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Levels and enantiomeric signatures of organochlorine pesticides in Chinese forest soils: Implications for sources and environmental behavior☆

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ABSTRACT

We investigated the levels and distributions of organochlorine pesticides (OCPs) in 159 background soil samples collected from 30 forested mountain sites across China. The sum of DDT was the most abundant OCP, with the concentrations of 0.197–207 ng/g and 0.033–122 ng/g in the O-horizon and A-horizon, respectively. High concentrations of OCPs usually occur near agricultural regions or high consumption areas. The spatial distribution was mainly influenced by the emission sources and soil total organic contents (TOC). The chiral compounds were generally nonracemic in the soils and showed preferential degradation of (−) *o,p*′- dichlorodiphenyltrichloroethane, (+) trans-chlordane, and (−) cis-chlordane in both the O- and A-horizons. The enantiomeric fraction (EF) distributions of chiral OCPs displayed no differences across the forest sites in the O-horizon or the A-horizon. Comparing the deviation of EFs from racemic (DEVrac = absolute value of 0.500 - EF) with environmental parameters, we found that DEVrac of cis-chlordane demonstrated a strong positive correlation with TOC ($p < 0.05$) and the C/N ratio ($p < 0.01$). This relationship suggests that these factors could affect the microbial activity and significantly impact the extent of enantioselective degradation of chiral compounds in the soils. Fresh and historical applications of DDT and historical chlordane and endosulfan uses may be prominent sources of OCP accumulation in Chinese forest soils.

1. Introduction

Organochlorine pesticides (OCPs) are classified as persistent organic pollutants (POPs), due to their persistence, toxicity, bioaccumulation, and long-range atmospheric transport (LRAT) potential (Huang et al., 2013; Huang et al., 2017; Luis Sanchez-Osorio et al., 2017; Mahmoud et al., 2016; Yu et al., 2015). Although their production and application have been prohibited or limited in a growing number of countries, these compounds are still detected as substantial residue in various environmental matrices, such as soil, air, water, sediment, dust, and biota (Bidleman et al., 2012; Lu and Liu, 2015).

Several OCPs, such as trans- and cis-chlordane (TC and CC) and *o,p*′-dichlorodiphenyltrichloroethane (*o,p*′-DDT), are chiral chemicals comprised of two enantiomers. These chiral chemicals are racemic in technical products (Wiberg et al., 2001). The enantiomers have identical physicochemical properties (e.g., partition coefficients, water solubility, and vapor pressures in the soil, water, and air), and the enantiomer proportions do not change with transport or abiotic reactions (Bidleman et al., 2012; Huang et al., 2013; Kurt-Karakus et al., 2005; Li et al., 2006). However, because of the different molecular configurations of the enantiomers, they

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often have different toxicological properties and may undergo biodegradation at different rates in the environment (Zhou et al., 2014). The enantioselective degradation of chiral chemicals can enrich one enantiomer and results in nonracemic residues (Bidleman and Falconer, 1999). Therefore, the enantiomer proportion is a valuable marker of biological activity and can offer a particular advantage for tracing sources and fate pathways (Genualdi et al., 2011; Kurt-Karakus et al., 2005).

Forests play a pivotal role in the global fate and distribution of POPs due to the forest canopy effect. With canopy enhanced atmospheric depositions, forest soils can act as a principal receptor and reservoir for POPs because of their strong affinity to soil organic carbon (OC) content (Xu et al., 2015; Zheng et al., 2015). Although the fate of OCPs in soils has been widely investigated, with a considerable amount of research conducted on OCPs in Chinese soils, most of the research has focused on agriculture or local background soils (Luo et al., 2019; Sun et al., 2009; Wong et al., 2012; Zhang et al., 2011). The distribution patterns and environmental behavior of OCPs and their chiral chemicals may vary with land-use types and research regions. Nevertheless, there is minimal information on OCPs in Chinese forest soils, especially for the national-scale dataset.

China covers 134 million hectares of forested land, including boreal, temperate, subtropical, and tropical biomes (Fang et al., 2001). The contaminant levels, distributions, and enantiomeric signatures in vast geographic-scale forest soils could reflect the influence of emission sources, the LRAT potential of the contaminants, and environmental variability (Meijer et al., 2003; Schuster et al., 2011). Studying the chemical distribution patterns and enantiomeric signatures in Chinese forest soils is an effective means to assess the sources, environmental processes, and fates in China, which is a substantial region of OCP contamination and distribution worldwide (Jiang et al., 1999; Meijer et al., 2003; Zheng et al., 2015).

In this study, 30 mountain sites across China were chosen to i) identify the levels, spatial distributions, and enantiomeric fractions of the selected OCPs in the background forest soils, ii) estimate possible influences of environmental variables on contaminant distribution, and iii) assess the environmental sources and pathways of the pollutants.

2. Experimental section

2.1. Monitoring design

This study assessed 30 mountain sites throughout the country (shown in Figure S1). In all, 82 locations and 159 forest-soil samples (including 77 O-horizon and 82 A-horizon samples) were collected from May 2012 to March 2013. Details on the characteristics of sampling locations are shown in Table S1 and our previous study (Zheng et al., 2014).

2.2. Soil sampling

Three trenches (approximately 5 m apart) were dug at each sampling site. The soil layers were categorized according to color and vertical structures. The samples were collected from each trench separately, stored, and transported immediately to the laboratory. They were kept at −20 °C until further analysis. The sampling processes are described in our previous study (Zheng et al., 2014).

