

Original Research

Air-Soil Exchange of Organochlorine Pesticides in a Traditionally Agricultural Region in China: Base on the Bark/Air Partitioning Model

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Abstract

Willow barks were collected for OCP analyses in the middle reach of the Huaihe River (MRHR), China. Σ OCPs in the tree barks were 16.00-50.35 ng g⁻¹ (mean: 27.60±7.48 ng g⁻¹, dry weight). HCHs were the dominant OCPs in the bark samples. The historical usage of technical HCH and DDT considerably impacted the HCHs and DDTs in the barks. Heptachlor, Aldrin, Isodrin, etc., have never been used in China, but they were frequently detected in the barks, indicating their unknown usage or atmospheric transportation from other source regions. Volumetric air concentrations of OCPs were estimated using a model for bark/air partitioning. Calculated air concentrations of Σ DDTs and Σ HCHs were 0.16±0.04 and 10.38±4.13 ng m⁻³, respectively. The results of air-soil exchange were: HCB, HCHs, and Heptachlor presented net volatilization; DDTs preferred net deposition; Endosulfan-I and Endosulfan-II might be in equilibrium or presented a weak trend of deposition; and Aldrin was in equilibrium.

Keywords: OCPs, Huaihe River, Tree bark, Passive air sampler, Air-soil exchange

Introduction

The majority of organochlorine pesticides (OCPs) are categorized as persistent organic pollutants (POPs) [1, 2].

Because most POPs are semi-volatile, their important pathway for transport is through the atmosphere [3, 4]. Soil contacts directly with the atmosphere and acts as a sink of POPs from the atmosphere [5, 6]. The air-soil exchange is regarded as a crucial process for understanding the environmental behaviors of OCPs. Most OCPs have been restricted or banned for decades, and their atmospheric concentrations have decreased

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gradually. Hence, OCPs stored in the soil may volatilize into the atmosphere, causing secondary pollution [5, 7, 8]. Moreover, OCP released back into the atmosphere by soil may undergo long-range atmospheric transport, affecting the levels and distributions of OCPs on regional/global scales. What are the current levels and air-soil exchange direction of OCPs in traditionally agricultural regions in China after decades of prohibition and restriction? Currently, is soil becoming a secondary source for OCPs instead of a sink in traditionally agricultural regions? It is challenging to comprehend these problems due to the lack of relevant research on the air-soil exchange of OCPs in agricultural regions.

Generally, research on the air-soil exchange was conducted by simultaneously sampling both the soil and the air [5, 6, 9]. Atmospheric samples can be collected using active air samplers (AASs) or passive air samplers (PASs). However, conventional active air samplers are inconvenient for fieldwork since they need pumping devices and electrical sources [10]. Similarly, PASs using artificial materials (XAD resin and polyurethane foam [PUF]) as passive sampling media still need to be deployed and recalled, and these devices are often lost (in our previous studies), especially when they were deployed in urban regions. Some people will destroy the devices out of curiosity [10-12]. Natural PASs, such as tree barks, have lower sampling costs as they do not require deployment and are easier to obtain from the paired bark and soil samples [13-15]. In addition, tree barks can reflect air concentrations over several years, while PUF or XAD-based PASs can only reflect air concentrations over several months [16]. Hence, tree barks may be more suitable for research on air-soil exchange as the soil concentrations also reflect long-term concentrations. Currently, many previous studies have already investigated the methods to extrapolate the volumetric air concentrations using tree bark concentrations [16, 17]. This study intends to use the extrapolated air concentrations from tree barks to estimate the air-soil exchange of OCPs. This work will provide some useful experience for using natural PASs in exploring the environmental behaviors of POPs.

The Huaihe River Basin, located in the transition zone between the southern and northern climates of China, drains an area of 270,000 km², serving about 190 million residents [18]. The Huaihe River Basin is adjacent to the middle-lower Yangtze Plain (MLYP), which is one of the most populous and economically developed, as well as the most POPs-contaminated regions in China [19-21]. Hostage to the prevailing southeast monsoon, POPs can migrate from the MLYP to the adjacent Huaihe River Basin through a series of geochemical behaviors, i.e., re-volatilization from the soil, atmospheric transportation, and deposition, or the so-called "grasshopper effect" [22]. Our previous study found that OCPs were widely detected in the sediments and soils of the middle reach of the Huaihe River (MRHR), including some OCPs that had never been used in China [23]. However, the atmospheric

concentrations and the air-soil exchange of OCPs in this region are still not fully understood. In December 2018, tree barks were collected in the MRHR for OCP analyses. This study aimed to 1. investigate the residual levels, distributions, and sources of OCPs in the barks from the traditionally agricultural region; 2. evaluate the reliability of tree barks as passive air samplers; 3. investigate the air-soil exchange of OCPs.

Material and Methods

Sampling and Sample Treatment

Twenty-nine tree barks were collected along the MRHR (accounting for ~80% of the total watershed area). Willow, as the dominant species in the study area, was selected as the sampling species. Tree bark can accumulate both gaseous and particle-phase POPs simultaneously from the surrounding air. About 200 g of bark were collected from each willow by the river with trunk diameters around 30 cm at a height of 1.5 m in two different directions. Lyophilized tree bark samples were extracted by ASE 350. Prior to extraction, PCB30, PCB65, PCB204, and pentachloronitrobenzene (PCNB) were added as surrogate standards. Extracts were purified using gel permeation chromatography (BIO-Beads S-X3 resin) for lipid removal and further purified using silica/alumina columns. DDTs and HCHs were commonly used pesticides in China. During the 1950s and 1980s, there were roughly 4.46 million tons of HCHs and 0.44 million tons of DDTs into the environment in China [24]. A total of 23 OCPs were targeted in this study (Table 1), including commonly-used pesticides (DDTs and HCHs), rarely-used pesticides (Chlordane and Endosulfan), and never-used pesticides (Heptachlor, Aldrin, Endrin, and Dieldrin). OCPs were analyzed using an Agilent GC-MS (7890N-5977B, equipped with a 60 m × 0.25 mm × 0.25 μm HP-5MS capillary column). Before GC-MS analysis, 2,4,5,6-tetrachloro-m-xylene was added as an internal standard.

