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Atmospheric processes of persistent organic pollutants over a remote lake of the central Tibetan Plateau: Implications for regional cycling

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Abstract

Atmospheric processes (air-surface exchange, and atmospheric deposition and degradation) are crucial for understanding the global cycling and fate of persistent organic pollutants (POPs). However, such assessment over the Tibetan Plateau (TP) remains uncertain. More than 50% of the Chinese lakes are located on the TP, which exerts a remarkable influence on the regional water, energy, and chemical cycling. In this study, air and water samples were simultaneously collected in Nam Co, a large lake on the TP, to test whether the lake is a "secondary source" or "sink" of POPs. Lower concentrations of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) were observed in the atmosphere and lake water of Nam Co, while the levels of polycyclic aromatic hydrocarbons (PAHs) were relatively higher. Results of fugacity ratios and chiral signatures both suggest that the lake acted as the net sink of atmospheric hexachlorocyclohexanes (HCHs), following their long-range transport driven by the Indian Monsoon. Different behaviors were observed in the PAHs, which primarily originated from local biomass burning. Acenaphthylene, acenaphthene, and fluorene showed volatilization from the lake to the atmosphere; while other PAHs were deposited into the lake due to the integrated deposition process (wet/dry and air-water gas deposition) and limited atmospheric degradation. As the dominant PAH compound, phenanthrene exhibited a seasonal reversal of air-water gas exchange, which was likely related to the melting of the lake ice in May. The annual input of HCHs from air to the entire lake area (2015 km^2) was estimated as 1.9 kg $year^{-1}$, while those estimated for PAHs can potentially reach up to 550 kg $year^{-1}$. This study highlights the significance of PAH deposition on the regional carbon cycling in the oligotrophic lakes of the TP.

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1. Introduction

Since the past century, large quantities of persistent organic pollutants (POPs), such as organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs), have been discharged into the global environment. Soils, water bodies, and snow/ice are generally considered as reservoirs or sinks of these pollutants (Dalla Valle et al., 2005; Froescheis et al., 2000; Guglielmo et al., 2012). However, due to the influence of global warming (Komprda et al., 2013; Noyes et al., 2009), growing evidence indicates that POPs previously stored in reservoirs can be re-released back to the environment (Ma et al., 2011). For example, air-soil exchange of OCPs has showed the re-emission of OCPs from past contaminated soils in Europe (Ruzickova et al., 2008), North America (Kurt-Karakus et al., 2006), and India (Chakraborty et al., 2015). Modeling results have suggested that large parts of the global ocean have been losing dichlorodiphenyltrichloroethane (DDT) via volatilization (Stemmler and Lammel, 2009). In addition, air-sea exchange of PAHs has revealed that the seawater in the Mediterranean has turned into a temporary secondary source of PAHs, which is related to biomass burning in that region (Mulder et al., 2014). Moreover, melted sea glaciers have released large quantities of POPs back into the atmosphere in the polar regions, which has led to increased POP levels in air and water (Jantunen et al., 2008; Wong et al., 2011).

Similar to the polar regions, the Tibetan Plateau (TP) has been regarded as a "convergence" of POPs (Wang et al., 2016). Due to the continuous use of POPs in the surrounding countries and the "cold trapping" by the TP, the enrichment of POPs in the TP environment has been reported (Sheng et al., 2013; Wang et al., 2015). However, the TP has experienced great warming (Liu and Chen, 2000), and results of the air-soil exchange of POPs have indicated that the Tibetan soils are acting as a sink of DDT and higher molecular weight PAHs, but are a potential secondary source for hexachlorobenzene (HCB) and hexachlorocyclohexanes (HCHs) (Wang et al., 2014; Wang et al., 2012). This shows that the cold temperature over the TP might not be sufficient to trap volatile POPs. More studies on the air-surface exchange of POPs over the TP are therefore needed to test the role of the terrestrial and aquatic ecosystems of the TP in the regional cycling of POPs.

Known as "Asia's water power", the TP contains the headwaters of many major rivers in Asia, which provide water sources for about one-sixth of the world's population (Yao et al., 2012). The TP also has large numbers of remote lakes that are important components of water bodies. Low temperature, oligotrophic conditions, and the long duration of ice-cover are distinct features of these lakes. Based on

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the higher atmospheric concentrations of α-HCH in summer, Xiao et al. (2010) deduced that these enhanced concentrations may be caused by the thawing of lake ice, which promotes the re-evaporation of α-HCH. However, the study did not include measurements of POP levels in lake water or the corresponding air-water exchange analysis (Xiao et al., 2010). Therefore, it is still unclear whether the lake water of the TP is the secondary source of a large number of POPs. Furthermore, biomass burning is a widespread activity over the TP (Hu et al., 2015). A recent study demonstrated that the locally sourced biomass combustion particles contributed substantially to the black carbon (BC) loading of the TP glacier (Li et al., 2016). Given that PAHs and BC both originate from incomplete combustion of biomass, regional air-water exchange of PAHs would also contribute to the overall air-surface exchange of carbon.

We therefore conducted air and water sampling in a remote lake on the TP, and assessed the air-water gas exchange, and the dry and wet deposition processes of OCPs, PCBs, and PAHs. The aims of this study were to ascertain whether the Tibetan lake represents a secondary source of POPs, to investigate the influence of seasonal lake ice melting on the gas exchange of different POPs, and to estimate the contribution of PAH exchange to the lake carbon budget.

2. Materials and methods

2.1 Site description

Nam Co Lake (30°30′–30°56′N, 90°16′–91°01′E, 4718 m) is located in the north of the Nyainqentanglha Mountains, on the central TP (Figure 1). It is the second largest lake in Tibet with an area of 2015 km^2 and a maximum depth exceeding 90 m (Wang et al., 2009). The climate of Nam Co is relatively cold and windy with an annual average temperature of ~0 ℃ and an annual wind speed of ~4 m/s. The regional climate also has large seasonal variation: the Indian Monsoon dominates summer (May to September) and the westerlies control winter climate (October to April) [see the Supplement (S), Figure S1]. High temperatures and precipitation are usually observed in summer (Figure S2), and the lake begins to thaw from the beginning of May and melts completely by the end of May, which coincides with the onset of the Indian Monsoon. During the winter, the lake is covered by ice due to the subzero temperatures (Figure S2) and maximum instantaneous wind speeds reaching up to 9.9 m/s.

The dominant land cover in Nam Co is alpine steppe and meadow, and the local residents herd yak and sheep that graze around the lake. Biomass burning occurs for heating, cooking, transport, and religious reasons. Near the southeastern shore, the Nam Co Monitoring and Research Station for Multisphere

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Interactions (NCMORS) is operated by the Chinese Academy of Sciences (Figure 1b). This station not only facilitates the consecutive collection of field samples used in the current study, but also provides local meteorological parameters for flux calculations.

2.2 Air and water sampling

An active air sampler (AAS) was deployed on the roof of NCMORS (Figure 1b) and the air monitoring was conducted for two consecutive years from September 2012 to September 2014. The flow rate of AAS was 60 L min^{-1} and the air samples were collected every 2 weeks with a volume of approximately 600 m^3 for each sample. The air stream passes first through glass fiber filters (GFFs 0.7 μm, Whatman) to collect the total suspended particulates (TSP) and then through polyurethane foam (PUF, 7.5×6 cm diameter) to retain the POPs in gas phase. In total, 47 air samples were collected. Details regarding the sampling period, average air temperature, and wind speed are given in Table S1. All harvested PUF and GFFs were stored at -20 ℃ until extraction.

To determine the POP levels in water, two sampling programs were conducted. First, 15 sites around the Nam Co Lake (surface lake water, 0–1 m depth) were selected to obtain the spatial distribution of POPs in lake water (Figure 1b), which provides a direct over-view of POP contamination over the lake. Second, monthly water samples were collected at a site close to NCMORS (Figure 1b) from May to September, 2014 (water samples were not obtained during winter due to the ice cover). This provided information regarding temporal variations in POP levels, isomer ratios, and the enantiomeric fraction in lake water. Furthermore, coupled with the monthly average air concentrations of individual POPs obtained, this allowed us to investigate the air-water gas exchange of POPs (direction, flux, and monthly variations).

Water samples (200 L) were filtered with GFFs to obtain the total suspended particulate matter (SPM), and then pumped through an XAD-2 resin column to collect the dissolved phase compounds. For each sampling month, triplicate samples were collected. In total, 15 samples for the spatial study and 15 samples for the temporal study were collected. XAD columns were kept at 4 ℃ until extraction. The lake water properties (salinity and temperature) are provided in Table S2.

2.3 Sample extraction and analysis

The chemical extraction and cleanup methods are detailed in Text S1 for each sample type [air (PUF plug), TSP, water (XAD column), and SPM]. POPs were analyzed on a gas chromatograph with an ion-trap mass spectrometer (GC-MS, Finnigan Trace GC/PolarisQ) operating under MS–MS mode.

