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Long-term trends of atmospheric organochlorine pollutants and polycyclic aromatic hydrocarbons over the southeastern Tibetan Plateau

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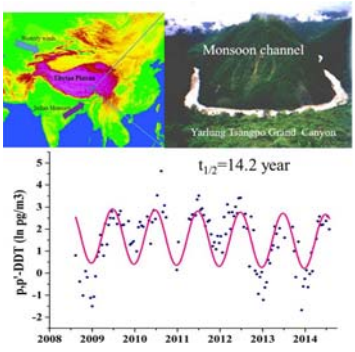
HIGHLIGHTS

- Decline trends were observed for α, γ-HCHs, *o,p′*, *p,p′*-DDTs and PAHs.
- Sources have shifted from technical HCHs to lindane and from technical DDTs to dicofol.
- The long half-lives of HCH, DDT indicated that they will persist in the TP for a longer period.

GRAPHICAL ABSTRACT



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ABSTRACT

Long-term monitoring in remote regions is essential for revealing pollution trends at the global scale but relevant studies remain limited. In the present study, a six-year continuous monitoring of atmospheric persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) was carried out at Lulang in the southeastern Tibetan Plateau (TP). Average concentrations of hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), dichlorodiphenyltrichloroethanes (DDTs), polychlorinated biphenyls (PCBs) and PAHs were 13.5, 8.9, 41.7, 1.8 pg/m^3 and 6.2 ng/m^3, respectively. Obvious seasonality was found for all the target compounds. HCHs, DDTs and PCBs had their highest concentrations in summer (monsoon season) and lowest in winter, which is consistent with the fluctuation of the Indian monsoon. Meanwhile, HCB and 5–6-ring PAHs showed opposite variations, possibly induced by local sources and the westerly flow in winter. Declining trends were observed for most of the chemicals, except *o,p′*-DDE, HCB and PCBs. A declining trend in the α/γ-HCH ratio indicated a shift from technical HCHs to lindane. An increasing trend in the *o,p′*/*p,p′*-DDT ratio suggested a likely shift from technical DDTs to dicofol. For PAHs, the contribution from high-temperature combustion has increased recently. The half-lives of α-HCH, γ-HCH, *o,p′*-DDT, *p,p′*-DDT were 6.1, 108, 77.6 and 14.2 years, respectively. The half-lives of γ-HCH, *o,p′*-DDT and *p,p′*-DDT were higher than those in the Arctic, indicating these compounds will persist in the TP for a longer period. The temporal trends in atmospheric POPs were possibly induced by emissions in India and likely driven by wind speed in Lulang. This study contributes toward a better understanding of the behavior and transport of POPs in the TP region.

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1. Introduction

Persistent organic pollutants (POPs) are stable in the environment, able to undergo long-range atmospheric transport (LRAT), and spread all over the world (Wania and Mackay, 1993; Wania et al., 1999). Not least because of their toxicity, POPs have aroused global attention (Stockholm Convention, 2001), resulting in several global and regional conventions and agreements having been signed with the aim to eliminate or reduce emissions of these pollutants. However, to monitor the effect of emission reduction measures, continuous observations of POPs in all parts of the environment (atmosphere, water, soil, vegetation, etc.) are required (Hung et al., 2010; Odabasi et al., 2015). Among these, atmospheric contamination monitoring is considered valuable and versatile for assessing anthropogenic influences on the environment (Hung et al., 2016; Kallenborn et al., 2013; Meijer et al., 2008).

Many international long-term atmospheric monitoring programs for POPs, such as the European Monitoring and Evaluation Program (EMEP), the Integrated Atmospheric Deposition Network, the Arctic Monitoring and Assessment Program (AMAP), Global Atmospheric Watch, and so on, have been established to cover Europe, the Great Lakes Basin, the Arctic, Antarctic, and some background regions of the world (EMEP, 1998; GLWQA, 2012; Hung et al., 2001; Hung et al., 2010; Kallenborn et al., 2013). These programs are devoted to measuring the levels of atmospheric toxic chemicals, determining the LRAT potential of these chemicals in remote regions, and evaluating the effectiveness of regulation measures. Data from these programs generally point toward decreasing trends for most POPs after the ban of these pollutants (Becker et al., 2012; de la Torre et al., 2016; Hung et al., 2005; Hung et al., 2001; Meijer et al., 2008). Thus far, the longest monitoring record is that of AMAP (over 20 years), which provides opportunities not only for investigating the global environmental regulation of POPs (Becker et al., 2006; Hung et al., 2016; Kallenborn et al., 2013), but also the connection between climate warming and POP variation (Ma et al., 2011).

