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Passive Air Sampling of Organochlorine Pesticides, Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers Across the Tibetan Plateau

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So far there are limited data on persistent organic pollutants (POPs) in the atmosphere of the Tibetan Plateau. XAD 2-resin based passive air samplers were therefore deployed for 1 year (between July 2007–June 2008) at 16 locations across the Tibetan Plateau. Based on previously reported sampling rates (R) derived in the north and south America, and their correlations with atmospheric temperature and pressure, R values in the present study were in the range of 2.2–3.3 m³ d^{−1} (average = 2.7 ± 0.3). Derived air concentrations (pg/m³) ranged as follows: DDTs, 5–75; HCHs, 0.1–36; α -endosulfan, 0.1–10; HCB, 2.8–80; sum of 15 PCBs, 1.8–8.2; and sum of 9 PBDEs, 0.1–8.3. The highest DDTs occurred at Qamdo, where the sampling site is near to farm land, indicating the spatial distribution of DDTs across the plateau may be influenced by scattered local usage of DDT. Higher levels of HCHs were observed at sites with high elevation (>4000 m) and close to the China-India border, indicating possible long-range atmospheric transport. The highest levels of HCB, PCBs, and PBDEs were found at a site impacted by forest fire during the sampling campaign.

Introduction

Persistent organic pollutants (POPs) are known to undergo long-range atmospheric transport (LRAT), reaching remote regions where they have never been produced or used. In order to better understand the key processes that control POPs distribution, environmental data are needed from all regions of the globe. The United Nations Environmental Program (UNEP) recommended several target media - air, bivalves, biota, and human milk - as suitable for regional or global scale monitoring studies (1). The atmosphere is particularly important, because it reflects ongoing emissions, responds rapidly to efforts at source reduction, and is key to the global dispersal of POPs. Air data are required to improve the understanding of atmospheric transport and the air-

surface exchange of POPs and to validate atmospheric POPs transport models (2).

Atmospheric monitoring of POPs traditionally relies on high volume air samplers. However, active air sampling requires trained operators and electricity supply which is rarely found at truly remote sites. In recent years, various types of passive air samplers (PAS) have been developed and used for POPs monitoring (3). PAS can be simple and cheap to use and therefore suitable for mapping the spatial distribution of POPs. The Global Atmospheric Passive Sampling (GAPS) project was initiated in December 2004 and has been monitoring POPs at 40 background sites on 7 continents using polyurethane foam disk samplers, deployed for 3 monthly exposure periods (2). Similarly, regional-scale efforts have been initiated in North America (4), South America (5), Europe (6), and Asia (7–9). PAS networks have been used to aid better understanding of region-specific sources, transport, and fate of POPs. Deploying samplers in monitoring networks over several seasons and years will yield data on temporal trends, to check on the effectiveness of bans and restrictions on use (10, 11).

Asia is a key area for study, because it is a major source/use region for many POPs, with scope for LRAT to the Arctic, the Pacific, and the Tibetan Plateau. However, so far, efforts have focused more on the source component (e.g., urban areas) than the dispersal to remote locations. PAS sampling campaigns have included China, Japan, Korea, Singapore, and India (e.g. refs 7–9). However, very little data have so far been produced in the hinterlands abutted by Central/East/South Asia - the Tibetan Plateau.

The Tibetan Plateau, with an area of over 2.5 × 10⁶ km² and an average elevation of >4000 m, is known as “the third pole of the world” and is the highest and most extensive plateau on Earth. The atmosphere over the Tibetan Plateau remains relatively pristine due to sparse human population and minimal industrial activities. Air masses over the Tibetan Plateau are mainly dominated by continental air from central Asia and maritime air from the Indian Ocean. Based on air mass trajectory analysis and ice core records of sulfate and black carbon, good correlations have been found between levels of pollutants in ice strata and trajectories originating from South Asia (12). Model predictions clearly show that the Tibetan anticyclone could ‘trap’ anthropogenic emissions lifted from South Asia (13). The Indian subcontinent has experienced heavy use of organochlorine pesticides (OCPs), such as HCHs and DDTs, while India continues the use of DDT to combat vector borne diseases which are prevalent in the monsoon season (8). Li et al. (14) reported very high levels of HCH in India in 1990, while recently attention has also been drawn to the processing of electronic (e-) waste (15). Monitoring data on POPs in soil, grass, and ice samples from the Tibetan Plateau (16–18) have suggested that it may be impacted by air masses derived from the Indian subcontinent as well as more local sources. This study was therefore conducted using PAS deployed at 16 sites across the Tibetan Plateau, to investigate the distribution of a range of POPs.