Quality Assurance and Quality Control (QA&QC)

Procedural blanks, sampling blanks, and matrix spike tests were conducted for QA&QC. Spiked recovery rates were 80%-110%, and the standard deviations of all the targets were <10% (n = 5). Surrogate recoveries of PCB30, PCB65, PCB204, and PCNB were 88±10%, 91±10%, 106±11%, and 96±11% in tree barks. Method detection limits (MDLs) of OCPs were 0.02-0.65 ng g⁻¹. No targets were >MDLs in the sampling blanks. Concentrations of OCPs in paired soils have been reported in our previous research [23].

Table 1. Descriptive analyses of OCPs in the tree barks of the MRHR (ng g⁻¹ dry weight).

Chemicals	Mean±SD (Median)	Range	DF ^a	Chemicals	Mean±SD (Median)	Range	DF
Hexachlorobenzene (HCB)	0.47±0.14 (0.44)	0.27-0.79	100%	Heptachlor epoxide B (HCE-B)	0.59±0.84 (0.08)	ND-2.98	34%
α-HCH	6.08±2.85 (6.33)	ND ^b -11.12	97%	ΣHeptachlors (ΣHepts)	1.70±0.99 (1.53)	ND-4.92	
β-HCH	4.42±1.55 (4.19)	0.99-8.25	100%	t-chlordane (TC)	0.07±0.03 (0.07)	ND-0.21	3%
γ-HCH	2.97±1.87 (3.34)	ND-7.03	93%	c-chlordane (CC)	0.10±0.08 (0.06)	ND-0.39	21%
δ-HCH	3.50±2.12 (3.55)	ND-7.80	93%	oxy-chlordane (OC)	1.64±0.96 (1.34)	ND-3.32	86%
ΣHCHs	16.96±6.37 (16.60)	3.24-29.84		ΣChlordanes	1.80±1.00 (1.63)	ND-3.68	
o,p'-DDT	0.21±0.10 (0.24)	ND-0.41	83%	Endosulfan-I	1.31±1.30 (0.99)	ND-4.21	59%
p,p'-DDT	0.34±0.23 (0.31)	ND-1.24	86%	Endosulfan-II	1.53±1.64 (1.22)	ND-5.88	59%
o,p'-DDD	0.12±0.08 (0.05)	ND-0.33	48%	ΣEndosulfans (ΣEndos)	2.84±2.75 (2.99)	ND-9.10	
p,p'-DDD	0.12±0.08 (0.12)	ND-0.30	69%	Aldrin	0.72±0.70 (0.70)	ND-2.49	59%
o,p'-DDE	0.38±0.17 (0.36)	0.07-0.75	100%	Endrin	0.27±0.42 (0.06)	ND-1.25	24%
p,p'-DDE	0.69±0.27 (0.73)	0.27-1.47	100%	Isodrin	0.79±0.91 (0.58)	ND-4.05	62%
ΣDDTs	1.87±0.50 (1.83)	1.06-3.16		Dieldrin	0.17±0.30 (0.04)	ND-0.85	17%
Heptachlor (HC)	1.01±0.59 (0.98)	ND-2.32	93%	ΣDrins ^c	1.96±1.47 (1.71)	ND-6.48	
Heptachlor epoxide A (HCE-A)	0.10±0.15 (0.06)	ND-0.83	10%	ΣOCPs	27.60±7.48 (27.68)	16.00-50.35	

Note: a. DF means detection frequency; b. ND means concentration was <MDL; c. ΣDrins means the sum of Aldrin, Endrin, Isodrin and Dieldrin

Calculation of Contribution Rates for the Technical and Dicofol-Derived DDT

The contribution rates of the two sources (technical and dicofol-derived DDT) to the residual of DDTs in environmental compartments can be calculated based on the *o,p'*-DDT/*p,p'*-DDT ratios in technical DDT, dicofol, and environmental samples. In this study, the equation from [25] was used in the calculation:

$$x = \frac{1.25 (7 - R_s)}{6.75 (1 + R_s)}$$

where *x* is the contribution rate of technical derived DDT and *R_s* is the ratio of *o,p'*-DDT/*p,p'*-DDT in the samples. 1-*x* is the contribution rate of dicofol-derived DDT. Samples with both *o,p'*-DDT and *p,p'*-DDT < MDL were excluded during the calculation. In samples with only one DDT isomer > MDL, half

of the MDL was assigned to the concentration value of the undetected isomer during the calculation. This approximate calculation will not distort the results of source identification.

Calculation of the Fugacity Fractions (ffs)

The fugacity of each compound in soil and air was calculated as follows [26]:

$$f_s = \frac{C_s RT}{0.41 \times \emptyset_{om} \times K_{OA}}$$

$$f_a = C_g RT$$

where *C_s* and *C_g* are concentrations of OCPs in soil and air (gaseous) respectively, *R* = 8.314 Pa m³ mol⁻¹ K⁻¹, *T* is the average air temperature in Kelvin, and *∅_{om}* is the content of organic matter in the soil. *K_{OA}* is the octanol-air partition coefficient of the compound.

