

## ***Interactive comment on*** “Seasonal and diurnal variations of Hg<sup>o</sup> over New England” *by* H. Mao et al.

H. Mao et al.

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***Interactive comment on*** 8220; Seasonal and diurnal variations of Hg<sup>o</sup> over New England 8221; *by* H. Mao et al.

*Anonymous Referee 2*

*Received and published: 6 December 2007*

*Long term measurements of ambient mercury concentrations are relatively scarce and this manuscript presents a novel analysis in the trends in ambient mercury concentrations and correlations with other atmospheric constituents that contribute to the community's knowledge of mercury pollution. The data presented in this manuscript show strong warm season diel trend and season trends in the ambient concentrations. Revisions showing the variability, uncertainty, and significance in measurements are*

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*needed to better support the conclusions in this manuscript. Further analysis of the warm season diel trends is needed to support the conclusion that nighttime deposition is driving the nighttime depletion of ambient concentrations.*

### General Comments

*More information should be provided supporting the assumption that the reactive gaseous mercury (RGM) fraction of the total gaseous mercury (TGM) concentration is negligible at the three sampling sites. This can be done by expanding on the RGM measurements. Was the RGM/TGM at a maximum during midday summer periods? What about cool season periods? Are the sample lines heated? Low RGM concentrations relative to TGM do not negate the accumulation of RGM on sample lines and possible subsequent evasion as gaseous elemental mercury (GEM).*

One of the co-authors (Jeff Sigler) is preparing a manuscript on the RGM measurements from TF, PM and AI. We cited this work as Sigler et al. (2007) (this should be rectified to be Sigler et al. (2008)) in our original manuscript. (Line 19, Page 17218) Therefore we had to keep the relevant information minimal here.

The sample lines are heated at the temperature recommended by Tekran. Based on preliminary analysis of RGM measurements in 2007 (to be included in Sigler et al., 2008), RGM is almost always <1% of TGM ( $\text{Hg}^{\circ} + \text{RGM}$ ) at both TF and PM. At TF, mean seasonal daily maxima of RGM occur during mid-afternoon and range from ~0.6 ppqv (summer and fall) to ~1.7 ppqv (spring). RGM levels tended to be higher from mid-winter to mid-spring.

*The authors liberal use of the word (8216;)significant(8217;) may be misleading. A measure of significance should be provided in cases where this wording is used. A measure of the variability and significance in correlations, diurnal and annual trends should be presented.*

The word “significance” has been clarified, replaced, removed, or further backed up

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with quantitative measures depending on its context. The significance of correlation and slopes has been tested and provided in the text now. See specific comments below.

*More data is needed to support the nighttime reductions in mercury and ozone concentrations by dry deposition. Is this supported by the diurnal variability in the wind direction? The Thompson Farm site is located near anthropogenic, natural terrestrial and oceanic sources/sinks of elemental mercury. Presumably a shift in the wind speed would greatly change the concentrations as air would be advected over sources or sinks of differing strengths. Further analysis is needed to show that the observed reduction in nighttime concentrations is from dry deposition and not seasonal shifts in the diurnal wind direction. Perhaps the lack of a nighttime drop and the muted nighttime drop in GEM concentrations at the Appledore Island and Pac Monadock are due to those sites relative homogeneity in surrounding land cover type.*

This nighttime depletion of  $\text{Hg}^\circ$ ,  $\text{O}_3$ , and a number of other chemical compounds occurs year-round whenever the nocturnal inversion layer occurs.  $\text{O}_3$  nighttime depletion was studied in great detail by Talbot et al. (2005), who demonstrated that it was caused by dry deposition and titration by NO from local mobile sources on nights with the occurrence of nocturnal inversion layer. On those nights wind speed is near zero. The mixing ratio starts to pick up shortly after sunrise, and the increase is gradual. This indicates that: 1.) the gradual increase in the morning is unlikely linked to the shift in wind direction (we assume that's what the reviewer meant) which would have caused abrupt change in  $\text{Hg}^\circ$  mixing ratios, 2.) the timing of the increase of  $\text{Hg}^\circ$  is far too early for the sea-land breeze switching, 3.) the  $\text{Hg}^\circ$  level in the marine boundary layer (at AI) was close to that at TF, which means even if when the sea breeze occurs, it is unlikely to observe a change close in magnitude to the diurnal amplitude provided in our paper, and 4.) the increase was associated with the vertical mixing down of the residual air with higher levels of  $\text{Hg}^\circ$  from the previous day as result of the growing planetary boundary layer due to the surface heating after sunrise.