2.3. Chemical analysis

After sieving to remove the particles larger than 2 mm, each soil sample was uniformly comprised of three subsamples. Thirteen compounds (α-endosulfan, β-endosulfan, HCB, Mirex, *o,p'*-DDT, *pp'*-DDT, *o,p'*-DDD, *pp'*-DDD, *o,p'*-DDE, *pp'*-DDE, CC, TC, and Heptachlor) were detected in this study. The sample preparation, instrumental analysis, and TOC analysis have been described in previous studies (Huang et al., 2013; Mai et al., 2005; Zheng et al., 2014), which are also reported in the supplementary information (SI).

2.4. QA/QC

In all, 20 repeated samples and 10 procedural blanks were analyzed to assess the contamination and stability. Each soil sample was spiked with 20 ng TCmX, PCB 198, and PCB209 as surrogates, and the recoveries were 62% ± 7.6%, 82% ± 4.9%, and 85% ± 3.7%, respectively. The reported results in this study are expressed on a dry weight basis (ng/g dry wt) and not corrected for recovery values.

For the chiral analysis, the racemic standards were repeatedly injected to calculate the reproducibility of the enantiomeric fraction (EF) measurements. EF is defined as $(+)/[(+)+(-)]$), and the $(+)$ and $(-)$ represent the peak areas of the $(+)$ and $(-)$ enantiomers, respectively. An EF of 0.5 indicates a racemic composition. If the EF for a particular standard fell within the 95% confidence interval, the substances were considered to be racemic. The average EF values of the standards were 0.503 ± 0.004 ($n = 25$) for TC, 0.501 ± 0.003 ($n = 25$) for CC, and 0.503 ± 0.006 ($n = 25$) for *o,p'*-DDT. More details can be found in the supplementary information (SI).

3. Results and discussion

3.1. Summary of target OCPs results

All thirteen target compounds were analyzed in each sample, and the concentrations in the two layers are individually presented in Table S2. The concentrations of OCPs in the O-horizon were generally higher (by an average factor of 2.31) than those detected in the A-horizon, probably due to the higher atmospheric deposition or organic matter content of the superficial O-horizon.

The $\sum_6$DDT (the sum of all isomers of DDE, DDD, and DDT) demonstrated the highest concentrations in this study. *pp'*-DDT was the dominant compound in most of the samples, followed by *p,p'*-DDE in both the O- and A-horizons. The concentrations of $\sum_6$DDT in the O- and A-horizon ranged from 0.197 to 207 ng/g (mean 9.47 ng/g) and 0.033−122 ng/g (mean 5.83 ng/g), respectively. These concentrations are significantly lower than those reported in Chinese agricultural soils from Hubei Province (nd−1198 ng/g) (Zhou et al., 2013) and Guangdong Province (mean 24.7 ng/g) (Li et al., 2006), German forest soils (mean 146 ng/g) (Aichner et al., 2013), Mexican soils (n.d.−360 ng/g) (Wong et al., 2010), and Czech mountainous forest soils (8.8−1908.3 ng/g) (Holoubek et al., 2009). Additionally, the measured concentrations are relatively higher than the values measured in other background soils, including Spain and the UK (0.02−4.73 ng/g with a mean value of 0.79 ng/g) (Cabrerizo et al., 2011) and Austria (n.d.−22.0 ng/g) (Weiss et al., 2000), which may be due to the higher consumption of DDTs in China (Li et al., 2006).

The mean concentrations of HCB in the O- and A-horizon samples were 0.712 ng/g (0.047−6.12 ng/g) and 0.203 ng/g (0.022−0.748 ng/g), respectively. The values are lower than those presented in Germany forest soils (mean 4 ng/g) (Aichner et al., 2013) and Czech mountainous forest soils (mean 1.5 ng/g) (Holoubek et al., 2009), yet comparable to those observed in the UK and Norway background soils (0.01−5.2 ng/g) (Meijer et al., 2003) and Sweden boreal soils (0.6 ng/g) (Bergknut et al., 2010).

TC, CC, and heptachlor are the primary components of technical chlordane (Dearth and Hites, 1991), and TC and CC are the most abundant chlordane isomers in the samples. The mean concentrations of TC and CC were 0.072 ng/g (0.008−0.215 ng/g) and 0.115 ng/g (0.017−0.333 ng/g) in the O-horizon and 0.035 ng/g (0.012−0.153 ng/g) and 0.058 ng/g (n.d.−0.239 ng/g) in the A-horizon, respectively. These concentrations were consistent with previous data from the UK archived soils (Meijer et al., 2001), western Canadian background soils (Daly et al., 2007b), and the eastern edge of the Tibetan Plateau (Liu et al., 2015), but higher than the values reported in the Peruvian Andes and Italian Alps (Tremolada et al., 2008). The concentrations of heptachlor were lower than TC and CC, ranging from n.d. to 0.141 ng/g (mean 0.026 ng/g) and n.d. to 0.091 ng/g (mean 0.017 ng/g) in the O- and A-horizon, respectively.

