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Atmospheric
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Interactive comment on “Seasonal and diurnal variations of Hg$^\circ$ over New England” *by* H. Mao et al.

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Interactive comment on "Seasonal and diurnal variations of Hg$^\circ$ over New England" *by* H. Mao et al.

Anonymous Referee 1

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The authors present a detailed analysis of long term monitoring of elemental mercury at two sites in New England: at Thompson Farm (TF, longer than 3 years) and Pac Monadnock (PM, longer than 1.5 years). These measurements were complemented by a short term monitoring at Appledore Island (AI) in the Gulf of Maine. Whereas mercury concentrations in air at PM appear to be similar to other mercury measurements in North America, mercury concentrations at TF show a number of atypical features

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which the authors ascribe largely to the coastal influence. The authors did a fine job to explain this atypical behavior in terms of sink processes but, in my opinion, tend to underestimate the role of emissions. They also tend to generalize the atypical features observed at TF. The discussion is at times difficult to follow because of frequent switching of the perspectives and a lack of precise wording. I recommend the publication after several factual and more extensive editorial revisions suggested below.

Factual comments:

The authors provide numerous statistically derived numbers such as averages and slopes of correlation lines. To judge the significance of their differences, especially of the frequently discussed slopes, it would be helpful to add standard deviations and the number of measurements used in the correlations.

The standard deviations and the number of measurements used in correlations have been added. See our response to specific comments below.

The statement 8220;Large interannual variability in warm season8230;.may be due to the role of precipitation patterns8230;8221; (page 17214, line 16) in the abstract and the pertinent discussion in the text neglects the possible role of mercury emissions from biomass burning. Emissions from biomass burning are highly variable from year to year and may explain the observed behavior equally well or even better.

Data from Canada (http://nfdp.ccfm.org) shows that total area burned in Quebec and Ontario were much higher in 2005 than in 2004. In 2004, there was more precipitation and fewer hectares burned in Québec and Ontario, where previous studies showed that fires can influence the northeast US (Sigler and Lee, 2003; DeBell et al., 2004). Hence, should emissions of biomass burning be the dominant effect, one would expect lower levels of Hg°, not higher, during the warm season in 2004 than in 2005. However, the steeper decreasing trend and the much lower annual minimum value in the 2005 warming season contradicts this piece of information. Moreover, the U.S. national data (http://www.nifc.gov/fire_info/fires_acres.htm) shows no significant difference in total

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burned area between 2004 and 2005 nationwide (and most of the burning takes place out west and, especially, in Alaska). Therefore, the impact of emissions from biomass burning was ruled out on the variation in Hg$^{\circ}$ levels from the warm season of 2004 to that of 2005. We have added this piece of information in the manuscript now. (Lines 10-21, Page 21 of the revised manuscript)

In the abstract the authors state: 8220;These trends could be explained by a homogeneous surface distribution of Hg0 over the North American continent in winter and/or rapid removal of mercury released from anthropogenic sources.8221; The more homogeneous distribution of longer lived species such as mercury in winter is rather a fact than a surmission. For alkanes it was demonstrated e.g. by Penkett et al (J. Geophys. Res. 98, D2, 2865-2885, 1993) and there is, to my opinion, no plausible reason to doubt it in the case of even longer lived elemental mercury. The sentence can also be read as if the anthropogenic elemental mercury were removed more rapidly than other elemental mercury which is hardly possible.

We agree with the reviewer with regard to the long lifetime of Hg$^{\circ}$ in winter and certainly we did not doubt the long lifetime of Hg$^{\circ}$ was likely the main controlling factor of the homogeneous distribution of the surface Hg$^{\circ}$. Here what we were trying to explain was the contrast between the large variability in anthropogenic tracers such as CO, NO$_y$, and CO$_2$ and the small variability in Hg$^{\circ}$; yet the primary sources of all these compounds are all anthropogenic in winter. What we found was such large interannual variability in CO, NO$_y$ and CO$_2$ was associated with the more meridional circulation patterns in winters of 2004 and 2005 which were conducive to the southward transport of the Artic air mass across the U.S., entraining anthropogenic emissions. Granted that Hg$^{\circ}$ is long-lived, one should expect just as much variability in Hg$^{\circ}$ levels as other anthropogenic tracers from winters of 2004 and 2005 to winters of 2006 and 2007. However, the observed relatively small variability in Hg$^{\circ}$ levels indicates fast removal of anthropogenic mercury. Our speculation is that the total mercury that remained in the atmosphere was relatively less enhanced compared to other anthropogenic tracers be-

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cause a significant portion of the anthropogenic mercury emission is reactive mercury which is removed quickly from the atmosphere. We had no intention to state that "*the anthropogenic elemental mercury were removed more rapidly than other elemental mercury* ".