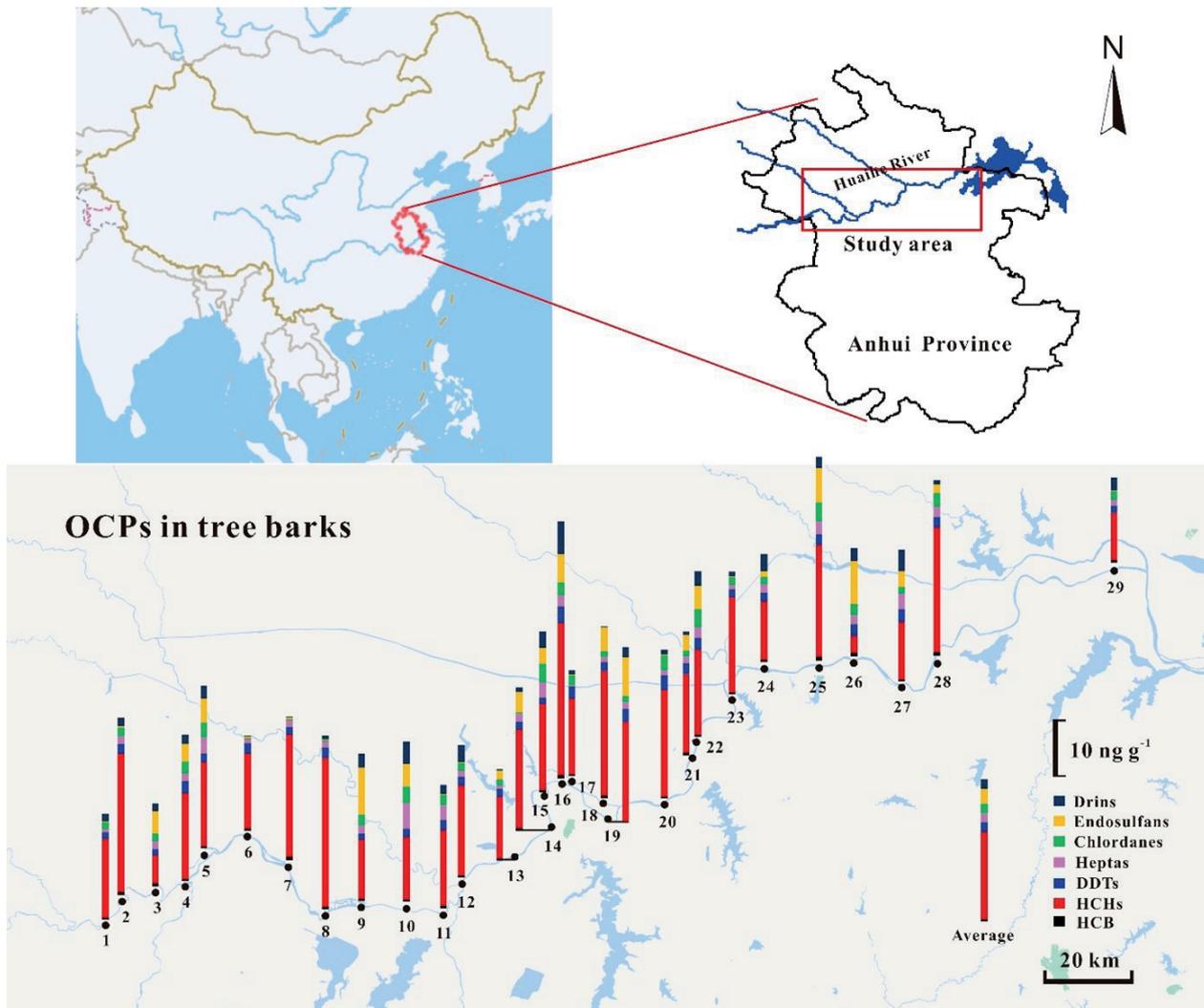


Fig. 1. Distribution of OCPs in the tree barks.

Fugacity fractions were used to infer the direction of air–soil exchange and can be calculated by dividing f_s with the sum of f_s and f_a :

$$ff = \frac{f_s}{f_s + f_a}$$

It's worth noting that the calculated air concentrations with tree barks are the sum of gas- and particle-phase concentrations. The gaseous concentrations used in the ff calculation were estimated by the proportions of gas- and particle concentrations:

$$\frac{C_p}{C_g} = B \times TSP \times K_{OA}$$

where C_g and C_p are the volume-based gas-phase and particle-phase concentrations of OCPs in the air. B is a constant ($1.5 \times 10^{-12} \text{ m}^3 \mu\text{g}^{-1}$ for OCPs). K_{OA} is the octanol air partition coefficient.

Results and Discussion

Concentrations of OCPs in the Tree Barks

The age of the willows was evaluated through their wood cores, which were collected by using an increment borer (Haglöf Sweden). The results show that all the willows are at least 20 years old. The age of the willow barks is undoubtedly less than 20 years (often several years); thus, collected barks have a similar exposure time to airborne OCPs and can reflect their atmospheric pollution over a long time scale.

Concentrations of total OCPs ($\sum\text{OCPs}$) in the barks ranged from 16.00 to 50.35 ng g^{-1} (mean = $27.60 \pm 7.48 \text{ ng g}^{-1}$) (Fig. 1). Total concentrations of different classes of OCPs ranked $\sum\text{HCHs}$ ($16.96 \pm 6.37 \text{ ng g}^{-1}$) $>$ $\sum\text{Endos}$ ($2.84 \pm 2.75 \text{ ng g}^{-1}$) $>$ $\sum\text{Drins}$ ($1.96 \pm 1.47 \text{ ng g}^{-1}$), $\sum\text{DDTs}$ ($1.87 \pm 0.50 \text{ ng g}^{-1}$), $\sum\text{Chlordanes}$ ($1.80 \pm 1.00 \text{ ng g}^{-1}$) & $\sum\text{Hepts}$ ($1.70 \pm 0.99 \text{ ng g}^{-1}$) $>$ HCB ($0.47 \pm 0.14 \text{ ng g}^{-1}$) (Table 1). Generally, HCHs accounted for $\sim 60\%$ of $\sum\text{OCPs}$ and were the most dominant OCPs in the tree barks (Fig. 1). Similar patterns were also observed

in the soils and sediments of the MRHR (accounting for >60% of \sum OCPs) [23]. The patterns were markedly different from those found in the environmental media of the adjacent MLYP, where DDTs were prevailing [7, 27-29].

