



## Spatial redistribution and enantiomeric signatures of hexachlorocyclohexanes in Chinese forest soils: Implications to environmental behavior and influencing factors



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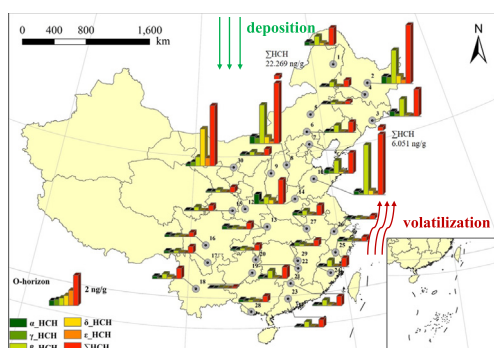
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### HIGHLIGHTS

- The secondary distribution pattern of HCHs was observed in Chinese forest soils.
- Temperature and precipitation mainly affect the HCH distribution in the O-horizon.
- The chiral  $\alpha$ -HCH showed preferential degradation of (–)  $\alpha$ -HCH in both soil layers.
- The transformation from  $\gamma$ -HCH to  $\alpha$ -HCH may alter the chiral  $\alpha$ -HCH in soils.
- C/N ratio may affect the enantioselective degradation of chiral pesticides.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Hexachlorocyclohexanes (HCHs) are a group of highly persistent pesticides. The concentrations of HCHs and the enantiomeric fractions of  $\alpha$ -HCH in the O- and A-horizons from 30 mountains across China were analyzed in this study. The concentrations of total HCHs ranged from 0.061 to 46.9 ng/g (mean 2.12 ng/g) and 0.046 to 16.1 ng/g (mean 0.792 ng/g) in the O- and A-horizons, respectively. The HCH residues were mainly derived from the historical applications of technical HCH and lindane. Higher concentrations of HCHs were typically found in northern China, and no significant correlations were found between historical technical HCH usage and HCH isomer concentrations in either the O- or A-horizons ( $p > 0.05$ ). Conversely, the concentrations of HCH isomers were significantly correlated with the environmental parameters (temperature and precipitation), thus indicating a typical secondary distribution pattern. Some HCH isomers tended to be transported northward under the long-term effect of monsoon. Chiral  $\alpha$ -HCH was non-racemic in soils and showed preferential degradation of (–)  $\alpha$ -HCH in both the O- and A-horizons. The transformation from  $\gamma$ -HCH to  $\alpha$ -HCH might alter the enantiomeric signatures of  $\alpha$ -HCH in soils. Moreover, the deviation from racemic of  $\alpha$ -HCH was positively correlated with the C/N ratio in the A-horizon ( $p < 0.01$ ), thus suggesting that the C/N ratio could alter the microbial activity and significantly affect the enantioselective degradation extent of  $\alpha$ -HCH in soils.

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## 1. Introduction

Hexachlorocyclohexanes (HCHs), owing to their persistence, semi-volatility, bioaccumulation, and toxicity, have been regarded as persistent organic pollutants (POPs) and banned by the Stockholm Convention in 2009 (Arias et al., 2023; Zhang et al., 2011). HCHs were once widely used as pesticides in the world in two formulations: technical HCH and lindane (Ding et al., 2022; Xu et al., 2013a). Technical HCH comprises  $\alpha$ -HCH (60 %–70 %),  $\beta$ -HCH (5 %–12 %),  $\gamma$ -HCH (10 %–12 %),  $\delta$ -HCH (6 %–10 %), and  $\epsilon$ -HCH (3 %–4 %), whereas lindane contains >99 % of  $\gamma$ -HCH (Li et al., 2006; Xu et al., 2012; Zhang et al., 2011). China had the highest production and historical application of technical HCH worldwide, and the total production from 1950s to 1983 was 4464 kt (Li et al., 2006; Xu et al., 2013b). After disabling technical HCH, 3200 t of lindane was still used in China between 1991 and 2000 (Li et al., 2001). The high usage of HCHs has resulted in their ubiquity in various ecosystems. Notably, long-term prohibitions on the use of HCHs have resulted in the reduction of primary emissions, which would promote secondary emissions of HCHs into the atmosphere from environmental reservoirs such as soils, vegetation, and water (Zheng et al., 2020). Therefore, the fate and redistribution of HCHs in the environment will still be a global concern for a long time in the future.

Several hypotheses have been proposed regarding the fate of organic pollutants. Based on the “global distillation model”, organic pollutants are driven by temperature and could be transferred from warmer regions to cooler regions along the latitudinal temperature gradient (Wania and MacKay, 1996). In addition, many studies have shown that organic matter (OM) is key in controlling organic pollutants in soils and sediments, and that high OM could retard the movement of organic pollutants to higher latitudes (Dalla Valle et al., 2005; Nam et al., 2008; C. Wang et al., 2023). However, some studies have suggested that the spatial distribution of organic pollutants is related to monsoon activity (Wu et al., 2023; Xu et al., 2013b). Meanwhile, the fate of organic pollutants remains ambiguous and requires further investigation.

