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Occurrence and air–soil exchange of organochlorine pesticides and polychlorinated biphenyls at a CAWNET background site in central China: Implications for influencing factors and fate

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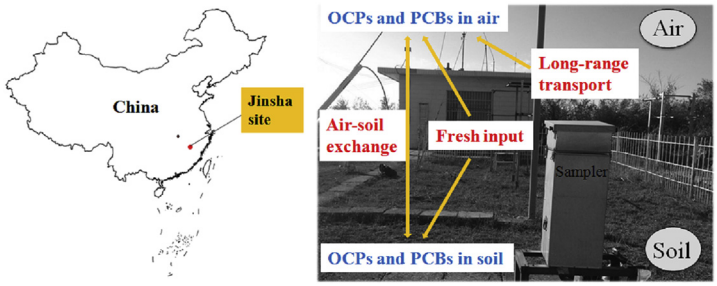
HIGHLIGHTS

- Air and soil samples were simultaneously collected at a central China background site.
- Concentrations of OCPs and PCBs in soil and air were lower or comparable with other remote/background sites.
- Soil was an important source for atmospheric *p,p′*-DDT, endosulfans, and chlordanes.
- Higher HCB concentrations in winter were attributed to the surrounding ongoing source.
- Atmospheric HCHs and PCBs were mainly influenced by long-range atmospheric transport.

GRAPHICAL ABSTRACT



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ABSTRACT

Ambient air and soil samples were collected between March 2012 and March 2013 at Jinsha, a regional background site in central China, to measure the concentrations of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). The average concentrations of total OCPs and total PCBs were 191 ± 107 and 39.4 ± 27.1 pg/m^3 in air (gaseous and particulate phase) and 0.585 ± 0.437 and 0.083 ± 0.039 ng/g in soil, respectively. The higher concentrations of *p,p′*-dichlorodiphenyltrichloroethane (*p,p′*-DDT) and *p,p′*-DDT/*p,p′*-DDE ratios in the soil indicated recent *p,p′*-DDT input to the soil. A strong positive temperature dependence and average fugacity fraction value > 0.5 were observed for *p,p′*-DDT, suggesting that volatilization of residual DDT in the soil was the main influencing factor on atmospheric *p,p′*-DDT. Highly average fugacity fractions (>0.7) of *trans*-chlordane (TC) and *cis*-chlordane (CC) and high TC/CC ratios both in the soil and atmosphere suggested fresh inputs. Higher gaseous concentrations of hexachlorobenzene (HCB) were observed in winter and negative temperature dependence was directly attributed to the surrounding ongoing source (e.g. fuel consuming activities), especially in winter. Overall, most targeted OCPs and PCBs were influenced by long-range transport, and fugacity fraction values indicated highly volatile compounds (e.g. α-hexachlorocyclohexane (α-HCH) and lower chlorinated PCBs) were volatilized and low volatility compounds (e.g. *p,p′*-DDE and higher

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chlorinated PCBs) were deposited at the air–soil interface. Knowing the source and sink of OCPs and PCBs can help to control their pollution in this area and provide a reference for other studies.

1. Introduction

Persistent organic pollutants (POPs) are a class of organic chemicals that have high persistence in soil, water, sediments or biota and can be transported over long distances in the atmosphere or water (Wania and Mackay, 1996; Fu et al., 2003). Because of their semi-volatility, POPs may volatilize from soils into the atmosphere after application. The processes of volatilization and deposition cause the soil to be an important source or sink for the regional or global cycling of POPs in the atmosphere (Jones and Voogt, 1999; Meijer et al., 2003).

Organochlorine pesticides (OCPs), one of the best-known POPs, are a series of man-made chemicals that were widely produced and used in China as insecticides from 1950 to 1983 (Fu et al., 2003; Wong et al., 2005; Jin et al., 2010; Tasdemir et al., 2012). China has prohibited the production, usage, and circulation of Dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs), chlordane and hexachlorobenzene (HCB) after signing the Stockholm Convention in May 2001. However, usage of DDT-containing dicofol, technical chlordane, lindane and endosulfan still continues in China, contributing to higher levels of OCPs pollution (Bidleman et al., 2002; Qiu et al., 2005; Wang et al., 2012a). Polychlorinated biphenyls (PCBs) are one of the target twelve POPs in the Stockholm Convention (Li et al., 2010). The production of PCBs in China was started in 1965, began to be restricted in 1974 and totally banned in the 1980s (Fu et al., 1997; Breivik et al., 2002). During the production period, about ten thousand tons of PCBs were produced as raw materials for the manufacture of transformers and power capacitors or as additives for paint. Transformer and power capacitor waste and the paint additives can lead to environmental pollution (Bi et al., 2002). Until recently, these compounds were still detected in the various environmental media (e.g. soil, atmosphere, etc.) in China (Wu et al., 2011; Cui et al., 2013; Yuan et al., 2014; Zhao et al., 2016).