Compared with previous studies carried out in China, \sum HCHs (16.96 ± 6.37 ng g⁻¹) in the barks of the MRHR were higher than those detected in tree barks of rural China (5.7 ± 12 ng g⁻¹), the upper Yellow River (median = 10 ng g⁻¹), Yunnan Province (0.10 ± 0.028 ng g⁻¹), and the Tibetan Plateau (2.7 ± 2.0 ng g⁻¹) [16, 30-32]. \sum DDTs in the barks (1.87 ± 0.50 ng g⁻¹) were lower than those detected in rural China (5.6 ± 6.5 ng g⁻¹), upper Yellow River (median = 110 ng g⁻¹), southern Jiangsu Province (6.6 ± 3.5 ng g⁻¹), and even the Tibetan Plateau (11 ± 9.3 ng g⁻¹), but were higher than those detected in Yunan Province (0.3 ± 0.42 ng g⁻¹) [16, 20, 29, 31]. Concentrations of HCB (0.47 ± 0.14 ng g⁻¹) were lower than those detected in the upper Yellow River (median = 9.9 ng g⁻¹), but were comparable with those in Southern Jiangsu Province (0.79 ± 0.34 ng g⁻¹) and Tibetan Plateau (0.32 ± 0.14 ng g⁻¹) [16, 29, 31]. Other OCPs were rarely reported in tree barks in China. This is probably because, compared with DDTs and HCHs, other OCPs were rarely used (e.g., Chlordane and Endosulfan) or never used (Drins and Heptachlor) in China [19, 33]. It's worth noting that these never or rarely-used OCPs were frequently found in different environmental compartments in China, including the atmosphere and soil, suggesting their wide distribution [7, 19, 33]. Overall, HCHs were the main OCPs in the tree barks from the MRHR, while the concentrations of DDTs, which have been extensively used historically in China, were relatively low, suggesting that HCHs should get greater attention in the study area. In addition, some pesticides that have never been used in China, including \sum Drins and \sum Hepts, have concentrations comparable to DDTs in the studied barks, indicating that the regional/global redistribution of OCPs after decades of prohibition and restriction is noteworthy.

Concentrations of OCPs in the soils of the MRHR have been reported in our previous publication [23]. \sum OCPs in the soils were 1.8 - 63 ng g⁻¹ (mean = 19 ± 12 ng g⁻¹). Similar to those in the barks, HCHs were the dominant OCPs in soils.

Compositions and Sources of OCPs

HCHs and DDTs

Despite the fact that the usage of technical DDT and HCH has been prohibited for decades in China, there are still some emissions of them recently, such as the usage of lindane (γ -HCH > 99%), dicofol, and DDT-containing antifouling paints [23]. In our previous study, α -HCH and p,p' -DDE were the predominant HCH isomers and DDT-related chemicals in both soils and sediments of the MRHR, respectively [23]. Similar results were also found in the barks (Fig. 2).

Overall, the proportions of HCHs in the barks were very similar to those in the soil samples. β -HCH has the highest K_{OA} among HCH isomers and is the most persistent. Moreover, α - and γ -HCH will be transformed into β -HCH in the environment [34]. Hence, the ratio of α/β -HCH will decrease gradually after the prohibition of technical HCH. In the barks, the mean of α/β -HCH was 1.5 ± 0.55 and was significantly lower than that in technical HCH (~ 5 - 14). Similar to those found in the soils and sediments of the MRHR, isomer ratios of HCHs in the tree barks suggested a significant influence of weathered technical HCH.

Ratios of DDTs and their degradation products were calculated to assess the contribution of weathered and fresh DDT [27]. The ratios of both (o,p' -DDD+ o,p' -DDE)/ o,p' -DDT and (p,p' -DDD+ p,p' -DDE)/ p,p' -DDT were >1 in all the tree barks, indicating a significant influence of decayed DDT. Moreover, the ratio of o,p' -DDT/ p,p' -DDT was calculated to interpret the contributions of technical DDT (0.2-0.3) and dicofol-derived DDT (7) [25]. The calculation results showed that technical DDT contributed $66 \pm 20\%$ of DDTs in the tree barks, and the contributions observed in the barks were slightly lower than those in the soils ($87 \pm 22\%$) and sediment ($74 \pm 30\%$) of the MRHR [23]. The higher contributions of dicofol-derived DDT found in the tree barks than those in sediment and soil samples might be ascribed to the heavy usage of dicofol in the adjacent area, such as the Taihu Lake region, and the facility of atmospheric transport of o,p' -DDT to the study area [35]. On the whole, DDT contamination in the MRHR was mainly derived from the historical usage of technical DDT.

Other OCPs

Except for DDTs and HCHs, other OCPs (HCB, Heptachlor, and oxy-chlordane) were also widely detected in the barks (detection frequency >86%). Furthermore, Endosulfan-I and -II, Aldrin, and Isodrin were detected in about 60% of the bark samples.

HCB was found to be a major OCP in the atmosphere of the MLYP, where pentachlorophenol (PCP) had been extensively used for schistosomiasis control [7]. However, HCB only accounted for 1.8% of \sum OCPs in the barks of the MRHR, indicating that PCP was not heavily used in this region.

Anhui Province was a hotspot of chlordane usage [36, 37]. In the tree barks of the MRHR, oxy-chlordane was found to be the major chlordane-related chemical and accounted for 91% of \sum Chlordanes (TC+CC+OC), indicating the main influence of decayed chlordane. Heptachlor has never been used as a pesticide in China; however, it can be released into the environment as an impurity of technical chlordane [37]. Concentrations of \sum Hepts (1.70 ± 0.99 ng g⁻¹) were comparable with those of \sum Chlordanes (1.80 ± 1.00 ng g⁻¹) in this study. Non-degraded heptachlor was the major form, accounting for 59% of \sum Hepts. A similar pattern was also found