Enantiomeric analysis is useful for determining the sources, processing, and fate of chiral compounds (Genualdi et al., 2011; Kurt-Karakus et al., 2005). The enantiomer proportions will not be changed by transport (advection, deposition, and volatilization) and abiotic reactions (photolysis, hydrolysis, OH radical attack) (Bidleman et al., 2012; Huang et al., 2013; Kurt-Karakus et al., 2005; Li et al., 2006). Conversely, the enantioselective degradation of chiral compounds is closely correlated with microbial activity, thus resulting in the accumulation of non-racemic residues (Bidleman and Falconer, 1999; Huang et al., 2013). Among the HCH isomers, only  $\alpha$ -HCH is chiral and manufactured as a racemic mixture of enantiomers (1:1) in technical HCH. Thus, the enantiomeric proportion of  $\alpha$ -HCH is useful for inferring the role of microbial degradation and the age of residue (Niu et al., 2013).

Soil, particularly the humus and topsoil of forested soil, is one of the largest receptors and reservoirs of hydrophobic substances, such as HCHs (Bergknut et al., 2011; Gong and Wang, 2021; Niu et al., 2016). Chinese forests encompass 134 million ha, which constitutes 22.56 % of the national terrestrial soil organic carbon stock (Fang et al., 2001; Xu et al., 2015). Most of them are located far away from major urban agglomerations and anthropogenic activities and can be regarded as background sites (Zheng et al., 2015). The transport of contaminants through atmospheric deposition into background soils primarily depends on the location, soil characteristics, and meteorological parameters (Niu et al., 2016; Tian et al., 2011). Therefore, research on the current concentrations and chiral compositions of HCHs in major reservoir compartments over a large spatial scale will allow us to determine key factors that affect the secondary distribution patterns of HCHs and understand their environmental behavior and fate. Moreover, China features a large land area, variable meteorological conditions, varied topography, and diverse ecosystems, which could significantly affect the global contamination and distribution patterns of HCHs.

To the best of our knowledge, few studies have examined the accumulation and chiral composition of HCHs in background forest soils over large

regional scales, particularly using national-scale datasets. In this study, O- and A-horizons soil samples were obtained from Chinese mountain sites to i) elucidate the concentrations, spatial trends, and enantiomeric fractions (EFs) of target compounds in forest soils and to ii) determine the primary environmental parameters affecting the distribution patterns of HCHs and chiral  $\alpha$ -HCH.

## 2. Experimental section

### 2.1. Sampling

Thirty mountains across boreal, temperate, subtropical, and tropical areas in China (shown in Fig. S1) were selected for this study between May 2012 and March 2013. In all, 77 O-horizon and 82 A-horizon forest soil samples (totally 159 samples) distinguished by color and vertical structure were acquired at 82 locations. Each soil sample contained three sub-samples. Vegetation litter and non-organic materials were removed meticulously. All samples were individually stored in polyethylene zip-bags, immediately transported, and cooled in the laboratory. Subsequently, the samples were freeze-dried, sieved (particles smaller than 2 mm), ground, and kept at  $-20\text{ }^{\circ}\text{C}$  until further analysis. Details of the sampling locations and processes have been reported in the previous study and are also presented in Table S1 (Zheng et al., 2014).

### 2.2. Chemical analysis

Five HCH isomers ( $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH, and  $\epsilon$ -HCH) were assessed in this study. Their concentrations were almost detected above the limits of detection. Sample preparation, instrumental, and total organic carbon (TOC) analyses have been described in previous publications (Huang et al., 2013; Mai et al., 2005; Zheng et al., 2014), which are also reported in the supplementary information (SI).

### 2.3. QA/QC

In total, 10 procedural blanks and 20 pairs of repeated samples were analyzed to evaluate the potential contamination and the repeatability of analysis. All soil samples were spiked with TCmX, PCB198 and PCB209 (20 ng) as recovery standards prior to extraction. The surrogate recoveries were  $62\% \pm 7.6\%$ ,  $82\% \pm 4.9\%$ , and  $85\% \pm 3.7\%$ , respectively. The reported results in this study are expressed on a dry weight basis (ng/g dry weight) and were not corrected based on the surrogate recovery results.

To analyze the chiral  $\alpha$ -HCH analysis, racemic standards were injected for replicate analysis to determine the reproducibility of the EF measurements. The EF is calculated as  $(+) / [(+) + (-)]$ , where (+) and (−) represent the peak areas of the (+)  $\alpha$ -HCH and (−)  $\alpha$ -HCH, respectively. An EF value of 0.5 represents a racemic composition; meanwhile, if an EF value is within the 95 % confidence interval, the corresponding soil sample is regarded as not strongly different from the racemic composition. The average EF value was  $0.502 \pm 0.004$  ( $n = 25$ ), based on the racemic standard. Further details are provided in the SI.

## 3. Results and discussion

### 3.1. Summary of HCH isomer concentration

The concentrations of HCH isomers in the O- and A-horizons are listed in Table S2. The total HCH ( $\Sigma_5\text{HCH}$ , which is the sum of  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH, and  $\epsilon$ -HCH) in the A-horizon ranged from 0.046 to 16.1 ng/g (mean 0.792 ng/g). These values were comparable to those of Czech mountainous forest soils (mean 0.86 ng/g) (Holoubek et al., 2009) and archived background soils in UK (0.1–10 ng/g) (Meijer et al., 2001), and slightly higher than those of the background soils in Spain and UK (n.d.–0.52 ng/g with a mean value of 0.06 ng/g) (Cabrerizo et al., 2011), mountain soils in western Canada (0.003–7.89 ng/g) (Daly et al., 2007b), and South Korean soils (n.d.–0.30 ng/g) (Khuman et al., 2022). The