More information on the chromatographic conditions is given in Text S2. The target compounds are as follows: HCHs (including α-HCH, β-HCH, and γ-HCH), HCB, DDTs (*o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDT, and *p,p'*-DDT), PCBs (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, and PCB 180), and 15 priority PAHs listed by the United States Environment Protection Agency (USEPA, without naphthalene), including acenaphthylene (Acel), acenaphthene (Ace), fluorene (Flu), 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), benzo[g, h, i]perylene (BghiP), and indeno[1,2,3-cd]pyrene (IcdP). Enantiomers of α-HCH were determined with a BGB-172 chiral column (see Text S2 for details). The chiral signature of α-HCH is expressed using the enantiomeric fraction (EF), which is equal to the ratio of peak areas of the (+)/[(+) + (−)] (Harner et al., 2000).

2.4 Quality assurance/quality control (QA/QC)

All analytical procedures were monitored using strict QA/QC measures. Prior to sampling, PUF and XAD resin were pre-cleaned using dichloromethane (DCM) for 16 h and GFFs were baked at 450 ℃ for 4 h. Six PUF field blanks, three XAD field blanks, and six procedural blanks were prepared; HCB, Phe, Ant, Fla, and Pyr were detected in the field blanks (Table S3). The definitions of the method detection limits (MDLs) are described in Text S3, and the derived MDLs are given in Table S4. The breakthrough of PUF plugs was checked in eleven split PUFs, and the results show that the individual POPs in the second half varied from 8% to 23% (Table S5), indicating good retention capacity. Certified surrogate standards (from Dr. Ehrenstorfer GmbH, Germany) were analyzed alongside each sample. The recoveries ranged from 71% to 94% for PCB 30, 79% to 105% for Mirex, and 65% to 92% for perylene-D12. The reported concentrations were subtracted by mean blanks but not corrected for recoveries. To check the reproducibility of the chiral analysis, the racemic standard of α-HCH was injected repeatedly and its average EF value was 0.499 ± 0.001 (n = 5).

2.5 Calculations of air-water gas exchange

Concurrent air and water samples were used to assess the status of air-water gas exchange in Nam Co Lake. The gas exchange direction can be determined by the ratio of fugacity in water (f_w) and air (f_a), giving the fugacity ratio (f_w/f_a) (Jantunen et al., 2015):

$$f_a = C_G R T_a \quad (1)$$

$$f_w = C_w H \quad (2)$$

where C_G and C_w are the gaseous and dissolved concentrations of target compounds in air and water, respectively, R is the gas constant (8.314 Pa m^3 mol^{-1} K^{-1}), T_a (K) is the air temperature, and H (Pa m^3 mol^{-1}) is the Henry's law constant. According to the method reported by Ruge et al. (2015), the POP concentrations retained by XAD were calibrated to derive the true freely dissolved POP concentrations in water (C_w, Text S4). H values were adjusted for the real water temperature and salinity of Nam Co by the procedure described in Text S5 (Cetin et al., 2006; Ma et al., 2010). Ratios of f_w/f_a >1 generally indicate volatilization, <1 indicates deposition, and equilibrium is reached at 1. Due to uncertainties, a significant deviation from equilibrium cannot be assessed in a range of 0.3–3 (Lohmann et al., 2009; Xie et al., 2011).

Net fluxes of air-water gas exchange (F_{AW}, ng m^{-2} day^{-1}) were quantified using the Whitman two-film model, which has been used in many previous studies (Iwata et al., 1993; Khairy et al., 2014):

$$F_{AW}=K_{ol}\left(C_w\text{-}C_G R\, T_a/H\right) \tag{3}$$

where K_{ol} (m s^{-1}) is the overall mass transfer coefficient, which contains contributions from the mass transfer coefficients of the water and air layers, K_w and K_a, respectively. They are related to the wind speed and compound-specific molecular diffusivity; a detailed calculation is presented in Text S6. Positive flux values indicate net volatilization, and negative values indicate net deposition.

2.6 Estimation of dry and wet deposition fluxes

In addition to the gas exchange, dry and wet deposition are also important processes that control the input of POPs from air to lake. Dry deposition fluxes (F_{DD}, ng m^{-2} day^{-1}) of atmospheric particulate-phase POPs can be calculated using (Gonzalez-Gaya et al., 2016) the following equation:

$$F_{DD}=0.864 V_D C_P \tag{4}$$

where V_D (cm s^{-1}) is the compound specific deposition velocity, C_P is the measured POPs concentrations in TSP (pg m^{-3}), and 0.864 is a unit conversion factor. V_D for each sampling period and compound was estimated using an empirical equation derived by Gonzalez-Gaya et al. (2014):

$$\log(V_D)=-0.261\log(P_L)+0.387U_{10}Chl_s-3.082 \tag{5}$$

where P_L (Pa) is subcooled liquid vapor pressure of chemicals that was corrected to the local temperature using the equations given in Table S6, U_{10} (m s^{-1}) is wind speed at 10 m height converted from the field-measured wind speed at 1.5 m (Table S1), and Chls is the surface chlorophyll concentration (mg m^{-3}, Liu et al., 2010).

Wet deposition fluxes (F_{WD}, ng m^{-2} day^{-1}) were estimated using the method established by Jurado et al. (2005):

$$F_{WD} = P(W_G C_G + W_P C_P) \tag{6}$$

where P is precipitation depth per day (m d^{-1}) derived from the data recorded in the NCMORS, and W_G and W_P are the gas and particle washout ratios, respectively. Assuming that equilibrium is attained between the gas phase and the dissolved phase in a raindrop/snow, W_G was estimated by (Wania et al., 1998a):

$$W_G = RT_a/H \tag{7}$$

In contrast to gas scavenging, particle scavenging by precipitation is a complex process controlled by meteorological conditions and the properties of the aerosols. Thus, the recommended values of W_P in literature (Franz and Eisenreich, 1998; Jurado et al., 2005) were adopted to consider the different particle scavenging by rain and snow.

3. Results and discussion

We determined the POP concentrations in air, TSP, water, and SPM separately; the full data sets are listed in Tables S7-S10. OCPs and PCBs were rarely detected in TSP (Table S8), and were therefore not considered in further discussion. Comparisons between the data from this study and previously published values for the TP and other remote regions are presented in Tables S11-S14.

3.1 Levels of POPs in air and water at Nam Co

The concentrations of POPs in the atmosphere and TSP in Nam Co are summarized in Figure 2 using box-and-whisker plots. Among the OCPs, HCB was the dominant chemical with an average concentration of 20 pg m^{-3} (Figure 2a), which was two times higher than that reported for southeastern TP (Sheng et al., 2013) and Mt. Everest (Li et al., 2006) (Table S11), but lower than the values in the Rocky Mountains (42 pg m^{-3}, Wilkinson et al., 2005) and the Arctic (64 pg m^{-3}, Su et al., 2006). The α-HCH (average 4.0 pg m^{-3}) and γ-HCH (2.1 pg m^{-3}) values in this study were much lower than those measured using a flow-through sampler (FTS) during 2006 to 2008 (48.7 and 7.9 pg m^{-3}, respectively) (Xiao et al., 2010). The DDT concentrations in the current study (0.8-46.4 pg m^{-3}) were lower than those observed for Lulang in southeastern TP (Table S11) (Sheng et al., 2013), which is the entrance of the Indian Monsoon. In spite of this, the levels of DDTs were still one order of magnitude higher than those for the Arctic (Table S11) (Su et al., 2008). Lower concentrations of $\sum_6$PCBs were also detected in air with an average value of 2.5 pg m^{-3}.

The sum concentrations of $\sum_{15}$PAHs in the atmosphere ranged from 0.5–13 and 0.1–3.4 ng m^{-3} in the gaseous and particulate phases, with averages of 2.2 and 0.6 ng m^{-3}, respectively. The 3- and 4-ring PAHs were predominant in both phases, including Phe, Flu, Fla, and Pyr (Figure 2b and 2c). The PAH levels in Nam Co were one order of magnitude lower than those reported for Lhasa (35.7 ng m^{-3}, Table S12), which is the capital city of Tibet with a large population, extensive tourism, and abundant religious activities (Gong et al., 2011). Compared with background levels in other regions of the world (Table S12), the PAHs in this study were comparable to the levels in Arctic air (Ding et al., 2007), but significantly higher than those from European mountainous regions (Fernandez et al., 2002).