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Regardless, we did plot up wind rose of  $\text{Hg}^{\circ}$  mixing ratios to address the reviewer's concern, and we found no correlation at all, which confirmed our points above. In Figure rp2-1 we're showing the data from summer 2004 at TF (right) as an example; all seasons revealed similar patterns. It shows: a.) the  $\text{Hg}^{\circ}$  mixing ratios (the radius) vs. wind direction ( $\theta$ ), and b.) wind speed (the radius) vs. wind direction ( $\theta$ ). There does not appear to be dependence of the  $\text{Hg}^{\circ}$  level on wind speed and direction.

The lack of nighttime depletion of  $\text{Hg}^{\circ}$  at PM and the dampened one at AI were caused by lack of nocturnal inversion layer at PM due to its high elevation (700 m, well above the nocturnal inversion layer) and possibly negligible dry deposition of  $\text{Hg}^{\circ}$  over water in the marine boundary layer (AI).

*The anomalies of GEM versus CHBr<sub>3</sub> are interesting but only scatter plots are presented. The diel variability of CHBr<sub>3</sub> may be useful in interpreting the data collected at Thompson Farm and Appledore Island. Given the discussion on oceanic influences on the mercury concentrations the relationship between ambient concentrations and wind direction at the Thompson Farm and Appledore Island site should be quantified with a scatter plot or concentration rose.*

We couldn't find meaningful relationship between the ambient levels of GEM and  $\text{CHBr}_3$ , and was more successful with their anomalies. The use of anomalies of GEM and  $\text{CHBr}_3$  ruled out the diel variability of  $\text{CHBr}_3$ .

With regard to the relationship between ambient concentrations of  $\text{Hg}^{\circ}$  and wind direction at TF and AI, please refer to our response to the previous comment.

*Changes in seasonal synoptic weather patterns and the seasonal variability in the boundary layer mixing depth should be discussed in the interpretations of the changes in the GEM mixing ratios. Could some of the changes in the ambient GEM concentrations arise from changes in the boundary layer depth or changes in the source of air parcels advected to the study sites.*

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The boundary layer mixing depth should not influence the  $\text{Hg}^{\circ}$  mixing ratio directly. However, the low mixing depth for the nocturnal boundary layer indicates the occurrence of the nocturnal inversion layer, which isolates the residual layer air mass bearing higher levels of  $\text{Hg}^{\circ}$  from the surface, and hence there was a net sink of  $\text{Hg}^{\circ}$  near the surface which leads to nighttime depletion of  $\text{Hg}^{\circ}$  on those nights. The mechanism of this phenomenon was discussed in details in Section 3, Line 23-29, Page 17220.

#### *Specific comments*

*1. Page 17215 lines 21-23: Given the reported annual and seasonal variability in this manuscript, the time of year of the measurements preferably the general characteristics of the measurement site, i.e. coastal, taiga, etc., by Poissant et al (2004) should be included.*

The year of the citation was mistaken; it should be Poissant et al. (2005), which has been corrected now. The time of the year of the measurements and the general characteristics of the site were included. (Lines 21, Page 2 - Line 1, Page 3 in the revised manuscript)

*2. Page 17216 lines 18-19: CMAQ Hg models the dry deposition of GEM using a resistance model that is temporally and spatially dynamic, as reported in Lin et al (2006). Defining a seasonal and domain mean as the deposition velocity of GEM is misleading. A range of values, preferably for forested or coastal land cover types, would be more applicable to the comparisons presented in this manuscript.*