concentrations of  $\Sigma_5$ HCH in the O-horizon ranged from 0.061 to 46.9 ng/g (mean 2.12 ng/g), which were significantly higher (average factor of 3.04) than those in the A-horizon, based on a *t*-test ( $p < 0.01$ ) (Table S3). However, this pattern between the two layers was reversed for all isomers when the concentrations of HCHs were TOC normalized. The concentrations of HCH isomers were higher than those in the O-horizon in >60 % of the samples after TOC normalization. This vertical distribution might be because that HCHs with lower molecular weights tend to be transported through dissolution into deeper soil layers (Xu et al., 2015). In addition, the relatively higher vapor pressure of HCHs would cause them to become unstable in the O-horizon and thus volatilize into the atmosphere, thereby further reducing the concentration of HCHs in the O-horizon. In the present study,  $\beta$ -HCH (mean 48 %) contributed most significantly to the  $\Sigma_5$ HCH concentrations in both the O- and A-horizons, followed by  $\alpha$ -HCH (mean 25 %) and  $\gamma$ -HCH (mean 13 %). Similar contributions ( $\beta$ -HCH >  $\alpha$ -HCH >  $\gamma$ -HCH) have been reported in the previous studies (Chakraborty et al., 2015; L. Wang et al., 2023). This is because, among the HCH isomers,  $\beta$ -HCH has the lowest water solubility and vapor pressure and the highest stability, thus rendering it more resistant in soils (Walker et al., 1999).

Studying the ratios of  $\alpha$ -HCH/ $\gamma$ -HCH is an effective approach to identifying the possible HCH sources. This is because the ratio of  $\alpha$ -HCH/ $\gamma$ -HCH in technical HCH ranges from 5 to 7, while lindane nearly contains 0 (Zhang et al., 2011). The HCH isomer ratios for each soil sample are presented in Table S4. The average values of  $\alpha$ -HCH/ $\gamma$ -HCH in Chinese forest soils were 1.91 (0.14–4.41) and 2.08 (0.35–4.56) in the O- and A-horizons, respectively, which were lower than those in technical HCH. The previous study shows that  $\gamma$ -HCH can be transformed into  $\alpha$ -HCH in soil, which will, to some extent, increase the ratios of  $\alpha$ -HCH/ $\gamma$ -HCH (Walker et al., 1999). Therefore, the lower ratios of  $\alpha$ -HCH/ $\gamma$ -HCH compared with that of technical HCH in the present study imply that lindane, as one of the pesticides, also affects the profiles of HCHs in Chinese forest soils.

Furthermore, the ratio of  $\alpha$ -HCH/ $\beta$ -HCH is of advantage to evaluate whether there were recent inputs of technical HCH in these locations (Tao et al., 2008). The  $\alpha$ -HCH/ $\beta$ -HCH ratios in this study ranged from 0.024 to 3.42 (mean 0.703) and 0.019 to 4.48 (mean 0.867) in the O- and A-horizons, respectively. All the ratios in these forest samples were much lower than that in the technical HCH (11.8), which indicates that no fresh technical HCH was applied to the Chinese forest soils.

### 3.2. Spatial distributions in forest soils

Significant spatial variabilities in HCH isomers were found in this survey, and the maximum concentrations of HCH isomers were two orders of magnitude higher than the minimum concentrations in the same soil layer. Fig. 1 shows the spatial patterns of HCH isomers in the O- and A-horizons. In general, samples from the northern region of China showed higher concentrations of HCH isomers compared with those from the southern region, which is consistent with the observation in Chinese surface soil (L. Wang et al., 2023). The highest concentrations of HCH isomers were measured at Site 8 and 10 in both layers, which are located in Hebei and Shandong provinces, respectively. Based on HCH usage inventories, the abovementioned two areas are among the top 10 provinces with the highest usage of technical HCH in China, ranking of 7 and 4, respectively (Li et al., 2001). Meanwhile, Eastern and Southern China, which had the largest amount of technical HCH, showed relatively lower concentrations of HCHs (Li et al., 2001; L. Wang et al., 2023). Additionally, the gridded total technical HCH usage until 1999 was obtained from the previous studies (Li et al., 2001; Xu et al., 2013b), but no significant correlations were found between the technical HCH usage and the concentrations of HCH isomers in either the O- or A-horizons ( $p > 0.05$ ). These findings suggest that other factors may have affected the distribution of HCH isomers in Chinese forest soils, which requires further analysis. Despite the significant variations in the HCH concentrations across the sampling sites, the spatial distributions of HCH isomers were significantly consistent in each soil layer ( $p < 0.05$ ). Significant correlations among the HCH isomers in both the

O- and A-horizons indicate similar sources or fates in these subregions (Table S5).

Previous studies showed that the Asian monsoon due to the strong thermal atmospheric circulations could form an effective northward atmospheric transport pathway, thus resulting in the discharge of  $\alpha$ -HCH from pollutant sources to Northern China (Tian et al., 2011; Xu et al., 2013b). Xu et al. simulated the sink regions of  $\alpha$ -HCH in China and discovered that a maximum overlap of 60 % between the monsoon margin and sink areas, which indicates that the sink formation processes might have been affected by Asian monsoon (Xu et al., 2013b). In this study, we discovered that the sampling sites with higher concentrations of  $\alpha$ -HCH were typically located in overlapping areas (Fig. S2), which suggests that  $\alpha$ -HCH or other POPs may migrate northward under the long-term effect of the monsoon and eventually be deposited in sink areas. Although the concentrations of  $\alpha$ -HCH were positively correlated between the two layers ( $r = 0.699$ ,  $p < 0.01$ ), the spatial pattern of  $\alpha$ -HCH in each soil layer showed discrepancies. As shown in Fig. S2a, the concentrations of  $\alpha$ -HCH in the O-horizon were obviously higher in northern China, despite the high usage of  $\alpha$ -HCH in southeastern China. However, the spatial differences of  $\alpha$ -HCH in the forest soil appeared to be inconspicuous in the A-horizon (Fig. S2b). These observations imply that the effect of monsoon is more prominent in the upper soil layer.

