Anonymous Referee #2

Review of manuscript acpd-11-32301-2011: "Speciated Mercury at Marine, Coastal, and Inland Sites in New England: Part I. Temporal Variability", submitted by H. Mao and R. Talbot to Atmospheric Chemistry and Physics (doi:10.5194/acpd-11-32301-2011).

Overview: *The manuscript entitled "Speciated Mercury at Marine, Coastal, and Inland Sites in New England: Part I. Temporal Variability", by H. Mao and R. Talbot reports on the inter-annual, seasonal and diurnal variability in speciated atmospheric Hg at three measurement sites in New England. The analysis draws upon measurements of gaseous elemental mercury (Hg°), reactive gaseous mercury (RGM) and particle-bound mercury (Hg_P) made at a marine site (Appledore Island), a coastal inland site (Thompson Farm) and an elevated inland site (Pac Monadnoc) from 2004–2010 (data availability was not the same for each site).*

A particular strength of this manuscript is that it compares the temporal variability of atmospheric Hg at three sites that, while located within a limited spatial domain (i.e., they are <200 km distant from one another), represent quite different local environments. The measurements from these sites therefore provide valuable information on factors influencing concentrations and speciation of Hg in the lower troposphere. Atmospheric Hg measurements provide key constraints in the development of models to describe the underlying processes governing the environmental cycling of Hg, yet the availability of such measurements is still limited at present.

My main criticisms are: (1) much of the discussion appears to be inconsistent/contradictory in comparison with tabulated data; (2) the results presented, and the associated discussion, are at times insufficient to support conclusions drawn; (3) grammatical errors are pervasive. These issues are discussed further below (see "Specific Comments"). The inconsistencies between the text and tables may be partly a result of the lack of a systematic statistical basis for describing the measurements, but they also suggest that the authors have not been careful in their analysis. These inconsistencies, together with grammatical errors detract from the value of the analysis and significantly weaken the paper.

While I feel this manuscript is relevant to the scope of ACP, my comments below highlight that major revisions are required before publication in ACP. I have provided a few suggestions on grammar under "Technical Corrections"; I have not highlighted every error I encountered.

Specific Comments

1. Introduction, page 32303, lines 1–3: The authors state that "Atmospheric mercury exists in three forms, gaseous elemental mercury (Hg°), reactive gaseous species (RGM = $HgCl_2$ + $HgBr_2$ + HgOBr +…), and particulate mercury (Hg_P)". This statement is misleading. RGM is 'operationally' defined as gas-phase oxidized Hg compounds which are collected on KCl-coated quartz denuders (after Landis et al., 2002) and thermally decomposed to Hg°. There exist major uncertainties regarding the chemical speciation of RGM. While the halides $HgCl_2$ and $HgBr_2$ are probable candidates for RGM species, their existence in the gas-phase has not been proven. Therefore, I would suggest that the authors clearly indicate that the compounds they have listed are 'probable' candidates for RGM.

These species were removed from the text (See line 61, page 3)

2. Introduction, page 32303, lines 15–16: Here the authors begin to discuss Hg concentrations reported in the literature and introduce units of ng/m^3 and ppqv. The authors typically present *their measurements in terms of ppqv and measurements from other groups in terms of ng/m3. For clarity, I suggest that the ng/m3 equivalent be provided for all ppqv quantities presented in the Introduction, since most other values reported in the literature are given in terms of ng/m3. Then, when the authors present their current results in Sections 2–4, it seems appropriate to use units of ppqv as long as the ppqv equivalent values are provided for any literature data cited in those sections. This will facilitate comparison between the authors' data and referenced literature data.*

We did provide the equivalent value of ng/m^3 in ppqv in lines 15-16, page 32303, and converted the numbers, from the first citation, in ng/m^3 to ppqv in line 15, page 32303. We also converted our value in ppqv to ng/m^3 in line 19, page 32303, when we cited our previous work.

Per the reviewer's suggestion, values in units of ng/m^3 have been converted to units of ppqv.

