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***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.**

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Author response to reviewers

We thank the two anonymous reviewers for taking the time and effort to read our paper and provide helpful criticisms. We are aware that we are presenting a novel dataset which requires careful interpretation, and are hopeful that the comments provided by the reviewers will help us produce a better manuscript. Below, we address the specific comments of both reviewers and propose changes in our final manuscript accordingly (abbreviated reviewer comments are included in quotations).

Anonymous Reviewer #1

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“Page 8738 line 25: The end of the sentence reads “as a source of Hg<sub>0</sub> using ambient measurements”. There are ambient measurements dealing with this and I believe at least a few should be mentioned.” “Page 8739 line 7-22. I believe that there are papers on measurements missing. For example there are new papers on atmospheric mercury measurements from the Mediterranean Sea area. I also think that some of the halogen papers should be mentioned.”

We will address these related comments together. A similar point was made regarding the need for additional references during the technical revision. The editor accepted our manuscript after requesting that we include more references on Hg measurements at coastal sites, specifically in the North Atlantic/Sweden and Mediterranean. We added a number of references (section 1, second and third paragraphs) to this section (e.g., work by Sprovieri, Pirrone, Hedgecock, Gardfeldt, Ebinghaus/Kock and others). Several citations were included in this section to note the reaction of Hg with halogens in the marine boundary layer (Sprovieri, Hedgecock and Pirrone, Laurier etc). We do feel that we have extensively cited relevant literature which supports the background information provided in section 1. If the reviewer can point to a very recent or specific study regarding the Mediterranean that we have overlooked or neglected that is essential here, we will cite it.

“Page 8742 line 24: The author is talking about sites and only giving one reference. There are several publications on mercury concentrations at coastal sites. Some more are needed here.”

We should clarify that we cite one particular study (Laurier and Mason, 2007) because it presents measurements from a coastal site in the eastern U.S., similar to our study, making it very appropriate in this instance. We will change the text to “coastal sites in the U.S.” for clarity (we are unaware of other RGM measurements at North American coastal sites).

“Page 8746 line 23: According to my knowledge 0.36 cannot be considered a cor-

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relation. So how can you base your calculations on this and state that this is “this tracer-based flux estimate is useful for Hg” (Page 8747 line 3-4)”

We acknowledge the weakness of the correlation in this same sentence (although we stress that any correlation is of interest here, given that the absolute concentrations of these species are almost never (even weakly) related at this site). We are well aware of the uncertainty involved in this calculation, as is described later in the section. However, we feel that the fact that the tracer-based estimate, despite high uncertainty, reasonably accounts for the observed Hg enhancement during the storm is testament to its usefulness.

“Page 8747 line 14-15: Maybe add some references on the mercury halogen chemistry.”

We will update the text here to include a reference.

Anonymous Reviewer #2

“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.”

In noting that the enhancement at both sites was statistically significant ( $p < 0.01$ ), we are referring to the data in the time series on 16 April (background levels to maximum)

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compared to the rest of the seasonal dataset. We disagree that an increase up to 227 ppqv at TF is “not rare as such.” Less than 4% of all 5-minute Hg<sub>0</sub> observations at TF in 2007 were > 200 ppqv. As noted in section 3.3, Hg<sub>0</sub> enhancements of this magnitude were unusual during rain events at TF in 2007. Sustained episodes (1-2 hours) of Hg<sub>0</sub> > 200 ppqv at TF were observed approximately once per month during spring/summer of 2007. An increase of this magnitude is rare at Thompson Farm, particularly over a period of ~12 hours (and during the morning), and this is the very point of the paper. In any case, we feel that the circumstances surrounding this particular enhancement are perhaps more important as a new result than the absolute value.

We began measuring TGM at TF in 2003, and added RGM measurements in late 2006. We will note this in section 2. The springtime mean of Hg<sub>0</sub> at TF in 2007 was ~179 ppqv and has varied between 157 and 179 ppqv from 2004-2008 (we will cite these numbers more explicitly in our revised version in addition to making a more explicit reference to our prior studies).

If the reviewer is interested, a broader discussion of Hg data at TF during 2007 and previous years can be found in our paper published very recently in ACP (Sigler et al., Gaseous elemental and reactive mercury in Southern New Hampshire, ACP, 9, 1929-1942, 2009) and also the multiple year data set prior to 2007 in Mao et al. (2008). These papers provide details on seasonal mean values at TF as well as the time frame of our ongoing Hg measurements.

As for the major enhancement of Hg<sub>0</sub> observed after the storm, we chose not to focus on this event because it appears to be a very different story, perhaps more appropriate for a future paper. Briefly, we observed a major enhancement of this sort in both 2007 and 2008 (unpublished data) at approximately the same time (late April) and under similar circumstances (the onset of a sudden warm, dry period after a cold, wet winter/early spring). These events occurred early in the morning and may be related to downward mixing of Hg<sub>0</sub> from aloft, and also occur under similar (northerly) wind directions. We have seen events of this magnitude at no other time and have no reason to suspect

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they are related to an oceanic source. We simply do not yet know whether these apparently repeating late-April events are related to sudden meteorological changes or to a seasonal combustion source.

“Note 2: The presence of elevated concentrations of the marine tracers. . . 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 (CH<sub>3</sub>Br and CH<sub>2</sub>Br<sub>2</sub>) 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?”

We are not sure which text is being referred to here. We note in section 3.3 (second paragraph) that enhancement of these species occurred during the storm, 15-16 April, and Figure 4a indicates that the enhancement did not begin until 15 April. We also compare pre/post storm levels of the halogen compounds in this section.

“Note 3: Regarding the correlation between CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub>, 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 CH<sub>2</sub>Br<sub>2</sub>/CHBr<sub>3</sub> 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?”

