



## Atmospheric Transport and Bulk Deposition of Organochlorine Compounds at Leigongshan Nature Reserve in Southwestern China

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### ABSTRACT

Atmospheric and bulk deposition samples collected at Leigongshan Nature Reserve (LNR) were analyzed to explore the status, transport, and deposition of atmospheric pollution—specifically, organochlorine compounds—in the foggy mountains of southwestern China. Prohibiting and restricting persistent organic pollutants in the surrounding areas has led to a decline in organochlorine pesticides and polychlorinated biphenyls (PCBs), but not hexachlorobenzene (HCB), in the air. Wet deposition is a factor that strongly influences the atmospheric input at LNR. Despite the relatively low atmospheric concentration levels of hexachlorocyclohexanes (HCHs) and HCB, heavy precipitation can increase the deposition of these compounds in summer. The airborne HCHs exhibited a “bimodal” pattern, with higher concentrations in spring and autumn and lower concentrations in summer, the latter of which are results of high surface input into the ground along the transport routes of these compounds from South and Southeast Asia to southwestern China. The HCB at LNR mainly originates in mainland China. The deposition fluxes are influenced by the enhanced washout of atmospheric particles in the rainy season and increased particle-associated content in winter. The potential sources of *o,p'*-DDT, *p,p'*-DDT, and PCBs are distributed widely over low-latitude western areas and eastern China. Atmospheric transport and deposition in spring and summer contribute a significant proportion of the total fluxes annually when air masses originating in Southeast Asia arrive, increasing rainfall at LNR. The foggy local weather may also enhance this deposition, eventually leading to the accumulation of pollutants at LNR.

**Keywords:** Air transport; Bulk deposition; Foggy mountain; OCPs; PCBs.

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### INTRODUCTION

Persistent organic pollutants (POPs) are a group of toxic, persistent, and bioaccumulative chemicals prohibited or restricted by a series of multilateral environmental agreements, such as the Stockholm Convention, the Basel Convention, and the Rotterdam Convention. Atmospheric transport and deposition are considered major pathways for the redistribution of these pollutants to pristine environments. To evaluate the air quality degeneration associated with POPs, air monitoring networks, such as the NJADN in

New Jersey (Van Ry *et al.*, 2002; Gioia *et al.*, 2005), IDAN for the Great Lakes (Hoff *et al.*, 1996; Melymuk *et al.*, 2011), and the AMAP for the Arctic (Hung *et al.*, 2016), have been established for extensive monitoring. Local-scale observations have also been conducted in Germany (Bruckmann *et al.*, 2013), Sweden (Bergknut *et al.*, 2011), and other European countries (Carrera *et al.*, 2002; Arellano *et al.*, 2015; Jakobi *et al.*, 2015). Relevant research has also been conducted in China (Wong *et al.*, 2004; Yang *et al.*, 2012; Liu *et al.*, 2013; Guo *et al.*, 2017), but most study data have been obtained from urban or suburban areas relatively close to the pollution sources. These observations provide extensive historical and current information on variations in air quality, which is useful to assess the effectiveness of national and international chemical control initiatives (Hung *et al.*, 2016).

To effectively implement the Stockholm Convention,

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the Chinese government is taking measures to reduce and eliminate pesticide POPs, polychlorinated biphenyls (PCBs), and dioxins (SEPA, 2007). Primary emissions of pesticides and PCBs generally show a decreasing trend in China (Wang *et al.*, 2005; Cui *et al.*, 2015). However, current application or emission still dominates the air in low latitude areas, such as Vietnam, India, or the Bay of Bengal. Distinct seasonal changes in prevailing wind directions and precipitation patterns caused by the Indian monsoons may result in atmospheric transport from those sources to pristine areas in western China such as the Tibetan Plateau (Sheng *et al.*, 2013). Moreover, the emission of historical residues of POPs in eastern China could also influence relatively clean regions in the west. A numerical study identified the influences of pollution sources in eastern China and India on sink accumulation in southwestern China (Xu *et al.*, 2013). Therefore, monitoring at the receptor sites in western China is essential to evaluate the pollution status and the transport and transfer processes.

In this paper, concurrent measurements of organochlorine pesticides (OCPs) and PCBs in both air and bulk deposition were performed at a mountaintop in Leigongshan Nature Reserve (LNR) of Guizhou Province, which is an important habitat for rare plant and animal species. Compared with the surrounding provinces, the historical usage of OCPs and PCBs is the lowest in Guizhou (Wang *et al.*, 2005). From a climatological perspective, this nature reserve, located within 100° and 110°E, delineates the South Asian and East Asian monsoon regions (Wang *et al.*, 2003); it thus has the potential to receive airborne pollutants transported from the regions lying to its east and west. A numerical simulation of the environmental fate of  $\alpha$ -HCH, performed after HCH restrictions were promulgated in Asia, suggested a potential sink in the surrounding areas (Xu *et al.*, 2013). Atmospheric observations at LNR may reveal the background air quality status in southwestern China and the possible atmospheric transport routes. Bulk deposition together with air monitoring can be used to assess the atmospheric loadings and the link between transport and deposition.

