

Residues of Currently and Never Used Organochlorine Pesticides in Agricultural Soils from Zhejiang Province, China

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S Supporting Information

ABSTRACT: Studies on residues of currently and never used organochlorine pesticides (OCPs) facilitate the assessment of the contamination level, distribution, sources, transportation, and trend of these selected OCPs in China. In this work we investigated the concentration levels of endosulfans and chlordane, which are currently used, and the never used aldrin and dieldrin in the province of Zhejiang, a rainy, and hilly tea-growing province in eastern China. The average/mean residue levels of OCPs was in the order \sum endosulfan > \sum chlordane > aldrin > dieldrin. The residue level was in good agreement with the usage of OCPs in Zhejiang. The spatial distribution showed that the residues of OCPs in soils from the mountain area were always higher than those in soils from the plains. The distribution characteristics were related to usage for current-use OCPs and temperature for never used OCPs. The isomeric ratios and enantiomeric fractions are useful tools to identify the degradation preference of contaminants. The wide range of ratios between *trans*-chlordane (TC) and *cis*-chlordane (CC) indicated that the degradation of the two isomers of chlordane was different at different sites. Nonracemic residues of TC and CC were observed in most soils; this is significant since the enantiomers have different toxicities.

KEYWORDS: organochlorine pesticides (OCPs), endosulfan, chlordane, dieldrin, enantiomers, China, soil

I INTRODUCTION

The United Nations Environment Programme (UNEP)/Stockholm Convention on POPs (persistent organic pollutants) listed 12 POPs (the dirty dozen) in 2004, among which 8 are organochlorine pesticides (OCPs): aldrin, chlordane, dichlorodiphenyltrichloroethane (DDT), dieldrin, endrin, heptachlor, mirex, and toxaphene.¹ Nine new POPs were adopted by the Conference of the Parties at its fourth meeting in May 2009, including several OCPs, α - and β -HCH, and lindane.² Current-use OCP endosulfan was recently classified as a POP by the Fifth Meeting of the Conference of the Parties³ and added to the Stockholm Convention in May 2011.

In China, DDTs and hexachlorohexacyclohexanes (HCHs) were banned from agricultural use in 1983, whereas chlordane was on China's 5 year exemption list and phased out in 2009 under the Stockholm Convention.⁴ Endosulfan is still on the list of allowable insecticides on crops at present in China.⁵ Aldrin and dieldrin were never industrially produced and used as an agricultural pesticide in China.⁴ Heptachlor (HEPT) was never applied in the purified form, but it is a component of technical chlordane, 5%.^{4,6}

Soils are still an important reservoir for POPs due to their persistence even though production of some POPs was stopped

30 years ago. Along with the oceans, POPs in soils are the major secondary source to air.^{7–9} Many researchers have investigated OCPs in Chinese soil, among which is the only nationwide concurrent air and soil monitoring program, the Chinese POPs Soil and Air Monitoring Program (SAMP). It was started in 2005 by the International Joint Research Center for Persistent Toxic Substances (IJRC-PTS), an international research institute currently joined by more than 10 universities/institutes from 6 countries (China, Canada, the United States, Vietnam, Japan, and South Korea). The objective of this program is to study and relate both temporal and spatial trends of POPs in the air and surface soil in China. This program collected both air and soil samples from around 100 sites across China; the results from this program have led to several publications,^{10–14} to which the results presented in this paper are compared.

Zhejiang province is an eastern coastal mountainous province of China, where hills and mountains account for 70% of the

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total area, while plains and basins make up 23%, and the remainder is composed of rivers and lakes. Zhejiang was also one district that had the highest OCP application in the country.⁴ In 2006 and 2007, soil monitoring in agricultural lands in 11 prefecture-level divisions of Zhejiang province was carried out, and OCP POPs were measured. The results for HCH (including α -, β -, γ -, and δ -HCH) were published,¹⁵ and those for DDTs are being prepared. In this paper we report the results for other OCP POPs, including endosulfan, chlordane (*trans*- and *cis*-chlordane (TC, CC)), heptachlor (including HEPT and HEPX), aldrin, and dieldrin. Since chlordane was still used as an insecticide in termite prevention and control in the sampling year in Zhejiang, chlordane and endosulfan were together classified as currently used OCPs. The enantiomeric signature of TC and CC was also determined in this study since it is a useful tool in helping to identify sources, emissions, atmospheric transportation, and redistribution of OCPs.^{16–18}

