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Persistent organic pollutants in mountain air of the southeastern Tibetan Plateau: Seasonal variations and implications for regional cycling

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ABSTRACT

In order to provide more conclusive evidence of monsoon-driven transport of persistent organic pollutants (POPs) to the Tibetan Plateau (TP) and assess the potential influence of forests on the fate of these pollutants, passive air samplers were consecutively deployed during 2008–2011 on Sygera Mountain (3800 m–4400 m). Higher DDTs levels were observed in the monsoon season (20.5–57.4 pg m^{-3}) than the non-monsoon season (9.2–27.4 pg m^{-3}), which confirmed that the Indian monsoon plays a key role in driving the atmospheric transport of DDTs to the TP. The similar DDT isomer ratios to the South Asia further suggested that Sygera Mountain is likely a receptor region of Indian subcontinent. By comparing the difference in concentrations between forest and clearing sites, it was found that the forest canopy can reduce airborne DDTs by a factor of 2, indicating strong absorption of DDTs by the Tibetan forest.

1. Introduction

Persistent organic pollutants (POPs), such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), are characterized by their toxicity, environmental persistence and potential to bioaccumulate. These compounds are able to undergo long-range atmospheric transport (LRAT) and reach remote areas where they have never been produced or used (Evenset et al., 2004; Kallenborn et al., 1998; Pacyna and Oehme, 1988). Thus, atmospheric data are particularly important, in order to understand the transportation processes of POPs (Hoh and Hites, 2004; Hung et al., 2010). Air monitoring has traditionally relied upon high-volume samplers, but these are expensive pieces of equipment and require an electricity supply, which limit their applicability in remote areas (Harner et al., 2006). Recently, passive air sampling (PAS) techniques have been developed and used for POPs monitoring (Shoeib and Harner, 2002). PAS is simple and inexpensive and therefore suitable for mapping the spatial distribution of POPs (Pozo et al., 2006). Deploying PAS in monitoring networks over several seasons and years will yield data on temporal trends (Pozo et al., 2009).

By using PAS, spatial surveys have been conducted on continental (e.g., Europe (Jaward et al., 2004a), Asia (Jaward et al., 2005b), and North America (Shen et al., 2004, 2005)) and global scales (Pozo et al., 2009, 2006). Besides, PAS campaigns have included various environmental gradients, such as the latitudinal (Jaward et al., 2004b), altitudinal (Estellano et al., 2008) and urban to rural (Harner et al., 2004). In one such study, the percentage of more volatile PCB congeners became higher with increasing latitude along a transect from 10°N to 82°N (Shen et al., 2006)—a phenomenon called the "global distillation" of POPs. Elsewhere, in terms of altitude, higher atmospheric concentrations of POPs have been observed at high-altitude sites of the Andean plateau where are susceptible to LRAT (Estellano et al., 2008). Combining with air mass trajectory analysis and seasonal variations of POPs, the LRAT pathway of POPs from the source region to a remote location can be depicted (Liu et al., 2010). Indeed, PAS is particularly appropriate for monitoring POPs in remote or alpine environments (Klanova et al., 2006); however, relevant research over the Tibetan Plateau (TP) remains limited.

The TP, with an average elevation of more than 4000 m, is known as "the third pole of the world". The atmosphere remains

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relatively pristine due to sparse human population and minimal industrial activities. However, it is adjacent to the Indian subcontinent, where dichlorodiphenyltrichloroethane (DDT) and lindane (γ-hexachlorocyclohexane, HCH) has been applied (Chakraborty et al., 2010; Pozo et al., 2011). By using active air sampler (AAS), we previously found that atmospheric concentrations of DDTs and PCBs in the southeastern TP are strongly linked to the cyclic patterns of the Indian monsoon (Sheng et al., 2013). Full details of the campaign are given elsewhere (Sheng et al., 2013). Thus so far, there have been two PAS studies aimed at examining the levels of pollution on the TP. Wang et al. (2010) deployed XAD-based PAS across the TP and found higher OCP levels occurred at sites close to the China–India border; while Xiao et al. (2010) observed that concentrations of POPs peaked in the monsoon season, based on monthly air samples using a flow-through sampler (FTS) at Lake Nam Co. However, a limitation of the above two studies is that the sampling periods were restricted to a one-year exposure time. To provide more detailed and robust seasonal data for assessing how the air circulation pattern (Indian monsoon) influences the transport of POPs, a more long-term PAS program is needed.

In the present study, the intention was to use a PAS network over a longer period of time (2008–11), to gain insights into how concentrations of OCPs and PCBs change spatially and temporally over Sygera Mountain. This mountain represents the western branch of the Yarlung Tsangpo Grand Canyon in the southeastern TP, which provides a "channel" allowing pollutants to climb up into the TP (Sheng et al., 2013). The climate of the region is mainly controlled by the Indian monsoon. As mentioned above, the study was a follow-up to the previous AAS work (Sheng et al., 2013), and comparing the PAS and AAS data will hopefully provide robust evidence regarding the monsoon-driven transport of POPs. Additionally, the landscape of Sygera Mountain is dominated by various forest types and forest canopy would have a significant influence on the regional fate of POPs (McLachlan and Horstmann, 1998; Wania and McLachlan, 2001). It is therefore imperative to explore to what extent the Sygera forests accumulate and filter the POPs transported to the TP. A better understanding of these processes will help to comprehend the sources, transportation, and fate of POPs in temperate alpine environments.

