Survey of organochlorine pesticides in the atmosphere and soil of two typical landforms of Southern Anhui Province, China: Sources and air-soil exchange

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ABSTRACT

Organochlorine pesticides (OCPs) were detected in the atmosphere and soil of Southern Anhui, China. The average concentration of $\sum$OCPs in the atmosphere along the Yangtze River (YR) was 950 ± 400 pg m^{-3}, and was higher than that in the Huangshan Mountain (HM) which was 560 ± 120 pg m^{-3}. The average concentration of $\sum$OCPs in the soil along the YR was 4.4 ± 1.9 ng g^{-1}, and was lower than that in the HM which was 8.3 ± 2.3 ng g^{-1}. Fugacity fraction (ff) values of DDTs, endosulfan I, and γ-HCH found in Southern Anhui were <0.3, suggesting obvious net gaseous deposition. For HCB, almost all the sites in Southern Anhui had ff > 0.7, suggesting obvious volatilization. For α-HCH, sites in the HM showed obvious net volatilization, and both volatilization and deposition of α-HCH could occur along the YR. The α/γ-HCH values in the atmosphere were lower than that in the technical HCH mixtures, probably indicating the inputs of lindane. Patterns of DDT congeners indicated that atmosphere of Southern Anhui was largely influenced by external fresh input of technical DDT. In the HM, atmospheric endosulfan I, p,p'-DDT and o,p'-DDT mainly came from other source regions by the atmospheric transportation, while both local soil re-emission and external input would have influence on the atmospheric α-HCH. For atmospheric HCB in the HM, re-emission from local soil might be the primary source. Air back trajectories analysis showed high levels of OCPs found along the YR might attributed to the atmospheric transport from the lower reach of the Yangtze River basin.

1. Introduction

Organochlorine pesticides (OCPs), such as hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethane (DDTs), have been of great global concern because of their toxicity and environmental persistence (Feng et al., 2011; Liu et al., 2009). China is a large producer and user of OCPs in the world (Liu et al., 2009). Although the production of some OCPs has been banned in China for many years, such as technical HCH and DDT, the historically heavy usage of these chemicals has resulted in ubiquitous pollution in various environmental matrixes (Feng et al., 2011; Liu et al., 2009). On the other hand, some OCPs were still being use

for agricultural purposes in recent years (Jia et al., 2009). For example, usage of lindane (almost pure γ-HCH) in China has been estimated to be approximately 3200 tons between 1991 and 2000, and the usage of endosulfan in China was about 25,700 tons between 1994 and 2004 (Jia et al., 2009; Li et al., 2001). Furthermore, the usage of some chemicals containing OCPs as impurities may lead to the constant contamination, such as dicofol which contains o,p'-DDT as an impurity, and pentachlorophenol which contains hexachlorobenzene (HCB) as an impurity (Qiu et al., 2004; Zheng et al., 2012).

Due to their persistence and semi-volatility, OCPs can migrate through the atmosphere from emission regions to the remote areas where they are not, or never have been used (Scheringer, 2009; Wu et al., 2010, 2011, 2014). Hence, the pollution of OCPs is a global problem. As the rapid response of air concentrations to changes in primary emissions, the atmosphere is expected to an important media for understanding the global distributions and environmental fates of OCPs. Atmospheric monitoring of OCPs traditionally

relies on active air samplers (Shoeib and Harner, 2002). However, active air sampling requires electricity supply which is rarely found at truly remote sites (Shoeib and Harner, 2002). In recent years, various types of passive air samplers (PAS) have been developed and used for air monitoring. Polyurethane foam (PUF) disk based PASs, which are simple and low cost, have been successfully used in atmosphere monitoring ranging from regional to continental in scale (Estellano et al., 2012; Pozo et al., 2009, 2012).

Soil is a major terrestrial reservoir of OCPs. However, soil may not be considered as a permanent sink, as OCPs also tend to violate from soil to the atmosphere (Harner et al., 2001; Meijer et al., 2003b). Soil-air exchange has been characterized as a key process driving the environmental fate of OCPs on regional and global scales (Cabrerizo et al., 2011; Degrendele et al., 2016; Ruzickova et al., 2008; Sultana et al., 2014).

Anhui province is located across the basins of the Yangtze River (YR) and the Huaihe River. Geographically, Anhui province is divided into two parts by the Yangtze River, Northern and Southern Anhui. There are two typical landforms in Southern Anhui (36 500 km^2), the plains along the Yangtze River occupying an area of about 10%, and a series of mountains and hills which accounts for the other 90% (Hu, 2007). Southern Anhui is a traditional agricultural region with wide distribution of rice paddies, tea lands, and tobacco lands (Hu, 2007; Yue et al., 1990). Historically, OCPs had been widely used for agricultural and nonagricultural purposes in this region, such as seed and soil treatment in variety of crops and for vector control (Li et al., 1996; Yue et al., 1990). Previous studies had found high levels of OCPs in different environmental matrixes around the Caohu Lake, which lies in the central of Anhui province and is one of the largest lakes of China (Ouyang et al., 2012, 2013). However, no study had clarified the levels and distribution of OCPs in the environmental matrixes of Southern Anhui as yet. In the current study, eleven paired air and soil samples were collected along the YR (YR 1–6) and in the Huangshan Mountain (HM, HM 1–5) in 2013. The PAS apparatus using PUF disks as sampler medium were used for the air collection. The objectives of this study are 1. to analyze the levels, sources and spatial trends of OCPs in the soil and atmosphere of two typical landforms of Southern Anhui, 2. to evaluate air-soil exchange fluxes of OCPs in this region.