In the lake water, the average dissolved concentrations of α-HCH, β-HCH, γ-HCH, HCB, and PCB 28 were 9.9, 85.2, 7.0, 7.6, and 1.9 pg L^{-1}, respectively; while DDT-related compounds were below MDLs in most cases for both dissolved and SPM phases (Table S9 and S10). The current measured HCH concentrations were approximately two orders of magnitude lower than values reported for the Yamdrok and Co Ngoin Lake in 2002 (Table S13) (Zhang et al., 2003). Two possible reasons for this discrepancy are: i) the inter-annual variation of POPs, i.e., the concentrations declined rapidly since 2002; and ii) the uncertainties caused by analytical and instrumental method (electron capture detector in Zhang et al. (2003) study and the MS detector in the current study). From a global perspective, the HCH concentrations obtained by this study were overall lower than those in European mountain lakes (Table S13). DDT class chemicals were rarely detected and only PCB 28 could be quantified in the Nam Co lake water. These features combined with the low levels of HCHs suggest that the POP levels in Nam Co lake water were close to the values reported for ocean waters, such as, the North Atlantic and Arctic oceans (with DDTs and PCBs mostly below the detection level, or <1 pg L^{-1}) (Gioia et al., 2008; Lohmann et al., 2009). By contrast, high levels of PAHs were found in the Nam Co lake water, ranging from 6.9 to 83.6 and 1.7 to 28 ng L^{-1} for the dissolved and SPM phases, respectively. The dissolved $\sum_{15}$PAH levels were one order of magnitude higher than those reported for Himalayan high-altitude lakes in Nepal (Table S14) (Guzzella et al., 2011) and the Great Lakes (Table S14) (Venier et al., 2014), and two orders of magnitude greater than values for open oceans (Table S14) (Ma et al., 2013) and European mountain lakes (Table S14) (Vilanova et al., 2001).

3.2 Possible sources

Long range atmospheric transport (LRAT) is considered an important source contributing to the occurrence of POPs in remote environments (Dalla Valle et al., 2005). Considering that the prevailing climate system operating over Nam Co in summer is the Indian Monsoon, if the seasonal pattern of a chemical is similar to that of the monsoon, monsoon transport may therefore be the source of POPs in Nam Co air. Thus, the interrelationship between monsoon intensity (Indian Monsoon Index, IMI, W m^{-2}) and POP concentrations was investigated (Figure 3). Figure 3 shows that α-HCH and *o,p'*-DDT displayed synchronous seasonal variation with the IMI. This suggests that monsoon transport was the principal reason for the occurrence of OCPs in the Nam Co atmosphere. In addition, isomer ratios can provide insight on the source and fate of the POPs. In this study, we found that the isomer ratios of *p,p'*-DDT to *p,p'*-DDE were broadly in agreement with those found for the source regions of India and the Bay of Bengal (Table S15) (Gioia et al., 2012; Zhang et al., 2008). Similar to other remote regions, such as, the Arctic (Hung et al., 2010), Antarctic (Baek et al., 2011), Rocky Mountains (Daly et al., 2007), and southeastern TP (Sheng et al., 2013), in which LRAT is the primary transport mode of POPs, the dominance of α- to γ-HCH was observed in the Nam Co atmosphere (Table S15). Results of isomer ratios associated with the seasonal variations supported the interpretation that OCPs in the Nam Co atmosphere had undergone LRAT. In contrast to OCPs, neither the gaseous nor the particulate phases of PAHs showed a clear and consistent seasonal variation during the two years of air monitoring (Figure S3), which is likely because there were primary emissions of PAHs surrounding the Nam Co region.

Apart from the seasonal trends, spatial distribution patterns can also provide valuable information on POP sources. The spatial distributions of POPs in the surface water across the Nam Co Lake are presented in Figure 4. First, HCHs showed a uniform distribution (Figure 4) without significant differences among the different regions of the lake (Table S16). The even distribution of HCHs in the water was most likely caused by the LRAT origins and relatively higher water solubility. Second, relatively high levels of HCB and PAHs occurred in water from the northwestern and eastern parts of the lake (Table S16 and Figure 4). The elevated HCB and PAHs in these regions were likely related to anthropogenic activity in the vicinity. As shown in Figure 1b, two townships (Baoji and Namco), which have the highest population around Nam Co Lake, are located in the northwestern and eastern corners of the lake. Following a traditional lifestyle, the residents use large amounts of local biomass (mostly yak dung) for cooking and heating (Xiao et al., 2015). High PAH concentrations have been reported in local Tibetan tents that were emitted mainly from burning yak dung (Li et al., 2012). A ratio of BaA/(BaA+Chr) = 0.33 was recommended as a specific diagnostic fingerprint for yak dung combustion (Li et al., 2012). The BaA/(BaA+Chr) ratios observed in our study (0.27±0.08 for air and 0.24±0.10 for water) were in good agreement with this diagnostic ratio. This suggests that local combustion emission is likely the source of PAHs in Nam Co. With the exception of PAHs, biomass combustion can also produce HCB (Bailey, 2001), which may be the reason for the higher HCB concentrations occurring around the townships. The spatial distribution of POPs in the Nam Co lake water highlights the important contribution of local sources for PAHs and HCB.

3.3 LRAT versus re-volatilization

From the above results, we found that LRAT is a key factor that determines the seasonality of the atmospheric HCHs and DDTs in Nam Co (higher concentrations occurred in summer). However, high temperatures generally occur during summer, which may promote the evaporation of chemicals from local surfaces (e.g., soils and water bodies). To what extent does this re-evaporation contribute to the atmospheric POPs? The Clausius-Clapeyron (CC) equation can be used to assess this probability (Wania et al., 1998b). If a strong relationship is found between the partial pressure of atmospheric OCPs and the air temperature, this indicates that volatilization may occur. Otherwise, low temperature dependence will occur in the case of LRAT. In the present study, the results of the CC equation are summarized in Table S17. The correlation with temperature (p>0.05, Table S17) for most chemicals was not significant, except for α-HCH, which displayed a relatively lower correlation coefficient (R^2=0.29, p<0.05, Table S17). This indicates that weak volatilization of α-HCH from local surfaces at Nam Co may exist, while the re-evaporation of other chemicals is limited.

Enantiomers of chiral POPs have been used to distinguish the contribution of LRAT and re-volatilization of POPs from surfaces (Bidleman et al., 2012). For example, technical HCH contains the (+)- and (-)-α-HCH enantiomers in a racemic proportion (EF=0.5). Abiotic processes (transport, hydrolysis, and photolysis) do not favor either enantiomer, while only biological processes, such as, microbial degradation in soils and water, show enantioselectivity and will alter the EFs of α-HCH (Ridal et al., 1997). Therefore, nearly racemic signatures usually indicate input from LRAT, while nonracemic signatures represent the influence of local microbial degradation. In the present study, both the enantiomeric signatures of α-HCH in air and water were measured simultaneously from May to September. As shown in Figure 5a, all the lake water samples showed a selective depletion of (+)-α-HCH, with EFs ranging from 0.318 to 0.449. This has previously been reported for other cold oligotrophic water systems, such as the Arctic Ocean (EFs: 0.393−0.438) (Lohmann et al., 2009). From Figure 5a, we found that extensive enantioselective degradation occurred in June and July, which coincided with the bacterial bloom period (Figure 5b) (Liu et al., 2013). Law et al. (2001) suggested that under low nutrient conditions, oligotrophic bacteria are able to use xenobiotic carbon sources, such as α-HCH. This implies that the Tibetan lake microbes can also metabolize, or cometabolize, α-HCH.

If high temperatures favor the evaporation of α-HCH from the lake water, depletion of (+)-α-HCH should be observed for air. However, the EFs of the air samples were overall racemic. This is similar to the racemic composition observed in the atmosphere over Indian regions (Huang et al., 2013), which is the potential source region of HCHs in Nam Co. With respect to the enantiomeric signature in air samples from June and July, only some (+) α-HCH depletion was observed in air (Figure 5a), indicating weak evaporation of α-HCH from the lake water. Combined with the EF values in air and water, the fraction of the contribution from lake water volatilization (*f*) can be quantified by (Huang et al., 2013):

$$f = \left(EF_a - EF_b\right) / \left(EF_w - EF_b\right) \quad (8)$$

where EF_a and EF_w are the EF values in air and water, respectively; and EF_b is the background EF value in air, which was assumed to be the average EF of the standard. The estimated results show that only 19% and 17% of atmospheric α-HCH came from water volatilization in June and July, respectively, demonstrating that LRAT is indeed the major source (more than 80%) of α-HCH. This result is in contrast with the conclusion of Xiao et al. (2010) that evaporation from Nam Co Lake largely contributed to the atmospheric α-HCH concentration. In that study, both levels and enantiomeric signatures of α-HCH in Nam Co lake water were absent.

