

Interactive comment on “The exchange of SVOCs across the air-sea interface in Singapore’s coastal environment” by J. He and R. Balasubramanian

J. He and R. Balasubramanian

eserbala@nus.edu.sg

Received and published: 24 November 2009

We thank the reviewer for the insightful comments.

Major Comment #1 The authors make the point that the sea surface is heavily impacted by organics (to the point where the microlayer represents a separate reservoir for the SVOCs). It would seem to me that air-sea exchange might be better described by transfer through film-covered interfaces. However, the relationships used to estimate the water-side air-water transfer velocities, k_L , are for clean surfaces. Perhaps the air-sea gas exchange flux components would be more accurately estimated using relationships for film-covered surfaces? The paper by Tsai and Lui (Tsai, W.-T. and Liu, K.-K. 2003. An assessment of the effect of sea-surface surfactant on global atmosphere-ocean CO₂ flux. J. Geophys. Res., 108(C4), 3127, doi:10.1029/2000JC000740) might

C7440

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Interactive
Comment

provide some insight on how to proceed along these lines. Major Comment 1 Response: In this study, we found that most of sea surface microlayer (SML) enrichment factors were greater than one. This suggests that the SML in Singapore's marine area has larger storage capacity (per volume) compared to the bulk seawater. It is therefore reasonable to assume that the SML would delay or reduce the transport of SVOCs across air-sea interface. In order to quantify the reduction in the transport of SVOCs, we applied the linear $K_{w,comp}$ (mass transfer coefficient across the water layer)- u_{10} relationship proposed by Asher (1997) for the sea surface with surfactant coverage to estimate the air-sea gas exchange fluxes as per the reviewer's advice. This calculation shows that the reduction in net fluxes of SVOCs across air-sea interface due to the influence of surfactants ranges from 21% to 51% for PAHs and from 23% to 51% for OCPs, respectively. However, the surface coverage scenario addressed in this work represents the maximum possible reduction in the net flux of SVOCs across the air-sea interface due to the influence of surfactants in the microlayer. More details are provided in the revised manuscript in Section 4.3.

Major Comment 2 Most of the fluxes and concentrations are listed with an associated "uncertainty" given as a +/- value. However, I suspect this is not a true uncertainty in the statistical sense that the number reflects the statistical variation in the value, but rather is the range of the observations. If my assumption is correct, and the uncertainty in any measured concentration is actually not so large as the range, it would be interesting to see histograms of the distributions of measured concentrations. If the fluxes are derived from pairs of numbers (e.g., in the case of the air-sea fluxes, one would need a water concentration and air-phase concentration), the distribution of fluxes could also be shown. The idea being that perhaps the authors could discuss whether there was any pattern to the distribution of the fluxes (i.e., correlation of air-water fluxes with tides or some other forcing) based on patterns in the distributions. Response: The variability of flux values reported in this study is believed to be due to changes in the occurrence levels of SVOCs in the multi-media system during the sampling period, and not due to the operational errors. The concentrations of SVOCs in air and rainwater are affected

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

by changes in their emission strengths, the prevailing meteorological conditions during the sampling periods and all atmospheric dynamic distribution processes such as gas/particle partitioning, particle and gas scavenging, etc. The occurrence levels of SVOCs in both water and air gas phase have been listed in Table 3. It is known that the concentration levels of SVOCs in the atmosphere and rainwater are critical to the flux estimation, and the uncertainty of these concentration values could be minimized by using appropriate quality assurance protocols for the entire experimental procedures. For estimation of air-sea gas diffusive exchange fluxes, parameters such as K_a and K_w (mass transfer coefficients across the air layer and water layer) were calculated by taking into account ambient atmospheric conditions while Henry's law constant was adopted from the literature. Error analysis was applied in a statistical sense onto this natural distribution process. In accordance with all the equations involved in this study, it can be seen that uncertainty in the estimated air-sea exchange fluxes was generally derived from systematic and random errors in the analysis. Systematic errors resulted from the values of H and also from uncertainties in the estimation of the mass transfer coefficient. To assess the random errors in the air-sea exchange fluxes, a propagation of error analysis (Shoemaker et al., Experiments in Physical Chemistry. New York: McGraw-Hill, 1996) was performed as explained in Section 4.3.5. The overall random error in the air-sea gas exchange fluxes was $\sim 36\%$ (mean, ranging between 26% - 64%). Overall, the error analysis showed that the major source of uncertainty in the estimation of the air-sea exchange flux was the calculation of the mass transfer coefficient. However, we could not evaluate the correlation of air-water fluxes with tides or some other forcing with the experimental and field data available in the present study. This point will be addressed in our future work.

Minor Comments: 1. Line 348: remove "etc" and enumerate examples. Response: Line 348 with "etc" that appeared in the original manuscript has been removed and one more scavenging mechanism "electrical charge effects" has been added.

2. Figure 4 is corrupt. Response: Figure 4 has been corrected and updated as Figure

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

6 in the revised manuscript.

Reference: Asher, W.E.: The sea-surface microlayer and its effects on global air-sea gas transfer, in *The Sea Surface and global Change*, edited by P.S.Liss and R.A. Duce, 251-286, Cambridge Univ. Press, New York, 1997.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 13235, 2009.

ACPD

9, C7440–C7443, 2009

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

C7443

