

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: 17 August 2009

We thank the reviewer for the constructive comments.

Major Comments:

Response: All the measured data in this study, of which values are greater than 1, are presented in single decimal place; those values less than 1 are written in two decimal places.

Since atmospheric sampling was conducted in this study for each event in a consistent manner (48 h at 250 L min⁻¹), monthly average concentrations were taken for yearly flux calculation. However, in the case of rainwater, the rainfall amount for each event varied. Hence, those concentrations were calculated as volume-weighted mean

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



(VWM) values. The standard error of the weighted mean (SEMw) was calculated according to the formula (Equation (1), see Figure 1) (Offenberg and Baker, 1997, Environ. Sci. Technol. 31, 1534-1538).

In this equation, P_i is the precipitation amount of sample i , X_i is the concentration in sample i , \bar{P} is the mean precipitation amount for samples 1 to n , and \bar{X} is the precipitation weighted mean concentration.

We believe that the variability of flux values reported in this study is not due to the operational errors, but due to changes in the occurrence levels of SVOCs in the multimedia system. The concentrations of SVOCs in air and rainwater are affected by the emission sources, 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 quality of field-measured data was assured by the quality control/assurance protocols used throughout the field sampling, sample extraction and analytical procedures.

For the air sampling (including dry deposition and wet deposition), the field work utilized the well-established procedures by using efficient and reliable instruments/samplers. A sampling artifact is prone to occur when gaseous SVOCs sorb to filter and particle surfaces, thus leading to an over-estimation of particle-phase SVOCs (Dachs and Eisenreich, 2000, Environ. Sci. Technol., 34, 3690-3697). Our sampling strategy here consisted of 24~48 h sampling. As the ambient temperature variations were small and relative humidities were uniform in this area, backup filters were used in this study to correct for gas adsorption of SVOCs to a front filter (Hart and Pankow, 1994, Environ. Sci. Technol., 28, 655-661). According to the method reported by Mader and Pankow, 2001 (Environ. Sci. Technol., 35, 3422-3432), it was found that less than 5% of mass recovered from the primary filter was sorbed onto a secondary filter. Breakthrough of SVOCs from the PUF can lead to under-estimated SVOCs gas phase concentrations. In this study, breakthrough was evaluated under field conditions by connecting three

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

one-inch plugs in series and analyzing them separately. For 48 h samples, measured SVOCs at the third plug were in the range of blank values. Three one-inch plugs used in series with the high-volume PUF sampler could therefore trap gas-phase targeted compounds effectively. The rainwater samples were collected by an automated wet-dry sampler (Model US-330, Ogasawara Keiki Seisakusho, Tokyo, Japan), which collected only rainwater with no interference from dust fall. All rainwater samples were stored in an internal refrigerator at 4°C by the automated sampler immediately after a rain event to minimize the loss of SVOCs as much as possible. The rainwater samples were brought back to the lab from the field site within 24 hours after each rain event.

For SSW and SML sampling, even though the samplers applied in this study were simple, their suitability and efficiency have been evaluated and reported in the literature (Harvey and Burzell, 1972, *Limnol. Oceanogr.*, 17, 156-157; Wurl et al., 2006, *Chemosphere*, 62, 1105-1115).

Regarding the sample extraction, all atmospheric samples and water filters were extracted separately under optimum conditions by Dionex ASE 200 (He and Balasubramanian, 2009, *Anal. Lett.* 42, 1603-1619; He et al., 2009, *Chemosphere*, 75, 640-648). All filtered water samples were extracted on the same day following collection via liquid-liquid extraction using 3×50 mL DCM aliquots in a two liter separatory funnel (EPA method 3510C). The analytical quality of the data obtained was determined using limit of detection (LOD), recovery, linearity, and by checking sampling artifacts, etc. During each set of extractions, the field blanks (filter and PUF plugs) were included. Detection limits were derived from the blanks and quantified as the mean plus three times the standard deviation of the concentration in the blanks. LODs for filter and PUF samples ranged from 0.14 ± 0.16 pg m⁻³ (4,4'DDE, filter blank) to 0.15 ± 0.07 ng m⁻³ (Naph, PUF blank). For water sample analysis, entire procedure blank tests were performed on organic-free water, and LODs for water samples ranged from 0.30 ± 0.17 ng L⁻¹ (Ind) to 1.9 ± 1.3 ng L⁻¹ (4,4'DDD). The reliability of all extraction procedures was assessed by using surrogate standards for targeted SVOCs. The pro-

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

Interactive
Comment

cedural recoveries of surrogates ranged from $86.7 \pm 6.8\%$ (anthracene-d10) to $97.2 \pm 13.9\%$ (benzo[e]pyrene-d12). Control calibration standards spiked with internal standards were analyzed regularly to check instrument performance during analysis.

As mentioned above, the concentration levels of SVOCs in the atmosphere and rain-water are critical to the flux estimation, and the uncertainty of these values could be minimized by using the quality assurance protocols for the entire experimental procedures. For air-sea gas diffusive exchange fluxes, more parameters were adopted from the literature. Error analysis was to be applied 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 in the values of H and particularly 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 by equation 2 (see Figure 2).

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

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

Interactive
Comment

$$(\text{SEM}_w)^2 = \frac{n}{(n-1)(\sum P_i)^2} [\sum (P_i X_i - \bar{P} \bar{X}_w)^2 - 2 \bar{X}_w \sum (P_i - \bar{P})(P_i X_i - \bar{P} \bar{X}_w) + \bar{X}_w^2 \sum (P_i - \bar{P})^2]$$

Fig. 1. Equation 1: The standard error of the weighted mean (SEM_w)

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

[Interactive
Comment](#)

$$\sigma^2(F) = \left(\frac{\delta F}{\delta K_{OL}}\right)^2 (\sigma K_{OL})^2 + \left(\frac{\delta F}{\delta C_{trubp}}\right)^2 (\sigma C_{trubp})^2 + \left(\frac{\delta F}{\delta C_a}\right)^2 (\sigma C_a)^2 + \left(\frac{\delta F}{\delta H}\right)^2 (\sigma H)^2$$

Fig. 2. Equation 2: The propagation of error analysis

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