## METHODS

### *Sample Collection and Site Description*

Starting from January 6, 2016, atmospheric and deposition samples were collected for 1 year at the top of Leigongshan Mountain (26.389°N, 108.205°E; 2178 m above sea level), which is within LNR (Fig. S1). Located in Leishan County, Guizhou Province, this nature reserve covers an area of 47,300 ha, with 88% forest coverage. It is a temperate area with mild temperature, abundant rainfall, and vertical climate variation. The annual average temperature at the top of the mountain is approximately 9.4°C, and the annual precipitation is 1300 mm. The monthly average temperature and precipitation are plotted in Fig. S2. The mountain is foggy year-round, with more than 300 foggy days each year. Because the mountaintop is characterized by dense fog and light drizzle, long-term dry deposition samples are difficult to obtain; thus, bulk atmospheric deposition samples were collected in this

study.

Using a modified Anderson-type high-volume air sampler operated at a rate of 430 m<sup>3</sup> day<sup>-1</sup>, 24-h air samples were collected once every 6 days. Atmospheric particulate and gaseous samples were collected using quartz microfiber filters (QFFs) (20.3 × 25.4 cm, Grade GF/A) and polyurethane foam (PUF) plugs (8.0 cm (length) × 6.25 cm (diameter)), respectively. Atmospheric bulk deposition samples were collected using stainless-steel funnels mounted 0.5 m above the ground. The continuous samples obtained within each month were combined, and the total monthly rainfall was measured using a calibrated jar. Deposition samples were filtered using glass microfiber filters (GMFs) (diameter = 4.7 cm, Grade GF/F) and passed through a chromatographic column containing a mixture of XAD-2 and XAD-4 (1:1) resin. Before sampling, the QFFs and GMFs were baked at 400°C for 4 h. The weights of the filters were measured before and after sampling. The PUFs and resin were pre-cleaned twice in a Soxhlet apparatus by using acetone and dichloromethane (DCM), and these materials were kept frozen until use. The stainless-steel funnels for deposition sampling were cleaned using ethanol and DCM. The deposition samples were analyzed after storage, transportation, and filtration. The pollutants in the dissolved and particulate phases do not necessarily reflect the original phase partitioning because submicron particles might have passed through the 0.7- $\mu$ m filter pores into the dissolved phase. Deposition was recorded as the sum of the target compound in the GMF and resin samples. Filters (QFFs and GMFs), PUFs, and resin columns were wrapped with clean aluminum foil, sealed in Teflon bags, and stored at -18°C until analysis.

### *Analytical Procedures*

Before laboratory analysis, QFFs and PUFs were spiked with internal standards, including 2,4,5,6-tetrachloro-*m*-xylene (TCmX), PCB-30, <sup>13</sup>C-PCB-28, <sup>13</sup>C-PCB-52, <sup>13</sup>C-PCB-101, <sup>13</sup>C-PCB-118, <sup>13</sup>C-PCB-153, <sup>13</sup>C-PCB-138, <sup>13</sup>C-PCB-180, and PCB-209 as recovery surrogates, after which they were separately Soxhlet-extracted using DCM for 48 h. Deposition samples were also spiked with the same standards, filtered by GMFs and absorbed by XAD resin, and then Soxhlet-extracted using DCM for 48 h. The extracts were concentrated to a volume of 1 mL by using a rotary evaporator and solvent-exchanged into hexane. Extract purification was performed using an alumina/silica column containing anhydrous sodium sulfate, 50% sulfuric acid silica, neutral silica gel, and neutral alumina. The purified extracts were evaporated to approximately 100  $\mu$ L under low nitrogen flow, following which 20  $\mu$ L of dodecane was added. Samples were concentrated to the final volume of 20  $\mu$ L. Then, <sup>13</sup>C-PCB-141 was added to each sample as an internal standard for analyzing OCPs and PCBs.

In total, 47 chromatographic peaks corresponding to 32 PCB congeners (PCB-8, -28, -37, -44, -49, -52, -60, -66, -70, -74, -77, -82, -87, -99, -101, -105, -114, -118, -126, -128, -138, -153, -156, -158, -166, -169, -170, -179, -180, -183, -187, and -189) and 11 OCP compounds (HCB,  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH, and *o,p'*- and *p,p'*-DDE, -DDD

and -DDT) were analyzed. The target compounds were detected and measured using an Agilent 7890/7000 GC-MS/MS in multiple reaction monitoring (MRM) mode with a capillary column (length = 50 m, ID = 0.25 mm, thickness = 0.25  $\mu\text{m}$ ; CP-Sil 8 CB, Varian). Sample (1  $\mu\text{L}$ ) was injected in splitless mode. The initial GC oven temperature was set at 80°C for 0.5 min, raised to 160°C at a rate of 20°C  $\text{min}^{-1}$ , to 240°C at a rate of 4°C  $\text{min}^{-1}$ , to 295°C at 10°C  $\text{min}^{-1}$ , and finally held for 10 min. High purity helium was used as the carrier gas, with a flow rate of 1.0  $\text{mL min}^{-1}$ . The instrumental settings of the GC-MS/MS were the same as those described by Huang *et al.* (2014) and Zheng *et al.* (2014).

### QA/QC

The sampling and experimental procedures were controlled through tests of breakthrough, recovery, lab blanks, and field blanks. A breakthrough test was performed by placing a smaller PUF plug below the main PUF in the sampler. The smaller PUF trapped only 0–3% of the compounds targeted in this study. Lab blanks were precleaned QFFs, GMFs, PUFs, and XAD resin. Filed blanks for collecting air samples were precleaned QFFs and PUFs exposed to ambient air for approximately 5 min, whereas those for the deposition samples were precleaned GMFs and XAD resins exposed to purified water at the sampling site. The lab and field blanks were stored and analyzed along with each batch of samples.