3.4 Atmospheric processes

3.4.1 Air-water gas exchange

Although some α-HCH evaporation was recorded in June and July, the air-water exchange process during the entire ablation period is of great concern as this is the main season transferring pollutants between air and water. Fugacity ratios (f_w/f_a) and net exchange fluxes (F_{AW}, ng m^{-2} day^{-1}) were quantified using paired air-water samples collected from May to September in 2014. The average exchange status (average of f_w/f_a) for HCHs, HCB, PCB 28, and PAHs during the ablation period is illustrated in Figure 6. Because of DDTs, Ant and Fla were not quantified in the lake water (Table S9) and were therefore excluded from the discussion. α- and γ-HCH had low f_w/f_a values ranging from 0.08 to 0.15, and 0.02 to 0.08, respectively (Figure 6a). The low f_w/f_a ratio suggests that α- and γ-HCH were overall prone to deposition from air to water during the ablation period. The deposition fluxes were -1.6 $\pm$0.4 ng m^{-2} day^{-1} for α-HCH and -1.0 $\pm$0.2 ng m^{-2} day^{-1} for γ-HCH, which are within the same order of magnitude as those reported for the Great Lakes (Khairy et al., 2014). Connected to the source of HCHs

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discussed above, this result implies that the following LRAT-deposition event of HCHs occurred in the ablation period of Nam Co Lake. In terms of β-HCH, PCB 28, and HCB, their f_w/f_a ratios overlapped with the equilibrium range but were on the edge of the deposition threshold ($f_w/f_a = 0.3$). Therefore, low deposition fluxes for β-HCH (-0.2 ng m^{-2} day^{-1}) and PCB 28 (-0.1 ng m^{-2} day^{-1}), and large variability for HCB (-1.0 ± 0.6 ng m^{-2} day^{-1}) were observed (Figure 7a).

The results of the air-water gas exchange for PAHs are presented in Figure 6b. The fugacity ratios of thirteen PAHs varied depending on their molecular weight and volatility (Figure 6b). Acel and Ace showed f_w/f_a values significantly higher than 3 (Figure 6b), indicating that the lake acted as a secondary source for these volatile chemicals. In addition, Flu was close to equilibrium but showed a tendency toward volatilization to the air. The f_w/f_a values for Phe covered a large range (from 0.3 to 3), showing a shift between volatilization and deposition (Figure 6b). Other high molecular weight (MW > 202) PAHs, including Pyr, BaA, Chr, Bbf, Bkf, Bap, IcdP, DahA, and BghiP, favored net deposition with f_w/f_a values lower than 0.3 (Figure 6b). Greater volatilization fluxes were observed for Acel, Ace, and Flu (3-ring), which could reach up to 203 ng m^{-2} day^{-1} (Figure 7b). Whereas, the gaseous deposition fluxes for high molecular weight PAHs were two orders of magnitudes lower and only varied from -1.0 to -4.6 ng m^{-2} day^{-1} (Figure 7c). Although average deposition fluxes of 339 ng m^{-2} day^{-1} were calculated for Phe, the deposition fluxes showed large variability (±604 ng m^{-2} day^{-1}). This result is broadly consistent with the exchange direction revealed by the f_w/f_a values, implying that the exchange of Phe between air and water may be reversed during the entire ablation period.

3.4.2 Reversal of the air-water exchange of Phe

In section 3.4.1, we observed that both the air-water exchange direction and the flux of Phe showed a large range of values and uncertainties. This raises a question about what drives this variation. The monthly calculated f_w/f_a and F_{AW} of Phe during the ablation period showed that the volatilization of Phe occurred during May and June, but deposition begun in July, which represents a reversal (Figure 8). Given that lake ice begins melting during May, the melted ice may discharge large amounts of accumulated PAHs into the lake, causing the relative enrichment (high fugacity) of Phe in the water, and triggering the secondary emission of Phe from the water to the atmosphere. This was confirmed by the increased water concentration of Phe found during May and June (Table S9). This is also the reason why a large uncertainty of F_{AW} was observed for Phe during the ablation period. Linked to the source of PAHs discussed above, the final exchange status of PAHs is the combined effects of the depositional input caused by biomass burning, the properties of the chemical, and the melting of lake ice.

Seasonal ice cover is an important feature of water bodies in cold regions. In the Arctic region, Jantunen et al. (2008) and Wong et al. (2011) both observed the occurrence of volatilization of POPs from seawater coincident with the breaking up of ice cover in the summer. The Nam Co Lake also undergoes long periods of ice-cover (Liu et al., 2013). During the winter, the lake surface is covered by ice and gas exchange is restricted, meanwhile dry and wet deposition exerts a significant influence on the input inventory of PAHs to the lake. Both of these two deposition processes are one-way (no volatilization), which keeps the contaminants being accumulated. As summer arrives, the lake ice begins to thaw and air-water gas exchange begins to dominate. On the one hand, after the higher accumulation of deposition, supersaturation of PAHs in the lake may occur. On the other hand, the fugacity capacity of ice is much higher than that of water, and therefore the decrease of the fugacity capacity during melting will increase the fugacity of the PAHs (Wania et al., 1998c), which also promotes their re-emission from the water. Although the seasonal ice cover did not show any obvious influence on the fate of OCPs and other PAHs, it played an important role in the fate of Phe, which was a dominant compound in the Nam Co atmosphere. The lake therefore acted as a secondary source of Phe in May and June, and shifted to a net sink during other months, which is likely driven by the seasonal freeze-thaw cycle of lake ice (Figure 8).

3.4.3 Atmospheric degradation

Reactions with the hydroxyl radical (OH) are an important removal process of gaseous POPs from the atmosphere. The resulting degradation fluxes (F_{deg}, ng m^{-2} day^{-1}) are dependent on the concentration of OH radicals in the air (Spivakovsky et al., 2000) and the compound-specific degradation rate constant (K_{OH}, cm^{3} molecules^{-1} day^{-1}). The K_{OH} values of gaseous OCPs and PAHs are from Brubaker and Hites (1998) and Keyte et al. (2013), respectively. Due to the lack of information on K_{OH} for β-HCH and BaA, their degradation fluxes (F_{deg}) were not considered in this study. The calculated F_{deg} values were averaged for individual POPs and are presented in Figure S4. The degradation fluxes for α-, γ-HCH, HCB, and PCB 28 ranged between 0.3 and 0.9 pg m^{-2} day^{-1} (Figure S4), 3 orders of magnitude lower than their F_{AW}. This indicates that the contribution of atmospheric degradation to their total inventory in the environment is negligible.

In contrast to the OCPs, the PAHs are more susceptible to photodegradation (Lohmann et al., 2009). In our study, lower molecular weight PAHs showed higher degradation fluxes, such as 4–184 ng m^{-2} day^{-1} for Phe, and 1–160 ng m^{-2} day^{-1} for Ant (Figure S4). These values are similar to those reported for F_{deg} in the remote atmosphere of the Atlantic Ocean (i.e., 7–120 and 9–50 ng m^{-2} day^{-1} for Phe and Ant,

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respectively) (Nizzetto et al., 2008). We observed relatively low F_{deg} values for 5- and 6-ring PAHs, ranging from 0.01 to 0.18 ng m^{-2} day^{-1} (Figure S4). Generally, the F_{deg} of all PAH compounds was one order of magnitude lower than their F_{AW}. OH depletion is the primary process that removes atmospheric PAHs, presumably causing the continuous volatilization of low molecular weight PAHs from the water. This raised questions about other processes that may have supplied PAHs into the lake water. On the other hand, OH degradation also decreases the input of high molecular weight PAHs into the water and it is unclear to what extent this degradation counteracts other deposition processes.

3.4.4 Atmospheric deposition

In addition to the gas exchange, dry and wet deposition are also important processes that influence the input of POPs from air to the lake. Dry (F_{DD}) and wet (F_{WD}) deposition was estimated using Equations 4 and 6, respectively. With respect to HCHs, HCB, and PCB 28, their dry deposition fluxes (F_{DD}) were negligible due to their low detection frequency in the particulate phase (Table S8). However, the average F_{WD} for α-HCH, β-HCH, and γ-HCH was -0.3, -0.9, and -0.4 ng m^{-2} day^{-1}, respectively, which is comparable to their F_{AW} levels. F_{WD} for HCB (-0.02 ng m^{-2} day^{-1}) and PCB 28 (-0.002 ng m^{-2} day^{-1}) was two magnitudes lower than their F_{AW}. In general, precipitation scavenging is most efficient in HCHs compared with the other chemicals (Carrera et al., 2002). Greater wet deposition fluxes of HCHs occurred in August (Figure S5), coinciding with the highest amount of precipitation in Nam Co. Combining the F_{AW} and F_{WD} of HCHs, the estimated annual input of HCHs from air into the whole lake (2015 km^2) was 1.9 kg year^{-1}. This result highlights the input of HCHs by the LRAT-deposition process during the ablation period (open water season). Snow scavenging of HCHs has been reported as an important clearing process in mountain regions (Kang et al., 2009). However, the transport of HCHs in winter is very limited due to the unfavorable air circulation patterns (westerly wind), ruling out the significant contribution of input of HCHs by snow scavenging.