Materials and Methods

Sampling and Site Characterization. Details of the sites and their locations are given in Supporting Information (SI) Table SI-1. The samplers have been described elsewhere (19). XAD resin PAS are designed for mainly collecting POPs that normally dominate in the atmospheric gas phase and can be used for long-term air monitoring because they have a high capacity for POP and continue accumulating over year-round

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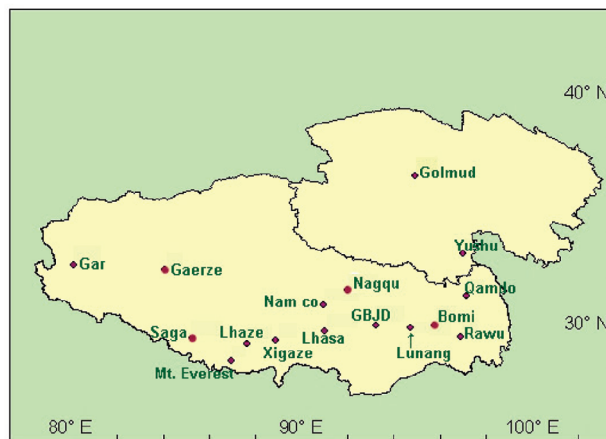
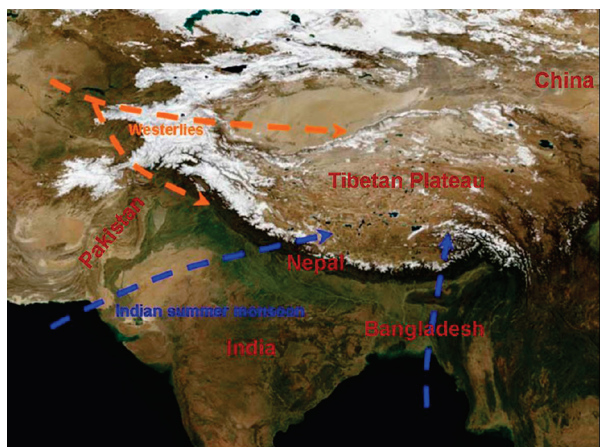


FIGURE 1. General pattern of atmospheric circulation systems over the Tibetan Plateau and map showing sampling sites. Site description: GBJD = Gongbog' Yamda.

monitoring (4, 19, 20). In this study, XAD-filled mesh cylinders were sealed in airtight containers with Teflon lids to avoid contamination during transit to the sites. Samples were taken at 16 sites across the Tibetan Plateau (Figure 1). The SI gives details of the sampling program (Text SI1) and annual average temperature conditions (Table SI1). Harvested XAD cylinders were stored in sealed, solvent rinsed, glass jars and sent by courier to Lancaster University. Upon receipt, the samplers were stored at -20°C until extraction.