EXPERIMENTAL SECTION

Materials. Standards of α -endosulfan, β -endosulfan, endosulfan sulfate, TC, CC, HEPT, HEPX, aldrin, and dieldrin were purchased from Dr. Ehrenstorfer GmbH, Augsburg, Germany. All solvents used were purchased from TEDIA, Fairfield, OH (high-performance liquid chromatography (HPLC) grade). Gases were of high purity at 99.999% (Hangzhou Jingong Gas Co. Ltd., China). Anhydrous granular sodium sulfate (analytical grade, Hangzhou Huipu Co. Ltd., China) was baked at 400 °C overnight before use. Neutral silica gel (Merck, silica gel 60) and alumina (Merck, Beckman grade 1) were activated at 180 and 250 °C for 12 h and then deactivated with 3% (w/w) and 6% (w/w) HPLC grade deionized water, respectively.

Sample Collection. Soil samples were collected from 58 agricultural sites across Zhejiang province in 2006 and 2007, as described by Zhang et al.¹⁵ At each site, soil samples ($n = 8$, upper 20 cm) were collected and pooled to obtain a representative sample for each field. Samples were placed in precleaned aluminum foil, sealed in plastic bags, and stored at 4 °C until extraction.

Extraction and Cleanup. Approximately 20 g of the wet soil was mixed with sodium sulfate and Soxhlet extracted with dichloromethane (DCM; 150 mL overnight). The extract was reduced to 100 mL by rotary evaporation and initially cleaned up and solvent-exchanged to 5 mL of hexane by online gel permeation chromatography (GPC) and a concentration and evaporation processes system. The GPC parameters used to separate the target and impurities were as follows: mobile phase (solvent), DCM; flow rate, 5.0 mL/min; column preclean time, 10 s; forerun, 1020 s; fraction, 1000 s; tailing, 300 s; solvent exchange, three times. The separation was achieved on a column (2.5 cm (i.d.) \times 40 cm) packed with Bio-Beads S-X3 of 200–400 mesh (GPC Ultra 10836, LCTech GmbH, Munich, Germany). The solution from GPC was further reduced, solvent-exchanged to isooctane under a gentle stream of nitrogen to a final volume of 1–2 mL, and further cleaned up using an aluminum/silica column containing 4 g of silica gel topped with 2 g of aluminum. The targets were eluted by 105 mL of hexane containing 30% (v/v) DCM, solvent-exchanged into isooctane under a gentle stream of nitrogen, and adjusted to a volume of 1 mL for analysis.

Analysis. Analysis of soils for OCPs was carried out with an Agilent gas chromatograph 6890 equipped with a nickel-63 electron capture detector (μ ECD) and a Zebtron MultiResidue-1 column (30 m, 0.25 mm i.d., 0.25 μ m film thickness; Phenomenex, Torrance, CA). Samples were injected in splitless mode (split opened after 1.0 min) at 100 °C. After a 0.5 min hold, the oven was programmed at 35 °C/min to 220 °C and 20 °C/min to 280 °C and held for 10 min. Other conditions were as follows: injector temperature, 250 °C; detector temperature, 300 °C; carrier gas, He at 3.4 mL/min; makeup gas, N₂ at 60 mL/min. Samples were quantified against seven standards that spanned the concentration range of the samples. The conformational analysis was carried out on an HP-5 column (30 m, 0.25 mm i.d., 0.25 μ m film thickness; Agilent Technologies Inc., Santa Clara, CA). The

initial oven temperature was set at 80 °C for 1 min and ramped at 10 °C/min to 200 °C, 1 °C/min to 225 °C (1 min hold), and 15 °C/min to 260 °C (5 min hold). The other chromatographic conditions were the same as those described above. Random samples were injected into an Agilent 7890 GC-5973 C mass spectrometer (Agilent Technologies) with negative ion mass spectrometry for confirmation of the analysis accuracy of the above method.

