

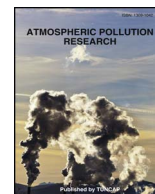
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# Polychlorinated biphenyls in two typical landforms of Southern Anhui province, China: Sources, air-soil exchange, and risk assessment

Xiaoguo Wu<sup>a,b,\*</sup>, Afeng Chen<sup>a,b</sup>, Siquan Wang<sup>b</sup>, Jiliang Zou<sup>b</sup>, Hanyang Liu<sup>a,b</sup>, Sa Xiao<sup>b</sup>

<sup>a</sup> Anhui Provincial Engineering Laboratory of Water and Soil Pollution Control and Remediation, Anhui Normal University, Wuhu, Anhui 241002, PR China

<sup>b</sup> College of Environmental Science and Engineering, Anhui Normal University, Wuhu, Anhui 241002, PR China

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## ABSTRACT

Polychlorinated biphenyls (PCBs) were detected in the atmosphere and soil of Southern Anhui, China. The average concentration of  $\Sigma_{26}$ PCBs in the atmosphere along the Yangtze River (YR) was  $32 \text{ pg m}^{-3}$ , and was higher than that in the Huangshan Mountain (HM) which was  $17 \text{ pg m}^{-3}$ . The average soil concentrations of  $\Sigma_{26}$ PCBs along the YR and in the HM were  $1.6$  and  $1.3 \text{ ng g}^{-1}$ , respectively. The mean percentages of tri-CBs were less than 40% in both air and soil samples. The percentages of penta- and hexa-CBs in air and soil samples were relatively higher than those in Chinese commercial PCBs and unintentionally produced PCBs. These homologue patterns indicated that PCBs in the environmental matrices of Southern Anhui might originate from other distant sources. In southern Anhui, most highly chlorinated congeners presented net gaseous deposition from air to soil, while lower chlorinated congeners preferred net volatilization from soil to air. PCBs in the environmental matrices of the HM were diluted with increasing altitude, suggesting that PCBs in this region might origin from some external sources, and be transported to the HM by atmosphere. Half of the sampling sites along the YR and one site in the HM had the cancer risks for  $\Sigma_{26}$ PCBs through the inhalation exposure higher than acceptable risk level of  $10^{-6}$ . Only one sampling site had the cancer risk for  $\Sigma_{26}$ PCBs through the accidental soil ingestion  $> 10^{-6}$ .

## 1. Introduction

Polychlorinated biphenyls (PCBs) are synthetic chlorinated organic chemicals which have no natural sources. Historically, PCBs were mostly applied in the products such as transformers and capacitors due to their thermal stability, excellent dielectric properties, and resistance to oxidation (Breivik et al., 2002; Cui et al., 2017a). These chemical properties, however, also contribute to the persistence of PCBs after they are released into the environment. Due to their characteristics of persistence, bioaccumulation and toxicity to biota and humans, PCBs are classified and regulated as persistent organic pollutants (POPs) under the Stockholm Convention (Breivik et al., 2007; Sun et al., 2016). Despite being restricted for several decades, extensively usage of PCBs has led to the ubiquitous contamination of the environment (Beyer et al., 2000; Wania and Su, 2004; Zhang et al., 2014; Sun et al., 2016; Cui et al., 2017a). The average air concentrations of PCBs at background sites may range from 1's to 100's  $\text{pg m}^{-3}$ , while average background soil levels were from 100's to 1000  $\text{pg g}^{-1}$  dry weight (Hornbuckle and Robertson, 2010). As a group of semi-volatile organic compounds (SVOCs), PCBs have spread globally via long-range

atmospheric transport (LRAT) (Gouin et al., 2004). Due to the direct connection facilitated by the LRAT, atmospheric levels are crucial for understanding the global distributions and environmental fates of PCBs. Moreover, soil also plays an important role in supplying the receiving PCBs from the atmosphere (Meijer et al., 2003; Cui et al., 2017a). Once released to the environment, PCBs may undergo several cycles of deposition and re-emission between the air and soil before achieving steady state (Cui et al., 2017a). The status of PCBs in the soil and air is mainly controlled by air-soil exchange. Hence, air-soil exchange is important for illuminating the distributions of PCBs in the air and soil.

In China, approximately 10,000 t of PCBs were produced in the decade from 1965 to 1975 (Ren et al., 2007; Xia et al., 2012; Cui et al., 2013). In consideration of the fact that the production of PCBs in China has been phased out for more than thirty years, the levels of PCBs in different environmental matrices should decrease gradually. On the contrary, PCBs in the atmosphere of China had increased by approximately one order of magnitude from 2004 to 2008 (Hogarh et al., 2012). This increasing trend might be attributed to the re-emission/volatilization of PCBs from environmental reservoirs, including soil. In addition, unintentionally emissions of PCBs recently, such as emissions

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\* Corresponding author: College of Environmental Science and Engineering, Anhui Normal University, Wuhu, Anhui 241002, PR China.

