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The soil – air exchange of OCPs and PCBs in the Tibetan Plateau: Emphasis on episodic transport of unintentionally produced PCBs

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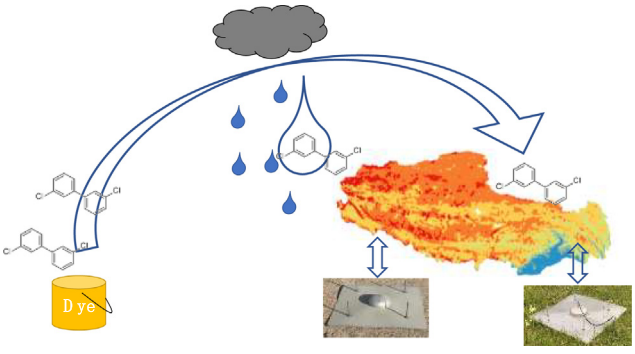
HIGHLIGHTS

- High air concentrations of PCB-11 were measured in the Tibetan Plateau.
- Episodic deposition/reemission events of PCB-11 were identified by fugacity method.
- cryoturbation and plowing are suspected to contribute to the reemission of PCB-11.
- The TP is acting as a secondary source of other OCPs and IP-PCBs.

GRAPHICAL ABSTRACT



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ABSTRACT

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in paired ambient and surface air fugacity samples were measured in the Tibetan Plateau (TP) from 2019 to 2022. The air concentrations of previously intentionally produced chemicals like dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) declined. Their soil – air exchange direction ranged from equilibrium to volatilization, suggesting that the TP is acting as a secondary source of most OCPs and PCBs with the pollution alleviation. However, considerably high atmospheric levels of PCB-11, an indicator of unintentionally produced PCBs (UP-PCBs), were recorded in the southern TP. Strong episodic long-range atmospheric transport (LRAT) and deposition of PCB-11 events took place mostly in summer. Those events associated with winds from potential sources and less rainfall interception along the air mass transport routes accounted for a significant fraction of overall atmospheric deposition in the TP. Meanwhile, cryoturbation and plowing are suspected to be important factors contributing to the reemission of PCB-11 from surface soil. The high abundance of PCB-11 and strong deposition/evaporation events highlights potential environmental and health risks of UP-POPs in the TP.

1. Introduction

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are typical persistent organic pollutants (POPs), which are persistent, bioaccumulative, and carcinogenic. Those chemicals will undergo long-range atmospheric transport (LRAT) and redistribute in the global environment, resulting in the occurrences in the cleanest region like the Arctic, the Antarctic, and the Tibetan Plateau (TP). To solve the global issue, countries agreed to eliminate or regulate the production, use, and release of POPs. To date, most OCPs and PCBs for agricultural or industrial usage have been ceased under the Stockholm Convention, except

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for the DDT (dichlorodiphenyltrichloroethane) exemption for vector-borne diseases control in developing countries. With the worldwide decline of those intentionally produced POPs (IP-POPs) like OCPs and commercial PCB products, relevant pollution was no longer prominent in the global environment. In contrast, there has been an increased awareness of unintentionally produced chemicals (UP-POPs). For example, HCB (Hexachlorobenzene) and PCBs were inadvertently released as byproducts of incomplete combustion processes and/or impurities in chemical processes using chlorine (Gong et al., 2017). Pigment production, combustion or wastewater treatment may also emit some PCB congeners (Hannah et al., 2022). PCB-11, a major constituent of UP-PCBs, has been detected in the air of the Arctic and Antarctic at significant concentrations, suggesting a ubiquitous presence of UP-POPs in the environment (Vorkamp, 2016). Since they were not routinely measured in field observations, the pollution status of those UP-POPs might be underestimated.

The TP is a pristine area known as "the third pole of the world". With a land area >2.56 million km^2, it has only an average of 7 people per square kilometer. Limited anthropogenic activities restricted local OCP and PCB emissions. However, the plateau is vulnerable to air pollution from adjacent areas such as China, India and other potential sources of regional significance. The northern TP can receive airborne POPs from central Asia via westerly wind (Zhang et al., 2018). With Indian summer monsoon onset, the southwest wind loaded with POPs emitted from the South Asia brought significant pollution to the southern TP (Gong et al., 2015). Sufficient investigation evidenced that the TP has already been contaminated by OCPs and PCBs through LRAT. Given the high altitude, low temperature and strong precipitation, the region was once regarded as a sink of POPs with considerable retention capacity. Wang et al. (2012) estimated that the Tibetan soils may be partial "secondary sources" of HCB, low molecular weight PCBs and hexachlorocyclohexane (HCHs), but will likely to be sinks for the less volatile DDE and DDT. High atmospheric concentrations in summer led to a clear seasonality on exchange with net deposition in summer but volatilization in winter in SOC-enriched soils, which is opposite to other regions in the world (Ren et al., 2019). Those observations suggest that the role of the TP might vary with time, location, and compounds.

