We'd like to thank the referees for their comments. We appreciate the details you've added to the paper.

Interactive comment on "Size distribution of atmospheric particulate mercury in marine and coastal atmospheres" by D. M. Feddersen et al.

Anonymous Referee #1

Received and published: 13 June 2012

Referee comments for Feddersen et al. (2012, ACPD)

General comments
Feddersen et al. are making an important contribution to literature. Very little is known about HgP, an issue the authors point out in the Introduction, and the authors are making a crucial step towards furthering our understanding of the size distribution of HgP in marine and coastal atmospheres. The authors have done a commendable job with the data collection and empirical analysis. Three major issues need to be addressed in the discussion:

1. In Section 2, Feddersen et al. describe how a whole suite of trace gases were measured in addition to mercury and yet the use of these trace gases to support source attribution is almost completely absent in the discussion. There is brief use of the trace gas information surrounding the discussion of Figures 9-10, but the use of trace gas as supporting evidence for marine versus continental/anthropogenic air masses seems necessary at multiple points throughout Section 4. I noted specific places in the discussion where using the trace gases could really help build the authors' case in terms of source attribution for HgP.

2. Be quantitative. There are too many places in the discussion were the authors only provide qualitative statements. The use of simple quantitative measures, such as correlation coefficients, would vastly improve the scientific robustness of many statements.

3. The discussion is lacking a synthesis statement about how the observations presented in this paper fit into the context of what we already know about HgP. I suggest adding a paragraph to the end of Section 4 and possibly extending the Conclusions to include some sort of discussion that tells the reader specifically how this work advances our knowledge of HgP cycling. This is a very new, exciting data set and the discussion needs a really clear statement at the end saying, "This is why our results are new and important and this is why it matters". There needs to be more thoughtful analysis and synthesis statement about how what Feddersen et al. saw at Thompson Farm and Appledore Island changes, challenges, or affirms HgP characteristics in previous literature.

Specific Comments
Page 14 591, title: Use of "atmospheric" and atmospheres" is slightly redundant. I suggest deleting "atmospheric", so you have the title "Size distribution of particulate mercury in marine and coastal atmospheres".

Atmospheric was removed in the title.

Page 14 592, line 3: Missing word “to” before “compare the seasonality”?

Thank you, it was added.

Page 14592, line 21: Should “Earth” be lowercase?

Yes, thank you.

Page 14592, line 25: These three forms are operationally defined. I suggest modifying the statement to read, “Mercury in the atmosphere consists of three operationally defined chemical forms. . .”

Done

Page 14593, lines 2 through 4: You need to include references for each potential oxidant (e.g. Hall (1995), Sommar et al. (2001), Calvert and Lindberg (2005), Holmes et al. (2006; 2010)). Also, HOCl is not typically viewed as a common oxidant, so what’s the justification for including it?

References were added. Correct, HOCl is not common and is removed.

Page 14593, lines 8 through 10: You say, “A few studies. . .”, but only provide Wang et al. (2006) as a reference. Are there other studies? If so, you should provide them. Also, is the work of Wang et al. really “confirming” that the majority of HgP resides in smaller particles? I suggest replacing “confirming” with “suggesting” since your work shows that it’s not always the case that HgP resides in smaller particles.

Correct, the way it was written was misleading. The paragraph was rewritten for clarification. Suggesting was used in place of confirming.

Page 14593, 2nd paragraph: Discussion of previous literature on size distribution of HgP omits Keeler et al. (1995) and Gildemeister et al (2005), both near Detroit.

Our apologies, they are now included.

Page 14594, Introduction: It would be helpful if you concluded your Introduction with a brief paragraph explaining what you’re going to do in this study and how it contributes to our broader understanding of atmospheric particulate mercury.

We included a paragraph explaining the study.

Page 14594, lines 17-26: Include a sentence explaining why you collected the trace gases that you did.

Included

Page 14596, line 4: Rather than “Our group”, better to use “AIRMAP has been collecting. . .”?

