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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal and diurnal variations of atmospheric mercury across the US determined from AMNet monitoring data" *by* X. Lan et al.

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Response to Reviewers:

Reviewer 1:

"Since the diurnal and seasonal cycles of atmospheric mercury at many individual AMNet sites have already been documented, including in papers by the coauthors, the value of this paper is in characterizing the AMNet system."

To the best of our knowledge, only 4 of 11 AMNet sites we discuss in this paper were presented in individual articles before, which are cited in the introduction sec-

tion (P10848, line 11-P10849, line 8). No synthesis paper has been published before to study the similarity and differences of the AMnet sites. This manuscript is the first one to do that.

"In addition, there are errors in grammar thoughout, such as subject-verb agreement, that impede understanding."

The senior co-author "R. Talbot" went through this manuscript several times before submission, and the lead author also took this manuscript to the English Writing Department of the University of Houston to correct any grammar issues prior to submission. In our opinion, this manuscript does not contain grammar problems that would impede understanding of the material. We will go through the manuscript carefully once more before resubmission.

"The manuscript contains major problems with the flow of its argument, and occasional jumps to conclusions that are not supported by the evidence provided. In the paragraphs below, I list the 3-4 most egregious examples. . .For example, Lan et al. write, "UT97 was heavily impacted by nearby anthropogenic emission sources" (P51), but then a few lines later they contradict themselves, saying, "The emission sources corresponding to UT97 were similar with UT96." The authors own Table 1 states that emissions near (<10km) from UT97 are 20,000 times larger than those near UT96, so the sources definitely aren't "similar"."

We mean the total emissions within 150 km, instead of most immediate emissions from 10 km radius. This is a discussion of GEM, which has a relatively long life time that enables its long-distance transport, so we believe a larger radius should be taken into consideration. For UT97, it should be 1.432+0.134+1.034*10-4=1.566 T/yr; for UT96, it should be 1.489+0.082+4.513*10-9=1.571 T/yr. That's why we say they are impacted by "similar" emissions. In the revised version, we will add up the total emissions within 150 km and add that column to Table 1. We believe that the reviewer misunderstood the distance–source relationship in Table 1. We will revise the text to make this point

clearer.

"The next sentence suggests that "UT97 could also capture long-distance transported mercury, which may include mining and/or Asian emissions." There are at least 3 major problems with this. First, there's already a better explanation (local emissions) for the mean difference between UT96 and UT97. Second, it is highly unlikely that plumes transported over hundreds or thousands of kilometers would impact site UT97, but not site UT96, 30 miles away. Third, I am not aware of any study that has conclusively identified Asian anthropogenic pollution at ground level in the North America, besides mountaintops, so this claim would require strong evidence that is not provided."

First, as we stated above, there's little difference between the local emissions at UT96 and UT97. Second, we agree that Asian emissions can also influence the UT96 site. We will modify this point in the text. Third, UT97 is at 1297 m elevation, which is showed in Table 1. It's not a ground level site. We will add the elevation height into the text to stress its importance. Jaffe et al. (2005) and Strode et al. (2008) showed the influence of Asian emissions to the United States. We will add these references in the revised version. (We are now not sure what caused the difference in GEM median mixing ratios between UT96 and UT97).

"Later, the authors attribute the diurnal cycle of GEM at UT97 to loss near the Great Salt Lake: "At UT97, the largest diurnal difference reached 55 ppqv, revealing the exceptionally large daily loss of GEM near the Great Salt Lake" (P58). As stated, this is unsupported speculation. I don't know what specific aspect of the diurnal amplitude leads the authors to implicate the lake, and it conïňĆicts with previous work by Peterson and Gustin (2008), who did not find large GEM loss in the same area."

The 55 ppqv difference is directly calculated from measurement data. It does not conflict with Peterson and Gustin (2008). Peterson and Gustin's work also showed a large diurnal loss in their Fig. 3 (P260). The daily losses were about 0.5 ng m-3 (= 56 ppqv) in June and about 1.0 ng m-3 (112 ppqv) in August, which were even

higher than we report in our paper. Both Peterson and Gustin's paper and our paper showed similar diurnal pattern with higher GEM at night and lower GEM in daytime. However, Peterson and Gustin did not report or point out the diurnal losses in the text. By comparing with other AMnet sites, we know that the daily loss of GEM at UT97 is significant. The Great Salt Lake has much higher salinity compared to the world's ocean; release of reactive halogens was measured from the lake by Stutz et al. (2002). Previous experiments conducted at the Dead Sea showed that reactive halogens released from a high salinity environment can induce GEM depletion (Obrist, 2010). Thus, we believe it is reasonable to implicate a possible contribution to GEM depletion from the Great Salt Lake.