The soil − air exchange is an essential process determines whether the TP acts as a sink or source of POPs. Clausius-Clapeyron equation of air concentrations which was widely applied to distinguish a region controlled by LRAT or local reemission might be invalid in the TP, because the temperature dependence of PCBs appears to be reduced or disappears at a low temperature environment (Carlson and Hites, 2005). Other laboratory experiments, traditional field measurements on the air and soil samples, and micrometeorological methods also have their limitations in estimating soil − air exchange (Degrendele et al., 2016). Recently developed fugacity samplers can take accurate soil surface fugacity samples (Cabrerizo et al., 2009) and thus were used in soil − air exchange assessment (Cabrerizo et al., 2011; Degrendele et al., 2016; Ren et al., 2019). In the present study, DDTs, HCHs, and indicator PCBs originated from intentionally produced commercial products (Gong et al., 2010; Gong et al., 2015; Sheng et al., 2013) were selected as representative IP-POPs in the TP. As a well-documented UP-PCB in air monitoring campaign, PCB-11 was considered as indicator of the pollution from overlooked IP-POPs in the TP. Paired 24 h ambient air and soil surface fugacity samples were collected from sites in the TP with four typical land cover types, namely, forest, farmland, pasture, and desert. First, the concentration levels and spatial patterns at the four sites of the TP were compared with previous dataset to outline the current status of IP- and UP-POPs in the air of the TP. Second, soil − air exchange direction and fluxes of those compounds were characterized to illustrate the role of the TP and to explore the mechanism that may cause atmospheric deposition/evaporation.

2. Materials and methods

2.1. Sampling

Sampling was conducted at four typical sites in the TP, including Lhasa (LS, farmland), Nam Co (NM, highland pasture), Lulang (LL, coniferous forest), and Nagri (NR, palaeochannel in a desert). LS site is about 30 km from the city center, and the other sites were far away from cities. NR site located in the west of the TP was cold and dry, whilst the other three sites in the southeast of the TP were characterized by relatively warm and wet summer (Fig. S1). Potential sources near the sampling sites were limited (Section 1 of Supporting Information (SI)). Surface soil properties varied with land cover changes. The average soil organic matter of surface soils (0–5 cm) at LS, NM, LL and NR were measured as 3.97 %, 3.93 %, 4.39 %, and 0.48 %, respectively (Zhang et al., 2022). Totally 35 paired ambient air and soil surface fugacity samples were collected from 2019 to 2022. Details on sampling site locations, periods, sample numbers and corresponding meteorological data are given in SI Table S1.

A soil fugacity sampler consists of low-volume air sampling system and a stainless-steel plate with a surface of 1 m^2, located 3 cm above the soil surface. The surface air equilibrated with soil was first pumped through a precleaned glass fiber filter (grade GF/A, 47 mm diam.) and then through a polyurethane foam (PUF, 2 cm diam. × 10 cm length) plug, by using an air pump at a flow rate of 8–10 L/min. Due to the low flow rates and the large surface contacting to soil, the soil fugacity sampler developed by Cabrerizo et al. (2009) ensured that the sampled air masses were in contact with surface soil for sufficient time to equilibrate. The device has been proved to be an effective device that can accurately determine soil fugacity in field studies (Degrendele et al., 2016), and avoid the overestimated soil − air partitioning of POPs in the TP (Ren et al., 2019). Successive 24-h ambient air samples were simultaneously collected by a high-volume active air sampler (AAS) operating at 300 L/min. Particulate and gaseous samples were retained by quartz microfiber filters (QFFs) (20.3 × 12.7 cm) and PUFs (6.5 cm diam. × 7.5 cm length) in the AAS, respectively. All the QFFs were baked at 450 °C for 8 h and the PUF plugs was precleaned by dichloromethane/acetone (DCM: ACE = 1:1 v/v). After sampling, all the sealed samples were delivered back to the lab and stored at −20 °C before analysis.

2.2. Sample pretreatment and analysis

Each sample was Soxhlet-extracted with DCM for 24 h. The extracts were concentrated, solvent-exchanged into hexane, and then purified by a multilayered chromatography column. After concentrated into a vial under a gentle stream of nitrogen, known quantities of ^{13}C-labeled PCB-141 were added as the internal standard. PCBs and OCPs were analyzed on Agilent Intuvo 9000/7000D GC–MS/MS with a DB-5MS Intuvo column (30 m × 0.25 mm × 0.25 μm, Agilent, Santa Clara, CA, U.S.A.) in a multiple reaction monitoring (MRM) mode. The detailed GC oven temperature program, injection mode, precursor and product ions of target compounds are presented in SI.