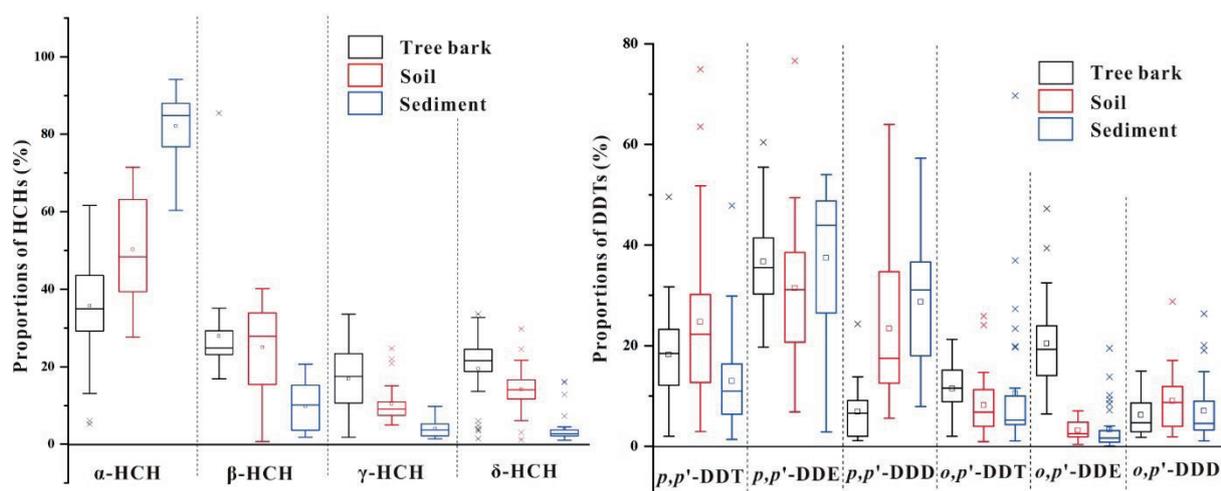


Fig. 2. The composition patterns of HCHs and DDTs in the tree barks, soils, and sediments of the MRHR (Notes: Soil and sediment data refer to our previous publication [23].)

in the soils of the MRHR [23]. This finding suggests there might be some unknown usage of heptachlor in the study area historically/recently [23].

The ratio of Endosulfan-I to -II in technical Endosulfan is 7:3 [37]. Owing to the faster degradation of Endosulfan-I than -II, the ratio of Endosulfan-I/-II will decline gradually over time. Generally, the ratio >2.3 indicates fresh input, while <2.3 suggests weathered Endosulfan. The mean value of the ratio was 1.1 ± 0.67 in the tree barks (samples with Endosulfan-I or Endosulfan-II $< \text{MDL}$ were excluded), suggesting the main influence of weathered Endosulfan.

Aldrin, Endrin, Isodrin, and Dieldrin had never been used in China before, but, they still could still be detected in some bark samples (Table 1) [37]. The concentrations of ΣDrins in the barks were similar to those of ΣDDTs , but were about an order of magnitude lower than those of ΣHCHs (Table 1). Drins in the barks might be mainly influenced by long-range atmospheric transport from other regions where these chemicals were used historically.

Volumetric Air Concentration Calculation

Considering the low cost and the convenience of tree bark sampling, air monitoring with tree bark is useful for understanding the sources as well as the pollution status of airborne POPs [14]. Quantitative or semi-quantitative estimation of volumetric air concentrations through POPs in barks is important for comparing the tree bark data with data obtained by other sampling methods [17]. A widely used bark/air partitioning model was used to estimate the volumetric air concentrations of OCPs from the tree bark concentrations [15-17]. The equations are as follows:

$$K_{\text{BA}} = \frac{C_{\text{B}}}{C_{\text{A}}}$$

$$K_{\text{BA}} = \left\{ 2 \times 10^{-6} (\text{LipCont})^{1.67} K_{\text{OA}}^{0.542} \cdot \exp \left[(-0.964 \Delta H_{\text{vap}} + 3.130) \left(\frac{1}{T} - \frac{1}{302.05} \right) \frac{10^3}{R} \right] + 210 \text{B} (\text{SSA})^{0.706} \left(\frac{P_{\text{ptn}}}{154} \right)^{-0.766} \right\} / (1 + \text{B} \times \text{TSP} \times K_{\text{OA}})$$

where K_{BA} is the coefficient of tree bark/air partitioning (dimensionless). C_{A} and C_{B} are the concentrations of OCPs in air and bark (ng m^{-3}), respectively.

Finally, the calculated K_{BA} ranged from 5.5 to 6.9. It was similar to the results of most previous studies [15-17]. Based on the K_{BA} , the volumetric air concentrations of the frequently detected OCPs were calculated (Table 2). The calculated concentrations of ΣHCHs and ΣDDTs were 10.38 ± 4.13 and $0.16 \pm 0.04 \text{ ng m}^{-3}$, respectively.

Calculated volumetric air concentrations of ΣDDTs ($0.16 \pm 0.04 \text{ ng m}^{-3}$) and Endosulfan-I ($0.31 \pm 0.31 \text{ ng m}^{-3}$) were comparable with those reported in Southern Anhui ($\Sigma \text{DDTs} = 0.24 \pm 0.16 \text{ ng m}^{-3}$, Endosulfan-I = $0.30 \pm 0.15 \text{ ng m}^{-3}$) and most other regions of China [7, 19, 38]. Air concentrations of the never-used OCPs, such as Aldrin and Heptachlor, were rarely reported in China; however, they presented considerable detection frequencies in the tree barks. The calculated volumetric air concentrations of them were about several hundred pg m^{-3} (Table 2).

Air-Soil Exchange OCPs

The fugacity fractions (ffs) were calculated using the soil and gaseous concentrations of OCPs to illuminate their gaseous air-soil exchange. It's worth noting that the air concentrations obtained from the bark/air partitioning model are the sum of gaseous and particle-phase concentrations. The gaseous concentrations used in the ffs calculation were estimated by the proportions of gas- and particle concentrations [17]. A value of