Recently, the transport and fate of OCPs and PCBs in the environment have been largely influenced by the process of soil–air exchange with the secondary sources becoming increasingly influential (Bidleman and Leone, 2004; Valle et al., 2005). The exchange directions of the chemicals between the soil and air can be characterized by the equilibrium between the two phases (Harner et al., 2001). There are many studies focusing on the soil–air exchange of OCPs and PCBs over the world (Meijer et al., 2003; Tasdemir et al., 2012; Wang et al., 2012b). Wang et al. (2012b) founded that HCB and lower chlorinated PCBs in Tibet were largely from the re-volatilization of the soil, whereas there were net deposition of DDTs to the soil. Li et al. (2010) reported global fugacity fraction (ff) for PCBs and the ff values were quite low at background sites in China, indicating that the background sites will likely continue to be “sinks” for PCBs. Růžičková et al. (2008) assessed air–soil exchange of OCPs and PCBs across central and southern Europe, the results showed that soil in background sites were sink for higher chlorinated PCBs, DDT, and γ-HCH while they were tend to be source for most of the PCB congeners, as well as for α-HCH.

Jinsha (JSH) is a regional background Chinese Meteorological Administration (CMA) Atmosphere Watch Network (CAWNET) site, which is located in a sparsely populated area in central China. To date, studies of environmental contaminants in air and soil were limited at JSH. Lin et al. observed the background concentrations of reactive gases and illustrated the impact of long-range atmospheric transport (LRAT) at JSH (Lin et al., 2011). Zhang et al. investigated the chemical compositions and seasonal variations of fine particles at JSH, finding that the high levels of $PM_{2.5}$ in winter were most likely caused by the LRAT from the north of JSH and strong regional emissions (Zhang et al., 2014). Since different economic development levels and historical usage in different areas, observations of OCPs and PCBs were mostly concentrated in the highly-polluted southeast coastal areas. To our knowledge, no studies on the occurrence of OCPs and PCBs at JSH (central China) have been published. This study was conducted to 1) investigate the concentrations and seasonal variations of OCPs and PCBs in air and soil at JSH; 2) assess the key influencing factors on atmospheric concentrations according to the results of temperature dependence and air–soil exchange; and 3) identify the potential sources and fate of the regional contaminants.

2. Materials and methods

2.1. Sampling site and sample collection

JSH (29°38′N, 114°12′E, 750 m.a.s.l.) is a regional background CAWNET site situated at the junction of Hunan, Jiangxi and Hubei provinces and geographically close to the center of China (Fig. 1). It is one of CAWNET sites across China operated by the CMA to monitor the meteorological data and concentrations of contaminants in the environment. The JSH site is on an isolated mountain peak, and the surrounding area is naturally scattered grasslands and is sparsely populated. During the whole year sampling period, the average temperature was 16.3 °C, and the average relative humidity was 78.6%. The prevailing wind directions were NNW, NW, ESE and SE, with an average wind speed of 3.7 m/s.

Air samples were collected for 24 h approximately every 6 days from March 2012 to March 2013, using a modified Anderson-type Hi-Volume air sampler which was operated at a rate of 0.3 m^3/min. Samples were also collected on days of very high pollution. A total of 64 samples were collected. Air particulates were collected on quartz fibre filters (QFFs) (Grade GF/A, 20.3 × 25.4 cm), and POPs in gaseous phase were collected by polyurethane foam (PUF) plug (length 8.0 cm, diameter 6.25 cm, density 0.035 g/cm^3). The QFFs were baked in an oven at 450 °C for 4 h to remove organic contaminants before use. The PUF plugs were precleaned using an Accelerated Solvent Extraction (ASE) extractor with 2 extraction steps, each last for 15 min at 100 °C and 1500 psi, using a mixture (1:1, V/V) of acetone and dichloromethane (DCM). The samples were sealed in glass bottles and stored below −18°C until analysis.

A total of 15 soil samples were collected approximately once a month around the air sampler (<10 m). About 1 kg of soil samples were taken from the top 5 cm of the soil after removal of the large stones and pieces of vegetation. After sieving through a 1.0 mm mesh to remove large particles and organic debris, the soil samples were sealed with aluminum foil and stored at 4 °C. About 30 g of soil samples were used to determine the contents of organic carbon, and 15 g were used for OCPs and PCBs analysis.