2.3. Quality assurance and quality control

Each atmospheric sample was spiked with 2,4,5,6-tetrachloro-m-xylene (tcmx), PCB-30, PCB-198, and PCB-209 as surrogates. The average recoveries were 71 ± 17 %, 86 ± 15 %, 88 ± 13 %, and 95 ± 15 % for tcmx, PCB-30, PCB-198, and PCB-209, respectively. Pre-cleaned PUFs and QFFs were shipped to sampling sites and exposed to local atmosphere for 5 min. Those field blanks were sealed, stored, and analyzed as other samples. Target OCPs and PCBs in the present study were listed in Table S2. Instrumental detection limits (IDLs) were the compound contents when a signal-to-noise ratio (S/N) was >3. For compounds above IDLs in the field blanks, their methods detection limits (MDLs) were calculated as the average plus 3 times of the standard deviation of field blank values. MDLs of other compounds were derived via dividing IDLs by sample volume. Measured values of ambient and surface air samples were corrected using the field blanks. The concentrations of OCPs and PCBs in the particulate phase were negligible as a result of low atmospheric particle content in the TP (Sheng et al., 2013), so the reported air concentrations refer to total concentration (gas plus particle phase). Totally 28 PCBs and 11 OCPs were tested in the present study (Table S2). Given that detection

rates of many compounds were <20 %, the following discussion focuses on the chemicals (α-HCH, γ-HCH, HCB, *o,p*-DDE, *p,p'*-DDE, *o,p*-DDT, *p,p'*-DDT, PCB-11, PCB-18, PCB-28, and PCB-52) with detection rate > 30 %.

2.4. Soil – air exchange flux calculation

Fugacity describes the potential of a compound to escape from one matrix to another. The ambient air (f_a, Pa) and surface soil (f_{sa}, Pa) fugacities were calculated as:

$$f_a = \frac{RT}{MW} \times C_a \times 10^{-12} \quad (1)$$

$$f_{sa} = \frac{RT}{MW} \times C_{sa} \times 10^{-12} \quad (2)$$

where R is the gas constant (8.314 Pa m^3 mol^{-1} K^{-1}), T is the air temperature (K), MW is the chemical molecular weight (g mol^{-1}), and C_a and C_{sa} (pg m^{-3}) are the measured ambient and soil surface air concentrations, respectively. The fugacity ratio of f_{sa}/f_a is an indicator of the soil – air exchange direction. A ratio > 1 indicates volatilization from the soil into air, whereas values <1 means net deposition. Given the uncertainties of concentration measurement, ln f_{sa}/f_a from −1.2 to +0.5 were considered as the soil – air equilibrium range (Cabrerizo et al., 2011).

In fugacity model, soil – air exchange flux (F, pg m^{-2} h^{-1}) can be estimated as:

$$F = D_{sa} \times (f_{sa} - f_a) \times MW \times 10^{12} \quad (3)$$

where D_{sa} is the overall soil – air transfer coefficient (mol Pa^{-1} h^{-1}). Details on D_{sa} calculation can be found in SI.

2.5. Back trajectory analysis

In order to explore the origin and atmospheric transport route, 5-day backward trajectories of each ambient air sample were calculated for different starting times corresponding to 0 to 24 h after sampling start time by the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model driven by the United States National Center for Environmental Prediction (NCEP) reanalysis dataset (Draxler and Hess, 1997; Draxler and Hess, 1998). The trajectories ended in 100 m above ground level at sampling site of each ambient air sample were clustered by HYSPLIT to identify where air masses are most frequently coming from. Other meteorological data of surrounding regions like temperature and precipitation were also obtained from the NCEP reanalysis dataset.