### 3.3. Effects of environmental parameters on HCHs

Environmental and geographical variables (such as soil TOC, temperature, precipitation, altitude, and latitude) can affect the distribution of hydrophobic contaminants (Tian et al., 2011; Xu et al., 2013b; Zhang et al., 2011). Linear correlations were used to investigate the effects of the environmental and geographical variables on the distribution of HCH isomers.

#### 3.3.1. TOC in soil

The distribution of hydrophobic compounds is believed to be governed by the TOC owing to their high affinity for OM (Zheng et al., 2020; Zheng et al., 2014). In the present study, although the concentrations of HCH isomers increase their abundance at higher TOC, only  $\epsilon$ -HCH and  $\gamma$ -HCH showed significantly positive relationships with the TOC in the O-horizon ( $r = 0.294$ ,  $p < 0.01$ ) and A-horizon ( $r = 0.225$ ,  $p < 0.05$ ), respectively. Weak correlations between the TOC and HCH isomers were observed in the previous study (Khuman et al., 2020). The relatively low dependence of the HCH isomers on the TOC is attributable to the lower *K*<sub>ow</sub> of the HCH isomers, which would affect the OM absorption capacity to the isomers. In addition, the high volatility of HCH isomers renders them susceptible to volatilization from the soil into the atmosphere.

#### 3.3.2. Latitude, temperature, precipitation, and altitude

The deposition, re-emission, and degradation processes of many POPs are related to temperature and precipitation, and correspondingly showing a dependence on the latitude (Zheng et al., 2015). In the O-horizon, all the HCH isomers were significantly negatively correlated with temperature and positively correlated with latitude (Fig. 2 and Table S6). This may be because the more volatile compounds tend to travel farther from their initial release point and their content tends to increase at high latitudes (low temperatures) through long-range atmospheric transport (LRAT), which is consistent with the global distillation model (Dalla Valle et al., 2005; Li et al., 2006). Meanwhile, a strongly negative correlation was observed between the concentration of each HCH isomer and precipitation in the O-horizon (Table S6). This result does not support the conjecture that wet deposition is a crucial method by which POPs enter the soil, thus causing a positive correlation between the contaminant concentration and precipitation (Niu et al., 2013; Zheng et al., 2020; Zheng et al., 2015). One of the reasons for the negative correlation was the synchronous change between precipitation and temperature ( $r = 0.692$ ,  $p < 0.01$ ). Therefore, partial correlation analysis was performed to analyze the correlation between HCH levels and precipitation. The significantly negative correlations were observed between some HCH isomers and precipitation (Table S7), thus

indicating that precipitation can affect the residue of HCH isomers in the soil, and the concentrations of HCH isomers in the O-horizon decreased as precipitation increased. This trend might be because the HCH isomers

are highly water soluble. Although precipitation can accelerate the atmospheric deposition of HCHs, the isomers can also be removed into the deeper soil layer via rainwater runoff and erosion. Owing to the ban on