"I don't understand why the authors don't consider diurnal lake or mountain breezes as the cause, especially since they think, reasonably so, in my opinion, that lake breezes are important at other sites. On the next page, Lan et al. suggest that "photochemical oxidation of GEM was likely a dominant factor controlling GOM" (P59). Again, the authors have not considered diurnal wind variations, which could be very important in the midst of large industrial and urban sources. Obvious alternatives explanations need to be discussed before concluding that photo-oxidation is "likely" or "dominant"."

We specifically stated the influence of the land-lake breeze: On page 10858, line 19, we stated "UT96, UT97 and NY95 showed distinct pattern ... it is possible that the special boundary layer structure and land/lake breeze in those areas caused the unusual variation pattern". We actually think that the lake-land breeze is an important factor for the GEM diurnal variation at UT97. For the case of GOM, we suggest that photochemistry is a dominant factor, because GOM presumably cannot be transported over long distances, and thus local production should be the major source for GOM instead of wind advection. In addition, the GOM diurnal variation at this site shows high mixing ratios during daytime and low mixing ratios at night. This variation matches the diurnal variation of solar radiation which strongly suggests a photochemical control on GOM. We will re-work the text to make our points clearer.

"On P55-56, the second and third paragraphs of this section state a lot of numbers without clear interpretations or significance. These could be condensed. Many explanations here are purely speculative, such as "the summer and fall GEM exhibited large interannual differences, which probably were the consequences of different annual meteorological conditions" (L8). Unless there is some additional evidence, these statements should be cut or, at the very least, clearly marked as speculations."

We will condense this part to make our points clearer. For the interannual time scale, anthropogenic emissions should be relatively constant compared with the meteorological factors, and thus it is not likely to cause the variations we observed. If we eliminate one of the leading factors, anthropogenic emissions, then changes in meteorological conditions is left as a leading candidate. We know that meteorological conditions are highly variable, and that's why we invoked them in our manuscript. They can directly influence biogenic emissions and/or deposition.

"Revisions to this manuscript, should also address the possible role of mercury emissions from soil, water, and vegetation as a cause for differences between sites. Since the sites range from deserts, forests, lake shores, and ocean coasts, natural mercury emissions are likely quite different across AMNet. The authors do recognize the importance of diurnal uptake and release of GEM on moistened vegetation, but should do more. The 2008 UNEP mercury assessment and Bash (2010) provide good overviews."

We agree that natural emissions are important factors. We will mention the role of natural emissions in the revised version. In general, natural emissions of mercury have very low flux values, and in our opinion, are not likely to influence the regional area in most cases.

"A recent of seasonal and diurnal cycles of mercury by Nair et al. (Atmos Environ, 2012) is clearly relevant to this manuscript; it should be referenced."

We will cite this reference in the revised version.

"P47 L11. GEM reactions with O3, OH, and NO3 are all controversial, as is stated in one of the cited references (Calvert and Lindberg 2005). This should be noted."

Calvert and Lindberg (2005) reported that O3 is unlikely to be an oxidant of GEM. We will clarify this in revised version. The current literature does not contradict OH and NO3 as oxidants of GEM.

"P47 L16. Misleading."GOM and PBM. . . are thought to be readily deposited on the order of 1–7 days near emission sources." Atmospheric oxidation of GEM is an important source of GOM and PBM, so GOM and PBM are frequently not deposited near where their constituent mercury atoms were emitted."

We agree. We will revise this sentence as: GOM and PBM. . . are thought to be readily deposited on the order of 1–7 days after they are produced.

"P56 L18. "Higher GOM mixing ratios in spring and summer may be due to the increased length of the growing season at this time." I don't know what this means. "

We mean that there is a stronger and longer exposure to solar radiation during the growing season, which favors GEM oxidation to GOM. We will clarify this in the revised version.

"P56 L19. Subsidence from the free troposphere is an important source of GOM at some sites (Weiss-Penzias et al. 2009). This may also contribute to seasonal cycles."

In our opinion, it is yet to be shown how important the free troposphere is as a source of GOM. To date, only very limited information is available to address this issue. We believe that adding this to the manuscript would only add more speculation at this time.