We report this regression slope as a way of establishing the presence of marine air with freshly emitted halogen species at TF. A similar regression slope of these species has not only been measured at Appledore Island, but also at other coastal and oceanic sites (Carpenter et al., 2003). We will make this point more clear by adding text explaining that this ratio (~0.15) is thought to be representative of fresh, co-located coastal marine emissions of these species based on previous research (e.g., Carpenter et al., Zhou et al. 2005). This ratio is typically not observed at inland sites (there is little correlation between these species at TF when the site is impacted by continental air masses).

“According to the text the author seem to consider the regression slope and the average

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concentration ratio to be the same. However, the present average concentration ratio seems to be more close to 0.5 than to 0.13!

This was a mistake on our part. We will change the reference to “average ratio” in the text to regression slope, which is correct.

“Note 4: As clearly is shown in Figure 4a, the concentrations of CH<sub>3</sub>I and CHBr<sub>3</sub> started to increase concurrent with the inflow of marine air early on the 15th of April, whereas the concentration of CH<sub>2</sub>Br<sub>2</sub> more or less is constant. Further on and throughout the storm (April 15 - 16) the CHBr<sub>3</sub> concentration is declining while CH<sub>3</sub>I increases and CH<sub>2</sub>Br<sub>2</sub> remains constant. However, in the text (bottom, p. 8) it is concluded that CH<sub>3</sub>I was somewhat positively correlated with CHBr<sub>3</sub> and also with CH<sub>2</sub>Br<sub>2</sub> during the storm. This is not correct. In fact CH<sub>3</sub>I and CHBr<sub>3</sub> are anti correlated and there is almost no correlation at all between CH<sub>3</sub>I and CH<sub>2</sub>Br<sub>2</sub> as also is indicated by the low r-values presented in the text.”

In this point (and in note 5 below), the reviewer highlights perhaps the greatest challenge of this type of study: how to elucidate relationships between Hg and halogen species which have disparate sources, relatively low measurement resolution, differing lifetimes in the atmosphere and in our experience generally show no correlation among them (e.g., Mao et al., 2008) yet, along with Hg<sub>0</sub>, were clearly enhanced at TF during this strong storm. In that sense, one of the more remarkable aspects of the data set, from our perspective, was the observation of even minor correlation between the time series of enhanced levels of Hg and the three halogen compounds. That being said, we dispute the reviewer’s assessment. Taking the time series of each halogen individually: CH<sub>2</sub>Br<sub>2</sub> may appear to be constant in Figure 4 and it certainly varies less than the other compounds, but it changes by ~70% (minimum to maximum) from 15 April to late afternoon on 16 April. CH<sub>2</sub>Br<sub>2</sub> normally shows little variation at TF (Zhou et al., 2005) and it was well-correlated with CHBr<sub>3</sub> during 15-16 April, as we describe in section 3.3. CH<sub>3</sub>I and CHBr<sub>3</sub> are not anti-correlated, in fact, (a point not made in our original manuscript), the relationship is strong from 15 April to ~13 UTC on 16 April

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( $r = 0.63$ ,  $p < 0.01$ ) but the positive correlation breaks down beginning  $\sim 13$  UTC on 16 April (coincident with the decrease in wind speed at TF). The same is true for CH3I and CH2Br2 (from 15 April to  $\sim 13$  UTC on 16 April, these two are much more strongly correlated:  $r = 0.8$ ,  $p < 0.01$ ). So, in our original analysis in section 3.3, we included data points beyond the storm peak which weakened the correlation. We did this so that we encompassed more or less the entire period during which TF was influenced by marine air, and because the Hg remained elevated compared to pre-storm levels during this time.

“Note 5: A strong correlation between Hg0 and the marine tracer CH3I is stated to have been observed during the nor'easter (top on p. 10). Obviously, there is a correlation as shown in Figure 4b. But the overall time-concentration pattern of CH3I is quite different in comparison to Hg. The increase in CH3I 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,  $r = 0.8$  ( $r^2 = 0.64$ ) 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.”

In fact, while a one-to-one correlation was not observed, the significant increase in both species beginning on 15 April is fairly synchronous. Indeed, mean CH3I on 14 April was  $\sim 0.2$  pptv, and increased to  $\sim 0.4$  pptv on 15 April and to  $\sim 0.9$  pptv on 16 April. In any case, while we agree that statistics do not prove a certain relation, our interpretation is that the correlation between Hg and CH3I is surprisingly strong, given that we previously have observed essentially no direct correlation between real-time mixing ratios of Hg0 and marine halogen species at TF (see Mao et al., 2008). The observation of simultaneous enhancement of these species and their correlation (even if weak) was the primary impetus for this paper.

“Minor comments The time axis in Figures 2a and 2b better have the same scale to improve a direct comparison.”

We will match up the scales.

“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?”

The Tekran 2537A measures TGM, but when in tandem with the 1130, Hg0 alone is monitored as RGM is stripped out. In section 2 (third paragraph), we state the 2537A continuously monitors Hg0 during the RGM sampling interval (we can add a more explicit statement to this section noting that we therefore refer to Hg0, and not TGM, measurements in the study).

“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/CH<sub>2</sub>Br<sub>2</sub> ratio was obtained is not accurately described. Halocarbon data during the period April 17 – 19 is missing. A comment on that is required.”

On the first point, we concur, particularly in light of the helpful references the reviewer provided, and will remove the reference to atmospheric pressure.

The Hg0/CH<sub>2</sub>Br<sub>2</sub> ratio was obtained using data from approximately 15 April (when winds shifted to easterly) through the end of 16 April. We will explicitly state this in section 3.4 (second paragraph).

The missing halocarbon data was due to a storm-related power outage (Hg and other systems were not affected). We will note this in the Figure 4 caption.

References:

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