After analysis of the residues, the samples were further concentrated for enantiomer analysis, which was done by capillary gas chromatography–electron capture negative ion mass spectrometry (GC–ECNI-MS) using a BGB-172 column (20% *tert*-butyldimethylsilylated β -cyclodextrin in OV-1701, 30 m, 0.25 mm i.d., 0.25 μ m film thickness; BGB Analytik AG, Switzerland) installed in an Agilent 7890 GC-5973 mass spectrometer. Samples (2 μ L) were injected splitless, and the split was opened after 1.0 min. The oven temperature program used for chiral separation was as follows: initial temperature of 90 °C, hold for 1 min, 15 °C/min to 160 °C, 1 °C/min to 190 °C, hold for 35 min, 20 °C/min to 230 °C, hold for 20 min. Helium was used as the carrier gas at a flow rate of 50 cm/s; injector and transfer line temperatures were set at 250 °C. The temperature of the ion source was 150 °C, and that of the quadrupole was 100 °C. The flow rate of methane was set at 40%. The monitor ions were (m/z 410 and 412) for TC and CC.

The elution orders on the BGB-172 for TC and CC enantiomers were confirmed by the single enantiomer collected from the outlet of the chiral JASCO LC-2000 series HPLC system (JASCO, Tokyo, Japan).¹⁹ For both TC and CC, the (+)-enantiomer eluted first. The results are agree well with the elution orders reported for these compounds.^{20,21} The elution order of enantiomers of chlordane on the BGB-172 was (+)-TC, (+)-CC, (–)-CC, (–)-TC.

Quality Control/Quality Assurance. Method blanks (solvent) were processed by extracting and analyzing 15 g of sodium sulfate using the same procedure as for the samples. Results from method blanks were used to assign method detection limits (MDLs), calculated as the mean of the method blank values plus 3 standard deviations. The MDL values were 0.05 ng/g for TC, CC, HEPT, and HEPX, 0.10 ng/g for α -endosulfan, β -endosulfan, and endosulfan sulfate, and 0.03 ng/g for aldrin and dieldrin. The results were not blank corrected. Analytical recoveries were monitored with the aid of the recovery standard decachlorobiphenyl (PCB209). The mean recovery for PCB209 was 78% \pm 9%. Data were not corrected for recoveries. Extraction procedures and recoveries of a standard containing all target compounds were assessed by spiking eight soil samples where residues were close to or below the detection limit. Recoveries ranged from 70% to 109%. A known quantity of pentachloronitrobenzene (PCNB) was added as an internal standard prior to gas chromatography electron capture detection (GC-ECD) analysis. Samples at each site were analyzed in triplicate. The acceptable residue values must meet the condition that the result difference between the columns is lower than 10%. A procedural blank was run with every set of 15 samples to check for the contamination from solvents and glassware.

The results of chiral analysis were expressed as the enantiomer fraction (EF), which was calculated by the areas of the (+)/[(+) + (–)] enantiomers. The precise integration of the enantiomer peaks and elimination of interferences is the key to ensure the quality of enantiomeric analysis. The limits for acceptable EF values were set as follows: (a) area ratios of the two monitored ions for samples and standards within \pm 5% and (b) agreement of EF values at each of the two monitored ions within \pm 5%.²² Racemic standards were injected into the GC–MS system repeatedly for every five samples to determine the reproducibility in measuring EFs. Average EF values of the standards were 0.501 \pm 0.003 for TC and 0.499 \pm 0.003 for CC, indicating the method is capable of highly precise enantiomeric analysis. Racemic standards were added to a control soil which contained very low residue levels before extraction. The EFs of recovered compounds are not significantly different from those of racemic compounds ($p > 0.05$), demonstrating that soil matrix effects did not alter the determination of the enantiomer fraction.

RESULTS AND DISCUSSION

OCP Residues in Soils. The concentration levels for individual OCPs and for all soil samples are given in Figure 1