Thank you, Done.

Page 14596, lines 24-27: Did you apply a blank correction of 25 pg? It’s ambiguous whether not a blank correction was actually applied.

Yes, we’ve made this clear in the text.

Page 14597, lines 2-4: Can you be more quantitative about “uptake by RGM was minimal”? And you need to provide a justification for your assumption that mercury loss is “the same each for impactor and each size fraction.” Because if mercury loss isn’t the same for each impact and each size fraction, your results and conclusions will be greatly affected.

We’ve expanded on the paragraph, RGM did not affect the measurements in lab at all, sorry for the confusion.

Page 14598, lines 2-3: I’m not convinced that the difference between the two impactors is “likely due to variability in the atmosphere”. How far apart were your impactors? If there several meters apart, then atmospheric variability might be a valid explanation, but the impactors are side by side, could something else be going on?

It’s a very small difference, it’s more probably differences in the impactors themselves, you are correct.

Page 14598, lines 3-4: The overall size distribution trends are similar for effective cutoff diameters >4μm, but the two impactors don’t agree at all for the cutoff diameters <4 μm. Can you explain this difference?

They still agree quite well, the differences may reflect their ability to determine aerosol size distributions.

Page 14598, lines 14-16 and Figure 3: Your explanations for why you observed more HgP in the daytime in the text of the paper and in the figure caption don’t match. In the text, you attributed the daytime/nighttime difference to RGM production during sunny days and in the caption of Fig. 3 you attribute the difference to sea salt generation. You need to be consistent. And what about the possibility of enhanced nighttime dry deposition? Or the possibility of a nocturnal inversion setting up and effectively cutting off the supply of free troposphere RGM from being entrained to your sampling site in the boundary layer?

Thank you for catching the discrepancy. There may be the possibility of RGM, a precursor to Hg^P, removed during a nighttime boundary layer inversion. This is also addressed in the diurnal cycle discussion.

Page 14599, line 10: The statement ". . . implying the transition from winter to summer cycling" is vague. Please be more specific. Exactly what part of the transition are you referring to? And how exactly is the cycling changing?

It refers to the transition from fine particles dominating in the winter to coarse particles dominating in the summer. The word "cycling" was changed to "distribution of particle sizes."

Page 14599, lines 12-14: "Thompson farm had more of an influence from fine particles during the first week which may be attributed to the source of air." You made all these trace gas measurements, can you use those to do source attribution for the air mass? Do you see elevated CO and SO2 when you see fine particles? Are the prevailing winds westerly? You have a lot of ancillary data to support your mercury measurements that you're not using.

There is no wind or SO_2 data for these two weeks at Thompson Farm. Source of the air parcels was determined using backward trajectories.

Page 14599, line 10: ". . . had marine origins." Again, can use your trace gas measurements to provide a more compelling argument that you actually think the air is of marine origin? Do you see elevated halogens?

Nor is there halogen data for Thompson Farm.

Page 14599, line 16: Do you mean Fig. 6a, not Fig. 6b?

Yes, the two were switched, thank you for catching the mistake.

Page 14599, lines 20-22: The statement, "the distribution of fine and coarse particles each location could reflect the influence of marine air on coastal air and vice versa." This is a weak statement. Can you provide evidence for such a statement? It may be true, but nothing you present in the discussion gives the reader a compelling reason to believe it.

An earlier study showed the influences of both sites on each other during the summer. This was made more clear in the text.

Page 14599, binds 24-25: The statement, "Table 3 summarizes the major findings of the campaign" seems out of place. You don't actually need Table 3. All of the major findings of your campaigns should be in the Conclusions.

Removed

Page 14599, line 29: You mention wind speed and rain. Does that mean you have meteorological measurements at Thompson Farm and Appledore Island? If so, you should present them and be more quantitative about the differences in wind speed and precipitation amount.

We've included the average wind speed and total precipitation data.

Page 14600, line 2: ". . . with the exception mentioned previously. . ." Not clear which exception you're talking about. You should state the exception explicitly here.