3. Results and discussion

3.1. OCPs and PCBs concentration levels in the ambient air

As a potential "sink" of POPs, atmospheric concentrations of OCPs and PCBs in the TP were well studies (Gong et al., 2015; Gong et al., 2010; Ren et al., 2019). The details on measured ambient air concentrations of each sample in the present study were presented in Table S4. The average concentration levels of IP-POPs here are compared with those reported values at each sampling site in Table S5 and Fig. S2. Generally, the concentrations of OCPs and IP-PCBs at all the sampling sites were lower than previous reported dataset in the TP. At Lhasa site, the concentration of γ-HCH declined an order of magnitude and DDTs decreased to half to one third of their concentration levels from 2006 to 2007 (Gong et al., 2010). Compounds at Lulang site also exhibited similar decline trend with the highest reduction of *o,p'*-DDT and *p,p'*-DDT, in comparison with the reported values between 2012 and 2015 (Ren et al., 2019). The air concentration of DDTs also declined at Nam Co, whilst the reduction rate of other OCPs is relatively slow. Atmospheric PCB-28 and -52 contents at that site were even higher than previous data (Table S5). It should be noted that those air samples were collected in summer when air concentrations of POPs were more than twice of those in winter (Gong et al., 2010; Ren et al., 2019; Sheng et al., 2013; Zhang et al., 2018). Considering the seasonality of atmospheric concentrations, OCPs and PCBs may also decline at Nam Co. The pollution alleviation was more notable at Ngari site, where the air concentrations were about an order of magnitude lower than the levels observed in 2010 (Gong et al., 2015) and 2014 (Ren et al., 2019). Tremendous efforts were devoted to regulate the pollution of POPs in the past decades, especially recent reduction of outdoor spray of DDTs in India (van den Berg et al., 2017). The decline of DDT-related compounds was prominent at the four sites, other OCPs were also decreased. The overall reduction trend of IP-POPs in the air of the TP confirms that international regulation effectively reduced the LART from Asian countries to the background atmosphere, consisting with conclusions based on other measurements on IP-POPs in the TP (Pan et al., 2013; Wang et al., 2016).

If considering PCB-11, PCBs were the dominant compounds in the air, followed by HCB, DDTs and HCHs. Average concentration of PCB-11 was 74.5 ± 92.0 pg m^{-3} (2.93–440 pg m^{-3}) in the TP, which is several times to tens of times of IP-PCBs in the present study. Field studies reported that the average concentrations of PCB-11 were 9 pg m^{-3} in the Arctic (Choi et al., 2008) and 15 pg m^{-3} in the Antarctica (Li et al., 2012), respectively. Relatively high levels ranging from 0.78 to 134 pg m^{-3} has been reported in the Antarctica (Baek et al., 2011). Compared with those reported levels, PCB-11 concentrations in the TP were within the high range of remote regions in the world (Table S6). National survey observed an average concentration of 35 pg m^{-3} in China (Zhao et al., 2020). Given the remoteness of the TP, the unusual enhancement of PCB-11 indicates the significance of unidentified sources. The highest concentration of 440 pg m^{-3} was recorded at Nam Co (NM-0624), exceeding the highest reported atmospheric level (248 pg m^{-3}) in urban areas of China (Zhao et al., 2020). It is also higher than the concentration of 307 pg m^{-3} in Cleveland, USA (Basu et al., 2009), which is the highest reported value according to the review of Mastin et al. (2022). Other OCPs and PCBs were also elevated in NM-0624. As a matter of fact, target chemicals in the air were significantly correlated with each other except for HCB (Table S7). The coefficient of determination (R^2) between PCB-11 and PCB-52 were 0.91 despite the differences on their physic-chemical properties and therefore LRAT and other environmental behaviors. A possible explanation of the strong correlation is that the two chemicals may come from similar source. PCB-11 and PCB-52 are the major PCB congeners in the azo-type pigment (Anezaki and Nakano, 2014). Although local pigment production was limited, the TP was surrounded by China and India, which hold major shares of the global azo pigments market (TMR (Transparency market research), 2020). The application of pigment may lead to PCB pollutions in the TP. It is expected that the consumer base of the two countries will increase in the coming years (EMR, 2022). By-products in pigments and paints, like PCB-11 and PCB-52, will be inevitably introduced into the TP. The relevance of those UP-PCBs in the TP may grow over time.

The Clausius–Clapeyron equation is widely used to preliminary distinguish LRAT from local reemission in the TP (Gong et al., 2015; Ren et al., 2019; Sheng et al., 2013). Low temperature dependence indicates LRAT, whilst strong temperature dependence denotes local reemissions. Gong et al. (2015) reported that the logarithm of partial pressure of HCHs, DDTs, endosulfans and 1/T were insignificantly correlated at Ngari in 2010. The correlation between OCPs and PCBs and temperature were also weak at Lulang in an air monitoring campaign conducted from 2008 to 2011 (Sheng et al., 2013). Later, a recent study at Lulang, Nam Co and Ngari from 2012 to 2015 found that HCHs and DDTs showed significant correlation (R^2: 0.23– 0.57) with temperature, but PCBs and HCB still showed low temperature dependence (Ren et al., 2019). Similarly, temperature-dependency (R^2: 0.32– 0.52, $p < 0.01$ and relatively steep slopes) was also found for HCHs and DDTs, but R^2 of 0.23 for PCB-28, PCB-52 or insignificant ($p > 0.05$) correlations for HCB suggest relatively weak temperature-dependency of those compounds in the present study (Fig. S3). PCB-11 showed a significant temperature dependence (R^2 = 0.43, $p < 0.01$). The re-evaporation trend means that historical input and accumulation of PCB-11 occurred in the TP. The correlations between air

concentrations of PCB-11 and other meteorological parameters like air humidity, soil temperature and humidity, boundary layer height and rainfall were also low. Given the high abundance of PCB-11 in the air, the atmospheric transport, deposition, and reemission of that compound should be further investigated by fugacity method.