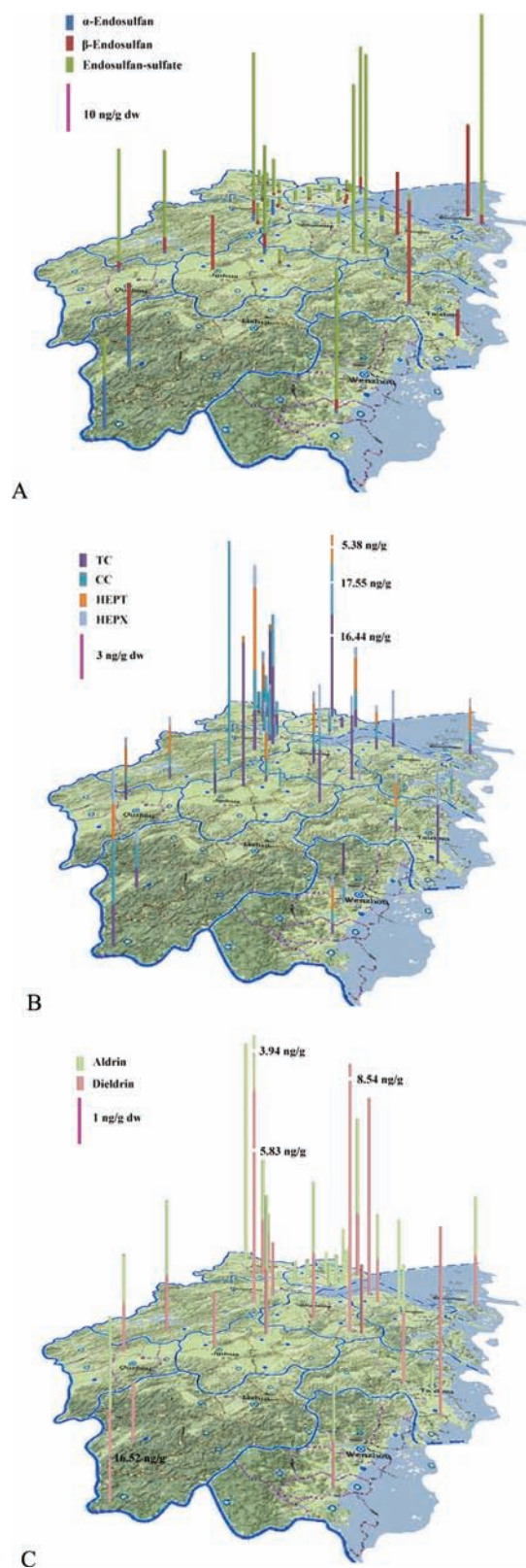


Figure 1. Spatial distribution of OCPs in agricultural soils in Zhejiang (A, endosulfans; B, chlordanes; C, aldrin and dieldrin).

and Table S1 (Supporting Information). Frequency distributions of concentration levels for all target compounds are presented in Table 1. The mass percentages of individual OCPs

Table 1. Frequency Distribution (%) for the Nine OCPs in 58 Soil Samples

OCP	≤BLD	BLD to 1 ng/g dw	1–10 ng/g dw	10–100 ng/g dw
α-endosulfan	72	5	21	2
β-endosulfan	52	22	17	9
endosulfan sulfate	41	0	40	19
TC	45	24	26	5
CC	48	17	31	3
HEPT	74	5	21	0
HEPX	55	28	17	0
aldrin	66	2	31	2
dieldrin	50	24	26	0

relative to total OCPs for all soil samples are illustrated in Figure 2. Endosulfans and chlordanes are two major OCPs in

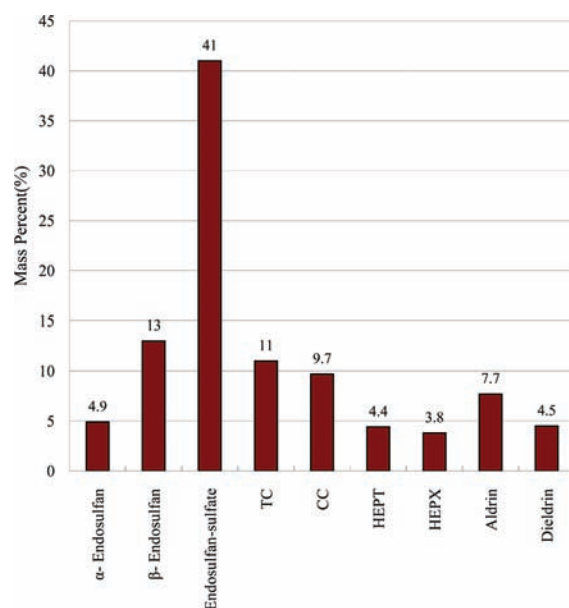


Figure 2. Mass percentage of individual OCPs relative to total OCPs for all soil samples.

