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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal changes in gaseous elemental mercury in relation to monsoon cycling over the Northern South China Sea" *by* C. M. Tseng et al.

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An item-by-item response to the reviewers' comments We thank the reviewers for their helpful comments and suggestions; their critiques have been addressed carefully, and the manuscript improved. The following is mainly detailed point-by-point responses (in red) to the reviewer #2's comments.

Firstly, we thank that the reviewer #1's comments for his positive recognition on the merits of our manuscript and acceptation of the revised paper.

And then, the following is regarding the reviewer#2's comments

General comments This paper presents data from 12 cruises on the South China Sea (SCS) showing enhanced GEM concentrations in winter relative to summer and an overall enrichment of several fold in this region relative to the global background. The authors use back trajectories and modeled differences in air-sea exchange from cruise means of dissolved elemental mercury (DEM) to conclude that the dominant controls of the observed variability are continental pollution sources and wind directions dictated by the East Asian monsoon cycles. This is a plausible hypothesis based on the data however the extent to which the ocean source has been explored is somewhat preliminary.

Thanks for appreciating the realistic hypothesis and findings we proposed and accepting the merits of the paper.

The authors report cruise averages for DEM with a sample size of three measurements if I am reading correctly (averaged over 4-6 hours) and model fluxes of Hg0 based on those values.

Actually, we collected mostly 6 samples per day, sometime up to 8 samples, during a cruise at the SEATS station under normal conditions. But, there were at least 4 samples per day sometime while the sea conditions were bad. Thus, there are 4-8 samples per day to have a cruise average for DEM. We made a statement more clear in Page 7, Line 149 for collecting samples in each interval of 3-6 hours for one-day run.

They use the relatively lower concentrations of averaged DEM in winter and undersaturaturation measured at this time to conclude oceanic evasion is not a probable source of the seasonal enrichment. I think this begins to build a good case for their argument but without simultaneous air-water measurements it is difficult to completely dismiss oceanic evasion as source because DEM can be so spatially and temporally variable. For example, the authors attribute diurnal variability in GEM to oceanic evasion acknowledging substantial variability that is not captured by three numbers?

We fully agree that automated simultaneously air-water measurements are desperately

needed for solving the issue of spatial and temporal variability in DEM. We can't ignore the possibility of the ocean evasion in winter since global warming and decadal climate variability may increase the Hg emission in the weak sink status in winter in the SCS. Actually, we did do simultaneously on-site air-sea measurements for the GEM (more high-resolution from 15 min to hours) and DEM (low-resolution by 3-6 hours). Thus, we'll develop the high-resolution air-sea Hg analyzer to quantify the more reliable contributions to the diurnal variability in GEM from oceanic evasion in future study. However, the seasonal changes we show in this manuscript, while based on low-frequent on-site measurement, are so large that we feel simultaneous measurements such as those that the reviewer calls for will represent refinements to our flux measurements, but should show the same trends. These trends include a dramatic increase in GEM at the same time that DEM is dramatically decreasing. Thus, changes in both sides of the air-sea boundary work to result in winter time invasion. . .a state in which the ocean is a net sink to the atmosphere. It is certainly true that the ocean would be a stronger net sink if no elemental Hg were present in surface waters at all, so to that extent the ocean is affecting the atmosphere in winter. However, our story is principally oriented to exploring the seasonal changes, and in that situation, the wintertime invasion is principally the result of increased GEM in the air, and related environmental conditions involved such as the lowest SST and enhanced vertical mixing.

Since methods/instrumentation (Anderson et al. – various papers) exists for these measurements I think the authors should slightly reframe their main conclusion to be that evidence points to continental sources and wind monsoon direction as the factors dictating seasonal differences in GEM and this confirming this with high resolution air/water Hg0 – measurements should be the priority for future research.

We'll reframe our main conclusion as mentioned by the reviewer comments to emphasize the importance of high resolution air/water Hg0 – measurements. However, and as mentioned in our response to the previous question, this will likely be a refinement and not dramatically change our conclusions. Please see the modifications in Page 15,

Lines 343-350.

Minor comments: Introduction: Many of the background references in the introduction seem out of date. For example: Line 21: Lifetime of Hg0 is well-established as several months to a year not 1-2 years.

Thanks for useful suggestions and updated references were added throughout the text and few references out of dates were removed. Please see those in Page 3, Line 53.

Introduction: I suggest the authors double check the number for fraction of global anthropogenic emissions from Asia. A few updated inventories have come out recently and should be acknowledged.

The numbers and references were updated in the final version of the manuscript in Page 3, Line 58,61.

Section 2.4 – Would be useful to present range across stand air-sea exchange models for fluxes instead of the one number from Wanninkhof since this is on the high end of modeled values. This could be easily bounded by the Liss and Merlivat and Wanninkhof models estimates to capture the potential range.

We had put the potential ranges of air-sea Hg fluxes bounded by the Liss and Merlivat (1986) and Wanninkhof (1992) and related information into the final version of our manuscript in Page 8, Line 174-179; Page 10, Lines 211-214, 217.