3.2. Soil – air exchange direction and fluxes

The direction of soil – air exchange can be estimated by the fugacity ratio of f_{sa}/f_a (Cabrerizo et al., 2011; Degrendele et al., 2016; Ren et al., 2019). The natural logarithm transformed f_{sa}/f_a ratios are plotted in Fig. 1. Most OCPs and PCBs distributed in the range from equilibrium to net volatilization, except for PCB-11. Previous soil – air exchange study found that most OCPs and PCBs, even PCB-138 and -153 with lower volatility, were subject to volatilization in the TP (Ren et al., 2019). Although higher chlorinated PCBs were generally below detection limits in the present study, other low volatility compounds like *p, p'*-DDT and *p, p'*-DDE still exhibited f_{sa}/f_a ratios higher than 0.53. DDT-class chemicals in the southern TP were delivered from India by South Asian monsoon (Sheng et al., 2013). Due to a large amount of DDTs applied in India, the TP was considered as a sink of DDTs (Ren et al., 2019; Wang et al., 2012). SOC-enriched soils like Lulang were identified as net DDT deposition region in summer (Ren et al., 2019). Recently, the production of DDTs in India has been restricted and the use has shifted from large scale application to indoor residual spraying (van den Berg et al., 2017). With the regulation of DDTs in India, atmospheric content of those compounds has depleted in the air of the four sites (Table S5). Samples collected in summer at those sites were now characterized as f_{sa}/f_a ratios ranging from equilibrium to net volatilization. Ren et al. (2019) estimate that surface soil in the TP has changed from "sink" to "secondary source in cold season", and now the soil seems to be a "secondary source in the whole year" of those substances.

The calculated soil – air exchange fluxes for target chemicals based on Eq. (3) were presented in Table S8 in SI. The average fluxes of HCHs were within the equilibrium ($< \pm 1$ pg m^{-2} h^{-1}) range. The fluxes of PCB-28, −52, *o,p*-DDE, *p,p'*-DDE, *o,p*-DDE, *p,p'*-DDT and HCB show net evaporation in the majority of TP samples, with an average of 1.41, 1.25, 3.41, 3.92, 0.05 and 2.91 pg m^{-2} h^{-1}, respectively. The levels of PCB-52, *p,p'*-DDE, *p,p'*-DDT were similar to another air – soil exchange study in the TP conducted from 2012 to 2015, whilst fluxes of HCHs, PCB-28 and HCB are about an order of magnitude lower than their reported values (Ren et al., 2019). Although the TP has become a secondary source of IP-POPs, but the strength of reemission is declining.

In contrast, equilibrium, volatilization, or deposition of PCB-11 can be observed during the sampling campaign. The estimated fluxes ranged