the soils of Zhejiang, due to their local usage. Endosulfans were found to be the most abundant compounds and accounted for about 60% of total OCPs in all the samples, followed by chlordanes, which occupied about 29% of total OCPs with 11% TC, 10% CC, 4.4% HEPT, and 3.8% HEPX. The other OCPs are in the order aldrin (7.7%) > dieldrin (4.5%). The distribution agrees well with the usage of OCPs in Zhejiang, suggesting the major residues of OCPs in the soils of Zhejiang at present is not due to long-range transportation but from their local use. However, the contamination of OCPs from long-range transport is not negligible because aldrin and dieldrin, the OCPs not used locally in Zhejiang province, account for ~12% of the compounds sought.

Endosulfans. Endosulfan, a currently used organochlorine insecticide, has been extensively used for over 30 years on a wide variety of food crops, such as grains, tea, fruits, and vegetables, and on nonfood crops, such as tobacco and

cotton.²³ As an insecticide, endosulfan has been used only in agriculture in China to control pests on cotton since 1994 and on wheat, tea, tobacco, apples, and other fruits since 1998.¹⁰ Total endosulfan usage for 11 years from 1994 to 2004 was approximately 25 700 t, including 14 000 t on cotton, 4000 t on wheat, 2900 t on tea, 2200 t on tobacco, and 1900 t on apples.¹⁰ In Zhejiang, endosulfan was mainly used to control pests on tea and amounts to about 40 t annually.²⁴ Technical endosulfan consists of ~70% α -endosulfan and ~30% β -endosulfan.²⁵ These two isomers have similar insecticidal properties but different physicochemical properties^{26,27} and, along with their metabolite endosulfan sulfate, are generally considered to be equally toxic; therefore, the endosulfans and their metabolites are the focus of many investigations.²⁸

Endosulfan was found in most soil samples in this study, and at least one of the three endosulfan components was found in 42 of the 58 agricultural soils sampled. Among 42 samples, 3 spanned MDL to 1 ng/g endosulfans and 24 samples had endosulfans in the range of 1–10 ng/g, while the endosulfan concentrations in the remaining 15 varied from 11 to 42 ng/g dry weight (dw), consistent with the concentrations across China which ranged from BDL (below detection limit) to 19 ng/g dw with a geometric mean of 0.12 ng/g dw.³

The previous study showed endosulfans could be detected in most air samples of the Tai Lake region with an average concentration of 307 pg/m³ and a maximum concentration of 888 pg/m³.²⁹ As northern Zhejiang is an important part of the Tai Lake region, the residues in the soils of the region might have a great contribution to the high concentration of endosulfans in the air of the Tai Lake region.

Chlordane. Chlordane production began in 1960 in China, and the pesticide was mainly produced by about nine manufacturers located in East China over the next 40 years. The total production and application amount of chlordane was about 9000 t in China with a peak production amount of 840 t occurring in 1999. Technical chlordane was widely used as a chemical barrier to prevent termite damage in building foundations in 18 provinces of China, which always suffer from termites in the rainy season. Zhejiang province had the highest application record of chlordane among 18 provinces of China to keep building foundations protected from termites.⁴

The major components of technical chlordane are TC (13%), CC (11%), heptachlor (5%), and *trans*-nonachlor (TN, 5%).⁶

In this study, TC was found in 32 of the agricultural soils, while CC was found in 30 of the 58 soils. Levels of chlordanes in samples above the MDL ranged from 0.13 to 16 ng/g for TC and from 0.86 to 18 ng/g for CC (Table 2). The concentrations were below 5 ng/g for TC and CC in most of the soils, which were in agreement with those across China.¹ In SAMP, the mean soil concentration of total chlordane (ng/g dw) was 0.25 and ranged from BDL at more than 10 sites in northern China to 24 at an urban site in the City of Xiamen. The residues of chlordane in agricultural soils in Zhejiang were much higher than in the Pearl River Delta, China (0.237–0.885 ng/g dw).³⁰ Even though chlordane was not largely used in agricultural soils and the residues were predominantly from the usage of technical chlordane as a termiticide in this area, the detection ratio and residues were relatively high in agricultural soils, indicating the contamination of chlordane has been transported from application sites to the uncontaminated zone in Zhejiang. The highest values of both TC and CC were found at the same site, implying that the surroundings of the site

