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Comment

Interactive comment on “Distribution and air-sea exchange of mercury (Hg) in the Yellow Sea” by Z. J. Ci et al.

Z. J. Ci et al.

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We would like to thank Dr. Joachim Kuss for the valuable and helpful comments and suggestions, which have helped us improve the manuscript. Please find our point-by-point responses to the reviewer’s comments below in bold.

General comments:

The paper “Distribution and air-sea exchange of mercury (Hg) in the Yellow Sea” by Ci et al. represents an important contribution to the understanding of marine Hg cycling in that region. The study area is of special interest since it is assumed to be affected

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by an increased mercury burden originated from eastern Asian countries. The authors present data of different Hg speciations in surface water and of GEM measurements in the atmosphere mainly to estimate the air-sea exchange of elemental mercury (Hg(0)). The paper is well structured and clearly written.

Response: We appreciate the reviewer's recognition of the merits of this work.

However some issues require a more detailed elaboration. Especially, more information about wind speed and surface water temperature are necessary to understand the calculated Hg(0) air-sea exchange fluxes. Moreover, the fluxes require recalculation by using a reliable estimate of the mercury diffusion coefficient and perhaps by application of average wind speeds (see specific comments).

Response: A new table (Table 1) has been added in the revised manuscript. This table includes the data of Station, Location, Time, DGM, GEM, Water temperature, Wind speed at 10 m, Supersaturation and the recalculated Hg(0) flux. [We have followed the reviewer's suggestion to recalculate the Hg(0) flux using the recently proposed diffusion coefficient of Hg(0) developed by Kuss et al. (2009). For the detail about the recalculated Hg(0) flux, see the response to P. 1519, L.7/8 of Specific comment below.]

[Reference:]

Kuss, J., Holzmann, J. and Ludwig, R.: An elemental mercury diffusion coefficient for natural waters determined by molecular dynamics simulation, *Environ. Sci. Technol.*, 43, 3183-3186, 2009.

The paper would also clearly benefit by including temperature and salinity depth profiles into the discussion.

Response: Figure 6 has been updated to add the sea water temperature/salinity

data of three vertical stations in the revised manuscript.

For some presented values the number of decimal places should be checked and adapted to the estimated precision of the method.

Response: We have followed the reviewer's suggestion to modify the number of significant digit of the presented values (including DGM saturation and Hg(0) fluxes). Please find more detail in the responses to P. 1513, L. 8 and P. 1526, L. 8 of Specific comments below.

Specific comments:

P. 1512, Lines 15/16: supersaturation, the term seems not adequate for trace compounds since it suggests something like sparkling mineral water. It is in fact just a disequilibrium. I'd propose to avoid the terms saturation/supersaturation throughout the manuscript.

Response: We have seriously considered the reviewer's suggestion. However, considering many papers published in past three decades, the terms, such as "saturation", "supersaturation" or "undersaturation" have been used and accepted extensively by the international community of mercury science to describe the status of Hg(0) in water (DGM) respect to Hg(0) in atmosphere (GEM), e.g., Kim and Fitzgerald, 1986; Mason and Fitzgerald, 1993; Leermakers et al., 1995; Amyot et al., 1997; Gårdfeldt et al., 2001; Rolfhus et al., 2001; Lamborg et al., 2002; Landis and Keeler, 2002; Feng et al., 2004; Fitzgerald et al., 2005; Narukawa et al., 2006; Zhang et al., 2006; Andersson et al., 2007; Strode et al., 2007; Soerensen et al., 2010; Sprovieri et al., 2010. So, we think that the usages of these terms are suitable and would not be misleading.

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[Reference]

Kim, J.P. and Fitzgerald, W.F.: Sea-air partitioning of mercury in the equatorial Pacific Ocean, *Science*, 231, 1131-1133, 1986.

Mason, R.P. and Fitzgerald, W.F.: The distribution and biogeochemical cycling of mercury in the equatorial Pacific Ocean, *Deep Sea Res.*, 40, 1897-1924, 1993.

Leermakers, M., Meuleman, C. and Baeyens, W.: Mercury speciation in the Scheldt Estuary, *Water Air Soil Pollut.*, 80, 641-652, 1995.

Amyot, M., Lean, D. and Mierle, G.: Photochemical formation of volatile mercury in high Arctic lakes, *Environ. Toxicol. Chem.*, 16, 2054-2063, 1997.

Gårdfeldt, K., Feng, X., Sommar, J. and Lindqvist, O.: Total gaseous mercury exchange between air and water at river and sea surfaces in Swedish coastal regions, *Atmos. Environ.*, 35, 3027-3038, 2001.

Rolfhus, K.R. and Fitzgerald, W.F.: The evasion and spatial/temporal distribution of mercury species in Long Island Sound, CT-NY, *Geochim. Cosmochim. Acta*, 65, 407-418, 2001.