Sample Preparation, Extraction, and Analysis. Prior to deployment, XAD resin was Soxhlet extracted using in turn methanol, acetonitrile, and dichloromethane (DCM). The XAD resin (60 mL of wet XAD in methanol) was transferred to a precleaned stainless steel mesh cylinder and dried in a clean desiccator. Dry cylinders were sealed in an airtight stainless steel tube with Teflon lids. Samples were extracted in a dedicated clean laboratory, which has filtered, charcoal-stripped air and positive pressure conditions. Each sample was transferred into the glass Soxhlet thimble and spiked with recovery standards of ^{13}C -labeled PCB congeners (^{13}C PCB-28, 52, 101, 138, 153, 180) and PBDE congeners (PBDE-51, 128, 190). Samples were Soxhlet extracted using DCM for 24 h. The extracts were first solvent-exchanged by hexane and loaded on the top of a fractionation column (2 g of 3% deactivated alumina/3 g of 6% deactivated silica). The first fraction was eluted by hexane and contained HCB, PCB, and DDEs. All HCHs, DDTs, endosulfans, and PBDEs were eluted by DCM and composed the second fraction. Both fractions were further cleaned on activated alumina/silica columns and gel permeation chromatography (GPC, containing 6 g of Biobeads SX 3). Before GPC cleanup, the first fraction was treated with concentrated sulfuric acid to remove possible interferences. Samples were finally solvent exchanged to 25 μL of dodecane containing PCB-30, $^{13}\text{C}_{12}$ PCB-141, and PBDE-69, 181 as internal standards. The samples were analyzed on a Finnigan-TRACE GC-MS system with a CP-Sil 8 CB capillary column (50 m, 0.25 mm, 0.25 μm), operating under single-ion monitoring (SIM) mode. Helium was used as the carrier gas at 1.0 mL min^{-1} under constant-flow mode. The oven temperature began at 100°C for 2 min and increased to 140°C at a rate of $20^{\circ}\text{C min}^{-1}$, to 200°C (10 min hold time) at a rate of $4^{\circ}\text{C min}^{-1}$, $4^{\circ}\text{C min}^{-1}$ to 300°C , and held for 17 min. The following compounds were monitored in the XAD samples: tri-PCBs 18, 22, 28, and 31; tetra-PCBs 44, 49, 53, 70, and 74; penta-PCBs 87, 90/101, 95, 99, 105, 110, 118, and 123; hexa-PCBs 138, 141, 149, 151, 153/132, and 158; hepta-PCBs 170, 174, 180, 183, and 187; octa-PCBs 194, 199, and 203; HCB; *o,p'*-DDT, *o,p'*-DDE, *p,p'*-DDT, and *p,p'*-DDE; and PBDEs 28, 47, 49, 99, 100, 153, 154, and 183. Quantification of α,γ -HCH, and α -endosulfan was performed on the same

instrument operated in negative chemical ionization mode with ammonia as the reagent gas.

Quality Control/Quality Assurance (QA/QC). All analytical procedures were monitored using strict quality assurance and control measures. Laboratory blanks (pre-extracted XAD resin filled cellulose thimbles) and field blanks were extracted and analyzed in the same way as the samples. Method detection limits (MDLs) were derived as 3 times the standard deviation of the mean field blank concentrations. However, most of the PCB and PBDE congeners and OCPs were not detected in the laboratory and field blanks, indicating contamination was negligible during transport, storage, and analysis. In this case the concentration of the lowest calibration standard was taken as the detection limit (0.03 ng/sample). MDLs ranged between 0.03 and 0.18 ng/sample for PCBs and PBDEs and between 0.03 and 1.3 ng/sample for OCPs. All reported values are field blank corrected but not corrected for the recovery rates. Analyte concentrations that were below the method detection limit (MDL) are reported as below detection limit (BDL) in the results. Recoveries were between 72% and 140% for $^{13}\text{C}_{12}$ PCBs and 56–158% for PBDEs. Lower variations between duplicate PAS were observed (Table SI 2).

Back-Trajectories/Wind Direction. The wind direction during the sampling period was determined by analyzing meteorological data from the National Center for Environmental Prediction (NCEP). Figure SI1 shows the wind direction and speed in the Indian monsoon season and nonmonsoon season. Five-day back trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model for 16 stations across the Tibetan Plateau at 1000 m above ground level at 6 h intervals for the whole year deployment (Figure SI2, 3). Clusters of trajectories were integrated based on the percent change in total space variance.

Results and Discussion

Introductory Remarks. A wind tunnel study has shown that the sampling rate (R) of the XAD resin PAS design is not strongly influenced by wind speed (19). The mass transfer of POPs to the XAD sampling resin is influenced by temperature, pressure, and compound molecular size (5, 19). A challenge for this study is that atmospheric pressure values on the Tibetan Plateau can be different from those in previous field campaigns. In field trials, uptake rates have varied between $\sim 0.5\text{--}2.1\text{ m}^3\text{ d}^{-1}\text{ PAS}^{-1}$. R is proportional to the molecular diffusivity (D_{air}) of substances, and D_{air} is proportional to $T^{1.75}$ and $1/P$ (5, 19). Therefore $R = K(T^{1.75}/P)$, where K is a constant. Reported R values from field studies are as follows: 0.5, 1, 2, and $2.1\text{ m}^3\cdot\text{d}^{-1}$ for Alert (256 K, 1010

TABLE 1. Estimated Volumetric Air Concentrations (pg m⁻³) from the Tibetan Plateau Sites^a