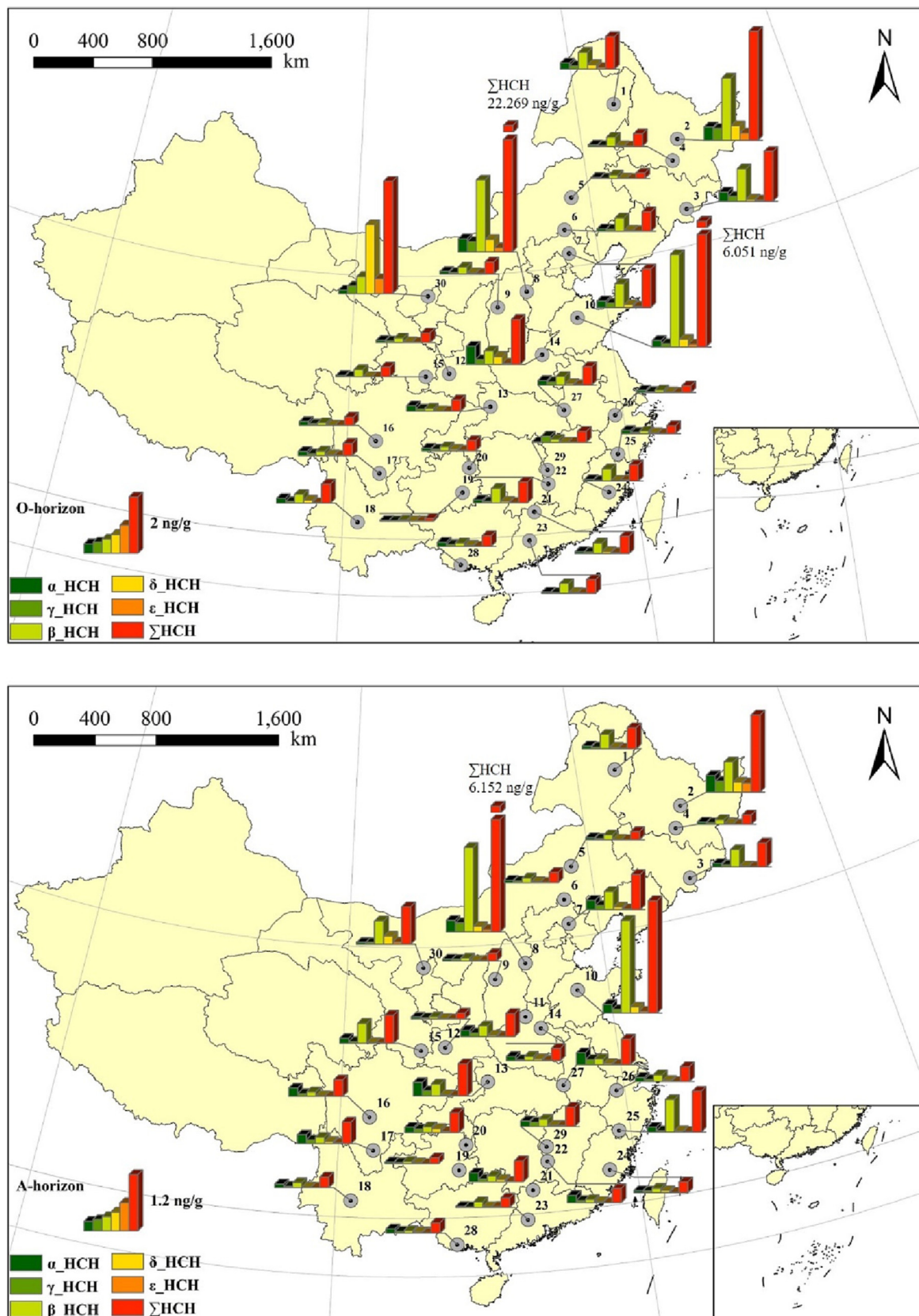


Fig. 1. Spatial distribution of HCH isomers in the O- and A-horizons (ng/g dry wt).

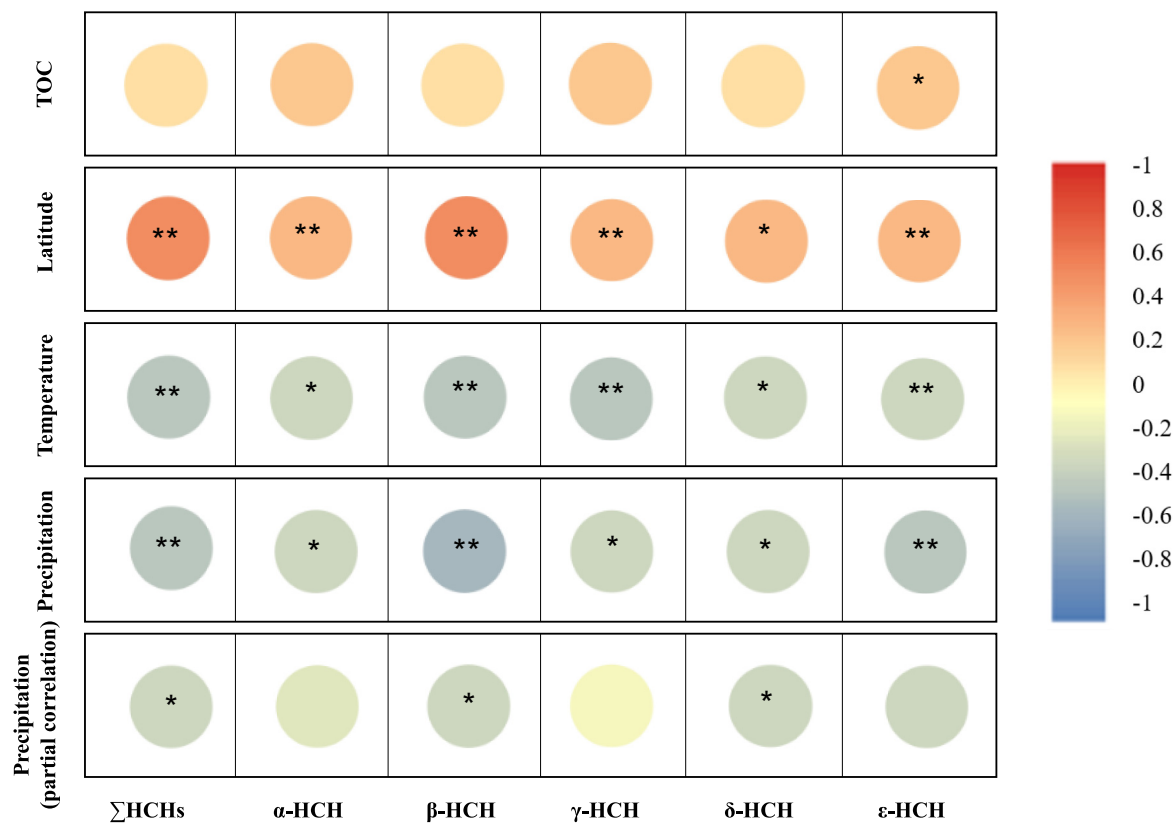


Fig. 2. HCH isomer concentrations against environmental parameters in the O-horizon.

Note: \* correlation is significant at the 0.05 level (2-tailed) and \*\* correlation is significant at the 0.01 level (2-tailed).