At the beginning of Chapter 4 the authors state that the time lag of seasonal Hg° maxima and minima against those of CO implies 8220;that other equally or more important oxidative processes beside reaction with OH and/or possible sources influence the annual temporal variation of Hg08221;. This is not quite true as even the species such as alkanes which are removed predominatly by OH show a time lag. As demonstrated convincingly by Bottenheim and Shepherd (Atmos. Environ. 29, 647-664, 1995), the lag increases with the increasing lifetime of the compound. The lag of mercury against CO and the seasonal amplitude at many sites can thus be viewed as an evidence for longer lifetime of mercury (in agreement with some other pieces of evidence) and as a suggestion of the dominance of OH reaction.

In the case of alkanes, difference of lifetime might be the controlling factor to the lag, but in the case of Hg°, it is much more complicated an issue. Our calculation shows that the oxidation of Hg° by OH was comparable to that by O_3 using the minimal O_3-Hg° reaction rate constant whereas negligible using the maximal constant. Research has suggested that Hg° oxidation by halogen radicals is much faster than that by OH and O_3. Therefore, we were being careful in speculating the causes for such a time lag.

Editorial comments:

The paper centers around the analysis of TF measurements, the PM measurements are only scarcely mentioned. This is understandable in view of the longer monitoring period at TF. But the PM measurements are more in line with other mercury monitoring in North America and the presentation of this would provide a better basis for the understanding the peculiarities of the TF measurements and prevent from their undue generalization. The long term mercury monitoring elsewhere in North America also

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needs to be referred to in more detail to underline the typical behavior at PM and the atypical one at TF.

In our opinion, PM is a pretty unique site, being at an elevation of 700 m. That was why we observed dampened temporal variation including diurnal, seasonal and annual cycles at PM. We presented and discussed this in great detail in comparison with measurements at TF in Section 3. However, in Section 4, we were focused on the relationships between Hg° and other anthropogenic tracers, and the measurements of those tracers at PM were not available with the exception of CO. That explains why we only showed CO-Hg° for PM. The availability of measurements of trace gases at TF and PM was more clearly stated now in Section 2 on Page 4 in the revised manuscript.

Abstract: The second sentence 8220;In comparison, Hg0 at Appledore Island 8230;.8221; reads as if seasonal variation were also measured at AI, which in view of two months long measurement is not true. The sentence thus needs rewording. For which season applies the statement 8220;Our analysis indicates that Hg0 had a regional background level of 732; 160 fmol/mol8230; 8220;? Or is the background independent of season?

We changed ”one summer” to ”two months” for the concern the reviewer had. (Line 3, Page 2 in the revised manuscript)

We added ”in winter” to clarify the season for the background level 160 fmol/mol. (Line 9, Page 2 in the revised manuscript)

The last sentence (8220;We caution that 8230;.) generalizes the observations at TF which in view of their peculiarities is highly questionable.

Based on our comparative analysis of the CO- and NOy-Hg° between the winters of 2004/2005 and 2006/2007, we found that in winters 2004 and 2005 the circulation patterns were more meridional; the Arctic air mass reached the southern U.S. and then veered toward the north arriving TF. Such air mass entrained fresh anthropogenic

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emissions. In comparison, the circulation pattern in winters 2006/2007 was much less meridional and the air mass arriving at TF was originated from southern Canada, which consequently contained much less fresh anthropogenic emissions. In this case, the CO-Hg$^{\circ}$ relationship reflects the ratio of loss of CO and Hg$^{\circ}$, instead of the ratio of CO to Hg$^{\circ}$ in fresh anthropogenic emissions. However, in literature, there's a tendency to seek the CO and Hg$^{\circ}$ emission ratio by examining the slope of CO vs. Hg$^{\circ}$. Therefore, we cautioned readers that in the flow regime such as the ones in winters 2006 and 2007,"the Hg$^{\circ}$-CO slope possibly reflects the ratio of Hg$^{\circ}$ loss relative to changes in CO more than their emission ratio". This discussion was elaborated in Section 7.2. We believe this statement is solid based on a careful analysis and logical inference.