3. Introduction, page 32304, lines 12–18: The authors summarize RGM measurements reported by Sigler et al. (2009) and refer to "a rural site on the southern New Hampshire coastline", "an elevated (700 m altitude) 185 km inland site" and "a marine site". Presumably these sites are the Thompson Farm (TF), Pac Monadnoc (PM) and Appledore Island (AI) sites discussed in the present manuscript. It would be helpful to refer to these sites by name if in fact they are the same sites. This will give the reader a much clearer basis for comparison.

Specific site names have been provided per the reviewer's suggestion.

4. Introduction, page 32304, lines 19–21: Here the authors use the terms 'background' and 'baseline' interchangeably. For consistency and clarity I suggest the authors first provide definitions for these terms and then choose one or the other if the terms can be defined similarly.

"Background" and "baseline" are two commonly used terms in atmospheric sciences. See Slemr et al. (2011), Ebinghaus et al. (2011), Wang et al. (2009, ACP). Considering the wide audience of ACP, we defined the terms per the reviewer's suggestion. Upon the first appearance of the two terms, we added that "t(T)heir analysis suggested that the baseline was the commonly used term "background level" in literature, which is obtained from a subset of data without direct anthropogenic influence". (See lines 107-109 on page 5)

5. Section 2, page 32305, lines 24–25: The authors state that "A Tekran 1130 denuder module operated in series with the 2537A provided continuous measurements of both RGM and Hg° respectively". This statement is not strictly true. While the Tekran 2537 provides continuous measurement of Hg° when operated alone, the 1130 and 2537 interfaced together only yield semi-continuous measurements of RGM and Hg°, with RGM and Hg° sampled typically every other hour (though here the authors indicate a 90 min sample cycle for their measurements). The authors' description should be corrected for completeness.

This statement has been revised to be: (See lines 143 – 144 on page 6)

"A Tekran 1130 denuder module operated in series with the 2537A provided continuous measurements of Hg° and semi-continuous data for RGM on a 90 minute sampling cycle."

6. Section 2, page 32305, lines 10–13: In their discussion of the performance of the denuder method for RGM quantification, the authors should acknowledge also that the collection/retention of ambient oxidized Hg species on KCl-coated quartz denuders is not well understood. For example, Lyman et al. (2010) demonstrate that denuder based RGM measurements may be biased low in the presence of elevated O_3 concentrations.

We are fully aware of these issues. In our opinion, a potential artifact of this nature may likely be site and instrument selective. We have not tested it, and therefore we cannot comment on its influence. It likely had no influence on the conclusions reached in our paper due to the few high ozone days in NH. Including every possible artifact in a paper is unreasonable in our opinion.

*7. Section 3.1, page 32307, lines 18–20: The authors state "The difference in the 10th percentile, median and 90th percentile values of Hg° between the three sites does not reveal distinct patterns **over the years**". Please clarify what years in particular are being referred to here.*

We meant over the years of the study period, which is November 2003 – August 2010. In the revised version, we made the new Figure 3 using the values from the original Table 1, and the original Table 1 is in the supplementary material section. Accordingly the text has been revised. This sentence was removed and specifics were provided instead. (See the text on page 8)

8. Section 3.1, page 32307, lines 18–20: The authors state "One exception was that the lowest 10th percentile values at TF in summer and fall were lower than PM by 11–44 ppqv over the period from 2004 to 2010". This statement is not consistent with data presented in Table 1. Table 1 shows that the 10^{th} percentile Hg° mixing ratio at TF during fall 2009 (95 ppqv) was in fact higher than that at PM (94 ppqv). This type of inconsistency occurs frequently throughout the manuscript as demonstrated in additional examples below. This discrepancy needs to be corrected.

It has been revised as follows: (See lines 192 – 195 on page 8)

"One striking feature is that the lowest 10^{th} percentile values at TF in summer and fall were lower than PM by 11 – 44 ppqv over the period from 2004 to 2010 except the fall of 2009 when the 10^{th} percentile value at PM (94 ppqv) appeared to be close to that at TF (95 ppqv)."