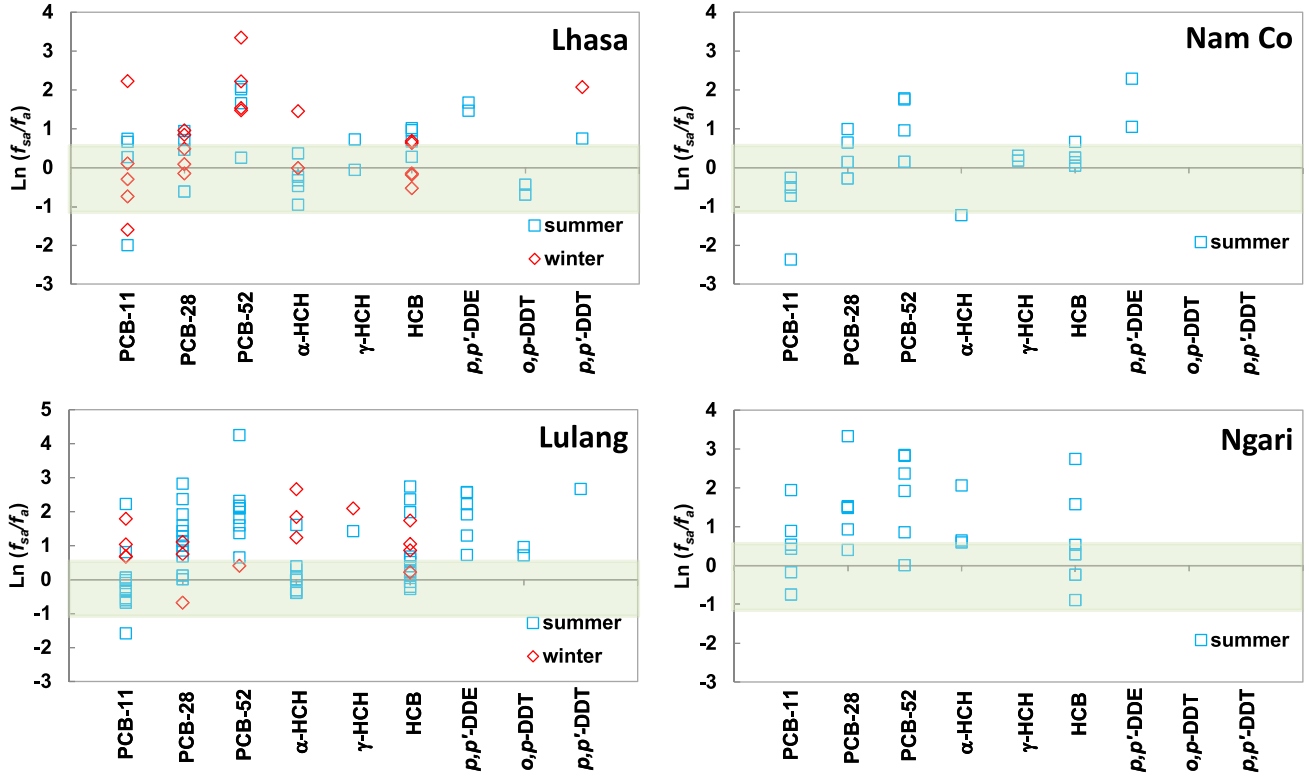

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Fig. 1. Surface-to-air fugacity ratios (f_{sa}/f_a) at four sampling sites. Shadowed areas indicate the equilibrium interval (−1.2 to 0.53).

from −211 to 165 pg m^{-2} h^{-1}, with an average of −8.65 pg m^{-2} h^{-1}. An overall deposition trend indicates that receptor sites were acting as a sink of PCB-11. Atmospheric concentrations at Ngari site were lower than other sites. As a desert site with low soil organic matter, Ngari has a low retention capacity for POPs and thus exhibited an overall reemission or equilibrium trend (Fig. 1). Except for that site, deposition tendency of PCB-11 ($f_{sa}/f_a < -1.2$) was measured at Lhasa, Nam Co and Lulang. Unlike relatively constant volatilization fluxes of PCB-28 and -52, the fluxes of PCB-11 were characterized by several deposition or volatilization events. Those events accounted for a significant proportion of the overall input/output fluxes to the TP (Fig. S4), suggesting that the emission-transport-deposition or reemission processes could be episodic in the TP.

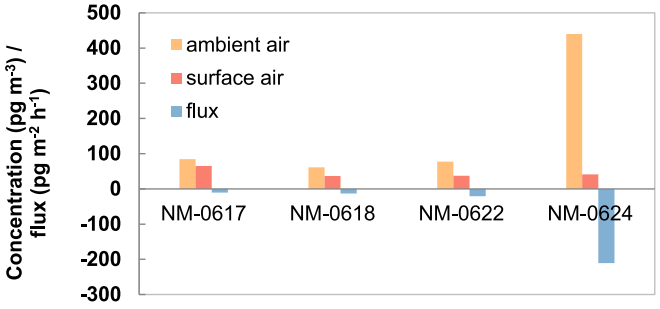

Fig. 3. ambient and surface air concentrations, and soil − air exchange fluxes of summer samples collected at Nam Co.

3.3. Deposition and evaporation events

Based on the calculated fluxes, deposition (NM-0624, LS-0802, LL-0728) and evaporation (LL-0802, LS-1130) events are identified. To explore the circumstances in which high deposition/evaporation events might occur, the synoptic atmospheric transport trajectories and weather conditions of those events were analyzed.

Fig. 2 presents the 5-day backward trajectories at Nam Co. Air masses back trajectories of NM-0617 and NM-0618 mainly came from relatively clean oceans. Later, the origin of air shifted to the northern India (NM-0622 and NM-0624), a potential source region of OCPs and PCBs (Zhang et al., 2008). PCB-11 is a chemical with considerable water solubility of 0.35 mg/L (Mackay et al., 2006). There is a rainfall center covering Nepal from June 18th to 20th, which might reduce airborne pollutants of NM-0622 when they traveled across there (Fig. 2, NM-0622). Since June 21st, daily precipitation along the air mass movement trajectories were generally <1 mm, both atmospheric concentrations and deposition of NM-0624 increased accordingly. The highest ambient air concentrations of PCBs (PCB-11, −18, −28, and − 52) in the present study was measured in NM-0624, whilst the surface air concentrations were comparable with other samples collected at Nam Co (Fig. 3). It further confirms that pollutants laden air of NM-0624 was likely delivered by a southwesterly air mass flow, rather than soil reemission.