Compared with OCPs, the close association between PAHs and the particulate phase accounted for their relatively higher deposition fluxes. The estimated dry and wet deposition fluxes for individual PAHs during the ablation and frozen periods, respectively, are provided in Table 1. We found that the F_{DD} values of PAHs for the ablation period are, in general, lower than those for the frozen period. For example, the F_{DD} of total PAHs increased by one order of magnitude from the ablation period (4.5 ng m^{-2} day^{-1}) to the frozen period (38 ng m^{-2} day^{-1}; Table 1). Two factors may lead to the increase of F_{DD} in winter: the increased wind speed during the winter season and the growing particulate-PAH concentrations due to the enhanced combustion activities in winter. Compared with other studies, the

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estimated F_{DD} for the total 15 PAHs (4.5–38 ng m^{-2} day^{-1}, this study) is broadly within the range reported for global oceans (8.3–52.4 ng m^{-2} day^{-1}) (Gonzalez-Gaya et al., 2014).

Wet deposition was found to be the dominant deposition process for the input of PAHs into Nam Co (Table 1). This was expected because precipitation scavenging of organic chemicals underlies the accumulation of pollutants in mountain regions (Tremolada et al., 2008). In addition, there was an obvious difference between the values of F_{WD} during the ablation and frozen periods. For the total 15 PAHs, the F_{WD} in the frozen period (702 ng m^{-2} day^{-1}) was approximately 5 times higher than that for the ablation period (161 ng m^{-2} day^{-1}), which may be due to the different precipitation types between these two periods (snow *vs.* rain). Snow has been suggested to be more efficient than rain for scavenging particulate-PAHs, which had a high concentration during winter in Nam Co (Table S8). Thus, although the precipitation of Nam Co in winter is low (less than 30 mm, Figure S2), the strong scavenging ratio of snow to PAHs combined with the relatively high particulate-PAHs concentration in winter caused the enhanced PAHs deposition in winter. The frozen season coincided with the period of high emission and high deposition of PAHs, implying a significant contribution of this season in the input of PAHs into the lake.

To calculate the comprehensive contribution of all above-mentioned processes, three groups of PAHs were classified in Table 1 based on their fate during the air-water exchange processes. PAHs (Acel, Ace, and Flu) showing volatilization behavior were placed into one group, PAHs with large F_{AW} variability between the status of volatilization and deposition were in the second group; and the remaining PAHs displaying deposition behavior were placed into the third group (Table 1). In this classification, although the air-water exchange direction and fluxes of Ant and Fla cannot be estimated, we still placed them into the second group because of their similarity to Phe in their physicochemical properties. For the volatilization group, the total outgassing from the lake was estimated to be approximately 126 kg per year, which cannot alone be supplied by their total deposition flux (sum of F_{WD} and F_{DD}). This suggests that there may be additional natural sources of PAHs in the lake, such as, degradation of pigments carrying aromatic structure and turnover of organic matter (Nizzetto et al., 2008). Regarding the deposition group (Pyr, BaA, Chr, Bbf, Bkf, Bap, IcdP, DahA, and BghiP), their total deposition flux (F_{AW}+F_{DD}+F_{WD}) will roughly cause the annual input of 208 kg high molecular weight PAHs into the lake. Although the F_{AW} of Phe was reversed and the total volatilization of Phe was estimated at around 26 kg year^{-1}, this loss will be complemented by the continuous deposition of Phe (~373 kg year^{-1}) from July to April. This indicates that the annual net input of Phe will be above 340 kg, which suggests that

Phe is the most dominant contributor in the total PAHs deposition. Considering the source of PAHs, the atmospheric deposition related to the regional biomass burning is assumed to be a potential anthropogenic carbon source to Nam Co Lake.

3.4.5 Uncertainties in flux estimation

Several factors were involved in the uncertainties of the flux estimation: (i) loss during sample extraction and clean-up; (ii) measurement errors; and (iii) accuracy of the parameters in meteorology and physicochemical properties. The air-water gas exchange flux (F_{AW}) is the most important contributor to the total inventory of PAHs into the lake. The uncertainty involved in F_{AW} was estimated by propagating the errors in C_a (30%), C_w (35%), K_{ol} (40%), and H (20%), which was 64%. These small errors demonstrate that the estimate of the gas exchange fluxes was relatively robust. By contrast, the confidence levels in the estimated F_{deg} and F_{WD} were a factor of 3–5, dominated by the uncertainty of K_{OH}, W_G, and W_P values for most PAHs in the study region. For example, the scavenging rates of PAHs by wet deposition were highly variable, which was caused by the complexity of the size distribution of aerosols, meteorological conditions, and the scavenging process (Jurado et al., 2005). Considering these aggregated uncertainties, the estimated fluxes here are only expected to capture the order of magnitude for the different processes. In addition, other input processes into the lake, such as, glacier meltwater, river runoff, and soil erosion may also occur in this study region, which will lead to an underestimation of the total input flux.

3.5 Implication for the regional carbon cycling

Lakes are increasingly recognized as an important component of the terrestrial carbon cycle (Tranvik et al., 2009). Nearly 50% of the area of Chinese lakes is located on the TP, with general oligotrophic conditions and a total lake area of >43000 km^2 (Zhang et al., 2014). Compared with other components, such as grassland and forest, organic carbon burial in Tibetan lakes has been largely ignored. Although our study only focused on one of these lakes (Nam Co, area = 2015 km^2), we can extrapolate the annual atmospheric deposition of PAHs into the remaining Tibetan lakes, and estimate it at 8.7 tons C, when expressed as carbon fluxes, which would become a significant allochthonous carbon source for these oligotrophic lakes. Because the Tibetan lakes are low in nutrients, bacteria in the lake have adapted to using a wide range of organic compounds and growing under starvation conditions (Liu et al., 2009). Recently, bacteria from the genus *Sphingomonas* were detected in Nam Co lake water and various glacier snows of the TP (Liu et al., 2013; Liu et al., 2009), and they were reported to have the ability to degrade PAHs (Leys et al., 2005). The presence of these bacteria in Nam Co suggests that the

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atmospheric inputs of PAHs can act as a carbon source to support the survival of Tibetan microbial communities. Despite the natural PAH background in the environment, increasing biomass burning has led to the accumulation of PAHs in the lake sediments, especially during the past 50 years (Yang et al., 2016). Therefore, the continuous atmospheric deposition of PAHs and its ecological impact deserve greater concern.

4. Conclusions

This study confirmed that the Nam Co Lake was still a net sink of HCHs, following the LRAT-deposition process, rather than a secondary source. By contrast, PAHs primarily originated from local biomass burning. Dominated by gas exchange and wet deposition, the air-water fluxes of PAHs to the whole Nam Co Lake were estimated to be 550 kg year^{-1}, providing a substantial carbon source for the oligotrophic lake. Among the PAHs compounds, Phe showed a distinct behavior with monthly reversals of the air–water exchange, which was most likely driven by the seasonal melting of lake ice. This hypothesis requires further investigation, and a passive sampling technique is recommended as a viable alternative to enhance the spatial coverage of the investigation of air-water exchange in the TP.

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738 **Table 1. Estimated fluxes (ng m^{-2} day^{-1}) of air-water gas exchange (F_{AW}), atmospheric degradation (F_{deg}), dry deposition (F_{DD}), and**
739 **wet deposition (F_{WD}) for individual PAHs during the ablation period and frozen periods, respectively.**

PAH	ablation period				PAH	frozen period		
	F_{AW}	F_{deg}	F_{DD}	F_{WD}		F_{deg}	F_{DD}	F_{WD}
				Volatilization compounds				
Acel	80 ±49	6 ±5	NA	-0.2 ±0.1	Acel	1 ±0.7	-0.02 ±0.001	-0.03 ±0.1
Ace	51 ±19	4 ±4	-0.003 ±0.002	-0.4 ±0.3	Ace	0.9 ±0.5	-0.01 ±0.01	-6 ±5
Flu	203 ±162	11 ±8	-0.1 ±0.02	-9 ±7	Flu	1.8 ±0.9	-0.2 ±0.2	-43 ±30
sum	**335**	**21**	**-0.1**	**-9**	**sum**	**4**	**-0.2**	**-49**
Phe	-340 ±604	82 ±67	-0.5 ±0.1	-42 ±35	Phe	10 ±4	-2.2 ±1.2	-345 ±237
Ant	NA	60 ±63	-0.04 ±0.03	-5 ±5	Ant	4 ±2	-0.11 ±0.05	-16 ±14
Fla	NA	5 ±5	-0.5 ±0.1	-20 ±18	Fla	0.5 ±0.3	-4.6 ±2.8	-93 ±64
				Deposition compounds				
Pyr	-145 ±154	20 ±21	-0.4 ±0.1	-18 ±17	Pyr	2 ±1	-3 ±1.5	-128 ±83
BaA	-19 ±23	NA	-0.1 ±0.1	-3 ±4	BaA	NA	-1.1 ±0.5	-15 ±10
Chr	-54 ±62	7 ±8	-0.5 ±0.3	-47 ±56	Chr	0.2 ±0.1	-4.7 ±2.3	-19 ±13
Bbf	-5 ±3	0.2 ±0.1	-0.6 ±0.5	-6 ±5	Bbf	0.02 ±0.01	-2.2 ±3.2	-4 ±8
Bkf	-2 ±1	0.2 ±0.1	-0.4 ±0.4	-2 ±1	Bkf	0.1 ±0.04	-3.8 ±1.9	-8 ±5
Bap	-2 ±1	0.2 ±0.2	-0.3 ±0.5	-3 ±1	Bap	0.04 ±0.03	-4.7 ±2.3	-16 ±10
IcdP	-2 ±1	0.7 ±0.5	NA	-2 ±2	IcdP	0.1 ±0.1	NA	-3 ±6
DahA	-1 ±0.7	0.1 ±0.1	NA	-0.1 ±0.2	DahA	0.01 ±0.01	NA	-0.6 ±1
BghiP	-2 ±0.4	0.02 ±0.01	-1 ±1	-3 ±1	BghiP	0.01 ±0.01	-12 ±6	-6 ±3
sum	**-231**	**28**	**-3**	**-85**	**sum**	**2**	**-31**	**-199**
Total PAHs	\	**196**	**-4.5**	**-161**	**Total PAHs**	**20**	**-38**	**-702**

740 NA: not available; For F_{AW}, F_{DD} and F_{WD}, positive values indicate volatilization, and negative values indicate net deposition.