9. Section 3.1, page 32307, lines 18–20: The authors state "The 10th percentile values at AI were ~110 ppqv for the three summers (2007–2010), lower than PM by 10–20 ppqv". This statement is not consistent with data presented in Table 1. Table 1 shows that the 10^{th} percentile Hg° mixing ratio at TF during summer 2010 (128 ppqv) was in fact higher than that at PM (125 ppqv). Perhaps the authors were referring to the years 2007–2009, not 2007–2010.

The statement was thus revised as follows: (See lines 195 – 197 on pages 8-9)

"The 10th percentile values at AI were ~110 ppqv for the three summers (2007 – 2009), lower than PM by 10 – 20 ppqv, whereas it rose to 128 ppqv at AI in summer 2010, close to that at PM."

10. Section 3.1, page 32308, lines 1–6: Here the authors define the time periods over which they calculated "decline and increase rates of Hg° in the warm and cool seasons". The time periods here are inconsistent with those given in the heading of Table 2. This discrepancy needs to be clarified.

The legend of Table 2 (Table 1 in the revised version) was corrected.

11. Section 3.1, page 32308, lines 10–12: The authors state that "Total seasonal increases were ~50 ppqv at AI, 52–69 ppqv at TF, and ~40 ppqv at PM (except ~20 ppqv in fall of 2005)". This statement is inconsistent with data presented in Table 2. Table 2 shows that at PM, the total seasonal increase was 20 ppqv in fall 2008. This discrepancy needs to be clarified. It seems that a more systematic, statistical discussion of the results would help in this case and in some of the others I have identified. For instance, the authors could compare the range in values for all sites or they could compare the mean values for all sites, rather than comparing approximate, conditional ranges with approximate, conditional means.

We added two metrics: mean values and ranges of the total increase and rate of increase. See new Table 1. Accordingly, the text has been revised. See lines 212 – 222 on pages 9 – 10.

12. Section 3.1, page 32308, lines 12–13: The authors state that "Mixing ratios of Hg° in the marine and coastal environments increased more than at ***a rural elevated location*** *during the cool season". I note several instances in the paper where the research sites are referred to in the abstract (e.g., "a rural elevated location") rather than by name. The actual site names should be used instead for clarity. Furthermore, the information provided in this paper does not warrant the broad generalizations suggested by referring to the sites in the abstract. For example, the sentence here is not demonstrated by the authors to be true in general for rural elevated locations.*

We are aware that results from this paper are regional, not universal, which is clearly reflected in the title of the paper. We had no intention to generalize about our results. Having said that, for the region we are focusing on it is beneficial to compare the environments that were represented by the sites. To avoid misunderstanding, we added specific site names in parentheses accordingly.

13. Section 3.1, page 32308, lines 25–26: The authors state that "the decline rate of Hg° during warm seasons at TF varied greatly from year to year compared to relatively small ranges at AI and PM with some exceptions". The authors need to more clearly state how they are using the data provided in Table 2. Considering all the data provided in Table 2, the range in 'warm' season decline rates at AI is in fact larger (−0.1 to −0.8 ppqv/day) than that for TF (−0.1 to −0.6 ppqv/day), which is contradictory to the description of the data provided in the text.

In the postscript below the original Table 2 (now the new Table 1), we explained that the numbers with asterisks were obtained from "seasons that were shorter due to missing measurement data and/or shortened study periods" and therefore these numbers should be used with caution in comparison.

We added more detailed information on those asterisked numbers. See the postscripts below the new Table 1. Without accounting for the asterisked numbers, the range of the rate of decline at AI was -0.1 – 0.2 ppqv/day and the same range for PM, whereas at TF the range was -0.2 – 0.6 ppqv/day. Therefore the statement we made was reasonable. We added these values to back up the statement. See lines 235 – 241, page 10.