E-mail address: [Wuxg1983@ahnu.edu.cn](mailto:Wuxg1983@ahnu.edu.cn) (X. Wu).

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from cement industry, steel industry and metallurgical industry, might also be responsible for the increasing atmospheric PCBs in China (Cui et al., 2013, 2015).

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<sup>2</sup>), the plains along the YR occupying an area of about 10%, and a series of mountains and hills which accounts for the other 90%. Southern Anhui, especially the plains along the YR, is an important part of the industrial transfer demonstration region (set up by the State Council of China in 2010). A large number of manufacturing enterprises, especially cement manufacturing enterprises which may lead to the unintentionally emissions of PCBs, had moved to this region since then. The HM is a national forest park and has also been declared a UNESCO (United Nations Educational, Scientific and Cultural Organization) world Heritage Site (cultural and natural heritage site). The HM comprises mesic forests (< 1100 m), deciduous forest (1100–1800 m) and alpine grasslands (> 1800 m).

The objectives of this study are to analyze the levels, sources and spatial trends of PCBs in the soil and atmosphere of two typical landforms of Southern Anhui, and to evaluate air-soil exchange of PCBs. Additionally, a preliminary carcinogenic risk assessment for the people living in this region was performed based on the acquired data.

## 2. Material and methods

### 2.1. Sampling

In the current study, eleven paired air and soil samples were collected along the YR (YR 1–6) and in the mountain ranges of “Huangshan” (HM, HM 1–5) in 2013. The passive air samplers using PUF disks as sampler medium were used for the air collection. The preparation, collection, storage and transportation of air and soil samples were accomplished according to previously established methods (Wang et al., 2017a). Briefly, PUF disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm<sup>2</sup>; mass, 4.40 g; volume, 207 cm<sup>3</sup>; density, 0.0213 g cm<sup>-3</sup>) were pre-cleaned by soxhlet extraction for 48 h using acetone and hexane (1:1 v/v), and then were dried in a vacuum drying oven. Passive air sampling was performed at all the sites for about two months, the details can be found in the supplementary material (SM, Table S1). 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<sup>2</sup> plot (four in the corners and one in the center), and thoroughly mixed to form a composite sample. Soil 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

Analysis of PCBs was accomplished by use of previously published methods with some modifications (Lam et al., 2008; Chen et al., 2011; Zhang et al., 2012). Briefly, 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 (1 cm inside diameter) 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 PCBs 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 PCBs was measured and the samples were analyzed separately in selective ion monitoring (SIM). Quantification of PCBs in the soils was performed using a GC (Agilent 6890) 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. Twenty six PCB congeners (PCB 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 180, 187, 189, 195, 206 and 209) were quantified in PUF and soil samples. Soil organic matter (SOM) quantity was determined by oxidation-reduction titration with ferrous ammonium sulfate (Sultana et al., 2014).

### 2.3. Quality control

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. Most congeners detected in the field and procedural blanks were at low levels (< 0.05 ng per sample), and were at least one order of magnitude lower than those found in real samples. Method Detection limits (MDL) of air samples were defined as mean of field blank with 3 times of the standard deviations (0.04–1.25 pg m<sup>-3</sup> for different congeners). MDL of soil samples were defined as mean of procedural blank with 3 times the standard deviations (0.0036–0.047 ng g<sup>-1</sup> for different congeners). Detailed values of MDL can be found in the SM (Table S2). For the undetectable congeners in blanks, the MDLs were calculated by using 3 times of the instrumental detection limits (IDLs). IDLs of different congeners were calculated from the lowest standards, extrapolating to the corresponding amount of analyte that would generate a signal to noise ratio of 3:1. 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 blanks and recovery rates.

### 2.4. Air concentration calculations

Details about method to derive air concentrations were published in previous publications (Shoeib and Harner, 2002; Harner et al., 2004; Pozo et al., 2006, 2012). Briefly, air concentration for the target chemicals were derived from the amount accumulated in the PUF disk (ng sampler<sup>-1</sup>) divided for the effective air volume (V<sub>air</sub>, m<sup>3</sup>) (Pozo et al., 2012). For the estimation of V<sub>air</sub>, Equation (2) from (Shoeib and Harner, 2002) was used; this equation considers the full uptake profile linear phase and the plateau phase. Details of the air concentration calculations can be found in the SM (Text S1). The equation and values for the various calibration parameters can be found in previous publications (Shoeib and Harner, 2002; Pozo et al., 2006). Effective gas phase sampling rate was set as 3.5 m<sup>3</sup> day<sup>-1</sup> for the calculation (Shoeib and Harner, 2002; Pozo et al., 2006). V<sub>air</sub> are given in Tables S3 (see SM) for PCBs.

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