The levels of endosulfan isomers and mirex were generally low in Chinese forest soils. The concentrations of α-endosulfan and β-endosulfan ranged from n.d. to 0.160 ng/g (mean 0.019 ng/g) and n.d. to 0.097 ng/g (mean 0.021 ng/g) in the O-horizon and n.d. to 0.039 ng/g (mean 0.009 ng/g) and n.d. to 0.185 ng/g (mean 0.011 ng/g) in the A-horizon, respectively. The mean concentrations of mirex in the O- and A-horizon samples were 0.011 ng/g (0.001−0.029 ng/g) and 0.005 ng/g (n.d.−0.019 ng/g), respectively. The concentrations of these compounds were lower than those reported in western Canada (Daly et al., 2007b) and the Tibetan Plateau (Chen et al., 2017).

Samples with detectable amounts of chiral compounds were also analyzed in this study. The wide range of EFs is presented in Table 1, and the data of the individual chiral OCPs for the two layers are shown in Table S3. The EFs of chiral compounds in the majority of soil samples were nonracemic, and the racemic proportion for each chiral OCP was less than 5%.

The EF of *o,p*′-DDT varied from 0.293 to 0.849 and 0.261 to 0.810 in the O-horizon and A-horizon, respectively. Preferential depletion of (−) enantiomer (EF > 0.5) was obtained in the O-horizon, while in the A-horizon, the residues of chiral *o,p*’-DDT ((+) (45.1%) and (−) (50%) depletion) were almost equally divided. The conditions in the A-horizon were in agreement with those reported in the Pearl River Delta soils (Li et al., 2006) and global background soils (Kurt-Karakus et al., 2005). The difference between the two soil layers could be attributed to the different soil properties, which are believed to be related to the activity of microbial community and the degradation preferences of chiral compounds (Bosch et al., 2015; Zhang et al., 2011).

For TC, the EFs ranged from 0.312 to 0.794 and 0.331 to 0.699 in the O- and A-horizons, while the EFs of CC ranged from 0.287 to 0.821 and 0.319 to 0.787 in the O- and A-horizons, respectively. The distribution of the EFs in these forest soils indicated that (+) TC and (−) CC were preferentially degraded in both the O- and A-horizons, which is consistent with the observations of the soils in Costa Rica (Daly et al., 2007a), Alabama (Wiberg et al., 2001), and Mexico (Luis Sanchez-Osorio et al., 2017). The (−) enantiomer excess for TC and the (+) enantiomer excess for CC were more than 75% and 60% in both layers, respectively.

3.2. Spatial distribution

Significant spatial variations in the OCP concentrations were found in this study. For example, the highest/lowest value of $\sum_6$DDT was up to 1050. On the contrary, possibly because of lower usage amounts or policy restrictions, the spatial variations of technical chlordane and mirex were relatively low. Fig. 1 shows the average concentrations of selected compounds in the O-horizon. Overall, substantial levels of OCPs were mostly observed in the large agricultural provinces or high pesticide consumption areas. For instance, the highest average concentrations of HCB and endosulfan isomers were displayed at site 8 in Hebei Province. This area is a common pesticide-use area and is also well known as a leading grain-producing area in China with plentiful pesticide applications historically (Wang et al., 2014). Furthermore, the DDT isomers revealed peak concentrations at site 10, located in Shandong Province. This region is densely populated with considerable agricultural and industrial activities, and DDT could be widely used on the cropland in this area for controlling insects (Xu et al., 2007). Mirex showed the highest average concentration at site 22 in Jiangxi Province, which previously had the most mirex consumption among all Chinese provinces (Wang et al., 2010).

In spite of the considerable variability in OCP levels across the 30 mountain sites, the spatial distributions of DDT isomers, endosulfan isomers, and chlordane compounds were notably consistent in each horizon. Significant correlations among the soil concentrations of isomers were found in both the O- and A-horizons (Table S4). Moreover, nearly all the spatial trends of OCP compounds (except for β-endosulfan) between the two layers were relatively uniform (Table S5). The results showed that emission sources could likely influence the distribution of OCPs, even at a sub-regional level. Additionally, although technical chlordane has been banned for many years and some provinces of China have never used any chlordane previously (Wang et al., 2013), chlordane compounds were still detected ubiquitously in the background forest soils. Therefore, the long-range atmospheric transport potential and relative persistence of chlordane may have caused its distribution in the forest soils (Huang et al., 2013; Niu et al., 2016).

The wide range of EFs presents a variety of enantioselective degradation rates and mechanisms in Chinese forest soils, but the spatial distribution of chiral OCPs have no evident trends across the forest sites in either the O-horizon or the A-horizon. However, the spatial distributions of chiral *o,p*’-DDT ($r = 0.487$, $p < 0.01$) and CC ($r = 0.429$, $p < 0.01$) were respectively consistent between the O- and A-horizons, suggesting the orientations and extent of enantioselective depletion were roughly the same in the similar environment.

The soil samples with the highest concentrations of *o,p*’-DDT showed EFs close to 0.5 in this study (0.496 in the O-horizon and 0.502 in the A-horizon), but no other samples with relatively high concentrations of the target compounds displayed the racemic patterns. In contrast, there were some soils with low OCP levels showing a racemic pattern. This result is in agreement with the results reported in Greenland and mainland Europe

Table 1
Summary Statistics for enantiomeric fractions of chiral OCPs in Chinese Forest Soil Samples.