Revision made upon suggestion, and the values are cited from the ongoing work from our group. (See Line 22 page 3 - Line 2 Page 4 in the revised manuscript)

*3. Page 17218 lines 12-13: Please specify (8216;)standard additions of  $\text{Hg}^0$  (8216;). Was this done using the internal permeation source of the Tekran? Were these spiked air samples? What were the concentration or loading of these (8216;)standard additions(8217;)?*

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“Standard additions of  $\text{Hg}^{\circ}$ ” was done using the internal permeation source of the Tekran. These were spiked air samples. The concentration of these standard additions was 2-3 times higher than ambient mixing ratios. This piece of information has been added now (Lines 4-6, Page 6).

*4. Page 17220 lines 10-11: A measure of the significance of the (8216;) significant almost daily downward propagation in its mixing ratio (8217;) should be reported.*

It was quantitatively elaborated on in the following statements in the original manuscript (Lines 11-14, Page 17220): “over this time period (March - September)  $\text{Hg}^{\circ}$  decreased at 0.5 - 0.6 ppqv  $\text{d}^{-1}$  in all years except for 2004, where the rate was 0.3 ppqv  $\text{d}^{-1}$ . These rates of decrease were a factor of 2 smaller than the subsequent increase during the colder month”.

*5. Page 17221 line 6: A measure of the significance of the summer trends in the PM site GEM mixing ratios should be reported.*

In this paragraph we were discussing the diurnal variability. It is not clear to us what the reviewer meant by bringing up the discussion of seasonal trends here. Moreover, as described in the original manuscript (Lines 14-17, Page 17220), the summer trends at PM were much less pronounced compared to those at TF.

*6. Page 17221 lines 11-13: (8216;) considerable interannual variability (8217;) should be quantified. How did the interannual variability compare to the seasonal variability? Are the seasonal values from different years significantly different?*

It has been quantified as “considerable interannual variability (20-30 fmol/mol) “(Lines 17-18, Page 9 in the revised manuscript), which is comparable to changes from season to season (e.g., decreases in  $\text{Hg}^{\circ}$  levels from winter to summer by  $\sim 30$  ppqv on average). As stated in Lines 11-12, Page 17221, “at TF there was considerable interannual variability (20-30 fmol/mol) in the seasonally averaged diurnal cycle of  $\text{Hg}^{\circ}$  for all seasons but summer (Figure 2a); this difference was most pronounced during the

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fall season“.

*7. Section 5: additional information is required to support the hypothesis that the nighttime depletion of GEM at TF is a result of dry deposition. Section 6 acknowledges that TF is located near a multitude of natural and anthropogenic sources and the analysis of GEM versus CHBr3 implicitly implies a predictable diurnal shift in wind directions. Estimates of scatter in mean values and significance in relationships in the measurement data should be presented in this section.*

The entire Section 5 was dedicated to proving the nighttime depletion of Hg<sup>0</sup> was a result of dry deposition. Honestly, we don't know what more additional information is needed at this point. On a night with visible nighttime depletion of Hg<sup>0</sup>, there tended to be coincident depletion in O<sub>3</sub> and NO<sub>y</sub>, and near zero wind speed. Figure rp2-2 shows wind speed for a typical night with nocturnal inversion layer, which clearly illustrates our points. Therefore, wind direction can hardly be the factor to cause the nighttime low levels of Hg<sup>0</sup> by advection.

*8. Page 17225 line 14: Please quantify the (8216;) significant day-to-day variation (8217;)*

This was quantified in the seasonal trend in Figure 8a as described in the text (Line 14). We removed “and exhibited significant day-to-day variation“ because the first half of the original sentence “total daily loss of Hg<sup>0</sup> during the 2004 warm season at TF varied from 12 fmol d<sup>-1</sup> in April to 5 ppqv d<sup>-1</sup> in fall“ already quantitatively suggested the significance of day-to-day variation.