2. Materials and methods

2.1. Sampling sites and program

Polyurethane foam (PUF)-disk passive air samplers (see Text S1 in the Supplementary Material for details) were deployed on Sygera Mountain (29°10′–30°15′N, 93°12′–95°35′E, Fig. 1). The samplers were set up in duplicate in forest sites along two opposite slopes of the mountain (Fig. 1). There were three sites (3800, 4200, 4400 m asl) located on the southern slope (*S*) and two sites (4200 and 4400 m asl) on the northern slope (*N*). In order to test the possible depletion of atmospheric POPs by the forest canopy, another pair of samplers was deployed in the clearing of N4400 m (Fig. S1). Only this one comparison (forest vs. clearing in N4400) was made because the Sygera Mountain is in a dense forest and there are no available clearing areas in the lower elevations. Detailed information regarding the forest coverage at each sampling site can be found in Table S1. The sampling periods comprised consecutive deployments approximately every three months from 2008 to 2011. Four periods in one year were conducted to derive the seasonal-resolved concentrations: spring, summer, autumn and winter, respectively (Table S2). In total, 115 air samples were taken.

The Southeast Tibet Observation and Research Station (STORS), operated by the Chinese Academy of Sciences, is located at the foot of Sygera Mountain (3300 m) (Fig. 1). A low-volume AAS was deployed in the open plain of the station and our previous study has reported the seasonal atmospheric concentrations of POPs in the Sygera Mountain region using this AAS (Sheng et al., 2013). This can be used for comparison with the PAS results of the current study. Additionally, automatic weather station (AWS) is installed both at the foot and the top (4400 m) of Sygera Mountain to record the meteorological parameters (Table S2). The results showed that the temperature dropped by ~7 °C from the foot to the top (elevation difference of 1100 m).

2.2. Sample preparation

PUF disks were pre-cleaned by Soxhlet extraction using dichloromethane (DCM) for 24 h and dried in a clean desiccator under vacuum conditions. Before sampling, the PUF disks were spiked with four depuration compounds (DCs) (PCB-30, -54, -104, -188), which were used to determine the site-specific sampling rates (Pozo et al., 2009). Details related to the DCs can be found in Text S2. The PUF disks were wrapped in pre-cleaned aluminum foil (baked at 250 °C for 24 h and rinsed with acetone) and stored in a sealed tin container for transport. Twelve field blanks were prepared to investigate the potential sample contamination during handling, transport, and storage.

2.3. Sample extraction and analysis

Each collected sample was transferred into the Soxhlet body and spiked with a mixture of surrogate standards [2,4,5,6-tetrachloro-m-xylene (TCmX) and decachloro-biphenyl (PCB-209)]. Samples were Soxhlet-extracted using DCM for 24 h. The extracts were first concentrated by a rotary evaporator and solvent exchanged to hexane. Then, the samples were loaded on the top of a chromatography column (from the top to bottom: 1 g of anhydrous sodium sulfate, 2 g of 3% deactivated alumina, and 3 g of 6% deactivated silica gel), eluted with a 30-mL mixture of DCM and hexane (1:1). The elute was further cleaned on gel permeation chromatography (GPC, containing 6 g of Biobeads SX3) with a 50-mL of mixture of DCM and hexane (1:1) to yield the OCP and PCB fraction. Finally, the fraction was solvent exchanged and concentrated to 20 μL of dodecane containing a known quantity of pentachloronitrobenzene (PCNB) as the internal standard.

All samples and blanks were analyzed on a gas chromatograph (GC) with an ion-trap mass spectrometer (MS) (Finnigan Trace GC/PolarisQ), using a CP-Sil 8CB capillary column (50 m, 0.25 mm, 0.25 μm) and operating under the MS–MS mode. Helium was used as the carrier gas at 1 mL min^{-1} under constant-flow mode. The oven temperature began at 100 °C for 2 min, ramped up at a rate of 20 °C min^{-1} to 140 °C, at 4 °C min^{-1} to 200 °C (10 min hold time), then at 4 °C min^{-1} to 300 °C and

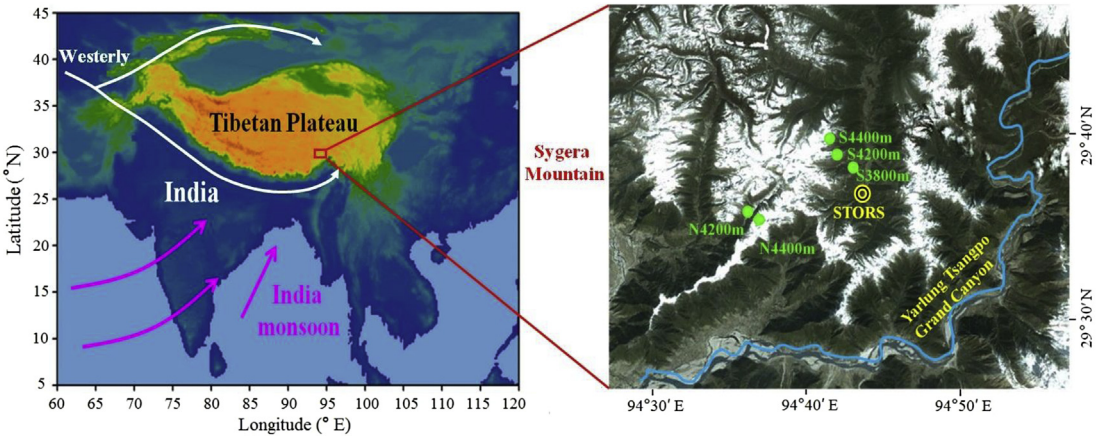

Fig. 1. General pattern of the atmospheric circulation systems over the TP and a map showing the locations of the PAS sites on Sygera Mountain. Sygera Mountain is denoted by the small rectangle; STORS is the Southeast Tibet Observation and Research Station.