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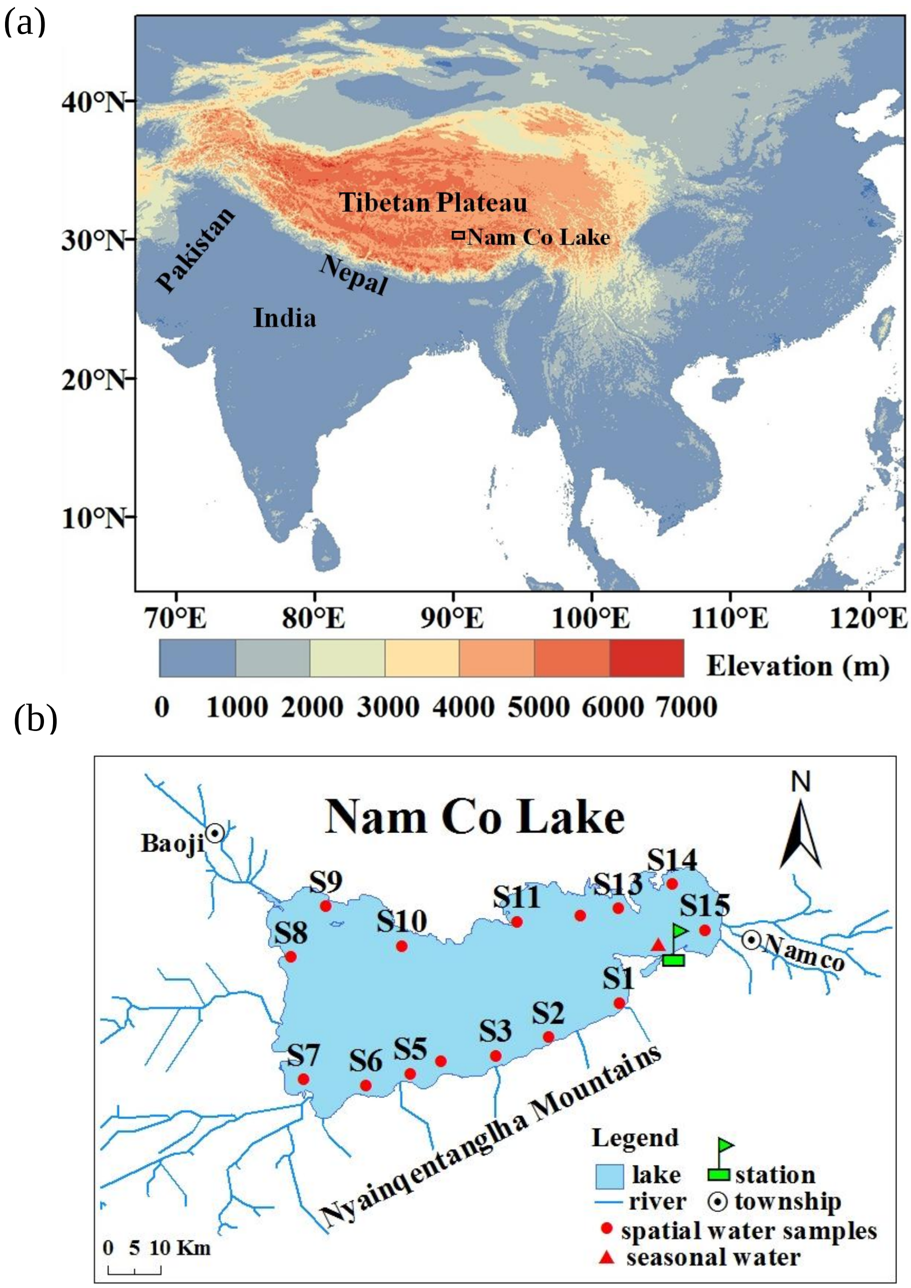

Figure 1. Location of Nam Co Lake on the Tibetan Plateau (a) and the sampling sites for air and lake water (b). The station refers to the Nam Co Monitoring and Research Station, and it is also the air sampling site; S01 to S15 represent the 15 sampling sites of surface water around the lake; the red triangle represents the sampling site of seasonal water from May to September.

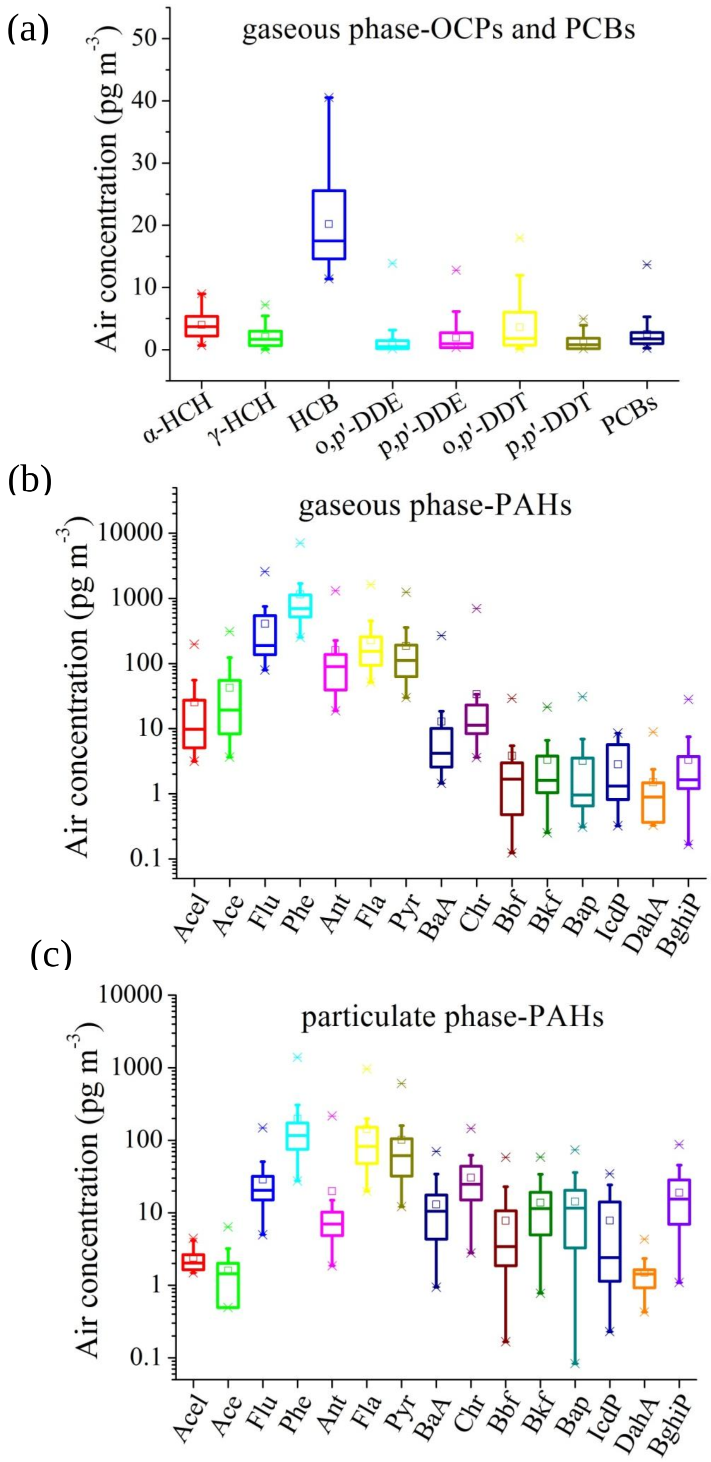

Figure 2. Air concentrations of gaseous OCPs and PCBs (a), gaseous PAHs (b), and particulate phase PAHs (c) in Nam Co. The boxes are defined by the 25th and 75th percentiles; whiskers mark the 10th and 90th percentiles; the median is represented by a horizontal line; the mean by a

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square; and outliers with an asterisk.