"P57 L9. The following paragraph contains many repetitions, such as listing the sites with strong GEM diurnal cycles."

We list the sites that have strong GEM diurnal cycles, and then discuss the prominent details of each site. We will condense this section to make our points clearer.

"P60 L16. This paragraph ïňĄrst repeats the 2 before it. Then I don't understand why MS12 speciïňĄcally is described as having very low GOM at night when several other sites have equally low or lower GOM during the same hours (e.g. NY20, VT99, OH02. . .)"

We agree with the reviewer and as a consequence we moved the first two sentences to the conclusion section. MS12 is special because it GOM level is not only low, but actually totally depleted because of high humidity at night. The time scale over which this phenomenon occurred is longer than at the other sites. We will clarify this in the revised version.

"Table 1. Missing elevations. Emission units are not SI. Change to kg or explain in footnote. Emissions from a belt 10-50km or 50-150km from a site are not obviously relevant. It would be more helpful to list cumulative emissions within 10, 50, and 150km."

Again, we agree with the reviewer. We will add the missing elevations and explain the emission units. We will put the cumulative emissions in Table 1.

Reviewer 2:

"The manuscript describes similarities and differences among the sites in great detail; however, a "large-scale picture of speciated mercury" is not clearly developed. The 11 AMnet sites analyzed in this manuscript only cover a limited geographic area, primarily the northeastern U.S., and do not reflect a large scale picture. Consequently, we have modified the sentence in the last paragraph in the introduction to reflect this. In many sections, observations are listed for each site and each season (e.g. Sections 4 & 5), and seem to lack focus. As a result of this organization, it is often difficult to extract the important points."

This manuscript first describes the characteristics of a three year time series, and then reports the seasonal and diurnal variation patterns we observed. In each section, we use separate paragraphs for each mercury species. Because of the large amount of

data, we believe this is the best way to report observations and make comparisons among different sites on the same time scale. We believe that the manuscript is organized in a logical fashion. We will further condense the description for observations with more focus on the important points.

"Additionally, while the authors attempt to provide explanations for the observations, their conclusions are generally not dissimilar to those found in previous studies (many of which are from co-authors) that analyzed temporal variation at fewer sites. Without a continental-scale picture of mercury, it is unclear what new contributions are provided by this work."

We report 3 years of data for 11 AMnet sites in this manuscript. To the best of our knowledge, only 4 of these sites were discussed in individual articles before, which are cited in the introduction (P10848, line11-P10849, line8). No detailed reporting for the rest of the 7 sites has been published. The contribution of this work includes reporting the ambient levels of speciated mercury, comparing their seasonal and diurnal variations, and providing possible explanations. This is a synthesis paper to study the similarities and differences of all the AMnet sites. Our manuscript shows that there is now consistency in the mixing ratios of mercury species at least in the eastern U.S., and mostly similar seasonal and diurnal characteristics. This is key information for researchers, and in particular modelers. This shows that there has been progress made in measuring and understanding of atmospheric mercury. This is a very important point, and for most atmospheric species, this is how we have developed an understanding of each.

"For these reasons, and because the manuscript is often difïňĄcult to follow and would require signiïňĄcant additional copy editing to address typos, run-on sentences, and tense problems, I recommend rejecting the manuscript in its current form. "

The senior co-author "R. Talbot" went through this manuscript several times before submission, and the lead author also took this manuscript to the English Writing De-

partment of the University of Houston to correct the grammar issues before submission. In our opinion, this manuscript does not have grammatical issues that impede its understanding. We will go through the manuscript carefully once more before resubmission.

Specific Comments: "1)P10846: Abstract should be condensed to emphasize the main, important points."

We will condense the abstract, especially the part that describes the diurnal variation patterns.

"2)P10851 L11-12: Are you referring to local emissions or total emissions with 150km?"

We refer to total emission within 150 km. We will clarify this point in the revised version.

"A reference is needed when attributing observations to transport of Asian emissions."

Jaffe et al. (2005) and Strode et al. (2008) showed the influence of Asian emissions to the United States. We will add these references in the revised version.

"3) P10852 L4: How do you distinguish the contribution of halogen chemistry converting GEM to GOM and low GEM emissions at coastal sites?"

We agree that it's difficult to distinguish the contribution of halogen chemistry and anthropogenic emissions. We have modified the text appropriately.

"4) P10859 L13: It is unclear why the sampling sites were divided into the two groups for analysis and what interesting results were found by using this method."

