



# Atmospheric partitioning and the air–water exchange of polycyclic aromatic hydrocarbons in a large shallow Chinese lake (Lake Chaohu)



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## HIGHLIGHTS

- Levels and distribution of atmospheric and water PAHs were studied in Lake Chaohu.
- The monthly diffusive air–water exchange flux were estimated by a two-film model.
- PAH16 levels in atmosphere and water were significantly correlated with temperature.
- Significant correlations between gas–particle partition and  $\log P_i^0$  and  $\log K_{oa}$ .
- PAH levels in water and gas were the most important factors for air–water exchange.

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## ABSTRACT

The residual levels of polycyclic aromatic hydrocarbons (PAHs) in the atmosphere and in dissolved phase from Lake Chaohu were measured by (GC–MS). The composition and seasonal variation were investigated. The diffusive air–water exchange flux was estimated by a two-film model, and the uncertainty in the flux calculations and the sensitivity of the parameters were evaluated. The following results were obtained: (1) the average residual levels of all PAHs (PAH16) in the atmosphere from Lake Chaohu were  $60.85 \pm 46.17 \text{ ng m}^{-3}$  in the gaseous phase and  $14.32 \pm 23.82 \text{ ng m}^{-3}$  in the particulate phase. The dissolved PAH16 level was  $173.46 \pm 132.89 \text{ ng L}^{-1}$ . (2) The seasonal variation of average PAH16 contents ranged from  $43.09 \pm 33.20 \text{ ng m}^{-3}$  (summer) to  $137.47 \pm 41.69 \text{ ng m}^{-3}$  (winter) in gaseous phase, from  $6.62 \pm 2.72 \text{ ng m}^{-3}$  (summer) to  $56.13 \pm 22.99 \text{ ng m}^{-3}$  (winter) in particulate phase, and  $142.68 \pm 74.68 \text{ ng L}^{-1}$  (winter) to  $360.00 \pm 176.60 \text{ ng L}^{-1}$  (summer) in water samples. Obvious seasonal trends of PAH16 concentrations were found in the atmosphere and water. The values of PAH16 for both the atmosphere and the water were significantly correlated with temperature. (3) The monthly diffusive air–water exchange flux of total PAH16 ranged from  $-1.77 \times 10^4 \text{ ng m}^{-2} \text{ d}^{-1}$  to  $1.11 \times 10^5 \text{ ng m}^{-2} \text{ d}^{-1}$ , with an average value of  $3.45 \times 10^4 \text{ ng m}^{-2} \text{ d}^{-1}$ . (4) The results of a Monte Carlo simulation showed that the monthly average PAH fluxes ranged from  $-3.4 \times 10^3 \text{ ng m}^{-2} \text{ d}^{-1}$  to  $1.6 \times 10^4 \text{ ng m}^{-2} \text{ d}^{-1}$  throughout the year, and the uncertainties for individual PAHs were compared. (5) According to the sensitivity analysis, the concentrations of dissolved and gaseous phase PAHs were the two most important factors affecting the results of the flux calculations.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds composed of two or more fused aromatic rings (Menzie et al., 1992). PAHs occur in the environment as complex mixtures of many components (Petry et al., 1996). They mainly originate from coal combustion, vehicle emissions, the coking industry, and the burning of biomass (Rogge et al., 1993; Kavouras et al., 2001; Xu et al., 2006). They have been a topic of concern because

of their potentially toxic, mutagenic, and carcinogenic properties (Khalili et al., 1995; Fernandes et al., 1997; Larsen and Baker, 2003). Therefore, 16 PAHs are included in the priority pollutants list of the US EPA. During last decades, the PAH emissions in China have been increasing greatly with the rapid population growth and economic development (Xu et al., 2006; Zhang et al., 2007b). China is suffering from severe contamination of PAHs from various sources, which poses a serious threat to ecosystems and human health (Xu et al., 2011, 2013). The emissions of 16 priority PAHs in China was estimated as 25 300 tons in 2003, and among various emission sources, biomass burning, domestic coal combustion, and coking industry contributed 60%, 20%, and 16% of the total

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emission, respectively (Xu et al., 2006). The higher PAHs emission density was found in the southeastern provinces, while the higher PAHs emission intensity and population-normalized emission were found in western and northern China (Xu et al., 2006).

A body of water can act either as a sink (Lohmann et al., 2006) or as a source (Zhang et al., 2007a) for PAHs in the environment. The atmosphere plays an important role in PAH contamination of water bodies (Simonich and Hites, 1995; Simcik et al., 1999). Wet deposition, dry deposition, and gas exchange across the air–water interface are the three major transport pathways for atmospheric inputs of organic pollutants into the Great Lakes (Franz et al., 1998). Unlike wet and dry deposition, gas exchange is a “two-way street” (McConnell et al., 1993). Therefore, gas exchange appears to be an important process that controls the concentrations and residence times of PAHs in natural water bodies (Pandit et al., 2006). Air–water exchange is a complex process controlled by many factors. In recent decades, much work has been done on the estimation of the air–water exchange of POPs (Nelson et al., 1998; Wania et al., 1998; Totten et al., 2001; Tsapakis et al., 2006). Two-film models were usually employed to estimate the exchange flux quantitatively. However, model uncertainty and the impact of parameters were seldom discussed.

