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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal and diurnal variations of Hg° 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 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 statement “Large interannual variability in warm season….may be due to the role of precipitation patterns…” (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.

In the abstract the authors state: “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.” 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.

At the beginning of Chapter 4 the authors state that the time lag of seasonal Hg0 maxima and minima against those of CO implies “that other equally or more important oxidative processes beside reaction with OH and/or possible sources influence the annual temporal variation of Hg0”. 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

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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.

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

Abstract: The second sentence “In comparison, Hg0 at Appledore Island ….” 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 “Our analysis indicates that Hg0 had a regional background level of ˜ 160 fmol/mol… “? Or is the background independent of season?

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

Chapter 3 on “Seasonal and diurnal variations” 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. The first sentence mentions TF and PM, but the discussion starting by the second sen-

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tence 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.

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

Page 17219, line 26: “annual” instead “nnual”

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.

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?

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.

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

Page 17224, last paragraph: “Total chemical loss of Hg0 through reaction with O3, OH, and NO3 was estimated using typical mixing ratios at TF….” reads almost as if OH and NO3 have been measured there. “assumed” or “estimated” is probably more correct. On the next page the source

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of OH data is given but where did the NO3 concentrations come from? The question is also how “typical” are these concentrations at an untypical site like TF.

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.

Page 17229, line 8: “source emissions” - one word suffice.

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.

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.

Page 17232, “Wintertime Hg0”: 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.

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.

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Page 17234, 2nd and 3rd paragraph: As already mentioned, more homogeneous distribution 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 Hg0 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 – that is just the reason why Hg0 and CO diagram for PM should be shown as a figure 3b).

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.

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

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

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

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

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?

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

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years.

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

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