

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

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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

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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 #1 comments and response

Specific Comments: Abstract – sentence 3 – suggests that learning more about wet only deposition can provide understanding of atmospheric cycling and deposition. Rewrite to include dry and occult deposition, which are also crucial to understanding these broader processes.

Response: The beginning sentence is re-written to include this information.

In the abstract and throughout, avoid using the statistical term “trends”. Use “patterns” when a statistical trend analysis has not been performed.

Response: True. The word trends has been removed and replaced with patterns.

In the abstract and in Section 2, Line 15 – the authors refer to the site as “rural” but they also write that it is located in a heavily-developed “megalopolis”. How is “rural” defined? It's unclear that this site should be thought of as rural within this broader urban context.

Response: The immediate surroundings of the site are rural however it is also located down-wind of several east coast cities. Revised to explain better (See lines 131-134).

Introduction (and throughout) – Hg-P is written with a superscript “P”, but I believe most

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other authors are using a subscript P. Please check and change if appropriate.

Response: Particulate mercury is written 3 different ways in the literature. For example, Zhang et al. (2009, Atmos. Environ.) use subscript and Mao et al. (2008, ACP) use superscript, many others use Hg(P). For consistency between publications written by these authors, we use the superscript notation for particulate mercury.

A reference to consider mentioning in the introduction is the 'state of the science' paper from the Mercury conference in 2006: Lindberg et al. 2007, Ambio Vol. 36, No. 1, February 2007.

Response: We have now included this paper in our discussion.

P. 4571 Line 9: after "seasonal trends" add "in wet-only deposition" – or specify which are wet-only versus total or dry deposition. Many of the papers referred to are discussing wet-only deposition.

Response: We have changed this to to wet-only and expanded the introduction to include a paragraph with information on RGM dry deposition.

P. 4571, line 29 – Are there no more recent references with information for urban deposition? It seems that there has been more work in this area recently. The authors might scan the publications arising from the 2006 Mercury conference, at least, to check.

Response: The authors consulted the publications from the 2006 Mercury conference and conducted database searches for more recent publications with information comparing urban to rural deposition. Engle et al. (2009) discuss differences in rural vs. urban deposition and is included as more recent reference.

P. 4572, Line 19-21: I disagree that MDN sites collect integrated weekly samples – and this sample type has not been defined. My understanding is that, like NADP collectors, the MDN buckets stay closed unless it is actually raining/snowing. Is this the case? If so, then the collections are wet-only event samples. The generic "integrated weekly" description implies, perhaps, that samplers were continuously collecting. Please pro-

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vide more details so readers can determine whether your sampling strategy was reasonable to compare with MDN. If there were different strategies, then there needed to be side-by-side comparisons of the two types to validate your results.

Response: Integrated, admittedly in retrospect a poor word choice, was used to distinguish between event-based vs. weekly collection methods. Integrated was not meant to represent wet + dry samples. MDN samplers collect wet-only samples. We have now changed the wording (see lines 101-102).

P. 4572, Line 25 – the way this sentence is written, it appears that all (the sum of) events can equal 5-17%, which sounds like a small percentage. What the authors mean is that a single event can contribute between 5-17% – please re-phrase.

Response: This sentence is re-written (see lines 105-106).

P. 4573, Line 9 – Is wet-only, event precipitation flux comparable to dry deposition measurements (which were not event based). I think the authors need to provide more description and rationale up front – in the Introduction or Methods – to define and provide evidence for comparability among the different sample types. Throughfall, total deposition, and occult deposition were not mentioned anywhere in the paper. Perhaps they could be included in an earlier discussion of sample types and what they represent.

Response: The introduction is edited to include a better description and discussion of the various types of deposition.

P. 4574 – It seems that, if much of this methodology is consistent with MDN, the authors could omit virtually all of this section and refer the reader to MDN methods, simply pointing out in this section any deviations from those methods. Also, please cite an EPA method for cleaning and preservation of sample bottles and samples.

Response: This section is shortened and edited to make it more clear how our methods were minor modifications of EPA and MDN methods.

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P. 4574, Line 14: Confirm that samples were preserved in their original collection container, as specified in EPA methods. Failure to do so before pouring off aliquots might result in loss of Hg adhered to container walls.

Response: Samples were preserved in their original collection container according to EPA methods. Added to text. See line 147.

P. 4575, Line 13: Begin first sentence with “Wet-only”.

Response: Done

P. 4577, throughout. Often chemical concentration and flux data are skewed left. Before performing statistical analyses, did the authors check data for the assumption of normality, and transform the data accordingly (usually, a log transform works)? If not, then parametric statistical results may not be appropriate. This could be a major issue in the presentation of results and conclusions based on those results.

Response: A non-parametric method (Wilcoxon rank sum test) was used to determine statistical differences between seasonal Hg wet deposition data. The authors incorrectly assumed normality when running correlations (i.e. Table 2). Not all of the data followed a log-normal distribution, therefore the non-parametric Kendall's τ method was applied to determine correlations. These non-parametric correlations did not alter the interpretation of the results.

P. 4577, Line 9. Awkward wording – after “. . .differences”, change to “among years for the same season. . .”

Response: This discussion of statistically significant differences between seasons was deleted in an effort to condense this section of the manuscript.

P. 4578, Line 9-18: There are many plausible reasons for elevated deposition at the TF site. Those listed here make sense, but the section is quite speculative and could be shortened – or, provide references from the literature that support some of the hypothesized mechanisms.