To determine the analytical recovery efficiencies, all collected samples were spiked with surrogates. The average recoveries of TCmX, PCB-30,  $^{13}\text{C}$ -PCB-28,  $^{13}\text{C}$ -PCB-52,  $^{13}\text{C}$ -PCB-101,  $^{13}\text{C}$ -PCB-118,  $^{13}\text{C}$ -PCB-153,  $^{13}\text{C}$ -PCB-138,  $^{13}\text{C}$ -PCB-180, and PCB-209 were  $60 \pm 9.6\%$ ,  $70 \pm 8.8\%$ ,  $63 \pm 4.1\%$ ,  $72 \pm 5.9\%$ ,  $75 \pm 4.7\%$ ,  $74 \pm 4.4\%$ ,  $79 \pm 8.3\%$ ,  $82 \pm 9.6\%$ ,  $87 \pm 13\%$ , and  $96 \pm 14\%$ , respectively. Because the recoveries were relatively stable, the data were not recovery corrected. The instrumental stability of GC-MS/MS was checked daily by using two series of OCP and PCB standards, and a relative standard deviation within  $\pm 15\%$  was ensured. The instrumental detection limits (IDLs) were integrated where the signal-to-noise ratio was 3 in the chromatograms of samples. The method detection limits (MDLs) were derived from the mean concentrations of the target compounds of the field blanks, in units of mass plus three standard deviations ( $3\sigma$ ). Target OCPs were not detected in field blanks of air particle samples. Target compounds in the field blanks ranged from less than the IDL to 0.17 ng for the other matrixes employed in this study. For compounds less than the IDL in the field blanks, the MDL was defined as the IDL. The MDLs of the target PCBs and OCPs ranged from 0.002 to 1.1  $\text{pg m}^{-3}$  for the air samples and from 0.05 to 2.5  $\text{pg L}^{-1}$  for the water samples (Table S1). The quantities of compounds in the samples were blank-corrected.

### Back-trajectory and Potential Source Contribution Function Analysis

Air mass movement was estimated through trajectory analysis. For the sampling days, 5-day air parcel back-

trajectories were calculated at 6-h intervals using the Hybrid-Single Particle Integrated Trajectory (HYSPLIT 4.8) model developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (<http://www.arl.noaa.gov/HYSPLIT.php>). Each trajectory was estimated at 500 m above ground level. Fig. S3 shows the monthly precipitation data from the Global Precipitation Climatology Centre provided by NOAA as well as the prevailing air mass backward trajectories clustered using HYSPLIT 4.8.

Potential source contribution function (PSCF) analysis (Hafner and Hites, 2003; Hoh and Hites, 2004) was employed to illustrate the spatial distribution of the potential sources. Back-trajectory lines are a series of points representing the position of the modelled air mass at each hour. All the hourly points in the trajectories generated by HYSPLIT 4.8 were sorted into  $1^\circ$  (latitude)  $\times$   $1^\circ$  (longitude) cells. Accordingly, the PSCF of each grid is defined as follows:

$$\text{PSCF} = N_{\text{high}}/N_{\text{all}}$$

where  $N_{\text{high}}$  is the number of endpoints corresponding to the measured pollutant concentrations higher than a given criterion threshold. In this study, all trajectories corresponding to the chemical concentrations  $>$  average +  $0.125 \times$  standard deviations were selected.  $N_{\text{all}}$  is the total number of endpoints falling in the grid cell. To avoid numerical uncertainties, grid cells with  $N_{\text{all}} < 10$  were excluded. The calculated PSCF represents the probability of a given cell being a potential source region for a specific observatory, rather than the strength of sources for a large region.

### Deposition Estimation

Deposition fluxes were calculated assuming equilibrium status for the compounds in the air and the rain. The predicted deposition fluxes are the sum of the dry particle deposition ( $F_{\text{dry}}$ ), the washout of the particle phase ( $F_{\text{part}}$ ), and the dissolved phase ( $F_{\text{diss}}$ ):

$$F_{\text{dry}} = C_{\text{part}} \times V_d \quad (1)$$

$$F_{\text{part}} = C_{\text{part}} \times \text{rain} \quad (2)$$

$$F_{\text{diss}} = C_{\text{rain}} \times \text{rain} = C_{\text{gas}} \times \text{rain} \times R \times T/H \quad (3)$$

where  $C_{\text{part}}$ ,  $C_{\text{gas}}$ , and  $C_{\text{rain}}$  are the concentrations of the target compounds in the atmospheric particle phase, gaseous phase, and rainfall, respectively.  $V_d$  is the reported dry deposition rates ( $0.2 \text{ cm s}^{-1}$ ) (Hillery *et al.*, 1998; Miller *et al.*, 2001), rain is the precipitation intensity ( $\text{m month}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the temperature, and  $H$  is the temperature-dependent Henry's law constant (Mackay *et al.*, 2006).