Chapter 3 on 8220;Seasonal and diurnal variations8221; is difficult to read because the authors switch several times between the discussion of seasonality and diurnal variation (and its amplitude). The discussion is further obscured by the missing reference to the monitoring site: e.g. in paragraph starting on line 18 of page 17220.

We discussed the diurnal variation of Hg$^{\circ}$ by season; we don't see how to isolate the discussion on the diurnal variation entirely from the seasonal one.

The first sentence mentions TF and PM, but the discussion starting by the second sentence is limited to TF only without saying so explicitly. The reader has thus to look at the diagrams to find out what is being discussed. Reordering and more precise wording of the entire paragraph are highly desirable.

That is the lead sentence of the discussion in the following three paragraphs which include TF and PM.

Page 17218, line 16: The sentence 8220;In most environments, a few minute sampling resolution for RGM is too short to contribute the measured TGM.8221; needs rewording. It is not the sampling time which determines the contribution of RGM to TGM but its percentage relative to TGM.

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What we meant was the amount of RGM that can be trapped within 5 minutes is below detection limit; we collect RGM for 2 - 3 hours in order to obtain detectable concentrations. To avoid misunderstanding, this sentence was reworded to be ”a few minute sampling resolution for RGM is too short to detect levels near the detection limit” (Lines 10-11, Page 6 in the revised manuscript).

Page 17219, line 26: 8220;annual8221; instead 8220;nnual8221;

Corrected.

Page 17222, paragraph starting at line 20: How was the background level deduced: from Hg/CO correlations or as an average of Hg concentrations for the lowest 10th percentile of CO? In both cases standard deviations should be given for the seasonally averaged Hg mixing ratios.

The wintertime background level of Hg° was deduced from the linear relationship between CO and Hg° at PM, $Hg^\circ = 116 + 0.23 \times CO$ from winter 2006 and $Hg^\circ = 134 + 0.21 \times CO$ from winter 2007, using the lower 10th percentile value of CO mixing ratios. Because the lower 10th percentile value of CO levels has been considered to be the background level, the Hg° level estimated based on this is logically considered to be the background one.

It is not clear to us what the reviewer was referring to by ”both cases”. The seasonally averaged Hg° mixing ratios and their standard deviations were indeed provided in Table 1.

Page 17222, last paragraph: The Hg/CO correlation at TF is obviously substantially worse than that at PM. Are the slope differences between TF and PM significant? Are the interannual differences at TF significant?

The slope differences between TF and PM are significant. P values and error estimates of the slopes are given now in the text. The interannual differences at TF are indeed significant based on our error estimates. See Lines 17-19, Page 10; Lines 19-21, Page

11; Line 6, Page 12 in the revised manuscript.

Page 17223, paragraph starting at line 13: Many of the gases investigated here correlate quite well with CO because, in a broader sense, they are tracers for industrial and residential activity. If CO does not correlate at TF as well as at PM, one should not expect good correlation of any of these substances either, irrespective of their sources and lifetimes. This reasoning applies also for SO2 discussed in the next paragraph.

Not all these compounds are correlated with CO owing to their different lifetimes.

Page 17223, last paragraph about correlations with SO2: The SO2 correlations at PM should be presented here and compared with those at TF.

No SO_2 measurements were available from PM.

Page 17224, last paragraph: 8220;Total chemical loss of Hg0 through reaction with O3, OH, and NO3 was estimated using typical mixing ratios at TF8230;.8221; reads almost as if OH and NO3 have been measured there. 8220;assumed8221; or 8220;estimated8221; is probably more correct. On the next page the source of OH data is given but where did the NO3 concentrations come from? The question is also how 8220;typical8221; are these concentrations at an untypical site like TF.

