and is defined differently by the sources cited. Prestbo and Gay 2009 define the northeast as NY, NJ, New England and the Province of Quebec and Canadian Maritimes. Vanarsdale et al., (2005) include a site in Pennsylvania, the New England States and New York, plus the Province of Quebec and Canadian Maritimes in their definition of northeastern North America. Keeler et al. (2005) refers to a site in Vermont. The phrase “numerous conditions” is clarified.

Page 4578: Please avoid conjectures without supporting evidence such as is the case in “possibly due to. . .precipitation”. The statement “First. . .indicate that more Hg is available. . .” needs to be more fully explained. It is not clear what you mean by more Hg is available. This may be re-written to clarify what you mean. Also, the sentence “Thus it is reasonable to hypothesize. . .due to anthropogenic emissions” needs additional clarification. What other factors could contribute to this? The reader is left with the feeling that these statements are supported by weak evidence. Please strengthen the lines of thought.

Response: We agree with the reviewer that this is speculative without supporting evidence. We emphasize this is an overview paper and thus we raised several possible causes for the observed patterns in Hg wet depsotion in comparison to MDN sites. We fully intend to conduct in-depth studies to quantitatively identify supporting evidence.

Page 4580: The section covering Anthropogenic Influences needs a lot of additional information. The data here should be used to help understand the mechanisms associated with diurnal and daily changes in RGM (and GEM) in the next section. Do you see patterns among the various measured mercury species and the other conservative and reactive gases that are measured? There is a wealth of information here which will help explain the patterns you see in the RGM (and GEM). Here, as is the case with precipitation and wet deposition, you should be careful running inappropriate statistics on variables that potentially auto-correlate. It seems logical that photochemistry plays a very important role in RGM and GEM concentration patterns (as is also the case with halogenated and other radicals). Additional discussion of this are warranted.

Response: We agree with the reviewer that patterns in other gases can be used to help understand observed patterns in RGM and GEM. Sigler et al. (2009) and Mao et al. (2008) have performed an in-depth look at relationships between gas phase mercury and other atmospheric gases such as CO, NOy and SO2 and JNO2 at TF. The purpose of this section is to investigate relationships between these gases and Hg in precipitation.

Page 4581: There needs to be additional data/discussion presented about the interplay among the various variables that influence the estimated Vd. The derivation and use of this equation is the most important part of your argument about RGM deposition. Please provide a more robust discussion on its derivation, and the uncertainties associated with its calculation. Comparisons with other data sets (sa Miller et al., 2005 and Engel et al., 2010) need to discussed within the context that these authors used different methods/components to estimate dry deposition of mercury. It is not clear that these comparisons are entirely appropriate. Miller et al. (2005) stated in their study that they have low confidence in their RGM deposition estimates. The importance of snow scavenging of mercury has yet to be determined. The research done at TF can provide very useful insights to this. Please expand on this.

Response: The authors agree that there are many variables that influence Vd however the derivation used here is intended to provide an order of magnitude estimate of Vd, which is stated in the text in lines 126 and 342. Our motivations here are simply to demonstrate the seasonal differences between wet deposition and RGM.

The Engle et al. (2010) and Miller et al. (2005) data sets were the only published data that include both Hg wet deposition and RGM dry deposition values over a one-year timeframe. Results from a study by Han et al. (2008, Environmental Pollution) are added, however their estimates are based solely on emission inventories and not measurement data. Additional information is added about the methods used by other authors and their confidence in estimating dry deposition of RGM. See lines 397-401, 403-404, 407-408.

The discussion about snow scavenging at TF is expanded see lines 315-339.

Page 4582: The authors use the phrase “total Hg deposition flux”. However, this paper only looks at wet deposition (as precipitation) and RGM dry deposition. Please avoid this since measurements of other types of mercury deposition are not covered in this paper. Also, the (estimated) ratios of wet mercury deposition (precipitation measured)

to dry RGM deposition (estimated), may be plausible, but they need to be discussed in terms of the uncertainty of the variables. How certain is the Vd estimate? Please provide additional information.

Response: The phrase “total Hg deposition flux” is changed to reflect that we only include wet deposition and RGM dry deposition. Again we state this is an order-of-magnitude estimation of Vd.

Page 4583-4584: Were the data used in Table 4 for Engles et al. (2010) study derived (calculated) by the authors, or where they taken from the article? This is unclear. Additional evidence needs to be provided to assist the reader in understanding the importance the discussion about ratios (wet mercury deposition in precipitation [only] and dry deposition of RGM).

Response: The authors calculated the ratios in Table 4 from Engle et al., 2010. The table is edited to include this information. In general little is known about RGM deposition compared to wet deposition based on the paucity of studies that include concurrent field measurements of both. This study provides information about the seasonality of RGM measurements and dry deposition.

Page 4596: Figure 4. One would expect auto-correlation of these variables.

Response: This figure has been deleted from the manuscript as the data may be auto-correlated because the precipitation rate is correlated to the total amount of precipitation, which is a component of the deposition variable.

Page 4598 Figure 6 – There is no reference to this figure in the text.

Response: This figure is now referenced and discussed in the text.

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