14. Section 3.1, page 32309, paragraph 2: Here the authors discuss trends in 'background' Hg° mixing ratio at the three research stations. If the calculated trends are statistically significant, this would be one of the more substantial findings of this paper. The authors calculate trends for each site and then compare the trends between sites and with other trends presented in the literature. It would be highly valuable to recalculate the trends for each site over similar time intervals when possible. For instance, the authors find no trend in 'background' Hg° at AI which had the shortest dataset. Do the trends calculated for TF and PM also disappear when only the time period of the AI dataset is considered? Are the TF and PM trends more similar when the TF trend is computed over the shorter PM data period? I suggest the authors include some statistical information on the trends they calculated as well (e.g., an indication of whether the trends are statistically significant).

We conducted the Student *t*-test from Wilks (1995) to test the significance of the trends at TF and PM. For the TF site, the t-value was -3.05, greater than the critical t-value 1.664 for one-sided t-distribution at the 95% confidence level. For the 64 monthly median background Hg° mixing ratios at Pack Monadnock, the t-value is 4.344, exceeding the critical t-value 1.671 for one-sided t-distribution at the 95% confidence level. Therefore, the decline trends at the two sites are statistically significant. This was added into the text. (See lines 262 – 267 on pages 11 - 12)

Regarding the reviewer's question on the rates of decline for the same 5.5 year period at TF and PM, the slope value of the regression line was 2.8 ppqv/year for TF and 7.1 ppqv/year for PM, resulting in a total decrease of 16 ppqv and 38 ppqv for TF and PM, respectively. We added this information into the text now. (See lines 274 – 278 on page 12)

For AI, it was 3.25 years of data. It is too short a data record for identifying a meaningful trend. Therefore, we stated in the text that "t(T)he trend at AI was inconclusive because of a limited number of years of measurements" (lines 24-25, page 32309). In response to the reviewer's question regarding the changes in background Hg° at TF and PM during the 3.5 years of AI data, we found total decrease of 10 ppqv at a slope value of -3 ppqv/year at TF and a total decrease of 4 ppqv at a slope value of -1.2 ppqv/year at PM for the overlapping time period.

15. Section 3.1, page 32310, lines 6–10: The authors state that "The complete time series of RGM at the three sites exhibited distinct annual cycles in the upper range of mixing ratios (Fig. 4). Specifically, the annual cycle in the 90th percentile RGM levels at AI and TF displayed maxima in spring and minima in fall, while at the inland site PM, values in all seasons were below the LOD (0.1 ppqv), except in springtime (Table 3)". These statements are largely inconsistent with the data *presented in Table 3. For example, Table 3 shows that there is no clear seasonal cycle in the 90th percentile RGM mixing ratio at AI; note that the 90th percentile RGM mixing ratio at AI peaks during summer in 2007, spring in 2008, and fall in 2009. Furthermore, 90th percentile RGM mixing ratios at PM were in fact >0.1 ppqv in all seasons except summer 2008. These discrepancies need to be corrected.*

The statement was describing the upper boundary of the time series in Figure 4, followed by specifics. The paragraph was rewritten to clear up confusion, and more detailed information was provided to back up our statements. Please see lines 279 - 290 on pages 12 – 13).

16. Section 3.1, page 32310, lines 12–16: The authors state that "RGM mixing ratios were generally lowest at PM, with median values and 90th percentile values hardly exceeding 0.5 ppqv throughout the 7 seasons, even though two coal-fired power plants are located nearby, Salem Harbor and Merrimack Stations 168 km south and 119 km north of PM, respectively". They conclude that this is evidence for rapid depositional removal of any RGM emitted from the power plants. It seems that additional analysis/discussion is necessary to support this conclusion. For instance, can it be shown that times with transport from sectors encompassing the power plants showed no significant enhancements in RGM? How frequently did meteorological conditions (i.e., winds, absence of precipitation) favor transport of RGM from the power plants to PM? If transport from the power plants to PM was predominantly disfavored, then the PM observations are not useful for characterizing dispersal of RGM from the plants.