	O-horizon			A-horizon		
chiral compounds	TC	CC	*o,p*’-DDT	TC	CC	*o,p*’-DDT
EF	0.312−0.694	0.287−0.821	0.293−0.849	0.331−0.699	0.319−0.787	0.261−0.810
mean	0.441	0.529	0.566	0.446	0.515	0.521
std dev	0.091	0.105	0.139	0.088	0.130	0.138
N	72	73	74	75	74	79

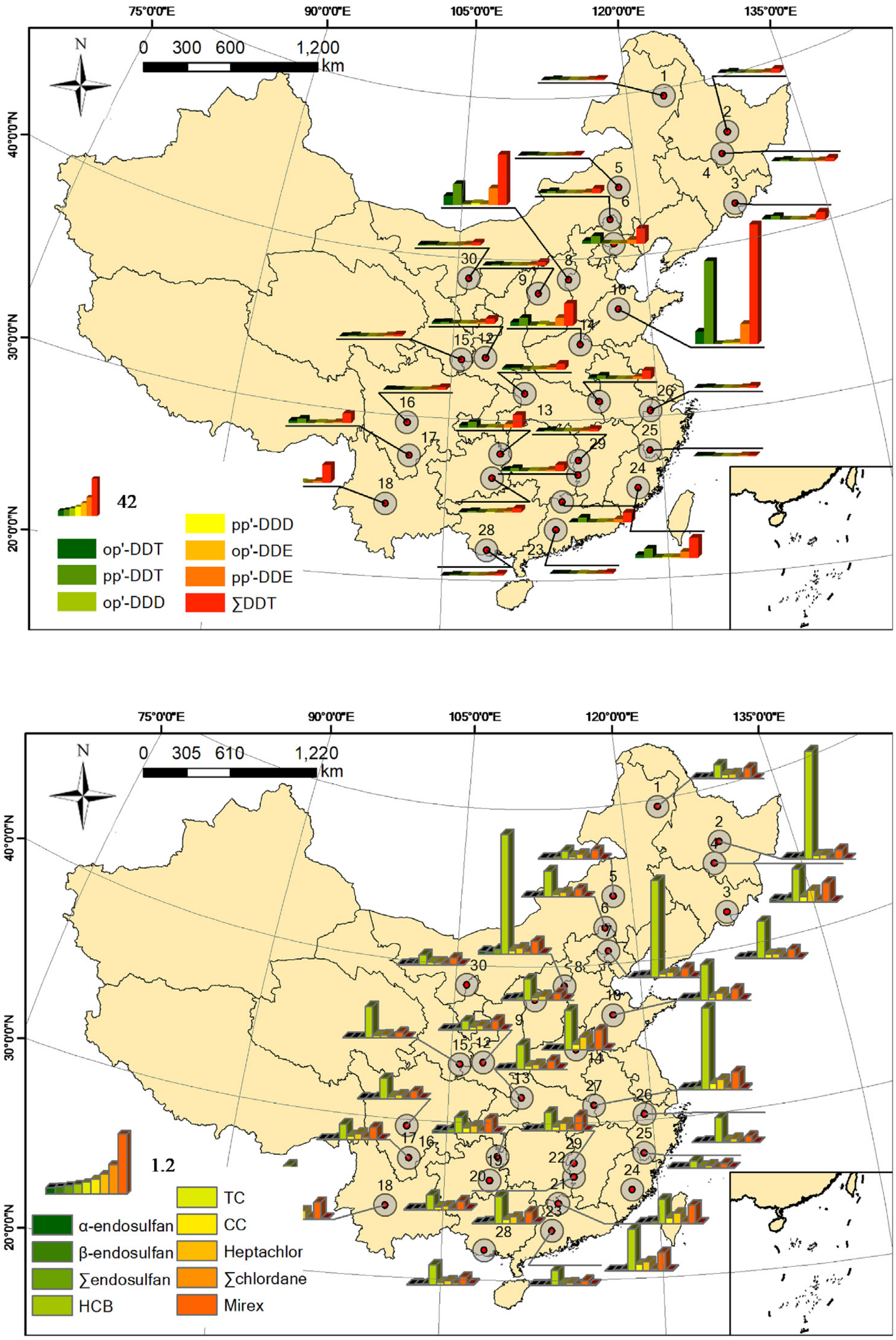

Fig. 1. Spatial distribution of target OCPs in the O-horizon. (ng/g dry wt).

(Kurt-Karakus et al., 2005), Canada and the UK (Wong et al., 2009), and Spain (Bosch et al., 2015). Moreover, no significant correlations were found between deviation of EFs from racemic (DEVrac = absolute value of 0.500 - EF) of chiral compounds and their concentrations in either the O-horizon or the A-horizon. Therefore, it is notable that even though the EF values could be used to estimate the age and degradation of chiral pesticides to some extent, the distribution of the EFs for the large-area soil samples was minimally associated with the OCP concentrations.

3.3. *Influence of environmental parameters*

It is believed that the distribution of persistent hydrophobic contaminants and the enantioselective degradation of chiral compounds could be affected by the environmental parameters (Tian et al., 2011; Xu et al., 2013; Zhang et al., 2011). Linear correlations were performed to explore the relationships of environmental factors with OCP concentrations and DEVrac of chiral OCPs. Some of the environmental variables and OCP concentrations were log-transformed to reduce the scatter and allow linear fits.

The relationships between OCP concentrations and TOC were analyzed individually for the O- and A-horizons. As expected, the majority of OCP compounds (total DDT, chlordane, α-endosulfan isomers, HCB, and mirex) had significantly positive correlations with TOC in both the O- and A-horizons (Fig. 2 and Table S6). These findings are in accordance with the observations from Greenland and mainland Europe (Meijer et al., 2003) and the Southeast Tibetan Plateau (Yang et al., 2013), which illustrate that TOC is a pivotal factor that controls the distribution of these compounds in soils.