HCHs, the concentrations of HCH isomers in the atmosphere have significantly decreased. Hence, the input of HCHs might be below the output in the O-horizon, thus resulting in a significant reduction in HCHs as rainfall increased. In addition, the concentrations of  $\beta$ -HCH in forest soils decreased with the altitude in the O-horizon ( $r = -0.227, p < 0.05$ ), thus indicating that elevation is a considerable factor influencing the distribution of HCH isomers in soils. Similar result has been reported for agricultural fields in 31 provinces or regions across China (Niu et al., 2013). Many physical and ecological factors contribute to the altitudinal distribution. In this study, the lower vapor pressure of  $\beta$ -HCH appears to be one of the most pivotal factors. This is because the less volatile  $\beta$ -HCH implies a lower LRAT potential; thus,  $\beta$ -HCH may be inclined to accumulate in soils at lower altitudes (Niu et al., 2013).

However, a completely different finding was obtained for the A-horizon. Few HCH isomers were significantly correlated with the environmental parameters (Table S6). Owing to the physicochemical properties of  $\beta$ -HCH as discussed above, only  $\beta$ -HCH was significantly correlated with the latitude, temperature, and precipitation ( $p < 0.05$ ). These results support the conjecture that the distribution of contaminants in the O-horizon is directly affected by atmospheric deposition, which is primarily associated with temperature and precipitation (Xu et al., 2015; Xu et al., 2013b). However, the atmospheric influence on the POPs would decrease as the soil depth increases; the HCH isomers in the “aged” A-horizon generally depend on their vertical transport and transformation processes (such as, leaching and vertical diffusion) in the soil column (Zheng et al., 2015).

### 3.4. EFs of chiral $\alpha$ -HCH

Despite the racemic mixture of  $\alpha$ -HCH in technical HCH, the preferential degradation of one enantiomer occurs via microbially mediated processes in soils, thus causing the EF to deviate from 0.5 over time (Kurt-Karakus et al., 2007). Therefore, the chiral signature of  $\alpha$ -HCH is used to identify the microbial degradation and the age of contaminants in

the various environmental matrices (Niu et al., 2013; Willett et al., 1998). In this study, all EFs of  $\alpha$ -HCH in the forest soils were non-racemic, and the EFs in the O- and A-horizons ranged from 0.435 to 0.815 (mean 0.613) and 0.189 to 0.847 (mean 0.617), respectively (Table S5). Preferential degradation of (–)  $\alpha$ -HCH was observed in most cases, which is similar to the results reported for Greenland and mainland Europe soils (Kurt-Karakus et al., 2005), Costa Rican soils (Daly et al., 2007a), and natural soils in Guangdong Province (Li et al., 2006). The wide range of EFs indicates variable enantioselective degradation mechanisms and rates in Chinese forest soils. Generally, higher EFs of  $\alpha$ -HCH were observed in higher latitudes (Fig. 3). The spatial distribution of chiral  $\alpha$ -HCH was uniform between the O- and A-horizons ( $r = 0.543, p < 0.01$ ), thus implying that the orientation and extent of enantioselective degradation were comparable in similar environments.

Both the EFs of  $\alpha$ -HCH and the  $\alpha$ -HCH/ $\beta$ -HCH ratio can be used to distinguish between past and recent inputs of HCHs. Therefore, one might expect that a low  $\alpha$ -HCH/ $\beta$ -HCH ratio corresponds to a significant deviation from the racemic mixture (DEVrac, calculated as the absolute value of  $(0.500 - EF)$ ) of  $\alpha$ -HCH. The highest EFs of  $\alpha$ -HCH were 0.815 and 0.847, which were recorded at Site 6 in the O- and A-horizons, respectively. Accordingly, low  $\alpha$ -HCH/ $\beta$ -HCH ratios were observed at this site, i.e., 0.25 and 0.42 in the O- and A-horizons, respectively. Subsequently, the DEVrac of  $\alpha$ -HCH was compared based on the  $\alpha$ -HCH/ $\beta$ -HCH ratio at each sampling site; the results showed no significant correlation in either the O- or A-horizons ( $p > 0.05$ ). This may be because that the two tracers provide different types of information. The  $\alpha$ -HCH/ $\beta$ -HCH ratio considers all types of processes (biotic and abiotic), whereas the EF only reflects the microbial degradation. In addition, the previous studies have shown that the chiral compounds in higher concentration samples were racemic or close to racemic (Kurt-Karakus et al., 2005; Li et al., 2006). However, the EFs of  $\alpha$ -HCH at Site 8, which showed the highest HCH concentrations, were all non-racemic in both the O- and A-horizons. Moreover, the distributions of EFs in this study were unrelated to the concentrations of  $\alpha$ -HCH in both the