Lamborg, C.H., Fitzgerald, W.F., O'Donnell, J. and Torgersen, T.: A non-steady-state compartmental model of global-scale mercury biogeochemistry with interhemispheric atmospheric gradients, *Geochim. Cosmochim. Acta*, 66, 1105-1118, 2002.

Landis, M.S. and Keeler, G.J.: Atmospheric mercury deposition to Lake Michigan during the Lake Michigan mass balance study, *Environ. Sci. Technol.*, 36, 4518-4524, 2002.

Feng, X., Yan, H., Wang, S., Qiu, G., Tang, S., Shang, L., Dai, Q., Hou, Y.: Seasonal variation of gaseous mercury exchange rate between air and water surface over Baihua reservoir, Guizhou, China, *Atmos. Environ.*, 38, 4721-4732, 2004.

Fitzgerald, W.F., Engstrom, D.R., Lamborg, C.H., Tseng, C.M., Balcom, P.H. and Ham-

merschmidt, C.R.: Modern and historic atmospheric mercury fluxes in northern Alaska: Global sources and Arctic depletion, *Environ. Sci. Technol.*, 39, 557-568, 2005.

Narukawa, M., Sakata, M., Marumoto, K. and Asakura, K.: Air-sea exchange of mercury in Tokyo Bay, *J. Oceanogr.*, 62, 249-257, 2006.

Zhang, H., Dill, C., Kuiken, T., Ensor, M. and Crocker, W.C.: Change of dissolved gaseous mercury concentrations in a southern reservoir lake (Tennessee) following seasonal variation of solar radiation. *Environ. Sci. Technol.*, 40, 2114-2119, 2006.

Andersson, M.E., Gårdfeldt, K., Wängberg, I., Sprovieri, F., Pirrone, N. and Lindqvist, O.: Seasonal and daily variation of mercury evasion at coastal and off shore sites from the Mediterranean Sea. *Mar. Chem.*, 104, 214-226, 2007.

Strode, S.A., Jaeglé, L., Selin, N.E., Jacob, D.J., Park, R.J., Yantosca, R.M., Mason, R.P. and Slemr, F.: Air-sea exchange in the global mercury cycle, *Global Biogeochem. Cycles*, 21, GB1017, 2007.

Soerensen, A.L., Sunderland, E.M., Holmes, C.D., Jacob, D.J., Yantosca, R.M., Skov, H., Christensen, J.H., Strode, S.A. and Mason, R.P.: An improved global model for air-sea exchange of mercury: High Concentrations over the North Atlantic, *Environ. Sci. Technol.*, 44, 8574-8580, 2010.

Sprovieri, F., Pirrone, N., Ebinghaus, R., Kock, H. and Dommergue, A.: A review of worldwide atmospheric mercury measurements, *Atmos. Chem. Phys.*, 10, 8245-8265, 2010.

P. 1512, Line 18: Please check the precision of the determination (e.g., 23 ± 15 ng m⁻² h⁻¹).

Response: We have modified the number of significant digit of the presented values in the revised manuscript. According to the least number of significant digit of all relevant data, the precision of estimated Hg(0) flux is rounded off to

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one significant digit (see Table 1).

P. 1513, L. 8: toxin refers to methyl mercury, but the biogeochemistry of Hg is analyzed. I suggest to replace "this toxin" by "mercury".

Response: We have changed "this toxin" to "mercury" as suggested by the reviewer.

P1514, L.3: production - transformation reaction (since Hg is an element)

Response: We have changed "production" to "transformation reaction" as suggested by the reviewer.

P.1516, L.2: A sampling time of one minute is not much. What was the sample flow rate?

Response: The sample flow rate is 20 l min⁻¹. The value of flow rate has been added in the revised manuscript.

P. 1519, L.7/8: An estimation of the diffusion coefficient by the Wilke-Chang method is not the best choice for Hg(0). This is based on a correlation of D of organic compounds. Based on the study of Kuss et al. (2009) the D-Hg(0) is about 50% too high by application of the Wilke-Chang method. I suggest recalculation of the fluxes by using the recently proposed diffusion coefficient (Kuss et al., 2009).

Response: We have followed the reviewer's suggestion to recalculate the Hg(0) flux using the diffusion coefficient of Hg(0) [D] recently developed by Kuss et al. (2009),

$$D = A * e^{-Ea/RT}$$

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[for seawater, $A=0.02293 \text{ cm}^2 \text{ s}^{-1}$ and $E_a=17.76 \text{ kJ mol}^{-1}$]. The updated values of Hg(0) flux in all surface stations are presented in the added table (Table 1) in the revised manuscript. Correspondingly, all relevant data and discussions of Hg(0) fluxes have been modified in the revised manuscript.

[Reference]

Kuss, J., Holzmann, J. and Ludwig, R.: An elemental mercury diffusion coefficient for natural waters determined by molecular dynamics simulation, *Environ. Sci. Technol.*, 43, 3183-3186, 2009.