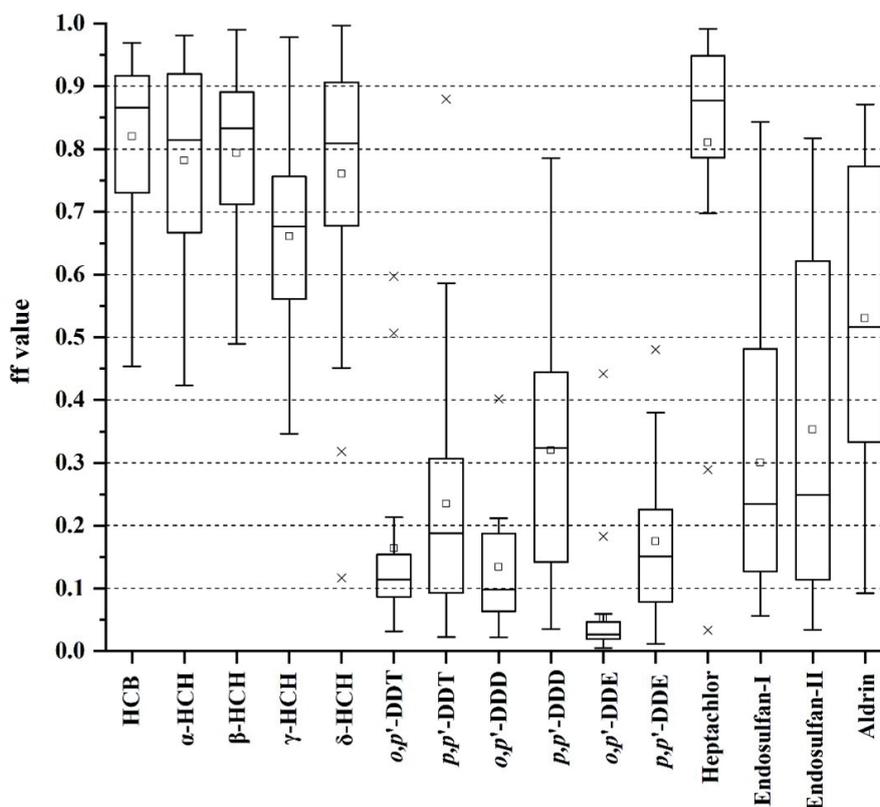
Table 2. Calculated air concentrations of OCPs (ng m⁻³)

Chemicals	Mean±SD	Range
HCB	0.90±0.26	0.52-1.52
α -HCH	2.67±1.28	ND-4.89
β -HCH	2.76±0.97	0.62-5.15
γ -HCH	1.52±0.96	ND-3.60
δ -HCH	3.43±2.08	ND-7.65
Σ HCHs	10.38±4.13	2.02-19.11
<i>o,p'</i> -DDT	0.02±0.01	ND-0.04
<i>p,p'</i> -DDT	0.03±0.02	ND-0.11
<i>o,p'</i> -DDD	0.01±0.01	ND-0.03
<i>p,p'</i> -DDD	0.01±0.01	ND-0.03
<i>o,p'</i> -DDE	0.03±0.02	0.01-0.07
<i>p,p'</i> -DDE	0.06±0.02	0.02-0.13
Σ DDTs	0.16±0.04	0.09-0.28
Heptachlor	0.58±0.34	ND-1.33
Endosulfan-I	0.31±0.31	ND-0.99
Endosulfan-II	0.36±0.39	ND-1.40
Σ Endosulfans (Σ Endos)	0.67±0.65	ND-2.15
Aldrin	0.22±0.22	ND-0.77

$ff = 0.5$ represents that the air-soil exchange of the target substance is in equilibrium, while $ff > 0.5$ and < 0.5 mean volatilization and deposition, respectively [7]. In consideration of the prediction error, ff between 0.3 and 0.7 is usually identified as equilibrium [6, 7].

The mean and median ff values of HCB, Heptachlor, α -, β - and δ -HCH were > 0.7 or even > 0.8 (Fig. 3). Therefore, these chemicals had a strong tendency to volatilize from the soil to the air, and soil was a "secondary source". This finding was partly attributed to their relatively low K_{OA} ($\log K_{OA} < 8$). However, the ff values of γ -HCH were obviously lower than those of other isomers (Fig. 3), while the K_{OA} values of all the HCH isomers were similar. Therefore, the air-soil exchange of a specific chemical was also influenced by the residual amounts in the environment and the use history. As discussed above, HCHs in the study area were significantly influenced by weathered technical HCH, and the usage of lindane (γ -HCH $> 99\%$) might be rare (Fig. 2). Hence, the residue of γ -HCH in soil was lower, and air-soil exchange is closer to equilibrium. For HCB and Heptachlor, a strong tendency toward volatilization indicated that there were still considerable residues in the soil. Again, the result suggested there might be historical/recent usage of Heptachlor in the study area.

Except for *p,p'*-DDD, the median ff values of all the DDT-related chemicals were < 0.2 (Fig. 3). The median ff value of *p,p'*-DDD was < 0.4 . Thus, all the DDTs presented a strong tendency for net deposition from the

Fig. 3. The ff values of specific OCPs.

air to the soil, and the soil was a “sink” for them. These results suggested there were ceaseless atmospheric sources of these chemicals in the study area and adjacent regions.

The median f values of Endosulfan-I and Endosulfan-II were about 0.2-0.3, and the first quartiles were about 0.4-0.6 (Fig. 3). The air-soil exchange of this chemical might be in equilibrium or present a weak trend of deposition. The f values of Aldrin were generally in the equilibrium range. There might be no continuous atmospheric input from them. For Aldrin, which was never used in China, historical atmospheric transport and subsequent deposition might be the primary source.

To sum up, the results of air-soil exchange indicated that the soil in the MRHR has transformed into a secondary source for several pesticides with relatively low K_{OA} , including HCB, Heptachlor, α -, β - and δ -HCH. Furthermore, this study provides some practical experience for employing tree barks in investigating the air-soil exchange of POPs based on the bark/air partitioning model.

Uncertainty Analysis

The present study revealed the residual levels and possible sources of OCPs in tree barks, calculated the OCPs concentrations in air based on the bark/air partitioning model, and clarified the current situation of air-soil exchange of OCPs in the studied traditionally agricultural area studied. Tree bark has been proven to be an effective nature passive sampler. The bark/air partitioning model employed in this study was established by Zhao et al. to calculate the volumetric air concentrations of POPs from tree bark concentrations [17]. This model has been demonstrated to effectively reflect the atmospheric pollution level of POPs, including OCPs, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and short-chain chlorinated paraffin, etc., at regional and global scales [15, 39, 40]. A recent study used the bark/air partitioning model to calculate theoretical air concentrations and successfully predicted the air-soil exchange of short- and medium-chain chlorinated paraffins in the Yangtze River Delta, China [40]. Although the uncertainty of calculating air-soil exchange using the bark/air partitioning model is inevitable, it is still informative to use this model to predict the air-soil exchange of POPs.