## RESULTS AND DISCUSSION

### Pollution Levels

Atmospheric OCPs and PCBs were mainly distributed in the gas phase of the air. The detection rate of the targeted

11 OCPs and 11 PCBs, including HCB, HCHs, DDTs, and PCB-8, -28, -37, -44, -52, -60, -66, -70, -74, -99, and -101, were > 80% in the gas phase samples. Detection rates in the particle phase were generally < 50%; hence, the air concentration results were calculated based on the total concentration. The average air concentration levels of OCPs and PCBs are summarized in Table S2. For compounds with concentration below the MDL, the mean concentration levels were calculated by assuming “not detected” data as equal to 1/3 MDL. Atmospheric OCP and PCB contamination at LNR is comparable with that recently reported for other regional background sites in China and worldwide (Table S2). The annual average concentrations of HCHs at LNR compare favorably with those at other background sites in China (Gong et al., 2017; Zhan et al., 2017), the Arctic (Bossi et al., 2016), and Sweden (Bidleman et al., 2017), whereas DDT levels were lower than those at other sites in China (Sheng et al., 2013; Gong et al., 2017; Zhan et al., 2017) and comparable with those at polar regions (Bossi et al., 2016; Bidleman et al., 2017) and European high Alpine stations (Kirchner et al., 2016). The mean HCB concentration at LNR was lower than that reported in other studies, except for the Tibetan Plateau (Sheng et al., 2013; Gong et al., 2017). Total PCB concentrations ( $\Sigma_{32}\text{PCB}$ ) ranged from 4.2 to 35  $\text{pg m}^{-3}$ , with an average of  $15 \pm 7.2 \text{ pg m}^{-3}$ . The average contribution of di-, tri-, tetra-, penta-, hexa-, and hepta-CBs were 17%, 35%, 37%, 7.9%, 1.9%, and 0.7%, respectively. The concentrations of seven indicator PCBs—namely PCB-28, -52, -101, -118, -138, -153, and -180—were compared with those reported in the literature. The average concentration levels were relatively high but lower than those found in central China (Zhan et al., 2017). The atmospheric concentrations of OCPs and PCBs at a background site in Guizhou Province were evaluated in a passive air sampling (PAS) campaign conducted in 2004 (Jaward et al., 2005); POPs sequestered through PAS were converted to air concentrations and are listed in Table S2. Compared with data in 2004, air concentrations of DDTs and high-molecular-weight PCBs reduced to low levels, whereas those of more volatile compounds, such as HCB and low-molecular-weight PCBs, either showed a slight decline or remained at the same levels.

The deposition concentrations at LNR were in the range reported at other remote sites. Volume weighted mean ( $\text{ng L}^{-1}$ ) concentrations in the deposition samples are listed in Table S3. Of the 43 target compounds, the following 7 were commonly detected in the deposition samples: HCB,  $\alpha$ -HCH,  $\gamma$ -HCH,  $p,p'$ -DDT,  $p,p'$ -DDE,  $o,p'$ -DDT, and PCB-28. HCB,  $\alpha$ -HCH,  $\gamma$ -HCH, and PCB-28 were found at relatively high concentrations. The average HCB concentration was within the range of 0.003–0.072  $\text{ng L}^{-1}$ , which were observed in the United States national parks (Hageman et al., 2006). HCH concentrations were lower than the range of 1.8–5.0  $\text{ng L}^{-1}$  obtained in French (Teil et al., 2004) and Atlantic Canadian background sites (Brun et al., 2008). DDTs, including  $p,p'$ -DDT,  $p,p'$ -DDE, and  $o,p'$ -DDT, were found at a low level and also lower than those in Atlantic Canada (Brun et al., 2008).

### **Effect of Meteorological and Atmospheric Parameters**

Meteorological and atmospheric factors, such as temperature, precipitation, wind direction, and particles, influence the air concentration (Wania et al., 1998; Tian et al., 2009) and deposition (Fernandez et al., 2003) of POPs. Linear regressions of the logarithm of the concentrations of OCP or PCB gas in air versus reciprocal temperature (i.e.,  $\ln(C_{\text{air}}) = m/T + b$ ) are widely used to distinguish temperature-dependent volatilization from various surfaces. A strong temperature dependence of  $p,p'$ -DDE was observed, with a high  $R^2$  of 0.66 (Fig. S4), suggesting that this compound is mainly influenced by volatilization. The correlations between  $\ln(C)$  and  $1/T$  of the other compounds were either nonsignificant ( $p > 0.05$ ) or weak ( $p < 0.05$  and  $R^2 < 0.2$ ), indicating that at LNR, revolatilization from nearby surfaces may not be the major source of most OCPs and PCBs in the atmosphere. The correlation between air concentrations and precipitation was nonsignificant.