Table 2. Enantiomeric Fractions of TC and CC^a

Sample	TC	CC	Sample	TC	CC
HZ 1	0.431±0.008	0.565±0.014	JH 1	0.612±0.013	0.518±0.026
HZ 2	NA	0.587±0.009	JH 2	0.485±0.020	NA
HZ 3	NA	0.569±0.013	JH 3	0.564±0.009	0.571±0.015
HZ 4	NA	NA	JH 4	NA	0.424±0.023
HZ 5	NA	NA	JH 5	0.909±0.017	0.516±0.007
HZ 6	NA	0.898±0.022	SX 1	0.292±0.010	NA
HZ 7	NA	0.421±0.011	SX 2	NA	NA
HZ 8	0.459±0.012	0.582±0.013	SX 3	NA	NA
HZ 9	NA	NA	SX 4	NA	NA
HZ 10	NA	0.592±0.006	SX 5	0.495±0.007	0.386±0.012
HZ 11	0.493±0.009	0.460±0.008	QZ 1	0.493±0.010	0.491±0.022
HZ 12	0.484±0.010	0.511±0.007	QZ 2	NA	NA
JX 1	NA	NA	WZ 1	0.517±0.021	NA
JX 2	NA	NA	WZ 2	NA	0.579±0.021
JX 3	NA	NA	WZ 3	0.493±0.016	0.490±0.009
JX 4	NA	NA	NB 1	0.396±0.018	NA
JX 5	0.521±0.009	NA	NB 2	0.417±0.008	NA
JX 6	NA	NA	NB 3	NA	NA
JX 7	NA	NA	NB 4	NA	NA
JX 8	NA	0.574±0.017	NB 5	0.494±0.014	0.407±0.009
JX 9	0.565±0.012	0.461±0.012	TZ 1	NA	NA
JX 10	NA	NA	TZ 2	0.436±0.020	NA
JX 11	0.493±0.020	0.466±0.014	TZ 3	NA	NA
HUZ 1	NA	0.569±0.009	TZ 4	0.493±0.013	0.513±0.026
HUZ 2	0.484±0.016	0.572±0.013	ZS 1	NA	NA
HUZ 3	NA	0.509±0.012	ZS 2	0.493±0.014	0.408±0.012
HUZ 4	NA	NA	LS 1	0.477±0.009	0.560±0.011
HUZ 5	NA	NA	LS 2	0.495±0.015	0.507±0.010
HUZ 6	NA	NA			
HUZ 7	0.493±0.009	0.473±0.010			

^aThe shaded EF values are not significantly different ($p < 0.05$) from racemic, which are demonstrated by Student's t test.

might have suffered from serious termite damage. Compared with the highest concentration of chlordane in farms in the Fraser Valley of British Columbia, Canada²¹ (1576 ng/g), and soils from the U.S. corn belt²² (752 ng/g), the highest residues of chlordane were very low in Zhejiang.

HEPT and HEPX. Heptachlor, a chlorinated cyclodiene insecticide, was isolated from technical chlordane in 1946. Technical-grade heptachlor contains ~72% heptachlor and ~28% related compounds, including about 20% *trans*-chlordane. Heptachlor epoxide is a soil oxidation product of heptachlor.²²

The mean soil concentration of heptachlor (ng/g dw) measured under SAMP was 0.12 and ranged from BDL to 2.0, with similar concentration levels among urban, rural, and background sites.¹ Similar results were found in the present work. Residues of HEPT were above the MDL in 15 soils with a range of 0.44–6.1 ng/g dw. HEPX had a higher detection ratio than HEPT and was found in 25 of 58 samples with levels ranging from 0.21 to 3.3 ng/g dw. Since HEPT is rapidly converted into HEPX or other metabolites,²² it is not surprising that the detection ratios of the parent are lower than those of its metabolite.

The purified form of HEPT was not used as an agricultural pesticide in China, but it is a component (~5%) of technical chlordane.⁶ The study on the relationship between the concentrations of HEPT + HEPX and chlordane indicated

the sum amount of HEPT and HEPX is significantly correlated with the amount of chlordane (Figure 3, $r = 0.42$, $p < 0.001$).