	Σ15PCBs	HCB	α-HCH	γ-HCH	α/γ-HCH	α-ENDO	<i>o,p'</i> -DDE	<i>p,p'</i> -DDE	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	<i>o,p'</i> -DDT/ <i>p,p'</i> -DDT	<i>p,p'</i> -DDT/ <i>p,p'</i> -DDE	Σ9PBDEs
Monsoon Region													
Bomi	8.2	80.0	8.6	4.7	1.8	3.2	2.6	5.5	15.2	4.0	3.8	0.7	8.3
Rawu	6.0	11.9	16.6	18.9	0.9	10.4	1.1	4.1	39.4	7.3	5.4	1.8	0.1
Lulang	5.5	19.5	1.8	0.6	3.2	0.9	3.3	4.5	32.9	7.5	4.4	1.7	0.6
Naqu	3.0	32.0	8.5	2.2	3.8	1.9	2.0	0.9	17.9	4.8	3.7	5.1	0.9
Namco	1.8	2.8	0.1			0.7	2.6		3.2	0.6	5.8		0.5
GBJD	4.9	26.2	7.8	2.4	3.3	2.4	3.9	7.7	31.9	7.4	4.3	1.0	2.2
Lhasa	4.4	66.2	4.6	1.6	2.9	0.8	2.5	6.4	24.9	6.9	3.6	1.1	0.9
Lhaze	3.0	22.5	1.6	0.8	2.0	1.0	1.0	1.0	9.6	2.6	3.8	2.5	0.6
Xikaze	7.1	29.2	3.7	1.4	2.6	1.8	3.7	5.8	30.7	12.7	2.4	2.2	1.3
Everest	4.2	28.3	5.8	7.0	0.8	1.4	0.1	0.4	4.0	0.6	6.2	1.7	0.5
Saga	3.2	19.9	4.8	1.6	3.1	1.3	3.2	5.6	28.1	8.9	3.2	1.6	1.4
Qamdo	7.3	19.6	1.5	1.3	1.1	1.1	8.2	13.4	41.9	11.4	3.7	0.9	0.8
Yushu	5.0	34.2	1.7	3.0	0.6	0.1	1.6	7.4	2.1	5.1	0.4	0.7	0.4
average	4.4 ± 1.4	28 ± 18	4.0 ± 2.3	2.4 ± 3	2.2	1.2 ± 1.3	2.9 ± 2	5.4 ± 3.7	19 ± 13	6.1 ± 3.8	3.7	1.8	1.1 ± 0.6
Westerly Region													
Golmud	4.2	60.4	4.0	1.4	2.9	0.7	2.1	1.6	1.9	0.7	2.8	0.4	1.1
Gaerze	3.9	5.2	3.1	3.1	1.0	4.5	0.1	0.8	5.1	2.2	2.3	2.8	0.1
Gar	5.0	7.9	3.5	12.3	0.3	4.3	0.9	1.8	8.8	2.0	4.4	1.1	0.2
average	4.4 ± 0.6	25 ± 31	3.5 ± 0.4	5.6 ± 5.9	1.4	3.1 ± 2.1	1.0 ± 1	1.3 ± 0.5	5.3 ± 3.4	1.6 ± 0.8	3.2	1.4	0.4 ± 0.6

^a BDL means below the detectable level; H/L ratio refers to the ratio between the highest and lowest value of the compound.

hpa), Burnt Island (280.3 K, 890 hpa), Point Petre (281.7 K, 850 hpa), and Costa Rica (296 K, 1003 hpa), respectively. Taking these values together (Figure SI-4) gives *R* positively correlated with $T^{1.75}/P$, with the following equation: $R = 0.16T^{1.75}/P - 2.14$ ($r^2 = 0.92$). Annual average temperatures and pressures of individual sampling sites in this study are listed in Table SI-3. Based on these values, sampling rates ranged from 2.2 to 3.3 m³ d⁻¹ giving an average of 2.7 ± 0.3 m³ d⁻¹ (Table SI-3). Results are presented here primarily as amounts of POPs sequestered over the sampling period (ng/sampler per year) and compared with data from other studies employing the same sampler and undergoing a year-round deployment (Table SI-4, 5). However, in order to make some general comparisons with other air measurements reported in the literature (Table 1, SI-6, 7), sequestered concentrations were derived using sampling rate at individual sites to yield volumetric air concentrations (pg/m³).