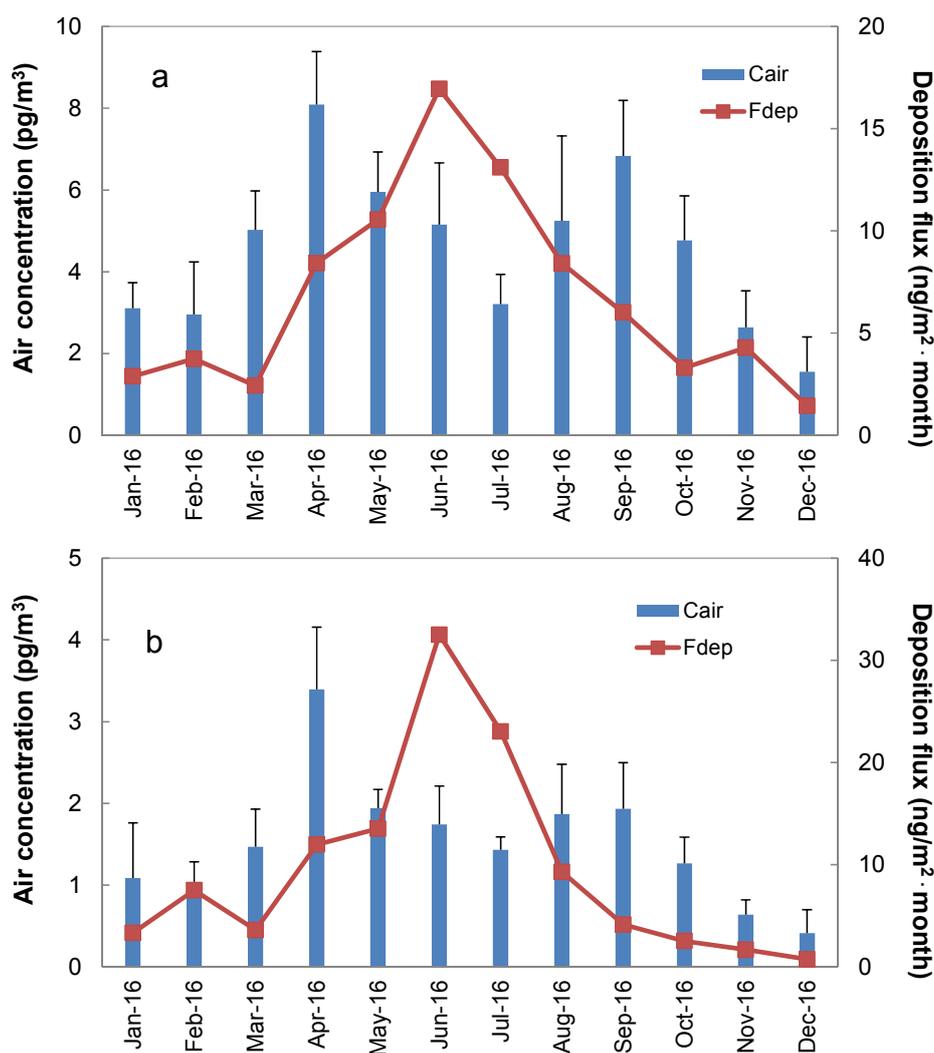
The effect of temperature and precipitation on deposition was investigated through linear regression analysis. A significant negative relationship was observed between  $\ln(C_{\text{dep}})$  of HCB and temperature (Fig. S5). This relationship is likely related to the tendency of atmospheric HCB to partition into particles during cold seasons given that HCB concentrations in the atmospheric particles increased in cold seasons (Fig. S6). The correlation between the concentrations of target compounds in the deposition samples and the total suspended particles was nevertheless nonsignificant. For  $\alpha$ - and  $\gamma$ -HCH with relatively high water solubilities, significantly high correlation coefficients of 0.97 and 0.92 were observed between precipitation and monthly deposition fluxes, respectively.

### **Transport and Deposition Trend of OCPs and PCBs**

The movement of airborne pollutants to remote areas entails three essential parameters, namely source emission, transport route, and favorable deposition condition at the receptor site. The following sections discuss the influence of these parameters on pollutant transport and deposition at LNR.

### **HCHs**

The seasonality of HCHs exhibited a “bimodal” pattern, with higher concentrations in spring and autumn and lower concentrations in summer (Fig. 1). Regarding other sites in the same latitudinal zone (Fig. S1; location details of the Tibetan and central China sites are shown in Table S1), this pattern was observed at the Tibetan Plateau but not at the central China site. Sheng et al. (2013) correlated this bimodal pattern to agricultural input of HCHs from India and rain scavenging in the rainy season. Zhan et al. (2017) attributed the high HCH levels in central China during winter to polluted air parcels originating from northern China. PSCF maps of  $\alpha$ - and  $\gamma$ -HCH reveal that northern China, Southeast Asia, and the Bay of Bengal are potential sources of HCHs in this study (Fig. S7). Most air parcels arriving at LNR passed through these potential sources from March to September (Fig. S3). The atmospheric concentrations of HCHs were high in March, April, and



**Fig. 1.** Seasonality of monthly mean air concentrations and deposition fluxes of (a)  $\alpha$ -HCH and (b)  $\gamma$ -HCH.

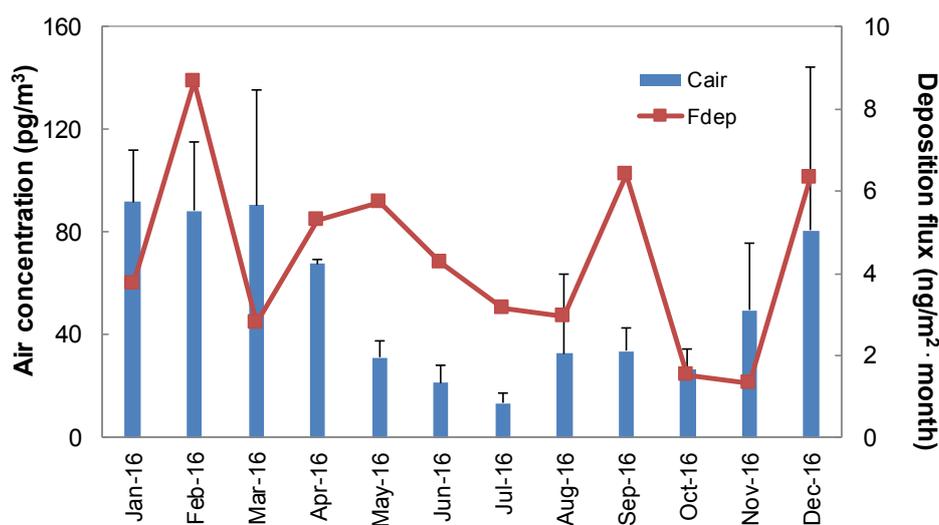
September and low from May to August, when many trajectories passed through precipitation centers over the Bay of Bengal and the South China Sea (Fig. S3, May–August).