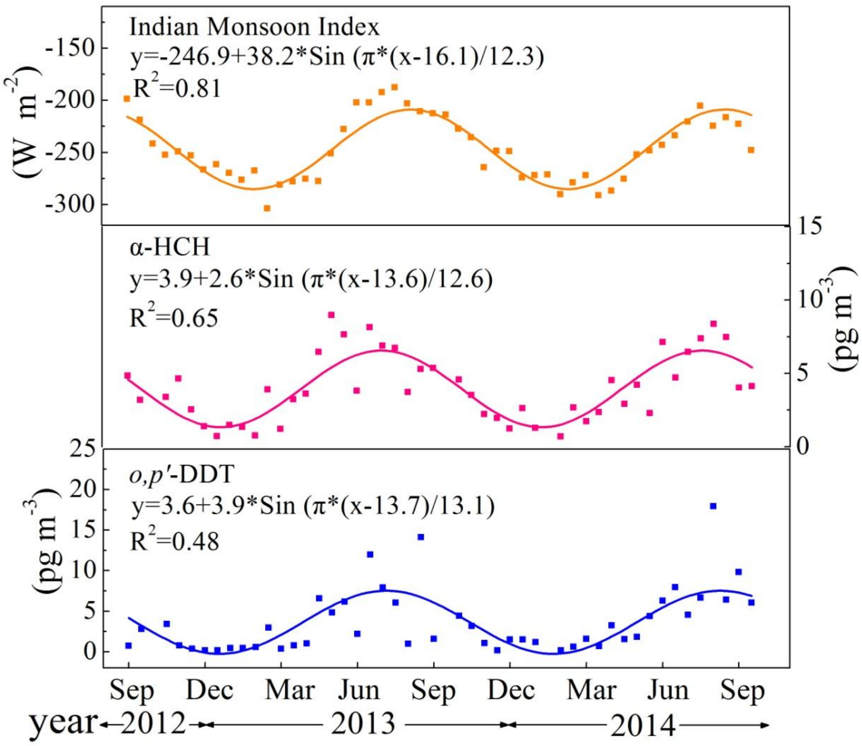

Figure 3. Seasonal patterns of Indian Monsoon Index, the atmospheric concentrations of α-HCH and *o,p'* -DDT.

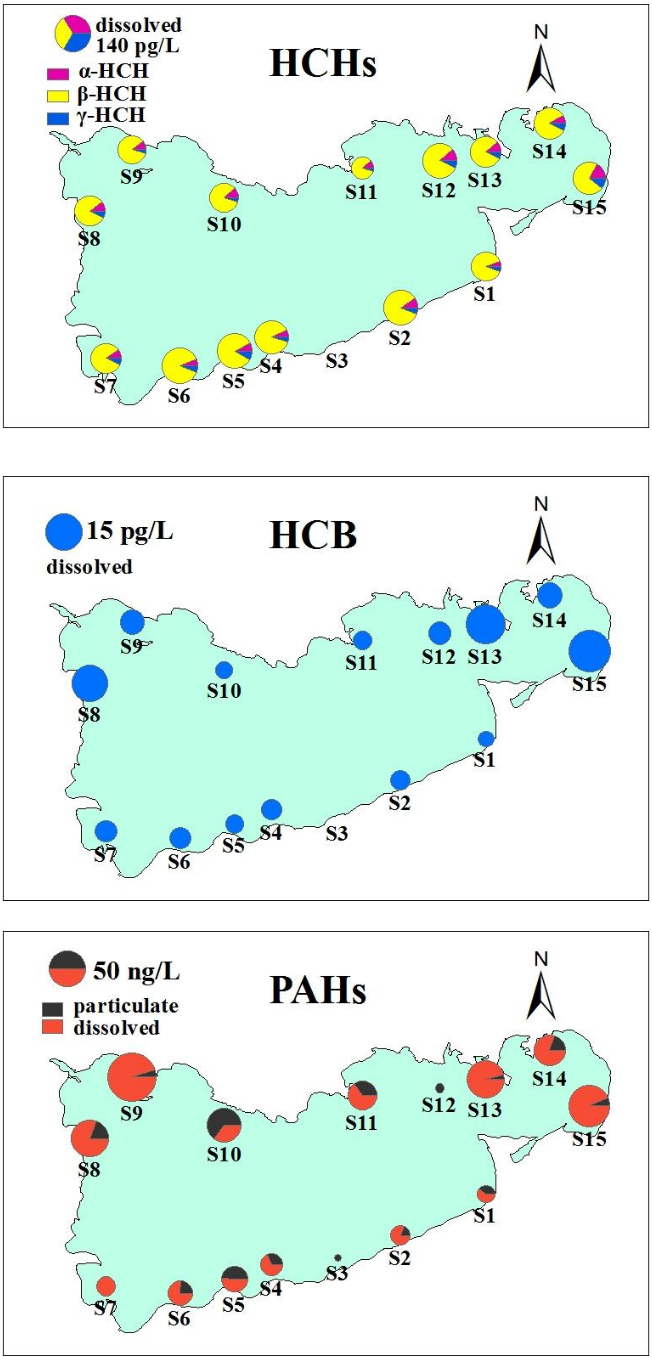

Figure 4. Spatial distribution pattern of HCHs, HCB, and PAHs in the surface water of Nam Co Lake.

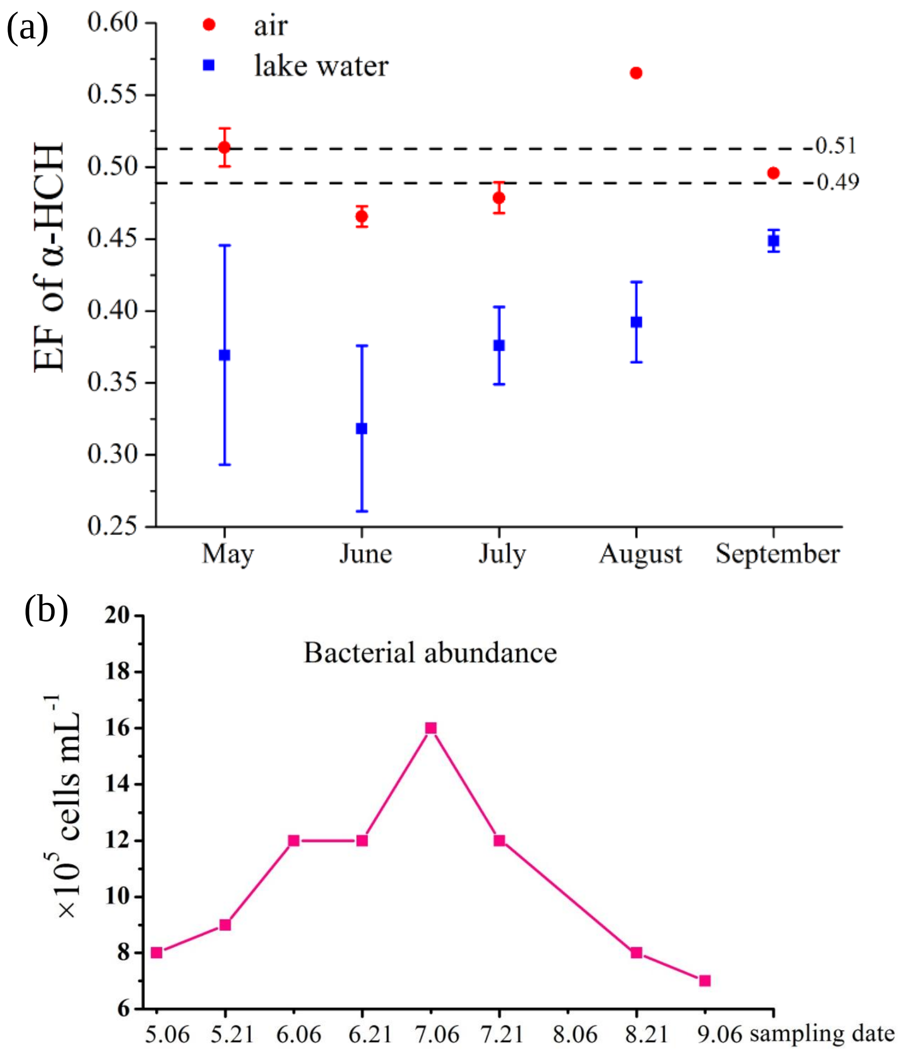

Figure 5. Enantiomer fraction (EF) of α-HCH in the air and surface water from May to September (a), and the seasonal bacterial abundance in Nam Co Lake water (b). The data of bacterial abundance was derived from Liu et al. (2013), which represents the total bacteria in the lake surface water.