P. 1519, L. 15: Also the term saturation is misleading.

Response: Please see the response to P. 1512, Lines 15/16 of Specific comment above.

P. 1523, L. 26: Were the acidified samples analyzed on board? The RHg/THg ratio might have been shifted due to the storage time (dissolution of e.g., particulate material).

Response: The sea water samples were acidified on aboard and all samples were determined for Hg in the lab on shore. After the cruise, water samples were transported soon to the lab and analyzed as soon as possible. At present, the RHg determination in water has not been standardized. The RHg fraction in water depend upon many variable, such as the container, the storage time, the analytical conditions and the ambient aqueous chemistry (Mason et al., 1993; Bloom, 1994; Parker and Bloom, 2005). In practise, different researchers adopt different storage and preservation methods to determine the RHg. For example, some researchers (e.g., Gill and Bruland, 1990; Leermakers et al., 1995; Balcom et al., 2008) determined the RHg by SnCl_2 reduction following an acidified storage period of days to weeks. This method is also used in our study.

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And others determined the RHg by acidifying the unacidified samples just prior to analysis and followed by SnCl₂ addition (e.g., Rolfhus and Fitzgerald, 2001) or by direct acidic SnCl₂ addition (e.g., Mason et al., 1998). There is no doubt that the application of different methods will obtain different RHg concentration and RHg/THg ratio. Therefore, as to compare the RHg concentration and RHg/THg ratio obtained by different studies, it is important to take account of the storage and preservation method adopted by the researcher.

To address the reviewer's concern, we have added some text in Section 2.4.3 [THg and RHg determinations] to further emphasize the influence of storage and preservation methods on the RHg determination.

[Reference:]

Mason, R.P., Fitzgerald, W.F., Hurley, J., Hanson Jr, A.K., Donaghay, P.L., Sieburth, J.M.: Mercury biogeochemical cycling in a stratified estuary, *Limnol. Oceanogr.*, 38, 1227-1241, 1993.

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Balcom, P.H., Hammerschmidt, C.R., Fitzgerald, W.F., Lamborg, C.H. and O'Connor, J.S.: Seasonal distributions and cycling of mercury and methylmercury in the waters of

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New York/New Jersey Harbor Estuary, *Mar. Chem.*, 109, 1-17, 2008.

Rolfhus, K.R. and Fitzgerald, W.F.: The evasion and spatial/temporal distribution of mercury species in Long Island Sound, CT-NY, *Geochim. Cosmochim. Acta*, 65, 407-418, 2001.

Mason, R.P., Rolfhus, K.R. and Fitzgerald, W.F.: Mercury in the North Atlantic, *Mar. Chem.*, 61, 37-53, 1998.

P. 1526, L. 24: I wonder if a flux of 55 ng/m²h can be realistic. This is 1.3 µg/m²d enough to fill a 500 m air column to 2.6 ng/m³ just in one day. This is at the upper end of average Hg emissions of industrialized areas. Perhaps it was lasting for a short period only. Was this flux value calculated by using a peak wind speed? This issue requires some discussion/explanation in comparison to contaminated air masses from land.

Response: Yes, this extremely high flux primarily resulted from the high wind speed. In the revised manuscript, we have added a new table (Table 1) including all relevant data with the Hg(0) flux calculation (e.g., DGM, GEM, Water temperature and Wind speed). This data will help reader evaluate the magnitude of relevant factors on the influence of the Hg(0) flux calculation.

P. 1528, L.8-L.12: Was the whole wind speed distribution used for the calculation of each flux? Please give some more details about the transfer velocity calculation (e.g., as table with all relevant data).

Response: Please see the response to the last comment.

P. 1528, L. 16: If vertical profiles are presented information about water density structure (temperature, salinity) are necessary. See general remarks. Especially if mix-

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ing processes, surface layer or bottom sediment re-suspension is discussed (P. 1528, L.25/26). Also the meaning of a $1.3 \mu\text{g}/\text{m}^2$ daily emission can be better judged.

Response: Figure 6 has been updated to add the sea water temperature/salinity data at three stations in the revised manuscript.

Technical corrections

P. 1513 L.16: have showed-have shown

Response: We have changed "have showed" to "have shown" as suggested by the reviewer.

P. 1513, L. 24: spicie-species (it is also singular).

Response: We have changed "spicie" to "species" as suggested by the reviewer.

P. 1526, L. 8: Please check the number of decimal places, i.e. the precision of the DGM saturation.

Response: We have modified the number of significant digit of DGM saturation value. According to the least number of significant digit of all relevant data, the precision of DGM saturation is rounded off to one significant digit.

References

Kuss, J., Holzmann, J. and Ludwig, R., 2009. An elemental mercury diffusion coefficient for natural waters determined by molecular dynamics simulation. Environmental Science and Technology, 43(9): 3183-3186.

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/11/C584/2011/acpd-11-C584-2011-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 1511, 2011.

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