However, comparing the OCP concentrations with other environmental factors (such as latitude, temperature, and precipitation), minimal significant correlations could be observed. The temperature had significantly negative correlations with α-

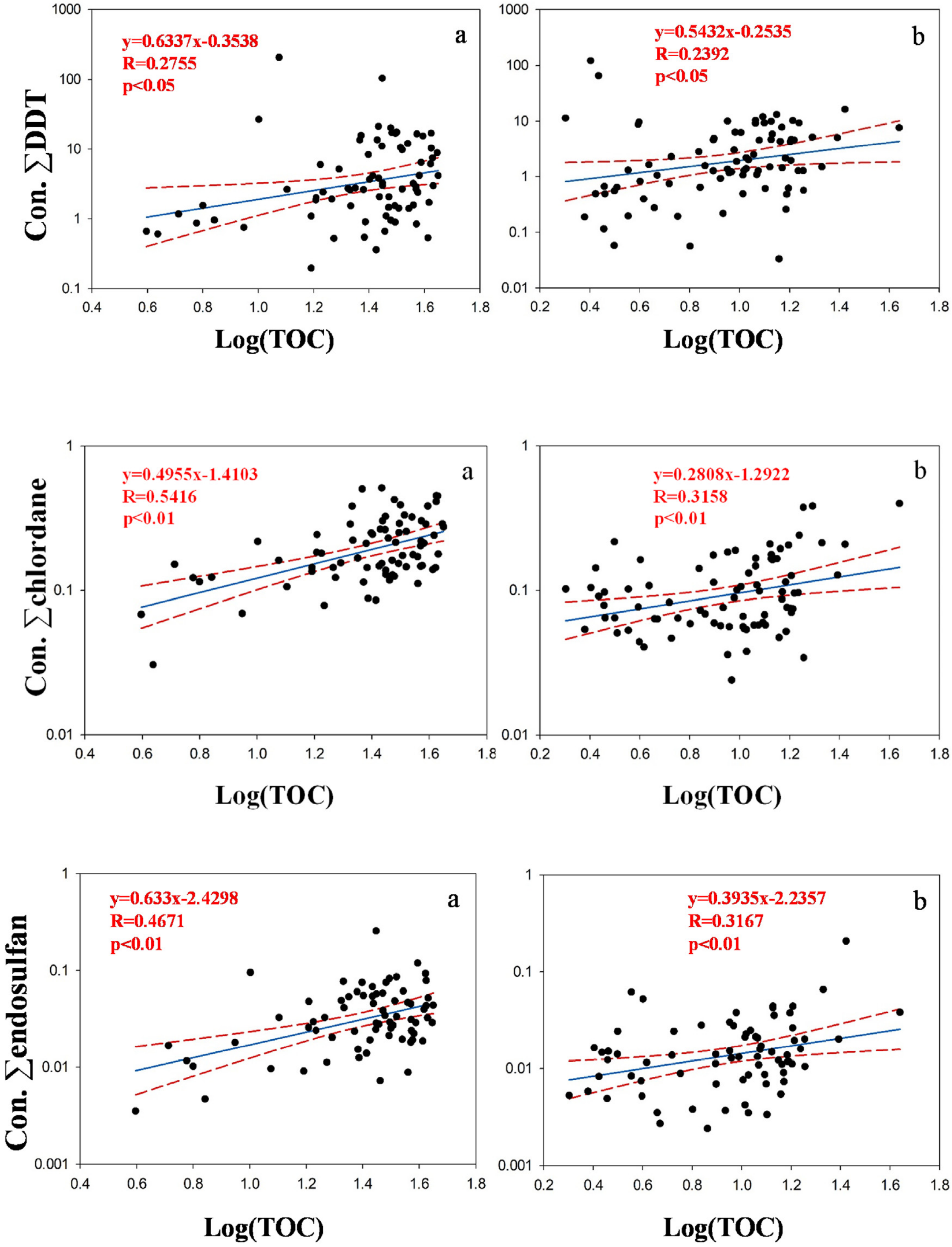

Fig. 2. OCP concentrations against environmental parameters in both the O- and A-horizons.

endosulfan in both the O- and A-horizons and with TC only in the O-horizon (Fig. 2 and Table S6). Possibly because of the higher volatilities of α-endosulfan and TC (Luis Sanchez-Osorio et al., 2017; Wang et al., 2012), they tend to transport from the emission points to lower temperature areas (Dalla Valle et al., 2005; Li et al., 2006).