The NO_3 concentration was given based on the measurements obtained during ICARTT 2004 (Ambrose et al., 2007, JGR).

Page 17228, paragraph starting at line 3: The warm season lifetime estimated here from observations at FT does not fit with the substantially longer lifetime suggested by the magnitude of seasonal amplitude and of maxima and minima delay against December 21 at TF. This inconsistency can be resolved if the short lifetime at TF were only a local phenomenon. For larger spaces, the behavior at PM seems to be more representative.

The lifetime of Hg° at TF varies seasonally, much shorter in summer and early fall possibly due to higher levels of halogen radicals, which are solar radiation dependent,

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and longer in winter and early spring due to less radicals of the kind. In the original manuscript, we clearly stated that ”our analysis indicates that deposition processes for Hg° are in fact very significant, and the lifetime of Hg° in the local planetary boundary layer at TF is short”. (Lines 9-10, Page 17228)

PM is an inland site, and thus it did not exhibit the kind of behavior in Hg° as suggested in the measurements at TF. However, it is a high elevation site, which results in its own idiosyncratic features in comparison to other low elevation locations.

Page 17229, line 8: 8220;source emissions8221; - one word suffice.

Corrected.

Page 17229, line 15: Is the correlation significant and what is the uncertainty of the slope? The same should be given for the AI measurements described below.

The correlation significance and the error estimates of the slope were given now. See lines 15-17, page 10 in the revised manuscript.

We did not examine the Hg°-CO relationship at AI.

Page 17231: The spectral analysis presented here is interesting but its result is probably not well explained. In fact, a week is just about the average period of changing weather situation at the latitude of New England and the accompanying change of air masses. To my opinion, the result just means that the change of air masses is responsible for 71% of the variance in 2005 and 32% in 2004. If this is correct than the next two paragraphs are of hardly any use.

Here we referred to all the periodicities $>$ 1 week. Whatever these cycles mean in physical processes, whether a changing weather situation in the region and the accompanying change of air masses, the difference in the variance of these cycles suggested the possible dominant causes for the interannual variability observed in Hg° as described, be the processes on time scale $>$ 1 week. Moreover, these processes are most likely large-scale instead of local-regional scale ones given the time scales. For instance, even if the main cause was the change of air masses only, it indicates that a shift in such changes from year to year could potentially cause large variability in Hg°. The following two paragraphs were meant to elaborate on this point because there are obviously many processes associated with weather changing that are on the time scale $>$ 1 week. Change in solar radiation could be one of those processes, which directly affects photodissociation reactions, which subsequently leads to changes in levels of halogen radicals, OH, and $O_(3)$. Changes in atmospheric circulation patterns (e.g. sea level pressure, SLP), temperature, moisture, radiation flux, or wind speed/direction are also ones of the aspects most relevant to weather changing, and thus we dedicated a paragraph to examining these variables.

Page 17232, 8220;Wintertime Hg08221;: As already mentioned the seasonal amplitude of Hg, CO, NOy, and SO2 concentrations reflect their atmospheric lifetime. The smallest seasonal amplitude of Hg0 just implies the longest lifetime. This is of course in disagreement with the general application of the short lifetime of mercury estimated here from the measurements at TF. The conclusion to me is that the observations at TF cannot be generalized.

The short lifetime of Hg° estimated in Section 6 was for the warm season in a coastal region where abundant halogen radicals are likely available for Hg° oxidation. Moreover, we must clarify one point that in Section 6 we were focused on warm seasons of 2004 and 2005, and in Section 7.2 we were discussing the interannual variability in Hg° during winters of 2004 - 2007. By no means did we intend to generalize about the finding of the short lifetime of Hg° over the warm season at TF.

Page 17233, paragraph starting at line 10: Correlation of Hg with NOy for NOy > 40 ppb is presented here for TF. How does it look like at PM? The transport of the Arctic air should also be recognizable in a distance of some 160 km at PM.

No NO_y measurements were available at PM.