Liss, P. S., Merlivat, L., (1986), Air-sea gas exchange rates: introduction and synthesis. In: Buat-Menard, P. (Ed.), The Role of Air-Sea Exchange in Geochemical Cycling, NATO ASI Series C: Mathematical and Physical Sciences, 185, 113-128. Wanninkhof, R. (1992), Relationship between Wind-Speed and Gas-Exchange over the Ocean, Journal of Geophysical Research, 97(C5), 7373-7382.

Section 3.1. Environmental conditions – Using the bounded estimates for air-sea exchange – how much of a modeled difference do you get in oceanic evasion with a mean wind speed difference by season of 3 m/s? This could help establish the rationale for

a continental pollution source of variability instead of an oceanic source.

We followed the review's suggestion to make estimates and statements via bounded ranges of air-sea fluxes for potential GEM diurnal variability and to establish the rationale for a continental pollution source of variability instead of an oceanic source as mentioned as above.

At the end of section 3.1 on diurnal variability there is a statement: "Overall, evasional Hg losses estimated as a significant source of Hg to the SCS air are confirmed convincingly" that seems to contradict the major premise of the paper. Also, I am not sure the source is "confirmed convincingly" and what does "significant" mean in this context (statistically)? Perhaps the authors meant to say that the diurnal variability in GEM may be explained by evasional losses. However, the magnitude of diurnal variability attributable to evasion is not as large as the seasonal difference, postulated to originate from continental sources.

We fully agree the reviewer's comment. The confusing words used in text will be removed and changed. We simply said that the diurnal variability in GEM might be explained by evasional losses from the SCS. However, the magnitude of diurnal variability attributable to evasion is not as large as the seasonal difference, postulated to originate from continental sources. Please see Page 10, Lines 221-224.

Section on Seasonal variability in GEM, page 12212 – lines 4-7 – Soerensen et al. in two paper in 2010 proposed an explanation for seasonal variability in GEM in coastal North American and European sites – and also ship cruises that should be acknowledged here.

Two referecnces by Soerensen et al. 2010 were added to the final version of our manuscript in Page 11, Line 241.

Soerensen, A. L. et al. (2010), An Improved Global Model for Air-Sea Exchange of Mercury: High Concentrations over the North Atlantic, Environ Sci Technol, 44, 8574-

8580. Soerensen, A.L., Skov, H., Jacob, D.J., Sørensen, B.T., Johnson, M.S. (2010). Global Concentrations of Gaseous Elemental and Reactive Gaseous Mercury in the Marine Boundary Layer. Environ Sci Technol 44, 7425-7430,

Same paragraph – the authors jump right into SST as a control on DEM and presumably evasion but this is not well explained. I don't think the SST difference is strong enough to explain a change in evasion. There is no reason to believe that SST is a good indicator of net reduction of Hg(II) except indirectly through UVA and UVB intensity as a control so I think the authors are confusing DEM concentrations and the physical exchange process

We certainly agree the Hg reduction in the surface water involves photochemical reaction. So, we do see the diurnal DEM variability during the cruises in warm seasons at the SEATS station (unpublished). In addition, a high averaged DEM (i.e, time-weighted mean during that cruise) was observed in a high SST season, suggesting a high production rate of Hg0 took place in summer. The results show the cruise averaged Hg correlated linearly with increasing SST (r2 = 0.81, n = 16 cruises, unpublished) between May 2003 and January 2007. This further indicates the SST as a control on the formation of Hg0 in seasonality. The seasonal DEM variability is closely related to the seasonal SST changes. Such a temperature dependence of DEM in the SCS offers an opportunity to explore some of the mechanistic controls behind Hg0 formation in the SCS. The apparent activation energy (Ea, kJ mol-1) of DEM production was calculated, using the Arrhenius equation; K=Ae-Ea/RT, at 140$\pm$20 kJ mol-1 for SST between 23 and 31 oC. The activation energy is similar to that estimated for surface waters in Swedish temperate lakes (about 125$\pm$5 kJ mol-1 at water temperatures of 0.5-23 oC, [Xiao et al., 1991]) and in Arctic lakes (about 150ïĆś40 kJ mol-1 between 11 and 15 oC, [Tseng et al., 2004]). This seemingly universal value can provide some clues regarding the reaction or reactions involved in the production of Hg0.

We added few references in Page 1, Line 249: Tseng C.M., Lamborg, C., Fitzgerald, W.F. and Engstrom, D.R.: Cycling f dissolved elemental mercury in Arctic Alaskan

lakes. Geochimica et Cosmochimica Acta, 68(6), 1173-1184, 2004.

Xiao, Z. F., J. Munthe, W. H. Schroeder, and O. Lindqvist (1991), Vertical Fluxes of Volatile Mercury over Forest Soil and Lake Surfaces in Sweden, Tellus B, 43(3), 267-279

Finally, we added some information regarding the GEM concentration comparison surrounding areas with the SEATS station in Page 12, Lines 273-279.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 12203, 2012.