An additional study was performed to compare the TOC-normalized concentrations with some environmental factors. Significantly positive relationships between the temperature and the TOC-normalized concentrations of some compounds were observed in the O-horizon (DDT isomers, chlordane, and mirex) and A-horizon (chlordane and mirex) (Table S7). These interesting correlations could be interpreted as collinearity between the temperature and source distribution due to the high consumption of dicofol, chlordane, and mirex in South China (Li et al., 2015; Qiu et al., 2005; Wang et al., 2010; Wang et al., 2013). This result further illustrates the importance of emission sources on the OCP distribution in China, and this correlation has also been observed between flame retardants and temperature in Chinese forest soils (Zheng et al., 2015). Because precipitation could accelerate atmospheric deposition, *op*'-DDE, chlordane, and mirex were significantly influenced by precipitation in the O-horizon, while heptachlor and mirex was significantly correlated with rainfall in

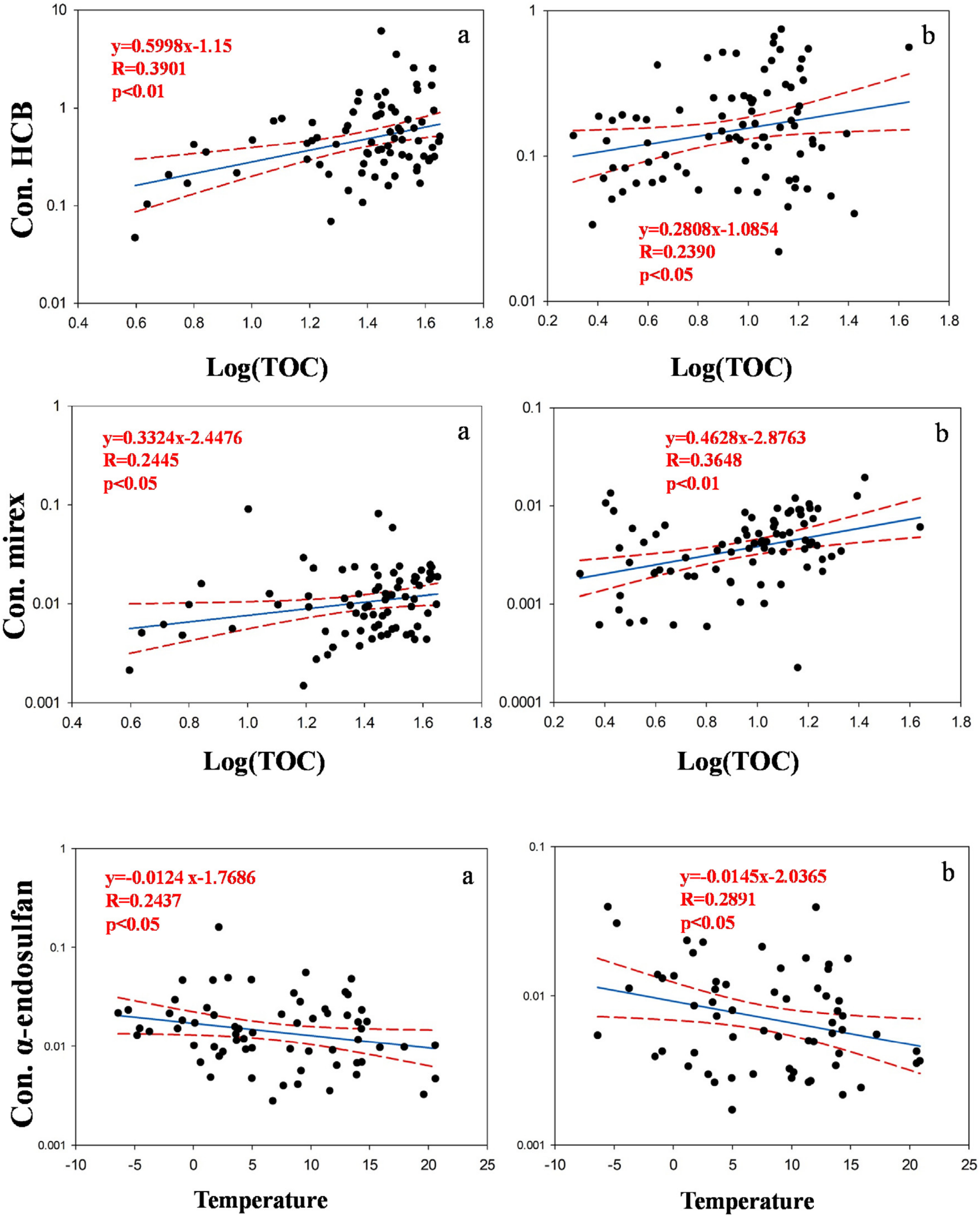

Fig. 2. (*continued*).

the A-horizon (Table S7). It is no surprise to find that relatively poor correlations between TOC-normalized concentrations and environmental factors in the A-horizon. This is because that the exposure pattern of mineral soil layer is not directly affected by atmospheric deposition, and the atmospheric influence decreased along with the increase of soil depth.

DEVrac of CC was notably positively correlated with TOC ($r = 0.253$; $p < 0.05$) in the O-horizon (Fig. 3), which has also been observed in Greenland and mainland Europe (Kurt-Karakus et al., 2005) and the Tibetan Plateau (Yuan et al., 2015). This result demonstrates that the microbial activity for enantioselective degradation may have been strengthened at the sites with higher TOCs. Furthermore, DEVrac of CC was found to have a strong positive correlation with the C/N ratio in the O-horizon ($r = 0.382$; $p < 0.01$) (Fig. 3). The soil C/N ratio is known to be substantially related to the microbial community composition, which could impact the extent of the enantioselective degradation of CC (Hogberg et al., 2007). The considerable correlations between DEVrac of CC and TOC or the C/N ratio imply that the forest soil microbes are processing the deposited chiral CC. In this study, the strong correlations had occurred only in the O-horizon potentially because of the properties of the O-horizon. The evidence has shown that a significant shift from the racemic values of chiral compounds were found among more carbon-rich and humic soils (Koblizkova et al., 2008). These results highlight that TOC and the C/N ratio, to some extent, reflect the strength of microbiological activity and could affect the magnitude of enantioselective degradation of chiral OCPs in Chinese forest soils and even possibly in other regions worldwide, which should be verified by further studies.