Lake Chaohu (30°58′–32°06′N/116°24′–118°00′E), which is located in Anhui Province, is the fifth largest freshwater lake in China. It is the primary source of drinking water for the provincial capital city, Hefei and for a medium city, Chaohu. Lake Chaohu covers an area of 753 km<sup>2</sup> and is located in one of the most developed areas in China, the Yangtze River Delta Economic Zone. The local sources of PAHs emission in the Lake Chaohu area are of complexity, due to the effects from the northwest Hefei city and eastern Chaohu City, the southern and northern rural areas, as well as from the lake tourism. The primary PAHs source in the urban areas is vehicle emission, while that in the rural areas is the combustion of biomass fuels (e.g. straw, firewood). The coal combustion in the nearby power plants is also an important PAHs source. In addition, the long distance transportation from the adjacent provinces is the secondary PAHs sources in Lake Chaohu area.

Some studies have examined the air–water exchange in China (Fang et al., 2008; Qiu et al., 2008, 2010; Li et al., 2009; Devi et al., 2011), but diffusive fluxes vary according to meteorological and geographical conditions (Bidleman, 1999). To understand the atmospheric influence of the Lake Chaohu aquatic system, it is necessary to study the specific pollution characteristics of atmospheric PAHs, identify the partitioning characteristics and to evaluate the exchange fluxes through the air–water interface. The aim of this study included the following: (1) to investigate the residual levels, composition characteristics and seasonal variation of PAHs in atmospheric samples and lake water; (2) to elucidate the partitioning of PAHs in gaseous and particulate phases; and (3) to investigate the uncertainty of estimates of the air–water exchange and the sensitivity of the parameters.

## 2. Materials and methods

### 2.1. Sample collection and pretreatment

Atmosphere samples and water samples were collected once a month from May 2010 to April 2011. The sampling sites are shown in Fig. S1 in the Supporting information. High-volume samplers were placed on the roofs of residential buildings on the island and on the Environmental Protection Agency building. Polyurethane foam (PUF) disks and glass fiber filters (GFFs) were used to collect gaseous-phase PAHs and particulate-phase PAHs. The average flow rate was 0.31 m<sup>3</sup> min<sup>-1</sup>. After sampling, both the PUF and the GFF were packed in aluminum foil and stored

at 20 °C. Twenty liters of water was collected from each sampling site. After shaking and mixing, a 1-L aliquot of each collected water sample was filtered through a 0.45- $\mu$ m glass fiber filter (burned at 450 °C for 4 h) using a filtration device consisting of a peristaltic pump (80EL005, Millipore Co., USA) and a filter plate with a diameter of 142 mm. Surrogate standards of 2-fluoro-1, 1'-biphenyl and p-terphenyl-d14 (J&K Chemical, USA, 2.0 mg mL<sup>-1</sup>) were added to the water samples to indicate the recovery before extraction.

In the laboratory, the PUF was Soxhlet extracted with a 150 mL 1:1 mixture of n-hexane and acetone for 8 h. The GFF was extracted with a 25 mL hexane/acetone mixture (1:1) using a microwave accelerated reaction system (CEM Corporation, Matthews, NC, USA). The microwave power was set at 1200 W, and the temperature was ramped to 100 °C over 10 min and then held at 100 °C for another 10 min. Both PUF and GFF extracts were concentrated to 1 mL by rotary evaporation at a temperature below 38 °C and then transferred to a silica/alumina chromatograph column for cleanup. The elution solution was collected, concentrated, converted to hexane solution, and then added with internal standards (Nap-d8, Ace-d10, Ant-d10, Chr-d12 and Perylene-d12, J&K Chemical Ltd., USA).

The water samples were extracted using a solid phase extraction (SPE) system (Supelco). C18 cartridges (500 mg, 6 mL, Supelco) were prewashed with dichloromethane (DCM) and conditioned with methanol and de-ionized water. A 1-L water sample passed through the SPE system and was extracted. The cartridges were eluted with 10 mL of dichloromethane. The volume of the extracts was reduced by a vacuum rotary evaporator (R-201, Shanghai Shen Sheng Technology Co., Ltd., Shanghai, China) in a water bath and was adjusted to a volume of 1 mL with hexane. Internal standards (Nap-d8, Ace-d10, Ant-d10, Chr-d12 and Perylene-d12) were added for the GC analysis.

### 2.2. Sample analysis and quality control

All samples were analyzed on a GC–MS (Agilent 6890GC/5973MSD). A 30 m  $\times$  0.25 mm i.d. with a 0.25- $\mu$ m film thickness HP-5MS capillary column (Agilent Technology) was used. The column temperature was programmed to increase from 60 °C to 280 °C at 5 °C min<sup>-1</sup> and was then held constant for 20 min. The MSD was operated in the electron impact mode at 70 eV, and the ion source temperature was 230 °C. The mass spectra were recorded using the selected ion monitoring mode. The concentrations of 16 PAHs were determined: naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorine (Flo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (Bap), dibenz(a, h) anthracene (DahA), indeno(1,2,3-cd)pyrene (IcdP) and benzo(g, h, i) perylene (BghiP).

The quantification was performed by the internal standard method using Nap-d8, Ace-d10, Ant-d10, Chr-d12 and Perylene-d12 (J&K Chemical, Beijing, China). All of the solvents used were HPLC-grade pure (J&K Chemical, Beijing, China). All of the glassware was cleaned using an ultrasonic cleaner (KQ-500B, Kunshan, China) and heated to 400 °C for 6 h. In the sampling process, three replicate samples were collected from each sample site. Laboratory blanks were analyzed with the true samples. The recovery methods and detection limits are shown in Table S1 in the Supporting information. The detection limits were in the range of 0.64–1.85 ng L<sup>-1</sup>. The PAH recoveries for gaseous phase, particulate phase and water varied from 46% to 124%; 47% to 119% and 21% to 122%, respectively.

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