General Comments on Ambient Concentrations. Total PCB concentrations (sum of PCBs 22, 28/31, 41/64, 44, 49, 52, 56/60, 70, 74, 90/101, 110, 138, 149, 151, and 153/132) were a few ng/sample and comparable to data from the Arctic (Figure 2, Table SI-4, 5). HCB values ranged from 2.5 to 61 ng/sampler; values of 18 ng/sampler has been reported for the Arctic (21). HCB air concentrations are quite uniform in the Arctic, with the *H/L* values (ratio of the highest to the lowest) ~2. The greater variability across the Tibetan Plateau suggests some primary emissions. Chemical usage is one possibility, another may be incomplete combustion (22, 23); low oxygen levels on the plateau lead to inefficient combustion in this area. Σ9PBDE values were also generally low, ranging from 0.08–2 ng/sampler (Figure 2, Table SI-4, excluding a high value at Bomi). These are similar to those reported for Arctic Alert (0.8 ng/sampler) and the CRM (1.2 ng/sampler) (24).

HCH, DDT, and endosulfan are also summarized in Table SI-4. Maximum values were in the tens ng/sampler range, higher than reported for the Arctic and CRM region (Table SI-5). The higher values on the plateau suggest closer proximity to source regions and scattered pesticide usage. This is discussed further below.

Comparison between volumetric air concentrations derived here and other studies indicates that the Tibetan Plateau has the following: i. PCB concentrations which are considerably lower than reported for other remote/rural areas in

China/India, European high mountains, and the Atlantic Ocean; ii. *p,p'*-DDT, *o,p'*-DDT, α- and γ-HCH concentrations about 2–10-fold lower than other remote and rural parts of China/India; however, similar levels of α-endosulfan to rural India; iii. higher level of *p,p'*-DDT than European high mountains (Table SI-7).

Air Circulation over the Tibetan Plateau and Possible Transport Pathways. Westerlies, blowing from the west to east, are blocked by the Tibetan Plateau into two flows - the southern and northern branch (see Figure 1, SI-1-right). In general, westerly branches are strongest in the winter and weakest during the summer. However, the Indian Monsoon dominates the plateau's climate - especially in summer - when air masses plume across the Indian subcontinent and Bay of Bengal and then lift toward the north, penetrating the barrier of the Himalayan Mountains and reaching the hinterland of the Tibetan Plateau (Figure SI-1-left). The westerlies, together with the monsoon system, are the prevailing meteorology of the plateau. Monsoon winds make a strong impact on the plateau's south side but are blocked from going further north (Figure SI-1-left). The plateau may therefore be considered in two parts - the monsoon region (MR) and the westerly region (WR) (Figure SI-5, Text SI-2). The height of the atmospheric boundary layer (ABL) over the plateau can extend to heights of almost 3 km (25). Details of the ABL over the plateau are given in Text SI-3. Cooling of glaciers/snow on the upper-mountain portions and heating of the valley surfaces play important roles in accelerating vertical exchanges. Sinking of the cold air leads to an important "pump-down" driving force for pollutant transport (26).

Evidence for LRAT of pollutants on the plateau has been found in glacier studies. For example, Xie et al. (27) observed a high level of n-alkanes in the Dasuopu glacier on the plateau, with the source being oil fires during the 1991 Gulf War. Recently, Xu et al. (28) observed good agreement between soot emissions in the India subcontinent and black carbon in southern Tibetan glaciers. In the present study, possible LRAT pathways were clustered by analysis of back trajectories, which is consistent with previous studies (28) (Figure SI-2, 3). Different parts of the Plateau will be more or less affected by prevailing LRAT inputs (Figure SI-2, 3). Moreover, most of the agricultural regions of Tibet are located in the valleys with lower elevation (<2000–3500 m). Scattered usage of