*9. Page 17227 second to last paragraph in section 5: Nighttime deposition velocities are typically much lower than daytime values. Are there published estimates of nighttime deposition velocities as high as the 0.17 cm s<sup>-1</sup>? This is larger in magnitude than the peak mid day deposition velocity reported in the modeling study of Lin et al. (2006).*

Not to our knowledge were there estimates of nighttime deposition velocities as high

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as  $0.17 \text{ cm s}^{-1}$ . That was the point we tried to make in this study that the dry deposition velocity used in current models in literature was largely small and hence the loss through dry deposition is underestimated.

*10. Page 17228 line 9: Please quantify or change the wording in (8216;) deposition processes for Hg<sup>0</sup> are in fact very significant (8217;). (8216;) very (8217;) can be eliminated from the sentence as it is not quantitative and adds little value.*

The word “very“ has been removed.

*11. Page 17229 second full paragraph: Was there no measurement of wind speed and direction? A wind direction filter would be a much better indicator of onshore transport.*

See our response to Comment #6.

*12. Page 17230 lines 16-17: Please quantify the (8216;) significantly lower Hg<sup>0</sup> levels (8217;)*

The “significant lower Hg<sup>0</sup> levels“ were quantified in Section 3. It was quantified by comparing the diurnal and seasonal variation between the two sites.

*13. Page 17231 lines 10-12: Weekly scale variances in the concentrations may be indicative of a dependence on synoptic weather patterns.*

It certainly can be, and that was why we examined the changes in temperature, moisture, wind field, and precipitation that are associated with synoptic weather patterns. Again we need to point out here that we included all periodicities on the time scale  $> 1$  week, not just weekly.

*14. Page 1732 line 13: Please quantify the (8216;) significant decreases in the maximum mixing ratios (8217;)*

This was one of the findings from Section 5 which was dedicated to quantitative discussion of the relationships of Hg<sup>0</sup> with a number of species and their interannual variability. The paragraph of Line 27 on Page 17222 to Line 12 on Page 17223 discussed

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quantitatively this “significant decreases in the maximum mixing ratios“. Specifically, it was stated that “the maximum mixing ratio of CO in winters 2006 and 2007 did not exceed 600 ppbv, whereas in winter 2003 CO peaked at close to 1000 ppbv. Lower maximum levels were also observed in CO<sub>2</sub> and NO<sub>y</sub> at TF in winters 2006 and 2007 compared to previous years, indicating that less polluted air masses arrived at the site. The Hg<sup>o</sup>-NO<sub>y</sub> relationship observed at TF in winter had large interannual variability in the slope values (Figure 6). Similar to the Hg<sup>o</sup>-CO correlation, the slope value increased by more than a factor of 2 from 0.50 ppqv/ppbv in winter 2004 to 1.22 ppqv/ppbv in winter 2006. The mechanisms driving this phenomenon are explored in Section 7.2“.

*15. Page 1732 lines 25-26: Please quantify or provide a citation for (8216;) near normal conditions in 2004 and 2005 to significantly warmer than normal conditions in 2006 and 2007(8217;)*

In the original manuscript, the remaining paragraph did follow up on this statement with numbers and citation. See Line 26 on Page 17232 - Line 4 on Page 17233.

*16. Page 17236 line 8: Please quantify (8216;) overall significantly lower Hg levels and steeper decreasing trend(8217;)*

These were quantified in Section 3, Lines 12-20, Page 17219 and Lines 9-13, Page 17220.

*17. Figure 2: Error bars should be added to the mean quantities in the figures.*

We added the standard deviation of means to the figures. See revised Figure 2.

*18. Figures 4 through 6 and 11: A p value should be added to the figures or in the text describing the figures.*

p Values added (Lines 17-19, Page 10; Lines 19-21, Page 11; Line 6, Page 12 in the revised manuscript).

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