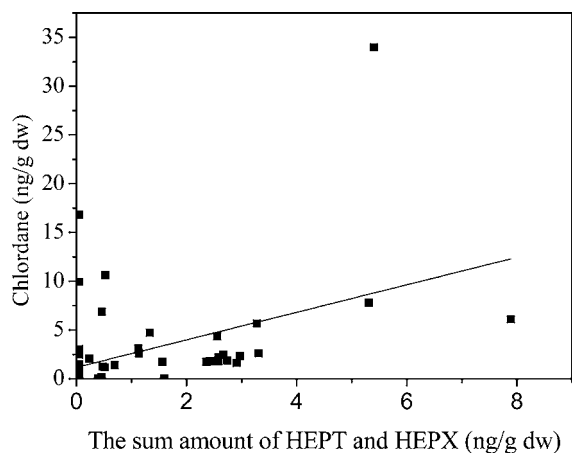


Figure 3. Significant relationship between the residues of chlordane and the sum residues of HEPT and HEPX ($r = 0.42$, $p < 0.001$).

The significant correlation suggested that the residues of HEPT and HEPX in soils in Zhejiang were mainly from local application of chlordane and not the result of long-range atmospheric transportation.

Aldrin and Dieldrin. Aldrin was found in only 21 of 58 samples with levels ranging from 0.70 to 8.5 ng/g for all of the soils except LS2, which contained 17 ng/g dw (Table S1, Supporting Information). The concentrations of detectable dieldrin in 29 samples ranged from 0.34 to 5.0 ng/g. The results were generally in agreement with the observations under SAMP which indicated the mean soil concentration of the drins, including aldrin, dieldrin, and eldrin (ng/g dw), was 0.88 and ranged from BDL to 30. The correlation between aldrin and dieldrin is significant ($r = 0.33$, $p = 0.006$) but is driven by the highest aldrin concentration (LS2), and removing this point resulted in a nonsignificant regression ($r = 0.18$, $p = 0.09$). Aldrin and dieldrin were never industrially produced and used in China.⁴ Therefore, it is postulated that their residues in sampled soils were mainly transported from other regions. However, illegal usage could not be excluded in some sites with high residues. Similar results were observed in a previous study which investigated the concentration of OCPs in surface water and sediments in Qiantang River, the largest river of Zhejiang, and found residues of dieldrin in most water and sediment samples.³¹

The wide distribution of never used aldrin and dieldrin possibly indicated that they have been continuously input into China by long-range atmospheric transport. Further studies are needed to better understand the environmental behavior and fate of currently used and never used OCPs in China.

OCPs in Mountain and Plain Agricultural Soils.

Zhejiang is a hilly province, where hills and mountains account for 70% of the total area with the rest being plains, rivers, and lakes. The climate records indicated the average annual temperature of the mountains is lower than that of the plains in Zhejiang. Moreover, the temperature difference between mountains and plains quickly increased during the period from 1981 to 2006, since the temperature in the plains increased much faster than that in the mountains assumably under the influence of climate change.³² The relationship between soil concentrations of HCHs and elevation, and thus temperature,

and also between soil concentrations and HCH usage were investigated in a previous study. Significant correlations were found between soil concentrations and elevation ($r = 0.52$, $p < 0.001$) and temperature ($r = -0.55$, $p < 0.0001$), but not between soil concentrations and total technical usage ($r = -0.24$, $p = 0.1$). This was considered as a typical *secondary distribution pattern*, in which the distribution of chemicals is governed by temperature and organic carbon in soil, not the usage of these chemicals.¹⁵

Similar research was carried out for other OCP POPs. A definition of mountain and plain sites used by ref 15 was used in this study: the areas with an elevation of <100 m are plains, while those with an elevation of >100 m are mountains. On this basis, out of the 58 sampling sites, 19 are mountains and 39 are plains. Σ chlordane (sum of HEPT, HEPX, TC, and CC) was used in comparing concentrations between plain and mountain sites. Figure 4 presents the mean concentrations of target OCPs