Included the exception that excessive rainfall scrubbed out the majority of the particulate mercury during the first week of summer 2009 at Appledore Island.

Page 14600, lines 4-5: ". . . the marine site is dominated by larger particles which affect the total HgP more than fine particles." Why would larger particles affect the total HgP more than fine particles? Removal processes? Larger particles contribute more mass? Provide your reasoning behind this statement because right now it's not clear what you're trying to get at.

Larger particles contribute more to the total mass, made clear in text.

Page 14600, lines 10-11: Again, what does it mean when you say "when larger sea salt particles reach the site, and it greatly influences the total HgP"? Be specific and provide your reasoning.

Again, made clear in text.

Page 14600, lines 24-25: I suggest removing the statement "and it is likely that had summer 2009 campaigns been conducted simultaneously, the size distribution of HgP would be similar." This statement is too much of the speculation. If you had several more years of data, you would have more justification in making this claim.

Agreed, the sentence was removed.

Page 14600, line 29: "Track each other nicely. . ." Please be more quantitative. Can you provide an r2 value?

Yes, correlation coefficients have been added where needed.

Page 14601, lines 3-6: Can you provide more evidence than "smoke smells"? For example, do you see elevated CO as a marker of combustion? Or other trace gases as indicators of biomass burning? I see that further down in the discussion you show hydrocarbon data – does this support the presence of fires?

We've included CO mixing ratios where needed in the text.

Page 14601, lines 20-21: "The green and red points correlate better than the black and red points. . ." Please provide correlation coefficient.

Included

Page 14601, lines 15 through page 14602 line for: This discussion is important, but the wording is unclear. Do you see an artifact at Appledore Island? At Thompson Farm? How big is the artifact, if present, in ppqv or even in %?

More details have been included in the discussion to clarify the artifact seen at Thompson Farm and to some extent, Appledore Island.

Page 14602, line 14: Generation of HgP due to "nighttime chemical reactions" is some-thing very new and potentially really interesting. Can you elaborate more about what's going on? Do you have a hypothesis for what the chemical reactions might be?

There is little information published about nighttime mercury reactions, but it may include the dissolution of Hg^0 into aerosols directly without oxidation of RGM.

Page 14602, lines 5-18: Some sites to do not see a diurnal pattern in HgP (e.g. Lyman and Gustin, 2009), so the fact that you do see a diurnal pattern of HgP and the fact that it looks like Hg0 is interesting and new and deserves a more thoughtful explanation. For example, why doesn't the diurnal pattern of HgP not look like the diurnal pattern of RGM if we expect a partitioning between RGM and HgP? And what does the fact that HgP looks like Hg0 tell us about the sources and sinks of HgP at your two sampling sites?

We've addressed this in the text. There does not have to be oxidation to RGM, it may not be the only precursor to Hg^P. The similar diurnal patterns could also be dissolution of Hg^0 directly into the aerosol occurring in the nocturnal inversion layer.

Page 14602, lines 20-23: What you justification for using an average deposition velocity of 0.5 cm/s? The deposition velocities can be highly variable depending on the wind speed and surface roughness. If you have wind velocity measurements, a better approach would be to use a simple resistance-in-series model (e.g Seinfeld and Pandis, 2006, Ch. 19).

We don't have the data to do the resistance-in-series model calculations.

Table 1: Shouldn't you also include Tekran HgP in your "sample type-time resolution"?

Yes, thank you, we've included Tekran resolution also.

Figure 1: Make the fonts bigger for the lat/lon coordinates and for the site names. If possible, use a map that doesn't have all of the streams and lakes on it, they make the text harder to read. Rather than having "Gulf of Maine" at an angle, orient it horizontally like the rest of the text and maybe move it up around 43.1 N.

We've put in a more simple map.

Figures 2-6, 8-12: Label y-axis "HgP" not "PHg", for consistency with the text in the body of your paper.

Thank you, done.

Figures 2-6: X-axis, should be “µm” not “um”.