For POPs with significant water solubility, such as  $\alpha$ - and  $\gamma$ -HCH, rainfall scavenging in the rainy season is a particularly effective method to remove these compounds from the air. The annual total  $\alpha$ - and  $\gamma$ -HCH deposition fluxes were 82 and 114 ng m<sup>-2</sup>, with atmospheric deposition fluxes from May to August contributing 60% and 68%, respectively; the relatively low air concentrations during these periods are likely achieved at the expense of high deposition from the air to the ground surface along the transport routes. The water solubility of  $\gamma$ -HCH (7.3 mg L<sup>-1</sup>) is higher than that of  $\alpha$ -HCH (1.5 mg L<sup>-1</sup>) (Mackay *et al.*, 2006); hence, wet deposition is more effective for  $\gamma$ -HCH and even significantly influences the  $\alpha$ -/ $\gamma$ -HCH ratio, a source indicator. Between May and July, the average  $\alpha$ -/ $\gamma$ -HCH ratio was 2.7 in the atmospheric samples, whereas it was only 0.62 in the deposition samples. For air samples, the average ratio increased from 2.2 in April to 3.1 in May, despite the similarity of the air mass back-trajectories of

these two months. These results imply that using isomer ratio indicators to distinguish between sources of relatively highly water-soluble compounds is difficult if the air mass passes through precipitation centers, such as the Bay of Bengal and the South China Sea. For example, the atmospheric  $\alpha$ -/ $\gamma$ -HCH ratios indicate technical HCH usage in the mainland of China, Vietnam, and the Kolkata region of India (Chakraborty *et al.*, 2010; Wang *et al.*, 2016) or Lindane use in the China Sea and the Bay of Bengal (Gioia *et al.*, 2012). Intensive precipitation over the sea areas may reduce the Lindane signals in the atmosphere when the air mass arrives at downwind receptors, such as at Tibetan and LNR sites.

#### HCB

HCB concentration exhibited clear seasonal variations, with elevated concentrations in winter months (Fig. 2), which was also reported in central China (Zhan *et al.*, 2017), the Tibetan Plateau (Sheng *et al.*, 2013), and other observation areas (Wang *et al.*, 2010). Decreasing the atmospheric concentration of HCB is difficult. Comparing the concentrations at the sites shown in Fig. S1, the annual



**Fig. 2.** Seasonality of monthly mean air concentrations and deposition fluxes of HCB.

average concentrations of HCB gradually decreased from east to west, with the highest in central China and the lowest in the Tibetan Plateau (Table S2). This spatial trend suggests that potential sources of HCB are likely located in central and eastern China. The PSCF map of HCB supports this assumption by indicating that the potential sources are widely distributed in southeastern, central, and northern China (Fig. S8). This spatial pattern is similar to that of airborne HCB measured in 2004 (Jaward *et al.*, 2005), suggesting that HCB concentrations at LNR are still influenced by these source regions, especially in the cold season.

The annual HCB deposition flux of  $52.1 \text{ ng m}^{-2}$  was close to those reported at other background sites (Arellano *et al.*, 2015). Elevated HCB deposition fluxes occurred not only in winter but also in summer (Fig. 2). The high fluxes in winter are mainly associated with elevated particle-associated HCB content in the air (Fig. S9). To a less significant extent, elevated gaseous HCB and TSP in the air may be related to high fluxes in winter. Unlike HCHs, HCB is a volatile compound with low water solubility, meaning that the HCB dissolution in rainwater during summertime is nonsignificant. The high concentrations in June and August likely reflect the enhanced washout of atmospheric particles during the rainy season.