2. Methodologies

2.1. Sampling

At each sampling site, PAS apparatus were deployed about 2 m above the ground. Sampling was performed at all the sites for about two months, the details can be found in supporting information (SI, Table S1). Before deployed for sampling, PUF disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm^2; mass, 4.40 g; volume, 207 cm^3; density, 0.0213 g cm^{-3}) were precleaned by soxhlet extraction for 48 h using acetone and hexane (1:1 v/v), and then were dried in a vacuum drying oven. The precleaned PUFs were wrapped in aluminum envelopes, double-sealed in polyethylene bags, and then transferred to the sampling locations. After sampling, exposed PUFs were wrapped in aluminum foil, double sealed in polyethylene bags, and kept at −20 °C until extraction. Three clean PUFs were treated as real samples, but exposed to the atmosphere only for about 1 min during the sampling and processed as field blanks.

Surface soil samples (0–10 cm) were collected using clean stainless steel spades. At each sampling site, five sub-samples were collected from a 100 × 100 m^2 plot (four in the corners and one in the center), and thoroughly mixed to form a composite sample. The samples were freeze-dried, ground to pass through a 60-mesh sieve and maintained at −20 °C prior to analysis.

2.2. Sample preparation and analytical procedure

PUF and soil samples (added with activated copper) were spiked with the surrogate standards (PCB30, PCB65 & PCB204 for PUFs, PCB65, PCB204 & pentachloronitrobenzene for soils) and Soxhlet extracted with mixture of hexane and acetone (1:1 v/v) for 48 h. Then, the extracts were concentrated to about 1 mL by rotary evaporation. For PUF samples, the extracts were purified by passing through chromatography columns packed with 4 g activated silica gel, 4 g deactivated alumina (5%) and 2 g anhydrous sodium sulfate from bottom to top. For soil samples, the extracts were purified by passing through chromatography columns packed with 5 g deactivated alumina (5%), 4 g deactivated silica gel (5%), 4 g acid silica (50% sulfuric acid), and 2 g anhydrous sodium sulfate from bottom to top. All the columns were pre-cleaned with 30 mL of n-hexane. The concentrated sample was added into the column and eluted with 50 mL hexane and 50 mL mixture of hexane and dichloromethane (1:1 V/V), which both of the fractions were collected and mixed. Eluates were spiked with internal standard (PCB24, PCB82 and PCB198 for PUFs, and 2,4,5,6- tetrachloro-m-xylene for soils) and concentrated to 100 μL under a nitrogen stream. All extracts were then kept in sealed vials at −20 °C prior to instrumental analysis.

Quantification of OCPs in the PUFs was performed using a GC (Agilent 6890) equipped with a mass-selective detector (Agilent 5973) in the electron impacting (EI) mode. The GC column used for quantification was a HP-5MS fused silica capillary having 0.25 mm i.d. × 60 m × 0.25 μm film. Standard of OCPs was measured and the samples were analyzed separately in selective ion monitoring (SIM). The most abundant ions were selected for quantification and two references ions were used for confirmation of each analyte in SIM mode. Quantification of OCPs in the soils was performed using a GC (Agilent 6890N) equipped with two Ni electron capture detectors. A dual column system was used for quantification. The two capillary columns were HP-5MS and DB-1701, both having 0.25 mm i.d. × 60 m × 0.25 μm film. Organic matter (OM) of soil samples were determined by oxidation-reduction titration with ferrous ammonium sulfate (Sultana et al., 2014).

2.3. Quality control

All analytical procedures were monitored using strict quality assurance and control measures. To check for reproducibility of PAS, three PAS apparatus were set on the campus of Anhui Normal University for 60 days. Variability of the triplicates was in the range of 7%–23%, and could mostly be attributed to the inherent variability in the analytical methodology (see SI Table S2). Three field blanks (for the PUF samples) and six procedural blanks (three for the PUF samples and three for the soils) were processed to check for field and laboratory contamination. All these blanks were extracted and analyzed in the same way as the samples. The instrumental detection limits (IDL) were calculated from the lowest standards, extrapolating to the corresponding amount of analyte that would generate a signal to noise ratio of 3:1. Method Detection limits (MDL) of air samples were defined as mean of field blank with 3 times the standard deviations (0.05–0.5 ng sample^{-1} for OCPs). MDL of soil samples were defined as mean of procedural blank with 3 times the standard deviations (0.010–0.079 ng g^{-1} for OCPs) (see SI Table S3). When the targets were not detected in the blanks, 3 times of the IDL was defined as the MDL. The average recoveries of PCB30, PCB65 and PCB204 in PUF samples (n = 17) were 74 ± 11%, 80 ± 12%, 83 ± 11%, respectively. The average recoveries of pentachloronitrobenzene, PCB 65, and PCB 204 in soil samples (n = 14) were 95 ± 9%, 106 ± 15% and 104 ± 10%, respectively. All reported values are not corrected with the recovery rates.