The reason for dividing the sites in two groups is for the convenience of reporting the variation amplitudes. As we found the sites in these two groups have very different variation amplitudes in springtime, we also found this difference to be consistent in summertime. We have modified the text to make this clear.

"5) P10855 L11-15: More information concerning this ïňĄre event is needed. When exactly did the ïňĄre occur? Need to better explain Figure 4."

The exact date of the fire is not really pertinent; it's when the emissions were transported to the U.S. that is important. The three sites shown in the Fig. 4 indicate the time frame of importance is from May 28 to June 3. We will describe the fire event and explain the Fig. 4 in more detail in the revised version.

"6) P10859: Observations are described for spring and summer but no analysis or explanations are provided."

This is a section to report the diurnal variation pattern of GOM. We provide detailed data analysis on P10859 and P10860. However, it is impossible for us to provide further explanations for the diurnal variation pattern with only mercury data. In the revised version, we will attempt to provide some possible explanations.

"7) Figures presented in both the manuscript and supplementary material seem to lack focus and their organization into sub-figures is difficult to follow. I think the paper would benefit from condensing a lot of material (including ïňĄgures) into fewer important points."

In our opinion, all the figures presented in the manuscript are necessary and none of it can be eliminated. Combining sub-panels into one panel complicates the figure greatly and makes it unreadable. The figures designed for manuscript and supplementary material are consistent. Each different color represents one site, and the same color is used in all plots for the same site. Besides, the scales of the sub-figures are set to be different to present the variations of mixing ratios. For the text, we will condense some information into fewer important points.

"8) The role of natural mercury emissions should be addressed further."

We agree that natural sources can also cause some differences among sampling sites. We will address the role of natural mercury emissions in the revised version.

Technical Corrections: The manuscript would beneïňĄt from additional copy editing. Some major concerns follow. "1)Table 1: Elevations for UT96 and NH06 are missing

along with the units."

We will add the missing elevations and explain the emission units.

"2)Units should be consistent throughout (ppqv or ng m-3)"

We report all mercury levels in ppqv for our data. However, ng m-3 is used in the citations, which is the original unit used in those articles. In this case, we provide the mixing ratio in ppqv right after ng m-3. We will check the units again to make sure ppqv is used for the mercury level.

"3)When time of day results are reported, AM or PM should be indicated and local standard time (LST) could be used instead of PST, EST, MST, etc"

In this manuscript, we always report time of day in the text by using the format: 14:00 LST, which, we think, should not cause misunderstanding. Local standard time is also used in our figures. The reason we use 14:00 format in the text instead of 2:00 PM is to be consistent with our figures (time axis). We will use LST instead of EST and CST in the revised version.

"4)P10850 L4-5: Tense should be consistent"

We will change “is” to “was” in this line 5 to keep the tense consistent.

"5)P10851 L11-14: References are needed. Also, it is unclear whether the emissions sources being similar at UT97 and UT96 is referring to emissions within 10 or 150 km"

We mean the total emissions within 150 km, instead of the most immediate emissions from 10 km radius. We will further clarify this point. For the Asian emissions, we will add the references of Jaffe et al. (2005) and Strode et al. (2008).

"6)P10854 L16: Why is this “interesting and surprising”? Isn’t this what we’d expect based on emission sources?"

The uptake of GEM and GOM by sea salt aerosols is not apparent from the monitoring

data. This is surprising. Sea salt aerosols can uptake GOM and produce considerable amounts of PBM. In the coastal environment, halogen compounds can also help convert GEM to GOM, which also help to increase the mixing ratios of PBM. Thus, it is not clear if anthropogenic emissions are directly important to the ambient levels at any given location. Our thinking is that chemical transformations may be more important at most coastal locations.

In addition, the Tekran instrument cannot measure the part of PBM associated with large particles (large particles from sea salt aerosol) efficiently. It is reported that the instrument can have as much as 3 times lower PBM mixing ratio than bulk filter collection (Talbot et al., 2011). We will further describe this point in the revised version.

"7)P10857 L24-27: References are needed."

Reference is in L28: (Kellerhals et al., 2003), we will also put it in L26 to make it clearer.

Additional Revisions:

One of our co-authors (MC) pointed out to us the Maryland site MD08 is really not coastal. In fact, it’s more than 300 km inland. Thus, we moved this site out of the coastal tgrouping and made the appropriate changes to the manuscript.

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