Again, thank you.

Figures 2 and 6: It’s difficult to see “a.” and “b.” in the bottom left corners. Make “a.” and “b.” bold and use larger fonts and move them to the top left corner of the plots where you have a lot of white space. Text in legend is too small, make larger – okay to use two lines for “Week 1 – Total 0.23 ppqv”, etc.

Done

Figure 7: It would be helpful if you could label the date of each figure. For example, put “26 July 2009” right on panel a. I also suggest putting the labels “a”, “b”, etc. right on the figures and not down in the corners.

Done

Figures 9-11: These figures are particularly difficult to read. Make all the fonts larger. It’s difficult to distinguish multiple lines. I suggest just plotting the data as solid lines rather than plotting the data as symbols (i.e. circles and triangles) connected with dashed lines. You can tell the reader the time resolution of the measurement in the figure captions. Figure 10, central panel: Use a color scheme with more contrast. It’s hard to tell hunter green, purple, and dark blue apart.

Done

Figure 12: The inset of the Hg0 diurnal cycle is illegible. The point you’re trying to make with this plot is a nice one, so I suggest re-plotting the Mao et al. Hg0 data in a separate panel right above your plot of HgP. Consider adding a second x-axis with local time in addition to UTC, or state in the caption that New Hampshire is noon local time is XX:00 UTC.

Done

Interactive comment on "Size distribution of atmospheric particulate mercury in marine and coastal atmospheres" by D. M. Feddersen et al.

Anonymous Referee #2

Received and published: 17 August 2012

I like this paper and it provides useful contraints on many parameters.

Some editorial comments.

Line 23, pg 14593: GEOS-Chem model does not have the % contribution to deposition in the NE US as high as 40-65%. This seems a little steep. See Atmos. Chem. Phys. Discuss., 12, 2603–2646, 2012.

You're right, it was lowered in the text to match the new reference.

Line 25-30, pg 14593. This sentence is very confusing. Are the authors saying that if one measures the fractions between 0.4 and 10 um, the dominant sources of Hg will be the ones listed?

We've removed the cut sizes to make the statement more clear.

Fig 8 and Fig 9, would be nice to see r2 data (Line 30 page 14600).

A correlation coefficient was given for Figure 8, however, it wouldn't be useful to give a coefficient for the hydrocarbon data in Figures 9 and 10. As you can see, sometimes elevations in isoprene lead to enhancements in Hg^P, but sometimes it doesn't. This suggests differences in the sources of the Hg^P. For example, the correlation coefficient between isoprene and the filters is 0.01.

Line 11-12, pg 14601: Authors use the word "correlated" but no statistics are given.

We'll change the word correlated, here we are doing a visual check on various hydrocarbons and not just one particular hydrocarbon correlation with the bulk filters.

Line 16, pg 14601: Don't understand the line "enhancements in HgP that were associated with those in hydrocarbons. You mean the data in Figure 9?

Yes, when various hydrocarbons are elevated, Hg^P is also elevated, which is shown in Figures 9 + 10.

Line 1, pg 14602: change "summer is at much" to "summer was at much" in general when speaking about data that was collected in the past it should be referred to in the past tense.

Thank you, done.

Line 20, pg 14601: again, when the word “correlate” is used, statistics should be provided.

Yes, thank you, it has been included.

Line 26, pg 14601: was removal of the PM2.5 elutriator on the Tekran inlet also done at Thompson Farm? If not, why only one site.

It was not removed, because it wasn’t expected that Thompson Farm was affected by larger particles.

The discussion in general on comparison with Tekran instrument is not very succinct. I think the comparison is useful but the explanation of results is not clear.

We’ve added more to the discussion to make it clear.

Line 17: pg 14602: Data “are” not “is”.

Changed, thank you.

Conclusions, pg 14603: This section is not complete. Conclusion #1 is too general to be of use. The results of the size distributions to distinguish between marine vs. continental sources of Hg should be summarized.

We’ve included more details about the results in the conclusion.