The Tibetan Plateau (TP) is regarded as the "Third Pole" of the Earth because of its low temperatures and pristine environment (Yao et al., 2013). Due to cold climate conditions, POPs tend to be trapped and deposited in these regions (Grimalt et al., 2001; Wania and Westgate, 2008). Although POP atmospheric monitoring programs have started on the TP, most previous research has concentrated on the spatial and short-term (seasonal) variations of POPs (Ren et al., 2017; Wang et al., 2010). For example, a passive sampling network based on the XAD-2 sampler revealed the spatial distribution of dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) across the TP and found relatively higher levels of these pollutants over the southeastern TP (Wang et al., 2010; Wang et al., 2016). Besides the spatial pattern, the levels of DDTs and HCHs were higher in summer (monsoon season) than that in winter over the southeastern TP (Ren et al., 2014). Given the southeastern TP is perennially downwind of India, the pollutants emitted in India will be transported to the TP.

India is still engaged in the large-scale manufacture and use of these banned chemicals (Sharma et al., 2014) – for example, DDT and HCH (NIP, 2011). Meanwhile, the densely populated Indo-Gangetic Plain (IGP) is another globally important source region for particulate-PAHs. Based on a three-year (2008–2011) monitoring program, the monsoon-driven atmospheric transport of DDTs and polychlorinated biphenyls (PCBs) and westerly-delivered particulate-PAHs were found to be able to penetrate the barrier of the Himalayan mountains to reach the southeastern TP (Lulang, Sheng et al., 2013; Wang et al., 2015). Given the concentrations of contaminants showed consecutive periodicity during the whole three-year sampling, this suggested the LRAT of pollutants from India to the southeastern TP is not an accidental event but a continuous process.

However, as compared with achievements in the Arctic, the above three-year atmospheric monitoring of POPs over the southeastern TP is very limited. For instance, the half-life characteristics of POPs in the Tibetan environment remain unclear, and it is also uncertain as to whether climatic parameters can influence POP levels. In this study, therefore, a three-year (2011–2014) atmospheric monitoring of Hydrophobic organic compounds (HOC) was carried out at Lulang and, combined with previous published results (Sheng et al., 2013; Wang et al., 2015), consecutive datasets (six years from 2008 to 2014) on the concentrations of OCPs, PCBs and PAHs were obtained. Our main aims in carrying out this work were to obtain information on the half-lives and annual variation of various pollutants, and reveal the factors that may control the temporal trends of POPs.

2. Materials and methods

2.1. Sampling site

Air samples were collected at the Southeast Tibet Observation and Research Station (STORS; 94.73°E, 29.77°N; 3330 m), which is located at Lulang, southeastern TP. The atmospheric circulation at Lulang is dominated by the Indian Monsoon in summer and the southern branch of the westerly flow in winter (Sheng et al., 2013). The prevailing wind – not only in summer but also in winter – is from the southeast direction, as determined from long-term meteorological observations (see Supporting information (SI) Fig. SI-1). More details on the sampling were reported in a previous study (Sheng et al., 2013).

2.2. Sampling program

A medium-volume air sampler (~100 L/min) was set up at STORS to trap both particle- and gas-phase chemicals via a glass fiber filter (diameter of 9 cm) and polyurethane foam plugs (PUFs; 7.5 cm × 6 cm in diameter), respectively. Typically, ~700 m^3 of air was collected over a two-week period. The observed data from 2008 to 2011 have been reported in previous studies that the PUF and filter samples were analyzed separately (Sheng et al., 2013; Wang et al., 2015). Based on the these studies, it was found that OCPs, PCBs and low-molecular-weight (LMW) PAHs were mainly in gas phase (collected by PUF) and high-molecular-weight (HMW) PAHs were mainly absorbed in particulate (collected by the filters, Sheng et al., 2013; Wang et al., 2015). In the present study, the sampling period was from 2011 to 2014, and the PUF and filter samples were combined to represent the total concentration of HOC in air. Therefore, combined with the previous data, the total (gas and particle) phase concentrations of HOC from 2008 to 2014 are analyzed in this paper. The meteorological parameters, including the air temperature, wind speed, wind direction and air pressure were recorded every 10 min during the sampling period by an automatic weather station at STORS. The average values of the parameters during the sampling periods are given in Table SI-1.

2.3. Analysis and quality control

The details of the chemical analyses have been published previously (Sheng et al., 2013; Wang et al., 2015); thus, only a summary is given here. The air samples were Soxhlet-extracted by 200 mL of dichloromethane for 16 h. Each sample was spiked with PCB-30, Mirex, phenanthrene-d10 and perylene-d12 as recovery surrogates. The extract was first purified on an aluminium/silica column (internal diameter of 8 mm), and then a gel permeation chromatography column. Known quantities of pentachloronitrobenzene, decachlorobiphenyl, anthracene-D10, and benzo(*ghi*)perylene-D12 were used as the internal standards. All the samples were analyzed by a gas chromatograph (GC) with an ion-trap mass spectrometer (MS) (Finnigan Trace GC/PolarisQ). The compounds were detected under MS-MS mode. The oven temperature of the system is given in Text SI-1. Compounds detected in this study included α-, β, γ and δ-HCH; HCB; *o,p′*-DDT, *o,p′*-DDE, *o,p′*-DDD, *p,p′*-DDT, *p,p′*-DDE and *p,p′*-DDD; PCBs-28, -52, -101, -138, -153 and -180; and 15 United States Environmental Protection Agency priority PAHs: acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU),