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Using a passive air sampler to monitor air–soil exchange of organochlorine pesticides in the pasture of the central Tibetan Plateau

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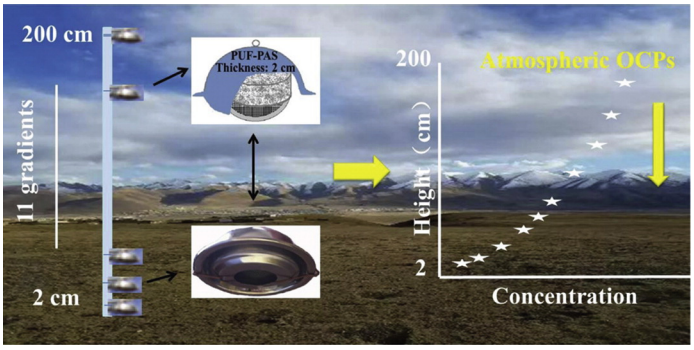
HIGHLIGHTS

- The modified PAS was a practicable device for capturing atmospheric OCPs.
- Mean concentrations of OCPs were all higher in summer than winter.
- Tibetan pastural soil was a sink of HCHs and DDTs.
- The environment of the pasture in the TP will remain pristine far into the future.

GRAPHICAL ABSTRACT



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ABSTRACT

Air–soil exchange is a key process controlling the fate of persistent organic pollutants (POPs). However, the "sink effect" of soil for POPs in Tibetan pasture has not been clear. In NamCo, in the central Tibetan Plateau (TP) where the land is covered by grass, a modified passive air sampler (PAS) (thickness: 2 cm) was tested. Using the PAS, the atmospheric gaseous phase organochlorine pesticides (OCPs) at 11 heights from close-to-surface (2 cm) to 200 cm above ground, in summer and in winter, were measured. Concentrations of OCPs in summer were higher than those in winter. Both in summer and winter, atmospheric concentrations of OCPs decreased with decreasing height from 200 to 2 cm, indicating that OCPs were being deposited from air to soil. Air deposition of OCPs was possibly driven by wind speed. Furthermore, based on air OCPs at 0–3 cm near the surface, the interface exchange of OCPs between air and soil was studied by the fugacity method. The results showed that pastural soil in the TP was a "sink" of OCPs even in summer. The mean deposition fluxes of α-HCH, γ-HCH and *o,p′*-DDT were 0.72, 0.24 and 0.54 pg/h/m^2, respectively, and it was estimated that the level of these pollutants in the soil will double every 24, 66 and 206 years, respectively. This study will contribute to the further understanding of global cycling of POPs in different land covers.

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1. Introduction

Persistent organic pollutants (POPs) are a group of pollutants that have long half-life and semi-volatility, which allows them to spread more easily over the world (Ballschmiter, 1996; Jones and de Voogt, 1999). The surface of the earth, e.g. soil, water and plants, consequently becomes a reservoir of these pollutants (Dalla Valle et al., 2004; Jurado et al., 2004; Sweetman et al., 2005). Driven by changes in temperature, atmospheric POPs exchange constantly with the surface (Wania and Mackay, 1993). Studies on air–soil gas exchange of POPs have found that remote soil is a "sink" (Cabrerizo et al., 2013), but polluted soil, such as industrial and agricultural soil, possibly becomes a secondary source of POPs (Harner et al., 2001; Kurt-Karakus et al., 2006).

When monitoring the air–soil exchange process, appropriate air sampling technology is crucial to the measurement of atmospheric POPs near the surface. Low-volume active air samplers (AAS) with reliable quantitative volume and high temporal resolution, collecting soil-equilibrated air close to the soil, have been used extensively to sample air POPs near the surface (Cabrerizo et al., 2009; Dobson et al., 2006; Gouin et al., 2005). Using the low-volume AAS, the air–soil exchange of POPs in various land-covers, such as agriculture (Wang et al., 2015c), e-waste recycling sites (Wang et al., 2016), rural background regions (Cabrerizo et al., 2011) and even the Antarctic (Cabrerizo et al., 2013), has been studied.

Compared with observing POPs at one height, vertical concentration gradients of POPs can be used intuitively to describe the air–surface exchange process (Kurt-Karakus et al., 2006; Majewski et al., 1990). In studies on farmland, AAS were set at four heights from 3 cm to 200 cm and concentrations were found to increase with decreasing height, which implied that POPs re-volatilized from soil to air (Cabrerizo et al., 2011; Kurt-Karakus et al., 2006; Meijer et al., 2003). Since AAS need a stable power supply, they are difficult to be deployed in remote regions. In contrast, passive air samplers (PAS) are easy to be operated, need no power and do not disturb the air (Gouin et al., 2005; Tao et al., 2009; Tuduri et al., 2012), which makes them more suitable for monitoring the vertical distribution of POPs in remote regions. Using the previous PAS, with a thickness of >10 cm, it is difficult to measure the air POPs close to the surface. Recently, however, Zhang et al. (2011) developed a small new PAS (thickness: 2 cm) and observed POPs at various heights from 5 to 520 mm above the ground. They found that atmospheric POPs deposited to background soil but evaporated from agricultural soil. However, comparable research on pasture, another land cover that is connected to human health, has received less attention.

The Tibetan Plateau (TP), with an average altitude > 4000 m, encompasses extensive natural pasture (area > 1.6×10^6 km^2), including the highest and largest alpine grassland in the world. Due to the cold climate, the TP has been seen as a "sink" of POPs. However, recent studies have revealed that Tibetan soil may be a secondary source of low molecular weight (LMW) POPs (Wang et al., 2014; Wang et al., 2012), with Wang et al. (2014) inferring that the direction of air–soil exchange for POPs in pastural regions possibly changes seasonally. Whereas these studies all adopted air data sampled by XAD-PAS at 1.5 m above the ground, research on the vertical variation of atmospheric POPs in the TP has been lacking, and no studies on the exchange of POPs occurring at the air–soil interface have been carried out. In this study, a modified PAS was applied to observe the vertical variations of atmospheric organochlorine pesticides (OCPs) in summer and winter, respectively, in NamCo region, in the central TP. The objective of the study was to investigate the seasonal variation in concentrations, direction and fluxes of air–surface exchange of OCPs in the pasture of the TP. This should then contribute to a greater understanding of the role that Tibetan pasture plays in air–surface exchange and global cycling of POPs.

2. Materials and methods

2.1. Sampling site

NamCo region, with an altitude higher than 4700 m, is located in the south of Chang Tang grassland. The NamCo Multisphere Observation and Research Station (NCMORS, 30°46.44′ N, 90°59.31′ E; 4730 m above sea level), operated by the Chinese Academy of Sciences, provides opportunities for in situ monitoring. Influenced by the westerly circulation in winter and the Indian monsoon in summer, the climate of NamCo is cold and dry in winter (October–April) but is warm and wet in summer (May–September). Additionally, the average annual wind speed reaches up to 4 m/s (Ma et al., 2009; Wang et al., 2015a). High wind speed will accelerate the turbulent exchange of atmosphere and subsequently have a possible impact on the air–surface exchange of atmospheric POPs.

2.2. Sampler

A new PAS was made of stainless steel, with a polyurethane foam (PUF) disk (6 cm i.d., 1.5 cm thickness, density 0.021 g/cm^3) as the absorbent material (Fig. 1). The PAS consisted of three parts from top to bottom: an upside-down dish, a mesh and a hollow dish (Fig. 1). The top stainless steel dish (diameter: 8 cm) protects the sampler against rain. The steel mesh (400 mesh) is put on the hollow dish to permit gaseous pollutants to enter the sampler. It also serves to hold up the PUF-disk. The hollow dish (4 cm i.d. opening, with diameter of 6.5 cm) is smaller than the top dish, which leaves a space between the two dishes to allow the air to circulate in the sampler (Fig. 1). As with the sampler of Zhang et al. (2011) that had a thickness of 2 cm, the sampler in this study could be used to collect atmospheric POPs close to the soil surface, but was designed with a larger surface (6.5 cm diameter) in order to capture more POPs. The modified PAS, with its thinner disk and greater specific surface area, can be used to observe gradients of air POPs, especially at heights close to the soil.

The PUF-disks were pre-cleaned with dichloromethane (DCM) for 24 h by Soxhlet extraction and dried in a clean desiccator under vacuum conditions. In order to determine the specific sampling rates of PAS, four performance reference compounds (PRCs) (PCB-30, -54, -104, -188, each PRC 400 pg/μL) were added uniformly into the PUF disks before sampling (Persoon and Hornbuckle, 2009; Pozo et al., 2009). For each PUF-disk, 15 μL of the PRC mixture were mixed with approximately 10 mL of n-hexane and then added evenly to both sides of the PUF-disk. The treated PUF-disks were wrapped in pre-cleaned aluminum foil and stored in a sealed tin container during transport.

2.3. Sampling design

The PAS was deployed as an array of 11 individual samplers, set along a gradient of 11 heights from 2 to 200 cm above the ground (Fig. 1). To avoid individual samplers blocking each other, they were distributed on two vertical stands set next to each other (Fig. 1). Six samplers were fixed non-uniformly at 2, 5, 10, 20, 80 and 200 cm on one stand and five were fixed at 3, 8, 15, 50 and 120 cm (Fig. 1) on the second stand. Three arrays, each comprising two stands, were positioned at random sites in pasture around NCMORS. PUF-disks sampling at the same height from the three arrays were mixed to form one sample. A composite surface soil sample (0–5 cm) from the three sites was collected during each sampling period.

Each sampling campaign lasted for approximately 2 months. Sampling campaigns were carried out in the summer (August–September 2013) and winter (October–November 2013), respectively. For each sampling period, two field blanks were prepared to investigate the potential contamination during handling, transport, and storage of the sample. To test the PAS, a low-volume AAS was deployed in NCMORS and sampled synchronously during the first sampled period (August–

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