Conclusions

OCPs were widely detected in the willow tree barks collected in the MRHR, China, and HCHs were the dominant OCPs. DDTs and HCHs were significantly influenced by the previous usage of technical DDT and HCH. Heptachlor, Aldrin, Endrin, Isodrin, and Dieldrin, which were never used in China, were also frequently detected in the barks, indicating their unknown usage or atmospheric transportation from

other source regions. The air-soil exchange of OCPs was evaluated using the fugacity model. The results indicated that soil was a “secondary source” for atmospheric HCB, HCHs, and Heptachlor; while the soil was a “sink” for DDTs. Other targets might present a weak trend of deposition or be in equilibrium.

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Conflict of Interest

The authors declare no conflict of interest.

References

1. WU X.G., LAM J.C., XIA C.H., KANG H., SUN L.G., XIE Z.Q., LAM P.K. Atmospheric HCH concentrations over the marine boundary layer from Shanghai, China to the Arctic Ocean: Role of human activity and climate change. *Environmental Science & Technology*. **44** (22), 8422, **2010**.
2. ZHENG Q., LI J., WANG Y., LIN T., XU Y., ZHONG G.C., BING H.J., LUO C.L., ZHANG G. Levels and enantiomeric signatures of organochlorine pesticides in Chinese forest soils: Implications for sources and environmental behavior. *Environmental Pollution*. **262**, 114139, **2020**.
3. BIDDLEMAN T.F., Atmospheric processes. *Environmental Science & Technology*. **22** (4), 361, **1988**.
4. WU X.G., CHEN A.F., YUAN Z.J., KANG H., XIE Z.Q. Atmospheric organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in the Antarctic marginal seas: Distribution, sources and transportation. *Chemosphere*. **258**, 127359, **2020**.
5. CUI S., FU Q., LI Y.F., MA J.M., TIAN C.G., LIU L.Y., ZHANG L.M. Modeling the air-soil exchange, secondary emissions and residues in soil of polychlorinated biphenyls in China. *Scientific Reports*. **7** (1), 1, **2017**.
6. WU X.G., CHEN A.F., WANG S.Q., ZOU J.L., LIU H.Y., XIAO S. Polychlorinated biphenyls in two typical landforms of Southern Anhui province, China: Sources, air-soil exchange, and risk assessment. *Atmospheric Pollution Research*. **9** (3), 569, **2018**.
7. WANG S.Q., WU X.G., ZOU J.L., CHEN A.F., TAO X.C., CAO Y.H. Survey of organochlorine pesticides in the atmosphere and soil of two typical landforms of Southern Anhui Province, China: Sources and air-soil exchange. *Atmospheric Pollution Research*. **8** (4), 619, **2017**.
8. WANG Y., LI Z.Y., TAN F., XU Y., ZHAO H.X., CHEN J.W. Occurrence and air-soil exchange of organophosphate flame retardants in the air and soil of Dalian, China. *Environmental Pollution*. **265**, 114850, **2020**.
9. QU C.K., ALBANESE S., LI J.J., CICHELLA D., ZUZOLO D., HOPE D., CERINO P., PIZZOLANTE A.,