Similarly, the 5-day backward trajectories of LS-0802 also passed over northern India (Fig. S5). Relatively high PCB-11 concentration (296 pg m^{-3}) and high deposition fluxes were observed at Lhasa. After August 3rd, the origin of trajectories gradually moved to eastern India and the South China Sea. Atmospheric concentrations and therefore deposition declined (Fig. S6). The westerly winds passed northern India were prominent in winter (Fig. S7). However, average air temperature of winter samples was about 10 °C lower than those collected in summer a (Fig. S8). As a chemical with a higher tendency toward volatilization, the emission of PCB-11 in source region is sensitive to temperature. Therefore, atmospheric concentrations at Lhasa were relatively low in winter. Indian monsoon activities lead to higher atmospheric concentrations in summer and lower values in winter over the TP (Sheng et al., 2013). A unique seasonality of "net deposition in summer but volatilization in winter" in the TP was ascribed to the low air concentrations of POPs in winter (Ren et al., 2019). Winter samples with relatively low PCB-11 concentrations like LS-1127 and LS-1130 characterized by weak deposition or evaporation (Fig. 4), but those with relatively high atmospheric PCB-11 concentrations like LS-1201 and LS-1204 exhibited deposition trend, confirming the effect of air concentration variations on soil − air exchange in the TP. It is interesting to note a net evaporation event (LS-1130). Ambient air concentrations of PCB-11 were similar for LS-1127 and LS-1130. The enhanced surface concentrations of PCBs for LS-1130 (Fig. 4) indicate that other factors may further lead to soil reemission, such as sorbed phase transport. McLachlan et al. (2002) considered that bioturbation, cryoturbation, and

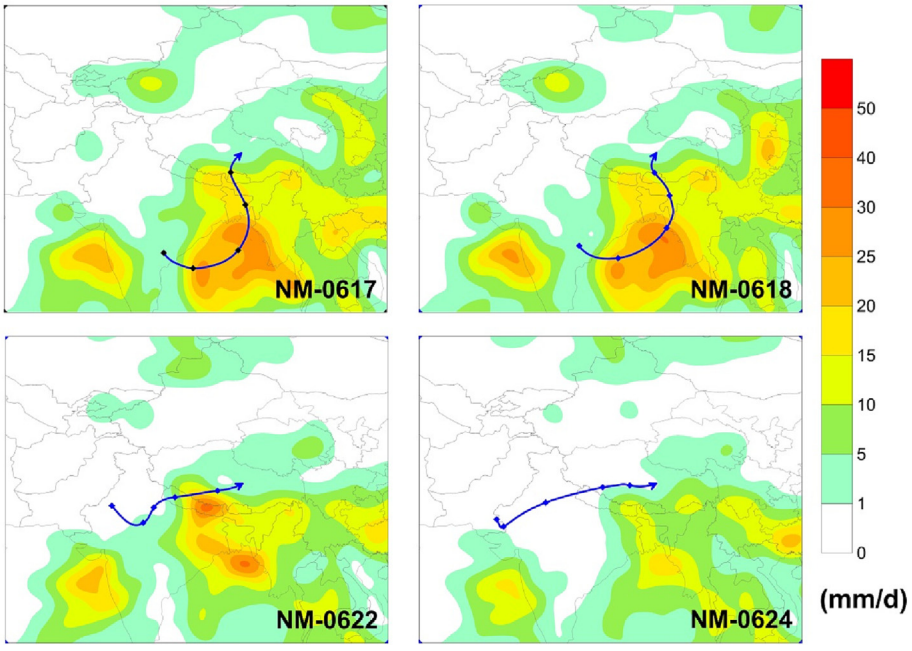

Fig. 2. five-day air mass back trajectories of samples collected at Nam Co. Air masses trajectories in the previous day of sampling often within the TP where significant sources were absent, so contour maps present the average precipitation from 5 to 2 days before sampling time to illustrate the meteorological data of potential source regions.