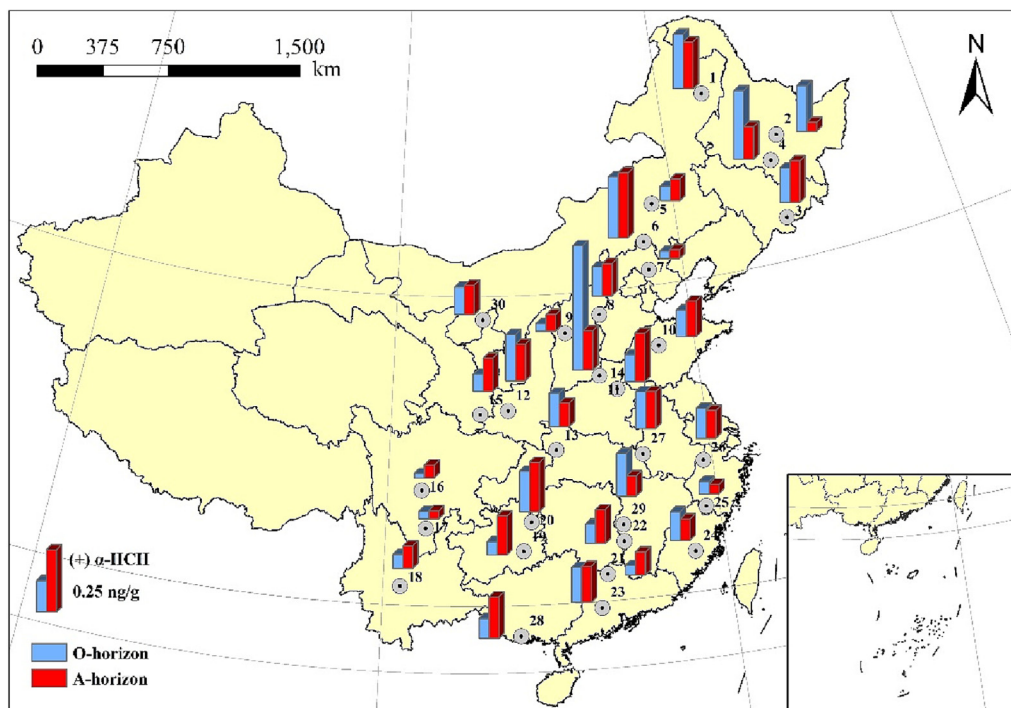


Fig. 3. DEVrac of  $\alpha$ -HCH in the O- and A-horizons (ng/g dry wt).

O- and A-horizons ( $p > 0.05$ ). This is because the distribution of HCHs over a large area depends on the combined effect of physical, ecological, and anthropological factors, which is more complex than the effect of microbial degradation.

Significantly negative correlations were observed between the DEVrac of  $\alpha$ -HCH and the  $\alpha$ -HCH/ $\gamma$ -HCH ratio in both O-horizon ( $r = -0.382$ ,  $p < 0.01$ ) and A-horizon ( $r = -0.254$ ,  $p < 0.05$ ). This implies that the soil samples with  $\alpha$ -HCH EFs closer to 0.5 indicated the higher  $\alpha$ -HCH/ $\gamma$ -HCH ratios. As discussed above, the  $\alpha$ -HCH/ $\beta$ -HCH ratios and the EFs of  $\alpha$ -HCH suggest no fresh input of HCHs into these regions. This result might be because  $\gamma$ -HCH can transform into the racemic mixtures of both enantiomers of  $\alpha$ -HCH via photolytic isomerization and biological degradation (Li et al., 2006; Walker et al., 1999; Yang et al., 2008). When the isomerized transformation of  $\gamma$ -HCH occurs, the  $\alpha$ -HCH/ $\gamma$ -HCH ratio and the proportion of racemic  $\alpha$ -HCH would increase, thus resulting in the EFs near 0.5.

### 3.5. Factors affecting enantiomeric profiles

The enantioselective degradation processes of chiral compounds are speculated to be mainly influenced by the activity of the microbial community and environmental parameters (Zhang et al., 2011). For the O-horizon, the DEVrac of  $\alpha$ -HCH was significantly positively correlated with the latitude ( $r = 0.331$ ,  $p < 0.01$ ) and negatively correlated with temperature ( $r = -0.277$ ,  $p < 0.05$ ). This indicates that the chiral  $\alpha$ -HCH at lower latitudes and higher temperatures is similar to a racemic mixture, which implies a fresh input of  $\alpha$ -HCH at low latitudes. However, technical HCH treatment has been banned in China for many years. Hence, the isomeric conversion of  $\gamma$ -HCH into  $\alpha$ -HCH in situ might be the best explanation for this observation. This inference is further supported by the negatively significant correlations between the DEVrac of  $\alpha$ -HCH and the  $\alpha$ -HCH/ $\gamma$ -HCH ratios in both the O- and A-horizons. This is because the microbial growth and metabolic activity are closely related to soil temperatures (Grayston et al., 2001), and higher temperatures can promote the biological degradation of  $\gamma$ -HCH. In addition, strong ultraviolet radiation (particularly in the summer) at lower latitudes can promote the transformation from  $\gamma$ -HCH to  $\alpha$ -HCH. Therefore, the transformation from  $\gamma$ -HCH to  $\alpha$ -HCH

might be a crucial contributor to the racemic  $\alpha$ -HCH in the soils, which is similarly observed in the previous study (Li et al., 2006). Moreover, a significant shift in the racemic values of chiral compounds was observed in carbon-abundant and humic soils (Kobližková et al., 2008). In this study, forest soils with much higher TOC and humic substances are typically found in northern China, which may positively affect the enantioselective degradation process. Therefore, the DEVrac of  $\alpha$ -HCH had the significant correlations with latitude and temperature might be caused by the combined effect of isomeric conversion and soil properties.