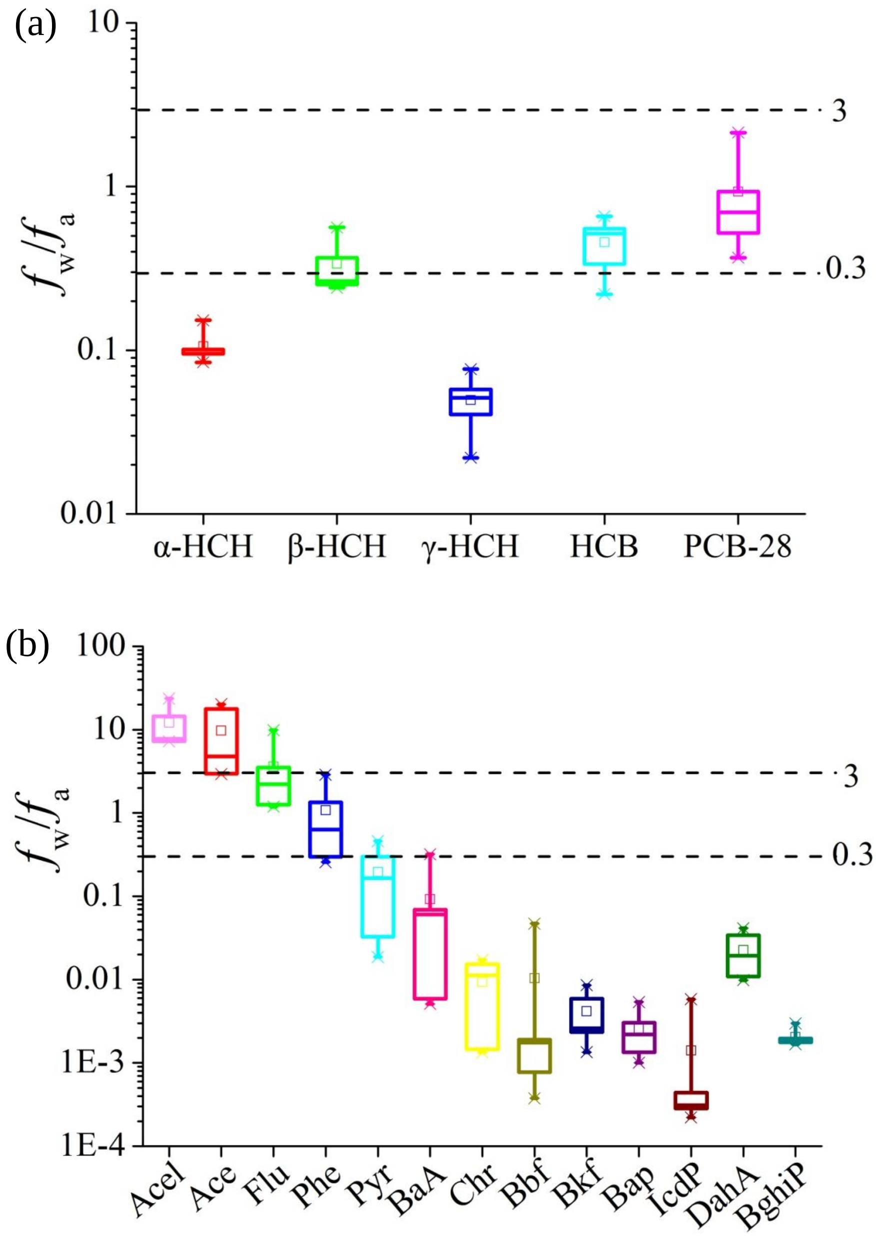

Figure 6. Water/air fugacity ratios (f_w/f_a) for OCPs and PCB 28 (a), and individual PAHs (b) in Nam Co Lake. The horizontal lines represent the uncertainty range, 0.3-3 was considered as equilibrium.

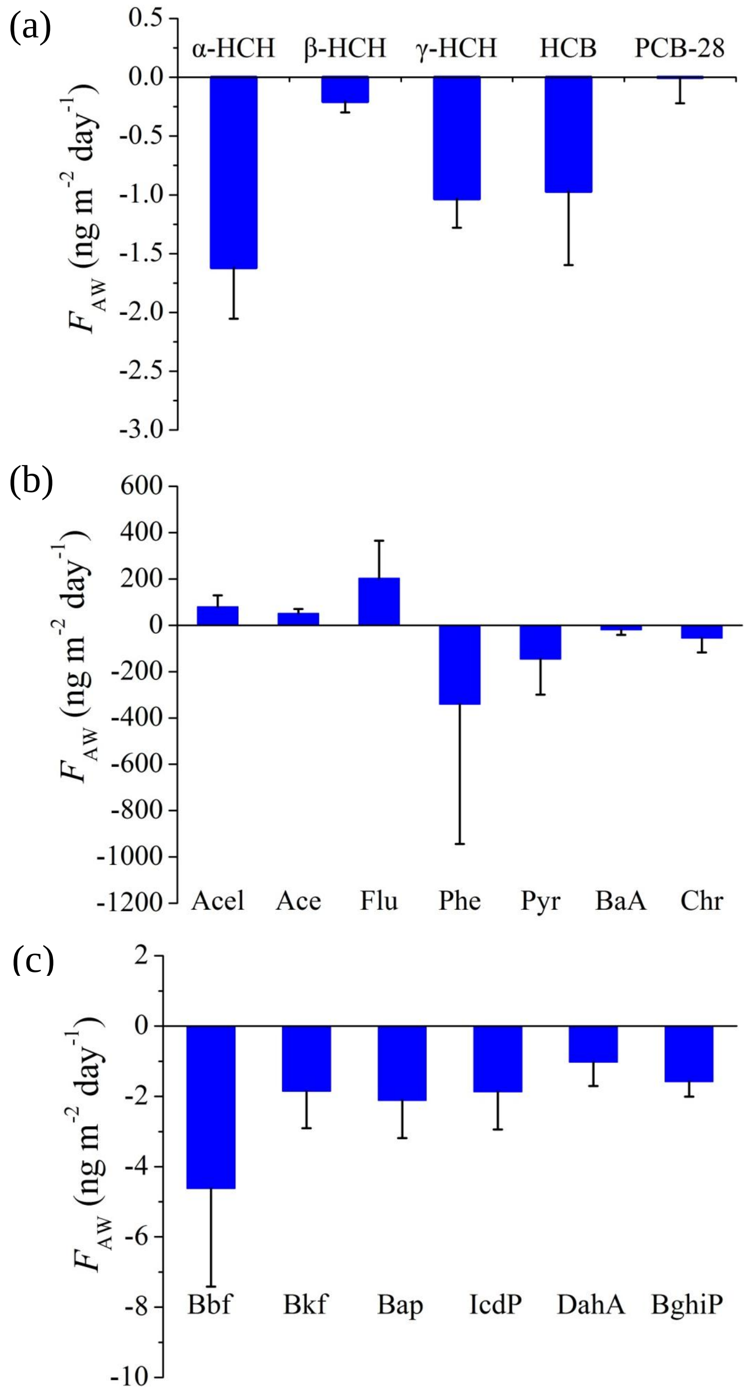

Figure 7. Average air-water gas exchange fluxes (F_{AW}) for individual OCPs, PCB 28 (a), and PAHs (b, c) in Nam Co Lake. Positive values indicate net volatilization, and negative values indicate net deposition.

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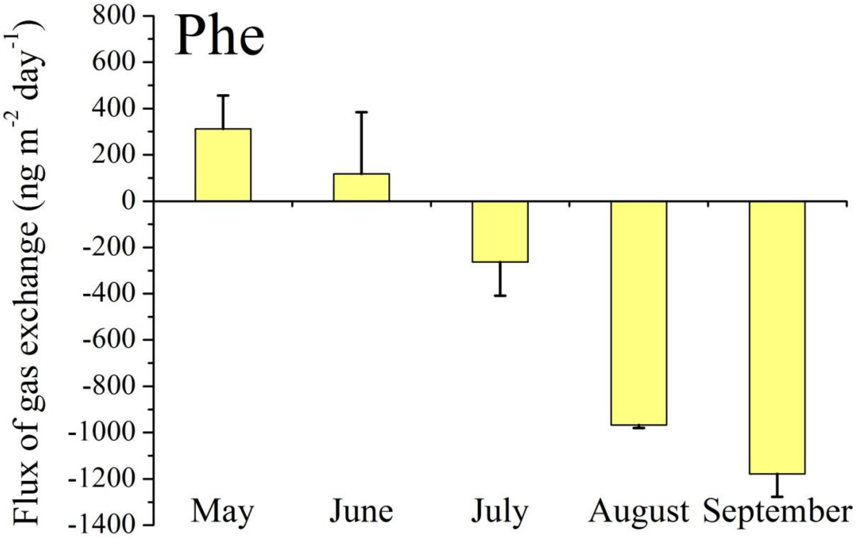

Figure 8. Reversal of the air-water gas exchange for Phe from May to September.