- DOHERTY A.L., LIMA A., VIVO B.D. Organochlorine pesticides in the soils from Benevento provincial territory, southern Italy: Spatial distribution, air-soil exchange, and implications for environmental health. *Science of The Total Environment*. **674**, 159, **2019**.
10. SHOEIB M., HARNER T. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environmental Science & Technology*. **36** (19), 4142, **2002**.
 11. POZO K., HARNER T., WANIA F., MUIR D.C., JONES K.C., BARRIE L.A. Toward a global network for persistent organic pollutants in air: results from the GAPS study. *Environmental Science & Technology*. **40** (16), 4867, **2006**.
 12. WANG C.F., WANG X.P., REN J., GONG P., YAO T.D. Using a passive air sampler to monitor air-soil exchange of organochlorine pesticides in the pasture of the central Tibetan Plateau. *Science of The Total Environment*. **580**, 958, **2017**.
 13. OISHI Y. Comparison of moss and pine needles as bioindicators of transboundary polycyclic aromatic hydrocarbon pollution in central Japan. *Environmental Pollution*. **234**, 330, **2018**.
 14. PEVERLY A.A., SALAMOVA A., HITES R.A. Locating POPs sources with tree bark. *ACS Publications*. **49**, 13743, **2015**.
 15. WANG X.Y., GONG P., WANG C.F., WANG X.P., POKHREL B., DOTEL J. Spatial distribution patterns and human exposure risks of polycyclic aromatic hydrocarbons, organochlorine pesticides and polychlorinated biphenyls in Nepal using tree bark as a passive air sampler. *Environmental Research*. **186**, 109510, **2020**.
 16. HE C., JIN J., LI G.Y., WANG Y. Exchange of organohalogen compounds between air and tree bark in the Yellow River region. *Chemosphere*. **153**, 478, **2016**.
 17. ZHAO Y.L., YANG L.M., WANG Q.Q. Modeling persistent organic pollutant (POP) partitioning between tree bark and air and its application to spatial monitoring of atmospheric POPs in mainland China. *Environmental Science & Technology*. **42** (16), 6046, **2008**.
 18. YU M.X., LIU X.L., LI Q.F. Responses of meteorological drought-hydrological drought propagation to watershed scales in the upper Huaihe River basin, China. *Environmental Science and Pollution Research*. **27** (15), 17561, **2020**.
 19. LIU X., ZHANG G., LI J., YU L.L., XU Y., LI X.D., KOBARA Y., JONES K.C. Seasonal patterns and current sources of DDTs, chlordanes, hexachlorobenzene, and endosulfan in the atmosphere of 37 Chinese cities. *Environmental Science & Technology*. **43** (5), 1316, **2009**.
 20. NIU L.L., XU C., ZHANG C.L., ZHOU Y.T., ZHU S.Y., LIU W.P. Spatial distributions and enantiomeric signatures of DDT and its metabolites in tree bark from agricultural regions across China. *Environmental Pollution*. **229**, 111, **2017**.
 21. WU X.G., LIU H.Y., YUAN Z.J., WANG S.Q., CHEN A.F., HE B.B. Concentration, exchange and source identification of polycyclic aromatic hydrocarbons in soil, air and tree bark from the Middle-Lower Yangtze Plain, China. *Atmospheric Pollution Research*. **10** (4), 1276, **2019**.
 22. WANIA F., MACKAY D. Peer reviewed: tracking the distribution of persistent organic pollutants. *Environmental Science & Technology*. **30** (9), 390A, **1996**.
 23. WANG S.S., WANG Q., YUAN Z.J., WU X.G. Organochlorine pesticides in riparian soils and sediments of the middle reach of the Huaihe River: A traditional agricultural area in China. *Chemosphere*. **296**, 134020, **2022**.
 24. CAO H.Y., LIANG T., TAO S., ZHANG C.S. Simulating the temporal changes of OCP pollution in Hangzhou, China. *Chemosphere*. **67** (7), 1335, **2007**.
 25. ZHANG C., LIU L., MA Y., LI F. S. Using isomeric and metabolic ratios of DDT to identify the sources and fate of DDT in Chinese agricultural topsoil. *Environmental Science & Technology*. **52** (4), 1990, **2018**.
 26. HARNER T., BIDLEMAN T.F., JANTUNEN L.M., MACKAY D. Soil – air exchange model of persistent pesticides in the United States cotton belt. *Environmental Toxicology and Chemistry: An International Journal*. **20** (7), 1612, **2001**.
 27. WU X.G., WANG Q., YUAN Z.J., HE B.B., LIU H.Q., WANG S.S. Concentrations, Sources and Ecological Risk of Organochlorine Pesticides in Urban Stream Sediments of Suzhou Industrial Park, China. *Soil and Sediment Contamination: An International Journal*. **31** (5), 655, **2022**.
 28. ZHANG L.F., DONG L., YANG W.L., ZHOU L., SHI S.X., ZHANG X.L., NIU S., LI L.L., WU Z.X., HUANG Y.R. Passive air sampling of organochlorine pesticides and polychlorinated biphenyls in the Yangtze River Delta, China: concentrations, distributions, and cancer risk assessment. *Environmental Pollution*. **181**, 159, **2013**.
 29. ZHOU L., ZHANG X.L., YANG W.L., LI L.L., SHI S.X., ZHANG L.F., DONG L., HUANG, Y.R. Levels and possible sources of organochlorine pesticides (OCPs) in camphor (*Cinnamomum camphora*) tree bark from Southern Jiangsu, China. *Environmental Science*. **35** (3), 1159, **2014** [In Chinese].
 30. NIU L.L., XU C., XU Y., ZHANG C.L., LIU W.P. Hexachlorocyclohexanes in tree bark across Chinese agricultural regions: spatial distribution and enantiomeric signatures. *Environmental Science & Technology*. **48** (20), 12031, **2014**.
 31. YANG R.Q., ZHANG S.J., LI A., JIANG G.B., JING C.Y. Altitudinal and spatial signature of persistent organic pollutants in soil, lichen, conifer needles, and bark of the southeast Tibetan Plateau: implications for sources and environmental cycling. *Environmental Science & Technology*. **47** (22), 12736, **2013**.
 32. YUAN H.D., JIN J., BAI Y., LI Q.X., WANG Y., WANG Q.H. Organochlorine pesticides in tree bark and human hair in Yunnan Province, China: Concentrations, distributions and exposure pathway. *Science of The Total Environment*. **580**, 1027, **2017**.
 33. NIU L.L., XU C., ZHU S.Y., LIU W.P. Residue patterns of currently, historically and never-used organochlorine pesticides in agricultural soils across China and associated health risks. *Environmental Pollution*. **219**, 315, **2016**.
 34. WALKER K., VALLERO D.A., LEWIS R.G. Factors influencing the distribution of lindane and other hexachlorocyclohexanes in the environment. *Environmental Science & Technology*. **33** (24), 4373, **1999**.
 35. QIU X.H., ZHU T., WANG F., HU J.X. Air-water gas exchange of organochlorine pesticides in Taihu Lake, China. *Environmental Science & Technology*. **42** (6), 1928, **2008**.
 36. WANG Q., ZHAO L.J., FANG X.K., XU J.H., LI Y.F., SHI Y.H., HU J.X. Gridded usage inventories of chlordane in

- China. *Frontiers of Environmental Science & Engineering*. **7** (1), 10, **2013**.
37. ZHANG A.P., FANG L., WANG J.L., LIU W.P., YUAN H.J., JANTUNEN L., LI Y.F. Residues of currently and never used organochlorine pesticides in agricultural soils from Zhejiang Province, China. *Journal of agricultural and food chemistry*. **60** (12), 2982, **2012**.
38. JAWARD F.M., ZHANG G., NAM J.J., SWEETMAN A.J., OBBARD J.P., KOBARA Y., JONES K.C. Passive air sampling of polychlorinated biphenyls, organochlorine compounds, and polybrominated diphenyl ethers across Asia. *Environmental Science & Technology*. **39** (22), 8638, **2005**.
39. GUÉGUEN F., STILLE P., MILLET M. Air quality assessment by tree bark biomonitoring in urban, industrial and rural environments of the Rhine Valley: PCDD/Fs, PCBs and trace metal evidence. *Chemosphere*. **85** (2), 195, **2011**.
40. ZHOU Q., XU C.Y., SHEN C.S., LI F., LIU S.R., AAMIR M. Congener profiles, air-soil exchange, and potential risks of short-and medium-chain chlorinated paraffins in demonstration zone of Yangtze River Delta. *Atmospheric Pollution Research*. **14** (1), 101639, **2023**.