However, the DEVrac of  $\alpha$ -HCH showed no significant correlation with either the latitude or temperature, and the linear relationship between the DEVrac of  $\alpha$ -HCH and the  $\alpha$ -HCH/ $\gamma$ -HCH ratio weakened in the A-horizon. This might be because the intensity of light exposure in the A-horizon was much weaker than that in the O-horizon, which subsequently weakened the conversion from  $\gamma$ -HCH into  $\alpha$ -HCH, thus affecting the EFs of chiral  $\alpha$ -HCH. The DEVrac of  $\alpha$ -HCH was only strongly correlated with the C/N ratio in the A-horizon ( $r = 0.349$ ,  $p < 0.01$ ) (Fig. 4). This is consistent with the finding that the DEVrac of CC had a positive correlation with the C/N ratio in forest soils (Zheng et al., 2020). The C/N ratio of soils, to some extent,

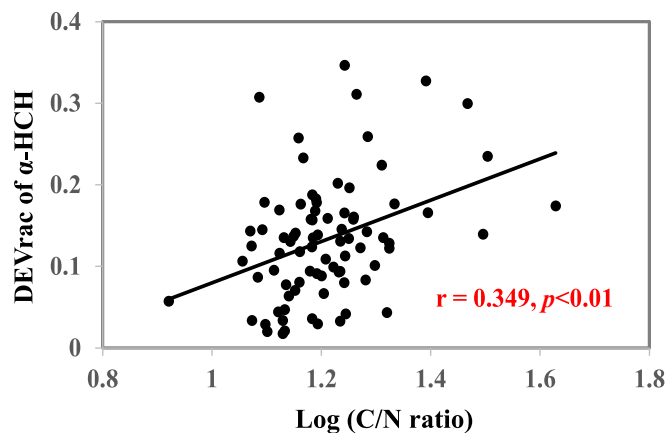


Fig. 4. DEVrac of  $\alpha$ -HCH against the C/N ratio in the A-horizon.

may reflect the microbial community composition, which may subsequently affect the extent of enantioselective degradation of chiral compounds (Hogberg et al., 2007). This positive correlation further highlights the fact that microbes affect the deposition of chiral  $\alpha$ -HCH in forest soils. However, insufficient information regarding the microorganisms in this study rendered it difficult to identify the mechanism of enantioselective degradation. Additionally, although the EFs of  $\alpha$ -HCH in the O-horizon were closely correlated to those in the A-horizon, the environmental parameters influencing the EFs of  $\alpha$ -HCH were not identical between the two layers.

#### 4. Conclusion

The concentrations and distributions of HCH isomers were measured in Chinese forest soils on a large geographical scale. The HCH isomers in forest soils dominated by  $\beta$ -HCH in this study were likely due to its lower water solubility and vapor pressure and higher stability compared with those of other HCH isomers. Historical applications of technical HCH and lindane contributed to the sources of HCHs in Chinese forest soils. High concentrations of HCH isomers were generally found in northern China, although a significant amount of technical HCH was applied primarily in southeast China. This indicates that primary emissions are no longer the major factor determining the spatial distribution of HCH isomers caused by the long-term prohibition of HCH products. Conversely, the environmental factors (including temperature, precipitation, monsoon, and soil TOC) significantly affected the secondary distribution pattern of HCH isomers, particularly in the O-horizon. However, the HCH isomers in the “aged” A-horizon were affected more significantly by their vertical transport processes in the soil column, instead of the atmospheric deposition. The EFs of chiral  $\alpha$ -HCH were all non-racemic, and the transformation from  $\gamma$ -HCH to  $\alpha$ -HCH might have a crucial effect on the EFs of  $\alpha$ -HCH in the forest soils. The DEVrac of  $\alpha$ -HCH increased along the latitudes of the O-horizon. This is attributable to the combined effects of different factors, such as the isomeric conversion process and different soil properties (e.g., TOC and humic substances), which affect the microbial degradation of chiral  $\alpha$ -HCH in the region. In the A-horizon, the DEVrac of  $\alpha$ -HCH was positively significantly correlated with the C/N ratio, thus suggesting that the extent of enantioselective degradation could be influenced by the C/N ratio.

In summary, this study revealed that environmental factors varying in different regions could form the secondary distribution patterns of HCH isomers on a large regional scale. Even at the same sampling sites, the driving factors can differ between the vertical soil layers. We can only speculate about the environmental behavior of HCH isomers in China; soils in southeast China received significant amounts of technical HCH owing to heavy application in the past. However, with the prohibition of HCH products, soils served as secondary sources for the release of HCH isomers into the air. Subsequently, HCH isomers could be transported to northern China and deposited in soils at high latitudes under the long-term effects of temperature, precipitation, monsoon, and soil TOC. Moreover, the EFs of  $\alpha$ -HCH in forest soils are not only related to enantioselective degradation, but also to the conversion between HCH isomers. Additionally, POPs with physicochemical properties similar to those of HCH isomers might exhibit similar environmental behaviors, as discussed above. These findings allow us to better comprehend the environmental fate of POPs in China, and even in the global perspective.

#### CRedit authorship contribution statement

**Qian Zheng:** Writing – review & editing, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Funding acquisition. **Yue Xu:** Data curation, Validation, Resources. **Zhen Cao:** Methodology, Formal analysis. **Shizhen Zhao:** Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition. **Haijian Bing:** Data curation, Resources. **Jun Li:** Data curation, Resources, Writing – review & editing. **Chunling Luo:** Data curation, Resources. **Gan Zhang:** Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition.

#### Data availability

Data will be made available on request.

#### Declaration of competing interest

The authors state that they have no known competitive financial interests or personal relationships, which may affect the work reported in this article. All authors were directly involved in the execution and/or analysis of this study. The contents of this manuscript have not been previously copyrighted or published. We declare that we have no commercial or affiliated interests that represent a conflict of interest in connection with the submitted work.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.165024>.

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