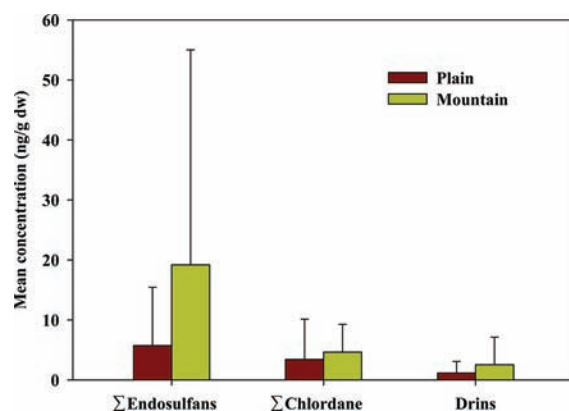


Figure 4. Mean concentrations of target OCPs in plain and mountain areas.

in soils in plains and mountains. It is interesting to note that all these OCPs had higher concentrations in mountain sites than in plain sites, similar to the soil concentrations of HCHs in the same province,¹⁵ which, however, does not necessarily indicate the secondary distribution pattern. Endosulfan was a currently used insecticide in the sampling year, and its distribution pattern should be a primary pattern, not a secondary pattern. The reason why its concentration in soil was higher in mountain areas than in plain areas is that this OCP was mainly used on tea in this province, and tea generally grows in mountain areas in Zhejiang province. On the other hand, aldrin and dieldrin have never been used in Zhejiang province; their existence in soil in the province is most likely from other areas where the insecticide has been applied through long-range transport. Thus, it is not unexpected that their distribution in soil appears as a “secondary pattern” or “cold condensation”.

With respect to chlordane, we do not have the usage data for the mountain and plain sites; however, it can be deduced that the distribution might also be a “primary pattern” by application records that show chlordane was continuously used until 2009 in China.⁴

Isomeric and Enantiomeric Composition of TC and CC. The ratio of TC to CC is variable in technical chlordane produced in different countries. Previous studies reported the ratios of TC to CC in environmental samples are significantly different from that in technical chlordane used in the district of sample collection.^{21,30,33} In the present study, both TC and CC

were below the MDL in 20 soil samples, 8 soils had only TC, and only CC was detected in 6 soils. In the remaining 24 soils with detectable TC and CC, the ratios of TC to CC ranged from 0.21 to 2.58, while the ratio in technical chlordane from the Chinese market is 0.76–0.87.³⁰ The results were similar to most of the published data^{22,30,33} and indicated the degradation rate of one isomer was not always more prevalent than that of the other isomer in Zhejiang agricultural soils.

The EFs of TC showed that (+)-TC was preferentially degraded in 10 of 26 samples in a sufficient amount for chiral analysis with EFs ranging from 0.292 to 0.484, (–)-TC in 5 samples (EF = 0.521–0.909), and racemate in 11 samples. For CC, 29 samples had sufficient amounts; the (–)-enantiomer was degraded in 13 with EFs ranging from 0.516 to 0.898, 10 soils showed selective degradation of the (+)-enantiomer (EF = 0.387–0.473), and racemic residue was found in 6 soils. This was approximately similar to the pattern observed in agricultural soils from the U.S. Corn Belt ((–)-TC, and (+)-CC were in excess in all soils with nonracemic compositions),²² soils from Alabama (enantioselective degradation of (+)-TC and (–)-CC was found in a large majority of samples),³³ soils from southern Sweden (all soils but one showed preferential degradation of (+)-TC and (–)-CC),³⁴ archived soils in the United Kingdom (the ranges of EFs are 0.40–0.48 for TC and 0.50–0.57 for CC),³⁵ and most of the global background soils (depletion of (+)-TC and (–)-CC).²⁰ The minimum TC EF of 0.292 in this study was higher than that of 0.237 in crop soils of the Pearl River Delta,³⁰ but far lower than that in most soils from other districts.^{20,22,33,35} The minimum EF of CC was 0.387 in this work, while it was 0.352 in Pearl River Delta soil³⁰ and 0.08 in background soils.²⁰ The maximum EF of TC and CC in the studied soils was 0.65 and 0.898, respectively, while the reported maximum EF of TC was 0.885 in Pearl River Delta soil,³⁰ and that of CC was 0.846 in background soils.²⁰ The enantioselective degradation of TC and CC is very significant for environmental risk assessment of chlordane due to differences in toxicity of the enantiomers and needs further study.

■ ASSOCIATED CONTENT

Supporting Information

Concentration levels of OCPs (Table S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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