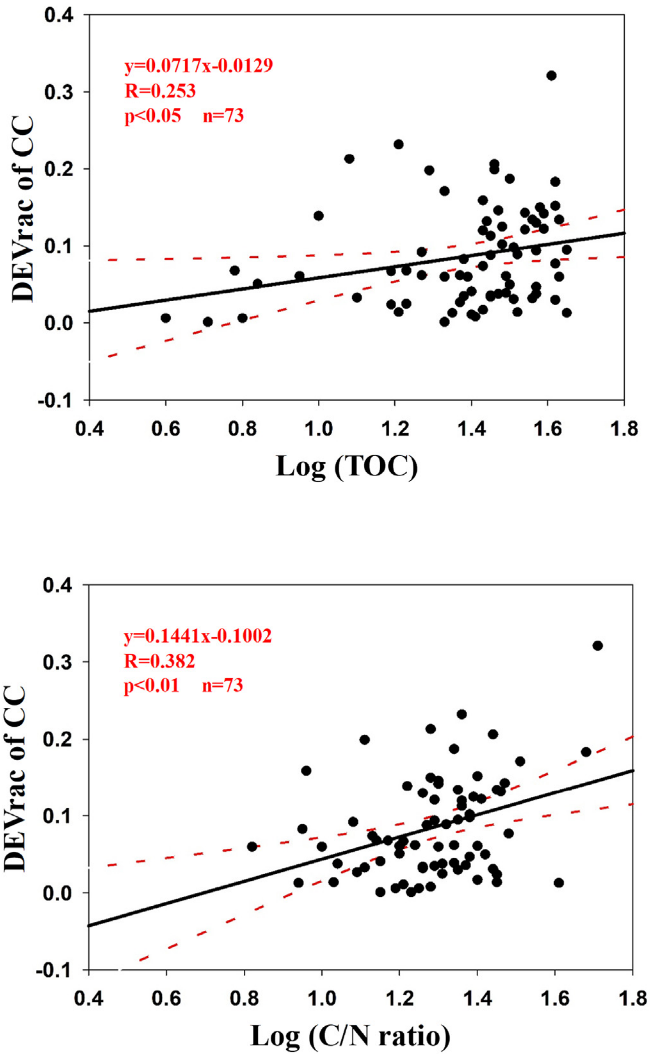

Fig. 3. DEVrac of CC against the TOC and C/N ratio in the O-horizon.

3.4. Assessment of sources

DDT isomers. DDT can be biodegraded into the stable and toxic DDE and DDD in soils (Yang et al., 2013). Typically, a low *DDTs/(DDEs + DDDs)* ratio indicates aged DDT, whereas a value much greater than 1 represents fresh inputs (Li et al., 2006). Therefore, samples with low *DDTs/(DDEs + DDDs)* ratios are expected for nonracemic *o,p'*-DDT (Bosch et al., 2015; Wiberg et al., 2001). In this study, the average ratios of *DDTs/(DDEs + DDDs)* were 1.66 and 1.52 in the O- and A-horizons, respectively (details shown in Table S8). Less than 30% of the ratios were below 1, which indicates that more than 70% of the soils have received fresh DDT (Bosch et al., 2015; Li et al., 2006). Furthermore, the average ratios of *o,p′*-DDT/*p,p′*-DDT were 0.47 and 0.36 in the O- and A-horizons, respectively. Similar ratios have also been observed in the native soils of Guangdong Province (Li et al., 2006). DDT could enter the environment by directly using DDT-containing dicofol and technical DDT. Most of the ratios were higher than that for technical DDT (about 0.25), but all ratios were lower than that for dicofol (about 7.0) (Qiu et al., 2005; Yang et al., 2013). The marketing and use of dicofol had not been halted in China until 2018; therefore, these DDT profiles could be partially caused by the residue of technical DDT and the current use of dicofol in Chinese agricultural practices during the sampling period (Ma et al., 2016; Yang et al., 2013).

Because *o,p′*-DDT is more volatile and metabolizes more quickly than *p,p′*-DDT in the environment, it was expected to observe lower *o,p'*-DDT/*p,p'*-DDT ratios than those of the technical DDT products (Bosch et al., 2015; Martijn et al., 1993). Interestingly, three soil samples (in sites 10 and 28) with considerably lower *o,p'*-DDT/*p,p'*-DDT ratios (<0.25) and higher *DDTs/(DDEs + DDDs)* ratios displayed the EF values for *o,p'*-DDT of approximately 0.5. This may be interpreted as a fresh application from the illegal use of technical DDT in small regions of China. A similar situation has also occurred for soils from Guangdong Province (Li et al., 2006). Therefore, DDTs in Chinese background soils have originated from the historical residue, the current use of dicofol, and a few fresh applications of technical DDT.

