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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Oceanic influence on atmospheric mercury at coastal and inland sites: a springtime noreaster in New England" *by* J. M. Sigler et al.

Anonymous Referee #2

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Review report on the manuscript:

Oceanic Influence on Atmospheric Mercury at Coastal and Inland Sites: A Springtime Noreaster in New England

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submitted to Atmospheric Chemistry and Physics Discussions

TGM and RGM were continuously measured at two inland sites in New England during the Noreaster event in April 2007. Peak TGM values, approximately occurring simultaneously at the two measurement sites, are interpreted as an effect of enhanced

emission fluxes of elemental mercury from the sea during the storm. Evidence in form of meteorological data and time series of simultaneous measured marine tracers are presented to prove the hypothesis.

General comments

This is a well written paper that presents original mercury measurement data obtained during a rare meteorological event. The discussion is focusing on to what extent elevated marine mercury fluxes caused by the storm can explain the observations at the two inland sites. The conclusion is that the storm at least partly was due to the elevated TGM values obtained at the 16th of April. Although it seems not unlikely that the TGM values observed actually was due to elevated mercury emissions from the sea it is questionable if the data presented really prove this.

Note 1: As stated in the text and shown in Figure 2b the increase in TGM during the 16th of April is relatively small, only about 30% in comparison to the days before the storm. However, the enhancement is claimed to be statistical significant relative to all springtime data obtained during 2007. What does this really mean? No statistics on springtime TGM data is presented. When was the mercury monitoring started at the two sites and what are the average TGM values at these sites? An increase from 175 to 227 ppqv, which was the case at Thomson Farm (TF) during the storm, is in my view not rare as such. Instead it is something which one can expect to happen many times per year also at real background sites. As shown in Figure 2b, much higher Hg concentrations than during the storm was obtained at TF after the storm. This is not commented in the text.

Note 2: The presence of elevated concentrations of the marine tracers (CH3I, CH2Br2 and CHBr3) supports the idea of a marine influence at the studied inland sites. However, there are a few unclear circumstances regarding this. According to the text was elevated values of two of the species (CH3Br and CH2Br2) observed already on the 14th of April, i.e. more than 24 hours before the wind direction changed and marine air

masses were transported to the two inland sites. What is the explanation to this?

Note 3: Regarding the correlation between CHBr3 and CH2Br2, which is thought to demonstrate the marine origin of the air mass, arrived to TF (on p. 8, l. 13). It is stated that the regression slope of CH2Br2/CHBr3 during the storm was 0.13 which is identical to the average ratio of these two species measured at the AIRMAP station on Appledore Island. It might be true, but what does it mean? According to the text the author seem to consider the regression slope and the average concentration ratio to be the same. However, the present average concentration ratio seems to be more close to 0.5 than to 0.13!

Note 4: As clearly is shown in Figure 4a, the concentrations of CH3I and CHBr3 started to increase concurrent with the inflow of marine air early on the 15th of April, whereas the concentration of CH2Br2 more or less is constant. Further on and throughout the storm (April 15 - 16) the CHBr3 concentration is declining while CH3I increases and CH2Br2 remains constant. However, in the text (bottom, p. 8) it is concluded that CH3I was somewhat positively correlated with CHBr3 and also with CH2Br2 during the storm. This is not correct. In fact CH3I and CHBr3 are anti correlated and there is almost no correlation at all between CH3I and CH2Br2 as also is indicated by the low r-values presented in the text.

Note 5: A strong correlation between Hg0 and the marine tracer CHÂň3I is stated to have been observed during the noreaster (top on p. 10). Obviously, there is a correlation as shown in Figure 4b. But the overall time-concentration pattern of CHÂň3I is quit different in comparison to Hg. The increase in CHÂň3I starts already 24 hours before an increase in Hg can be observed. My interpretation is that the correlation after all must be considered to be relatively weak. Also the correlation coefficient, r = 0.8 (r2 = 0.64) indicates this. One must also remember that it is not possible to prove a certain relation by help of statistics. The interpretation of the test ($p < 0.01$) is that it just failed to prove that the Hg/CH3I relation only is a result of chance. Another thing to consider regarding t-statistics is that the data should be normal distributed, which often not is

the case regarding airborne pollutants.

Minor comments The time axis in Figures 2a and 2b better have the same scale to improve a direct comparison. It is not clear whether TGM or Hg0 was measured. In chapter 2 it is clearly stated that total gaseous mercury (TGM) was measured using Tekran instruments. But further in the text Hg0 values are discussed. Was the Hg data obtained from the Tekran 2537A/1130 setup or from parallel Tekran 2537A measurements? Regarding the mechanism governing Hg0 emission and and outgasing of other dissolved gases from the sea surface (page 10). The emission is not likely to be related to the total atmospheric pressure, see the literature references given below. The description on how the Hg flux estimate was performed (on page 11) is not complete, i.e. how the Hg/CH2Br2 ratio was obtained is not accurately described. Halocarbon data during the period April 17 – 19 is missing. A comment on that is required.

Literature Liss P. S. & Slater P. G. 1974. Flux of Gases across the Air-Sea Interface. Nature Vol. 247, 181-183. Nightingale P.D., Malin G., Law C.S., Watson A.J., Liss P.S., Liddicoat M.I., Boutin J., Upstill-Goddard R.C. 2000. In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volative tracers. Global Biogeochem. Cycles, Vol 14, 373-387. Strode S.A., Jaegle′ L., Selin N.E., Jacob D.J., Park R.J., Yantosca R.M., Mason R.P., Slemr F. 2007. Air-sea exchange in the global mercury cycle. Global Biogeochem. Cycles, 21, GB1917, doi:10.1029/2006GB002766, 2007 Wanninkhof R. 1992. Relationship Between Wind Speed and Gas Exchange Over the Ocean. J. Geophys. Res., Vol 97, 7373-7382.

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