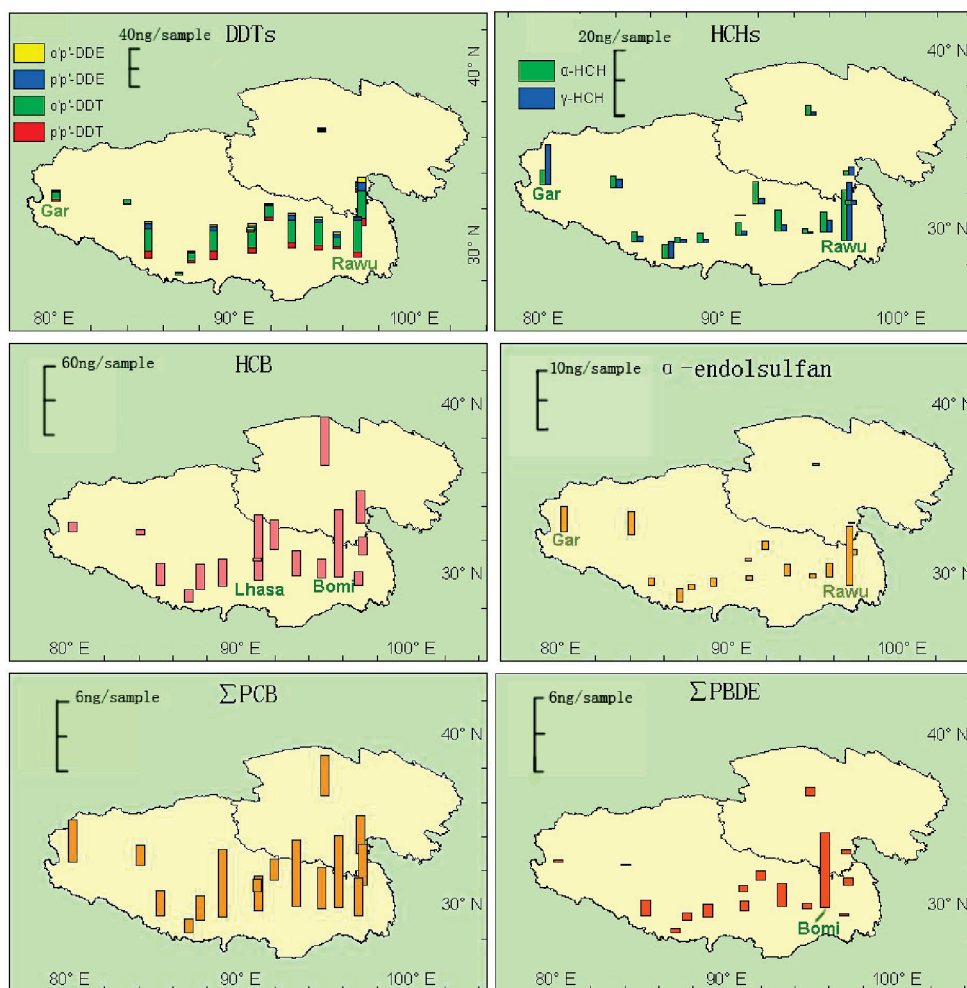


FIGURE 2. The spatial distribution of Σ DDTs, Σ PCBs, Σ PBDEs, α -, γ -HCH, α -endosulfan, and HCB (ng/sample) across the Tibetan Plateau. The bars center on the sample sites. Key: largest bar for DDTs, 61 ng/sample (site Qamdo, p,p' -DDT = 9.4, o,p' -DDT = 34, o,p' -DDE = 6.6, p,p' -DDE = 11); for Σ 15PCBs, 6.2 ng/sample (site Bomi); for Σ PBDEs, 6.3 ng/sample (site Bomi); for HCB, 61 ng/sample (site Bomi); for α -HCH, 16 ng/sample (site Rawu); for γ -HCH, 19 ng/sample (site Rawu); for α -endosulfan 10.3 ng/sample (site Rawu).

pesticides in these regions is possible. Considering the possible influence by LRAT and local contamination, it is appropriate to consider the spatial distribution of POPs across the plateau.

Spatial Distribution of Selected OC Pesticides, PCBs, and PBDEs. **DDT.** Useful information can be obtained by considering the distribution of total DDT (sum of p,p' -DDT, o,p' -DDT, p,p' -DDE, and o,p' -DDE) and the contribution of parent (o,p' -DDT, p,p' -DDT) and breakdown products (p,p' -DDE, o,p' -DDE). The ratios of the compounds which make up the total DDT signal and are sampled by the PAS reflect several factors, namely, are as follows: abundance in technical mixtures, vapor pressure/volatility, transport potential, reactivity, and partitioning to the sampler (5, 19). The DDT/DDE ratios did not show spatial differences, being with ~ 1 (Table 1) and suggesting that the p,p' -DDT found in plateau may not be due to recent usage. There are a few sites where both the levels of p,p' -DDT and the DDT/DDE ratios were higher where local fresh usage is possible. For example, the highest DDTs occurred at Qamdo, where the sampling site is near to farm land (Table SI-1). The higher o,p' -DDT/ p,p' -DDT ratio (average = 3.7 and 3.4 for MR and WR, respectively) and the dominance of o,p' -DDT (>50% of total DDTs) in air samples indicated a possible fresh o,p' -DDT input. One potential source is dicofol. Although local inputs cannot be excluded, this may be caused by relatively high o,p' -DDT concentrations in adjacent regions of India coupled with the higher LRAT tendency of o,p' -DDT under tropical climate