#### DDTs

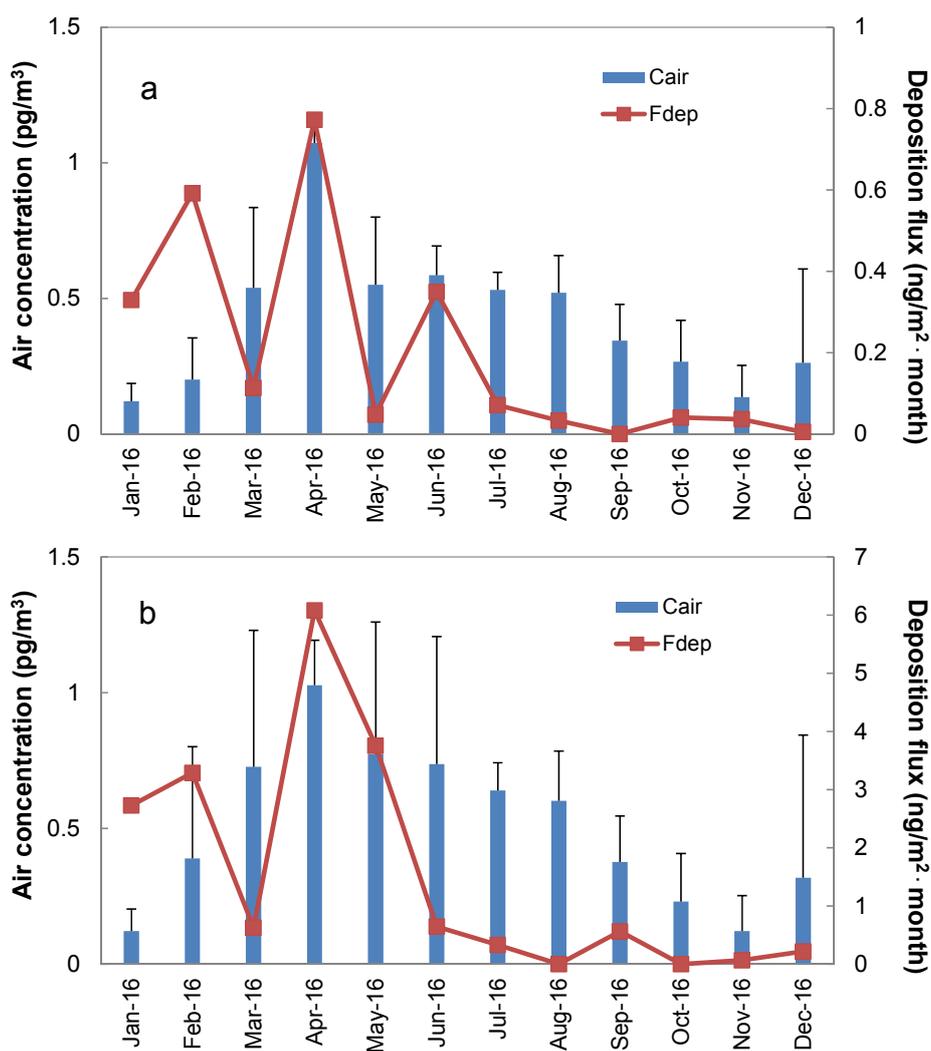
Seasonality was exhibited by *o,p'*-DDT and *p,p'*-DDT, with higher concentrations in spring and lower concentrations in winter (Fig. 3), which is quite different from the pattern observed for atmospheric DDTs at sites in the Tibetan Plateau and central China, which exhibited high levels in summer (Sheng *et al.*, 2013; Zhan *et al.*, 2017). The variation of *p,p'*-DDE at LNR was significantly correlated with temperature and therefore peaked in July (Fig. S10). By contrast, the highest mean concentrations of *o,p'*-DDT and *p,p'*-DDT were recorded in April. The potential source regions of *o,p'*-DDT are distributed in Southeast Asia, whereas those of *p,p'*-DDT include Southeast Asia and

eastern China (Fig. S11). The ratio of *o,p'*-DDT to *p,p'*-DDT, an indicator of DDT sources for technical DDT and dicofol, was  $0.98 \pm 0.58$  at LNR; this is consistent with the technical DDT use reported in Vietnam (Zhan *et al.*, 2017) and eastern China (Liu *et al.*, 2009).

Atmospheric fluxes of *o,p'*-DDT and *p,p'*-DDT peaked in April, accounting for 30% of the annual total fluxes. The deposition of DDTs with high  $K_{oa}$  is mainly controlled by atmospheric particles (Yue *et al.*, 2011). The observed deposition fluxes also follow the seasonality of particle-associated DDT concentrations (Fig. S12). In April, the air mass mainly originated from Southeast Asia, before precipitation centers had formed over the oceans (Fig. S3, April); nevertheless, rainfall at LNR started to increase (Fig. S2), which was favorable for atmospheric deposition. By contrast, the low DDT content in the particles and the precipitation amount led to relatively low depositions in cold seasons (Fig. S12); this is despite the air mass occasionally passing through potential source regions in eastern China in cold seasons, bringing about *p,p'*-DDT pollution.

#### PCBs

PCB congeners exhibited similar temporal trends, with high concentrations observed from April to August. The potential sources are presented in the PSCF maps in Fig. S13. The sources of tri-CBs are likely located in lower latitude areas, while those of tetra- and penta-CBs are distributed in central China as well. The map for hex-CBs exclusively displays a few clusters of high-probability cells over central China. Although relevant data on the source regions are limited, the air concentration levels of PCBs in Vietnam (Wang *et al.*, 2016) and India (Chakraborty *et al.*, 2013) have been reported to be higher than those in other Asian countries. The high atmospheric PCB concentrations over the South China Sea and the Bay of Bengal (Gioia *et al.*, 2012) could also contribute to PCB transport. PCB-28 was the only PCB congener detected in all deposition samples. The trends in monthly deposition fluxes were similar



**Fig. 3.** Seasonality of monthly mean air concentrations and deposition fluxes of (a) *o,p'*-DDT and (b) *p,p'*-DDT.

to those of air concentration (Fig. S14): The deposition flux was high in the rainy season, when air masses mainly arrived from the west.

#### *Comparison of Measured and Predicted Deposition Fluxes*

Fig. 4 compares the measured and predicted deposition fluxes at LNR. The similarity between the measured and predicted seasonal trends suggests a strong link between atmospheric input and deposition. The measured deposition fluxes were generally higher than the predicted equilibrium fluxes, except for compounds whose concentrations were close to the MDL, such as *o,p'*-DDT. Numerous studies have suggested that fog, clouds, and snow at high altitudes can scavenge organic pollutants from the atmosphere, often more efficiently than rain (Jakobi *et al.*, 2015). At LNR, our sampling site is a low-latitude site characterized by foggy weather. We suspect that the fog may induce higher deposition. In a previous numerical simulation, the  $\alpha$ -HCH sink in southwestern China was found to be related to atmospheric transport and strong deposition in the rainy season (Xu *et al.*, 2013). The measured deposition fluxes at LNR being higher than predicted indicates that deposition

input in the surrounding areas might be even higher than previously estimated.