Correlations have been made between DEVrac of *o,p'*-DDT and the *DDTs/(DDEs + DDDs)* ratios. No significant relationship was found in the O-horizon nor the A-horizon, despite nearly all the racemic samples showing high *DDTs/(DDEs + DDDs)* ratios. This result is consistent with those reported in Spain (Bosch et al., 2015) and Mexico (Luis Sanchez-Osorio et al., 2017), which consider that the EF of *o,p'*-DDT indicates enantioselective microbial degradation, yet the *DDTs/(DDEs + DDDs)* ratio reflects both biotic and abiotic pathways. Additionally, DDT is less volatile than DDE in the environment, and the sorption coefficient of *p,p'*-DDT is higher than *p,p'*-DDE in the soil (Bosch et al., 2015). The different physicochemical properties of the DDT isomers could increase the ratios to different extents, especially in the diverse environmental parameters nationwide. These properties could partly explain the nonracemic *o,p'*-DDT with relatively high *DDTs/(DDEs + DDDs)* ratios for the soil samples. Another possible explanation is that though the fresh *o,p'*-DDT via long-range transport into forest soils is nearly racemic, a significant amount of residual *o,p'*-DDT in the soils had been biodegraded. Therefore, the *o,p'*-DDT in the soils are still presented as nonracemic.

Chlordane compounds. The ratio between TC and CC has been widely used to analyze the possible chlordane sources and weathering processes occurring in the soil. F_{TC} is defined as the ratio of $C_{TC}/C_{(TC+CC)}$, and the values in the technical mixture were reported to be 0.61 and 0.54 in previous studies (Yuan et al., 2015). Although the proportion of TC is higher than CC in the technical mixture, TC is more volatile and more labile than CC, which could result in the loss of TC via volatilization and aerobic biodegradation and shift the F_{TC} toward lower values in the soil (Martinez et al., 2012; Yuan et al., 2015). In this study, the F_{TC} values respectively ranged from 0.23 to 0.55 (mean 0.38) and 0.16 to 0.59 (mean 0.38) in the O- and A-horizons (Table S8), which is consistent with the ratios observed in Mexico (Wong et al., 2010), the Italian Alps (Tremolada et al., 2008), and Western Canada (Daly et al., 2007b). The lower F_{TC} values and nonracemic TC and CC in Chinese background sites indicate substantially weathered chlordane in the soils. Moreover, the F_{TC} values for the soils were found to be significantly positively correlated with the TOC and negatively with temperature in both the O- and A-horizons (Figure S2), which suggests that higher TOC and lower temperatures could slow down the weathering processes.

Endosulfan isomers. The main components of technical endosulfan are α-endosulfan and β-endosulfan, and the α-/β-endosulfan ratio in the technical mixture is approximately 2.3 (from 2:1 to 7:3) (Chen et al., 2017; Weber et al., 2010). Due to their discrepancy in properties, the α-/β-endosulfan ratio can be used to identify their source and environmental behaviors in the environment. α-endosulfan is more volatile than β-endosulfan, and the organic carbon partition coefficient (log K_{OC}) of α-endosulfan (3.6) is lower than that of β-endosulfan (4.3). Additionally, the half-life of α-endosulfan (7–75 days) is shorter than for β-endosulfan (33–376 days) (Wang et al., 2012). These properties would result in the rapid dissipation of α-endosulfan and enrichment of β-endosulfan in the soils. Therefore, low α-/β-endosulfan ratios reflect that there are no fresh inputs in these areas.

In this study, the α-/β-endosulfan ratio ranged from 0.14 to 6.53 (mean 1.03) and 0.12 to 4.2 (mean 1.01) in the O- and A-horizons, respectively (Table S8). More than 90% of the samples exhibited ratios of less than that in the technical mixture, which implies that most of the endosulfan in Chinese forest soils have predominantly resulted from the historical applications.

4. Conclusions

We conducted a regional-scale analysis of OCP distributions and profiles in Chinese forest soils. The DDT isomers were the main component of OCPs in the soils, and high concentrations of target OCPs were generally found in the vast agricultural provinces or high consumption areas, indicating that the long-term application of pesticides had a significant influence on the distribution of pesticides in the background soil system. Most of the enantiomeric fractions of chiral *o,p*′-DDT, TC, and CC were nonracemic in the samples. The distribution of chiral OCPs showed no apparent trends throughout the forest sites in the O-horizon or the A-horizon. Soil TOC played an essential role in the regional distribution of the majority OCP compounds, and the temperature had significantly influenced the more volatile compounds (α-endosulfan and TC). DEVrac of CC was substantially positively correlated to TOC and the C/N ratio in the O-horizon, which implies that TOC and the C/N ratio may affect the extent of enantioselective degradation of chiral compounds. The sources of DDT in Chinese forest soils had been contributed by current treatments with dicofol DDT during the sampling period, historical usage, and a small amount of illegal application of fresh technical DDT, while chlordane and endosulfan were primarily from historical applications. Although the isomer ratios and enantiomeric fractions could both trace the sources and environmental processes of the target OCPs, they provide different types of information.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors have directly participated in the execution and/or analysis of this study. The contents of this manuscript have not been copyrighted or published previously. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted. The manuscript will not be copyrighted, submitted, or published elsewhere while acceptance by Environmental Pollution is under consideration.

CRediT authorship contribution statement

Qian Zheng: Writing - review & editing, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Funding acquisition. **Jun Li:** Data curation, Resources, Writing - review & editing. **Yan Wang:** Data curation, Methodology, Writing - review & editing, Investigation, Resources. **Tian Lin:** Data curation, Resources, Writing - review & editing. **Yue Xu:** Data curation, Validation, Resources. **Guangcai Zhong:** Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition. **Haijian Bing:** Data curation, Resources. **Chunling Luo:** Data curation, Resources. **Gan Zhang:** Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition.

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Appendix A. Supplementary data

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