We did not draw a conclusion here. We stated our observations were consistent with Fu et al. (2008) who suggested that fast dry deposition resulted in the low RGM levels at their location. The PM site is a regionally representative site (Mao et al., 2008), which was also stated in lines 132 – 135 on page 6. The PM observations were not meant to be used to characterize dispersal of RGM from the plants. The fact of no distinct influence from the nearby CFPPs proved again the site is regionally representative.

17. Section 3.1, page 32310, lines 20–23: The authors state "larger median and 90th percentile mixing ratios were observed in the marine environment than at the coastal and inland locations in all seasons except the winter, spring and summer of 2009 when RGM mixing ratios at TF were uncharacteristically higher". In contrast to this statement, Table 3 shows that the median and 90th percentile RGM mixing ratios at TF during summer 2009 were in fact lower than at AI. This discrepancy needs to be corrected.

Corrected.

18. Section 3.1, page 32310, lines 26–28: The authors state "Mixing ratios of Hg_P at AI and TF were close in magnitude to RGM levels and were mostly below 1 ppqv except the samples above the 90th percentile values in February 2009 and the ensuing spring at TF". In contrast to this statement, Table 4 shows that the 90th percentile Hg_P mixing ratio was also >1 ppqv at AI during fall 2009. This discrepancy needs to be corrected.

Corrected.

19. Section 3.2: Here the authors discuss diurnal variation in the three Hg forms measured: Hg°, RGM and Hg^P. For clarity, I suggest the authors provide separate, numbered sub-sections for each species.

New subsections were made for Hg°, RGM, and Hg^P.

20. Section 3.2, page 32311, lines 15–17: The authors state "The daily minimum occurred before sunrise and reached maximum values at ~14:00 UTC in spring and ~15:00 UTC in summer and fall". This sentence is somewhat confusing as written. Please clarify.

This statement was reworded:

"The daily minimum occurred before sunrise and the maximum at ~14:00 UTC in spring and ~15:00 UTC in summer and fall".

21. Section 3.2, page 32311, line 24: The phrase "at our local field site" should be replaced with the name of the site under consideration. While it can be deduced from the preceding discussion that the TF site is being referred to, this needs to be stated more clearly.

Clarified as "TF".

22. Section 3.2, pages 32311–32312: Here the authors compare diurnal variations in Hg° mixing ratios at the TF and AI sites. They indicate that during summer the diurnal trend at AI is opposite in phase to that at TF. The diurnal minimum at TF occurs during nighttime, while at AI the diurnal minimum occurs during the day. The authors attribute the nighttime minimum at TF to dissolution of Hg° in dew water beneath a shallow nocturnal inversion. They suggest that dissolved Hg° would largely be re-volatilized after sunrise. The authors attribute the daytime minimum at AI to net photochemical loss due to halogen chemistry. While these conclusions may be reasonable, I feel the data presented, and the associated discussion, are not sufficient to support the authors' conclusions that (1) nocturnal surface uptake at TF is completely reversible and (2) the diurnal cycle at AI is governed by net loss of Hg° during the day. What seems missing is a more detailed discussion of (1) the likely fate of Hg° dissolved in dew water and (2) the potential role of air-water exchange of Hg° in the marine environment at AI.

Please keep it in mind that this is Part I of a three part series serving as an overview. What the reviewer suggested was excellent points for an in-depth study but beyond the scope of this overview paper. Further, we did not draw conclusions just yet; we laid out speculations/hypotheses for in-depth studies.

23. Section 3.2, page 32312, line 20: I am not certain what the phrase "diurnal mixing ratios" is referring to. It seems the authors are referring to the amplitude of the diurnal cycle, but this should be clarified.

Clarified as “the diurnal amplitude”.

24. Section 3.2, page 32313, lines 18–21: The authors sate “Two unique features distinguished AI from TF. First, mixing ratios were close in range (0.2–1.5 ppqv) between all seasons except winter 2010. This implies that in the marine boundary layer there seemed to be net production of RGM in summer and spring as opposed to spring only in the coastal boundary layer.” The reasoning behind this conclusion is not sufficiently discussed for the reader to evaluate. Further analysis/discussion seems necessary to properly identify seasonal/diurnal variations in RGM production, loss and transport. In the preceding paragraph, the authors state that at TF “Nighttime mixing ratios were close to the LOD in summer and fall but were well above it in winters and springs of 2007–2009”. Does this imply a wintertime nocturnal source for RGM at TF during 2007–2009?