#### CONCLUSIONS

The atmospheric transport and deposition of OCPs and PCBs at LNR, a nature reserve in southwestern China, were investigated. Governments in Asia have prohibited or restricted POPs, as stipulated in the Stockholm Convention; consequently, atmospheric concentrations of POPs, aside from HCB, have exhibited a declining trend. Nevertheless, temporal shifts in the wind field can cause pollutants to be transported to LNR from neighboring regions, such as mainland China and South or Southeast Asia. Wet deposition, including that in the dissolved and particulate phases, acts as an effective transfer mechanism. The atmospheric transport and deposition of compounds with relatively high water solubility, such as HCHs, in the rainy season, when air masses mainly originate in western source areas, contributed to a significant proportion of the air input, and the low atmospheric levels of pollution at LNR are likely achieved at the expense of high surface input along the

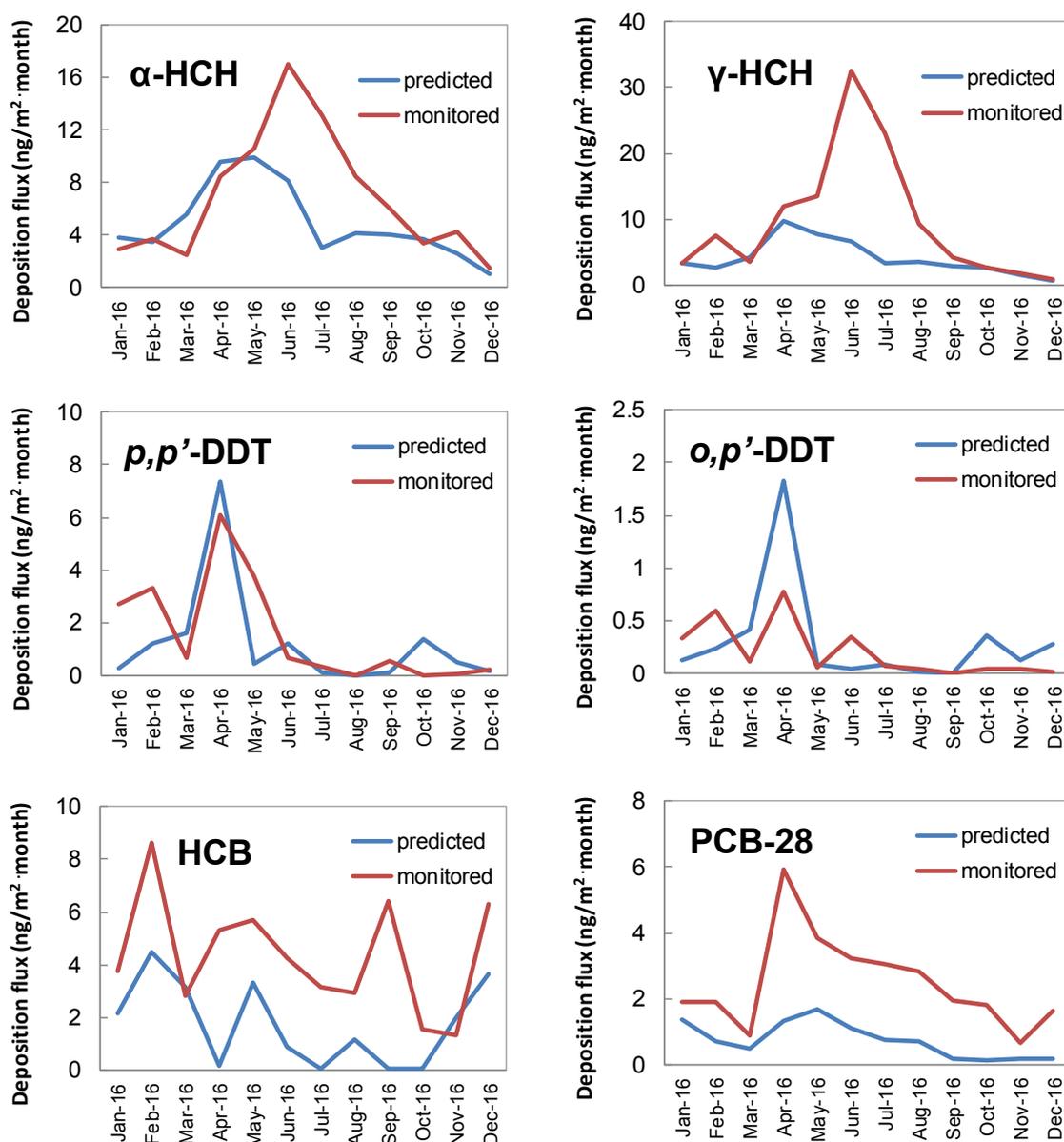


Fig. 4. Measured and predicted deposition fluxes at LNR.

transport routes. Washouts of particles via precipitation also influenced the total deposition of other compounds. The deposition trends of HCB and DDTs followed the temporal variations of their particle-associated content, with the highest deposition fluxes occurring in winter and April, respectively. Except for DDTs, the measured deposition fluxes were higher than the predicted equilibrium fluxes for all compounds, which may be related to the foggy weather at LNR.

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#### SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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