conditions (8, 29) (vapor pressure of o,p' -DDT is 5.5×10^6 mm). Levels of total DDTs were on average ~ 4 times higher in the MR than the WR (Table 1). LRAT under Indian Monsoon conditions and possible local usage may therefore both result in the relatively high level of DDTs in the MR of Tibet.

HCH and Endosulfan. Similar levels of α -HCH were observed in the MR and WR, while γ -HCH and α -endosulfan levels were relatively elevated in the WR. The highest levels of HCH and endosulfan occurred in sites close to the China-India border, namely: Rawu, Everest, and Gar (Table 1). Given that these 3 sites have elevations of >4000 m and local agriculture use of pesticides is extremely limited, LRAT presumably plays an important role. The α - to γ -ratio can be used to identify the source of HCH and as an indicator of LRAT (30). These 3 sites all exhibited low α/γ -HCH ratios (Table 1). This points to the influence of lindane usage on air concentrations/composition at the southern edge of the Tibetan Plateau. Lindane has been used in India since the ban on technical α -HCH in 1997 (31). The isomeric signatures of HCHs here coincide with the increasing use of lindane in the recent years. India is currently the world's largest user and producer of endosulfan (32). Typical westerly transport in the WR region presumably results in supply of endosulfan to the sites in west Tibet (Gar and Gaerze, Figure SI-3, Table 1).

HCB. Bailey and Barber et al. (22, 23) reviewed the global emission sources of HCB. There are industrial and agricultural

uses of HCB, together with emissions from incomplete combustion (22). Waste, coal, fuel, and biomass combustion can produce HCB (22). An interesting observation from this study is the relatively high loadings of HCB in areas where inefficient combustion at high altitude may be important - either in the more populated regions (Lhasa and Golmud) or at a site heavily influenced by forest fires during the study period (Bomi).

PCB. An interesting observation is that the tetra-chlorinated congeners are a major part of the total PCB composition of the samples (Figure SI-6). This is different from that reported previously for urban and background sites in other parts of China, where the tri-PCBs dominated (7, 9). Zhang et al. (8) also found tetra-PCBs dominating at rural sites in India, perhaps providing further evidence of this source region on the air composition of the Tibetan Plateau. Considering the transport potential of PCB congeners, lower chlorinated congeners can be efficiently degraded during LRAT, and higher chlorinated ones have less volatility and can be efficiently removed by particle-bound deposition. The intermediate chlorinated congeners therefore have greater LRAT potential (33).

PBDEs. As for HCB and PCB, the highest PBDE concentration was observed at Bomi, where forest fires had occurred (3 forest fires occurred near or during sampling period, namely: May 3rd, August 16th, and Jan 21st). Relatively high levels of other OCPs were found at this site as well (Table 1, Figure 2). High temperatures during forest fire events can promote re-evaporation of pollutants from soil or vegetation (34, 35). In the present study, BDE-47 accounted for 22–72% of total PBDEs, with BDE-99 at 14–47%. BDE-47 has a greater reported atmospheric travel distance than BDE-99 (33). These results therefore suggest both local and LRAT signals of BDEs on the Plateau.

This study confirms that XAD-PAS provide semiquantitative information and are particularly useful for this kind of long exposure time study in remote locations. Air mass transport in Tibetan Plateau shows obvious seasonality. Future work should focus on seasonally resolved data, to better investigate inputs from different transport processes. Local usage information should be gathered prior to sampling and OCP levels in agriculture region of Tibet should be considered.

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Supporting Information Available

Detailed information about sampling program, sampling rate at different sampling sites, original concentration data, back trajectory analysis, and other supplementary results.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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