“Further analysis/discussion” is imperative if we were to reveal the detailed chemistry and physics that might have been involved in producing/destroying RGM in the marine boundary layer. However, we have to stress again that this is an overview paper.

25. Section 3.2, page 32315, lines 1–3: The authors state “As aforementioned, RGM at AI was increased by 0.4 and 0.2 ppqv during the day in April and July, respectively, while Hg_P levels were quite constant throughout the day hovering around 0.1 ppqv in April and 0.3 ppqv in July.” However, diurnal variations during these particular months were not described previously in the paper. Elsewhere, the data are sorted by season, not by month. Please clarify.

The sentence was rewritten. See lines 415 – 417 on page 18.

26. Section 4, page 32316, lines 21–24: The authors state “Moreover, site differences suggest that at elevated inland rural locations interannual variability in ambient levels of Hg° is largely driven by processes in summer, while in the coastal and marine environments downwind of major source regions the net effect of all processes can vary greatly from year to year in all seasons but summer”. The wording here suggests the results are being generalized to a larger geographical region. This sort of language appears several times in the paper, yet the authors do not provide a clear explanation. Are the authors suggesting that their measurements are representative of the larger New England region or of all coastal environments downwind of source regions?

Undoubtedly results from this paper are regional, not universal. We had no intention to generalize about our results. Having said that, for the region we are focusing on it is beneficial to compare the environments that were represented by the sites. All discussion was set within the frame of this study. Revisions were made to reflect that.

27. Figure 9. The ordering of the seasons is different in this figure than in the other figures presented. I suggest changing this figure for consistency.

Figures have been remade, rearranged, omitted, and added in this revised version per reviewers’ suggestions.

Technical Corrections

1. Abstract, lines 26–28: The sentence "Diurnal variation in Hg_P was barely discernible at TF and AI in spring and summer with higher levels during the day and smaller but above the LOD at night." is not a complete sentence and needs to be reworded. The paper contains numerous sentences with a similar structure to this one. In such instances, where the authors try to use a single sentence to convey multiple pieces of information, I suggest the authors instead consider using several shorter, more concise statements.

This version of the manuscript has undergone major revisions.

2. Section 2, page 32306, lines 25–26: The sentence "A description of CO measurement can be found in Mao and Talbot (2004)" should read "A description of ***the*** *CO measurement**s** can be found in Mao and Talbot (2004)". The paper contains numerous sentences with a similar structure to this one with missing articles (e.g., "the", "an") and incorrectly pluralized nouns.*

Revisions have been made on this account throughout the manuscript.

However, in this particular case, the use of "CO measurement" is proper, because we were referring to a description of how CO was being measured.

3. Section 3.1, page 32307, lines 4–6: The authors state "The nearly 7, 5, and 3 yr datasets at TF, PM, and AI, respectively, reproduced the annual cycle with an annual maximum in late winter–early spring and a minimum in early fall as identified in Mao et al. (2008)". I take this to mean that the three sites had a similar, reproducible annual cycle, but the sentence should be reworded for clarity.

How else to express it?

4. Section 3.2, page 32312, lines 3–6: The sentence "This implies that the observed 40 ppqv Hg° dissolved in dew would largely be re-volatilized after sunrise ***if not all****, and thus the increase in Hg° mixing ratios between sunrise and 15:00 UTC in summer can be ascribed chiefly to Hg° re-volatilization from dew alone." is not grammatically correct as written. Please reword.*

Removed. See line 338, page 15.

5. Section 3.2, page 32315, lines 5–6: The authors state "This implies that the majority of the RGM+Hg_P ***production*** *during the summer is quite possibly lost through wet and dry deposition". Here, "**production**" should be replaced with "**produced**" or similar. Please reword.*

Reworded.