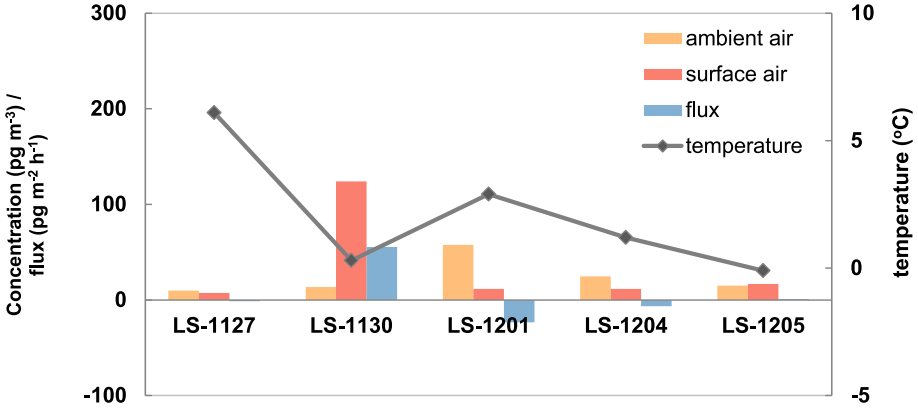

Fig. 4. ambient and surface air concentrations, soil − air exchange fluxes and average temperature of winter samples collected at Lhasa.

erosion into cracks formed by soil drying could play an important role of vertical transport of organic chemicals in soil. Average air temperature was around 0 °C and soil temperature ranged from −1.3 °C to 6.0 °C (Table S1) when the samples of LS-1130 was collected, which possibly means the occurrence of cryoturbation. PCB-11 of other samples taken at low air temperature (LS-1205 at −0.1 °C, LL-0222 at −1.5 °C, and LL-0223 at 0.1 °C) also exhibited a reemission trend (Table S8), implying the contribution of cryoturbation to the soil reemission in the TP. Besides low air concentrations, we suspect it may further facilitate the reemission of POPs in the wintertime.

Air masses of Lulang samples were mainly passed through central India, Bangladesh and Myanmar (Fig. S9), except for LL-0728. The air masses of the sample were originated from Xinjiang Autonomous Region. Xingjian has been previously identified as a potential source region of OCPs in the TP (Gong et al., 2015; Zhang et al., 2018). From July 29th to August 4th, the rainfall center distributed from the Bay of Bengal and Myanmar (Fig. S9). Heavy rain partly prevented the LRAT of OCPs and PCBs from the south to the TP, so LRAT declined in that period (Fig. S10). A significant evaporation event was observed at Lulang (LL-0801 and LL-0802). After a moderate rain from 30th to 31st July at Lulang (Table S1), air concentrations of PCB-11 remained a stable level (Table S4) whilst surface concentrations rapidly increased from 51.2 to 342 pg m^{-3} (Table S9). It indicates that the evaporation event could be induced by surface soil perturbation such as temperature increase or soil layer disturbance. Air and soil temperature change little from 31st July to 2nd August (Table S1). Bioturbation, like worms and plowing, is a major mechanism which vertically transports PCBs in soils (McLachlan et al., 2002). We suspect that earthworms and recorded picking-up mushrooms activities in 1st to 2nd August after rainfall may contribute to the evaporation event. Given the considerable accumulation of OCPs and PCBs in SOC-enriched forest soil at Lulang (Ren et al., 2019), bioturbation can be another emission factor in the TP that should not be neglected.

4. Conclusion

The pollution of IP-POPs in the TP has been alleviated, but high atmospheric concentrations of PCB-11 were recorded in the air. Elevated concentrations were associated with air mass originated from northern India and Northwest China, where pigments application and production could emit considerable PCB-11. The TP is acting as a secondary source of OCPs and IP-PCBs. In contrast, PCB-11 can be either deposited in the TP the ground surface or re-evaporated into the air, with an overall deposition trend. The contributions to overall deposition across the TP seem to be dominated by episodic LRAT in summer. High deposition events were characterized by meteorological conditions like strong emission in sources regions, favorable air mass transport route and less precipitation along the transport pathway. Given its large abundance and tendency toward deposit on surface soil in high deposition events, accumulation of PCB-11 in the TP may lead to considerable environmental and health risks. Regulation of those UP-PCBs in surrounding areas should be considered. In addition, cryoturbation and bioturbation are suspected to enhance the reemission of PCB-11 from ground surface back to the atmosphere. However, the present study is insufficient to accurate identify sources of PCB-11 in the TP. Due to limited dataset on UP-PCBs in potential source regions, it is still difficult to establish the essential link between sources and receptors. The contamination levels obtained by short-term active sampling in the present study focused on episodic transport/deposition/emission events. Relatively small date size may also ignore other important aspects like seasonal variations, mountain cold-trapping, and atmospheric transport over canyon. Those data gap should be addressed in the further study.

CRediT authorship contribution statement

Yue Xu: Conceptualization, data validation, Writing - original draft, Formal analysis.

Yang Wang: Conceptualization, Methodology, Writing - original draft, Writing - review & editing.

Chenmeng Yang: Sampling, data curation and validation, Writing - review & editing.

Shizhen Zhao: Methodology, software, Writing - review & editing.

Haiyan Zhang: Visualization, data curation, Writing - review & editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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