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Response: This section is shortened because it is highly speculative and not a main topic of the paper. A reference is added regarding the influence of polluted air masses on TF. A sentence is added suggested that a more in-depth analysis is necessary to understand the causes of these geographical differences in Hg wet deposition. See lines 247- 252.

P. 4579 Line 5-10: Does the solar radiation investigation make sense, if the authors collected using MDN-like samplers that keep the sample bottle stored inside the collector (in the dark)? Why would solar radiation affect Hg in those bottles stored away from light? Consider omitting this section – it is again fairly speculative and not a key finding of the study.

Response: Solar radiation should not affect the sample once it is collected because the sample bottle is stored in the dark. Solar radiation however affects atmospheric chemical reactions such as ozone photochemistry and halogen radical concentrations, which could subsequently affect the oxidation of gaseous mercury (see lines 277 to 280).

P. 4579, Line 18-19 – The reported correlation between precipitation and deposition is not particularly meaningful – deposition includes precipitation in its calculation, and thus, they are not independent variables. In fact, many (non-Hg) studies have shown that we expect greater concentrations of chemicals such as SO₄ in events with less precipitation, due to a washout effect later in rainstorms. The authors might peruse the literature to seek out such references and adjust their expectations and hypotheses to reflect these types of mechanisms. Also see page 4580, line 10+ - this explanation could account for some of the weak observed negative correlations. In general, the discussion of these various correlations is not strong – I suggest shortening it significantly.

Response: The correlation is between the maximum rate of rainfall measured in mm per hour and Hg deposition. The purpose of this was to examine potential differences

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between a light drizzle and a heavy downpour for example. There is a correlation between maximum hourly rainfall rate and total rainfall (Kendall $\tau = 0.57$ $p < 0.05$), which is used in calculating deposition. Due to this potential auto-correlation the information and figure (Figure 4) about rainfall rate and Hg deposition have been deleted.

P. 4581, Line 4+: The literature has made much of “ineffective scavenging” by snow in winter. This apparent phenomenon must be very carefully approached. At least one previous article on the topic misinterpreted an earlier publication and was subsequently widely cited. Also, it is crucial to define the form of Hg – and the authors have done a nice job doing so here, pointing out RGM specifically in the scavenging discussion. HgP could be affected by other mechanisms in winter. See Nelson et al. 2008 (Applied Geochemistry 23, pp. 384-398), which also used data from the ME98 MDN site referenced in the current manuscript. Importantly, this current manuscript provides more support for the concept that there can be significant deposition in winter, despite the “ineffective scavenging” hypothesis having led to many scientists dismissing winter deposition as unimportant. Again, this is new information that provides crucial evidence in that debate.

Response: We appreciate the reviewer’s insightful commentary here. This point is emphasized more in the abstract (lines 34-35), and revised text (lines 434-438).

P 4582 Line 20-24 – The information about RGM’s seasonal pattern, and comparing it to the seasonal wet deposition pattern, is the key contribution of the paper in this reviewer’s opinion. The work that supports it (comparing to other sites, to MDN) is useful and important to ensure data comparability, but if those sections were downscaled to focus on this important work, the paper would be stronger.

Response: The seasonal pattern in RGM and comparison to seasonal wet deposition is emphasized more in the revised text with the other sections somewhat downscaled as suggested.

P. 4584, around Line 15: Here the authors have an opportunity to be more specific

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in their summary – note that RGM dry deposition was greatest in winter, rather than simply saying there was seasonality. Make the difference between wet-only and RGM clear.

More specifics have been added (see lines 434- 441).

Tables: Table 1: is there a way to use bold font or some other visual technique to group similar seasons? Much of the paper focuses on differences among seasons, but the table (though informative and necessary), makes is difficult to compare. Note that the mean versus median suggests the data are indeed skewed left and might need to be transformed prior to statistical analyses that require the assumption of normality be met.

Response: Shading is added to distinguish the spring and summer seasons from the winter and fall.

Table 2: can symbols (*, etc) be used to indicate significance at a certain p level, rather than listing all the p values?

Response: As suggested by the reviewer a * is used to denote significance at a certain level.

Table 3: significant digits should be checked throughout the table. The table is useful, but another way to present the wet + dry information could be a stacked line graph. It would be visually appealing, but it would not be possible to include the ratio data – so this is a “take it or leave it” recommendation.

Response: The information presented in this table was changed to a graphical presentation. The authors agree a graph is more visually appealing than a table.

Figures: Figure 1: Can the figure be made more information-rich by perhaps putting a callout at each site that lists annual concentration and deposition of Hg for the project years? This would allow a reader to see how the sites compare, on an annual scale, at a glance.

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Response: The location of historical MDN sites was added to the text and Figure 1 as suggested by Reviewer #2. The annual wet deposition at each site for 2007 and 2008 has been added to Figure 1.

Figure 4: This graph demonstrates that log transforming the data would be much more appropriate and provide more statistically defensible results.

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.

Figure 5: For display clarity, it would be useful to put the Y gridlines on the graph, perhaps in gray or as dotted lines. It can be difficult to read values from a log scale without grid lines.

Response: Good point. Gridlines are added.

Figure 6: This is an interesting way to present the ratio data. Perhaps this figure obviates the need for the ratio column in Table 3, which might then be better presented as a stacked line graph (or stacked bar).

Response: A stacked bar graph representing the data presented in Table 3 has been added.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 4569, 2011.