Page 17234, 2nd and 3rd paragraph: As already mentioned, more homogeneous dis-

tribution of Hg0 in winter is a fact, not a surmission. The explanation 2) is unlikely for a) it is not specific for winter and b) RGM makes out only a small contribution to mercury measured at TF in every season. The discussion in third paragraph assumes implicitly a generally longer lifetime for CO than for elemental mercury. The amplitudes of the seasonal variation of CO and Hg° may be roughly comparable at TF but that is not generally the case at other sites in the northern hemisphere (and probably not at PM either 8211; that is just the reason why Hg0 and CO diagram for PM should be shown as a figure 3b).

We disagree that ”more homogeneous distribution of Hg0 in winter is a fact, not a surmise”, because, to our knowledge, so far no measurements are available to show distribution of Hg° on the hemispheric scale. The measurements of Hg° from a few individual locations suggested Hg° levels in winter were likely higher in the Arctic than at midlatitudes (e.g., Schroeder et al., 1998; Lindber et al., 2001; Dutchak et al., 2002). We do agree that the longer lifetime of Hg° in winter can possibly lead to a homogeneous distribution, which is inferred from our analysis.

The second explanation was reworded here to avoid misunderstanding. In explanation #2, we were discussing the anthropogenic emissions of RGM, not the ambient level of RGM, and thus this explanation was not meant to be ”specific for winter”, assuming in this study the seasonality of anthropogenic emissions was negligible. We were stating the fact that the emission of RGM comprised a large portion of the total mercury anthropogenic emissions (e.g. 34% of the emission from coal fire plants averaged in the U.S., Sullivan et al., 2006), and hence in winters 2004 and 2005 the increase in Hg° due to enhanced entrainment of anthropogenic emissions was relatively smaller compared to other anthropogenic tracers.

It is not clear to us which part of the discussion appeared to be assuming ”*a generally longer lifetime for CO than for elemental mercury*”. In the original manuscript we stated that ”Emitted CO is mostly retained in the atmosphere during winter due to its long lifetime, while RGM is likely removed quickly after entering the atmosphere” (Lines 27-

29, Page 17234). Clearly we were referring to the quick removal of RGM, but never Hg°. To further apply the point made above, the relatively small increase in Hg° and yet large increase in CO likely led to the relatively smaller slopes in winters 2004 and 2005.

Page 17236, paragraph starting at line 11: The decline, as defined here, will depend on the annual maximum which in turn will depend largely on the emissions. Large year to year variability of mercury emissions from biomass burning combined with a longer lifetime of Hg0 would lead to substantial interannual differences of mercury minima and maxima even if the sink processes remained constant. Several other comments to the abstract apply here as well.

Please refer to our response to the second comment on Page 1.

Table 1: Number of measurement for each season should be given because only then the significance of the interannual differences can be judged.

Numbers of measurements were given now. (Line 16, Page 7 and Table 1 in the revised manuscript)

Fig. 3: According to page 17217 CO was also measured at PM. Since a lot of the discussion concerns with the Hg0 8211; CO relationship, this relationship at PM should be also shown and the differences between TF and PM discussed in the text.

Revision made upon the reviewer's suggestion. (See Lines 8-10 on Page 10 in the revised manuscript and Figure 3b)

Figs. 4, 5 and 6: The uncertainty of the slopes and intercepts and r2 should be given.

The uncertainty is given now. (Lines 17-19, Page 10; Lines 19-21, Page 11; Line 6, Page 12 in the revised manuscript)

Fig. 6: The corresponding diagram for measurements at PM is missing.

NO_y measurements were not available at PM.

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Fig. 9b: If I understand the Fig 9a properly than it shows all the diagrams in Fig. 5 combined. But what is the meaning of black and red in the Fig. 9b?

All points were in black except the ones along the lower boundary of the NO_y-Hg$^\circ$ relationship which were highlighted in red, as indicated in the figure caption. The red coloring was meant to emphasize the well-defined linear relationships between NO_y and Hg$^\circ$ for the measurements with $NO_y > 40$ ppbv and $NO_y < 40$ ppbv along the lower boundary.

Fig. 10: The number of averaged days in a year is given in the text but should be given in the caption here as well. The three diagrams are not clearly ascribed to the pertinent years.

The number of averaged days in a year has been given in the caption upon the reviewer's suggestion. The three diagrams have been ascribed to the pertinent years.

Fig. 12: TF should be mentioned in the caption.

”TF” was indicated now in the Figure 12 caption.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 17213, 2007.