https://doi.org/10.17221/50/2019-SWR

Concentrations and sources of persistent organochlorine residues in the sediments and soils from an industrially impacted area in Anhui, China

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Citation: Yang J., Zhao Y.L., Zhen Q., Chen X., Zhang Y. (2020): Concentrations and sources of persistent organochlorine residues in the sediments and soils from an industrially impacted area in Anhui, China. Soil & Water Res., 15: 148–157.

Abstract: In this study, a typical site that had been contaminated by the chemical industry in the past was selected for investigation. To reveal the pollution status, 18 organochlorine pesticides (OCPs) and seven polychlorinated biphenyls (PCBs) in the surface soil and sediment samples were analysed by gas chromatography-mass spectrometry (GC-MS). The levels of the persistent organochlorine residues in the sediment ranged from 44.59–143.29 ng/g, whereas they were 13.94–97.91 ng/g in the soil. A principal component analysis identified that PCBs and dichlorodiphenyltrichloroethanes (DDTs) were the primary sources of the organochlorine residues in the study area. The *p,p'*-DDT/(*p,p'*-DDE + *p,p'*-DDD) values were all below 1, which indicated that the historical inputs of the technical DDT and dicofol were the major sources of DDTs rather than recent inputs. The composition diversity of the hexachlorocyclohexane (HCH) isomers showed that the main sources in the soil were the past use of pesticides, whereas the sediment sources might be due to the historical use of technical HCHs and recent lindane inputs. The ecological risk assessment showed that γ-HCH could pose the highest risks for benthic organisms, followed by DDTs and heptachlor epoxide. These compounds are known to bio-accumulate in fatty tissues. Therefore, routine monitoring of the persistent organochlorine residues in the area is needed and the health risks to local residents should be assessed.

Keywords: ecological risk assessment; OCPs; PCBs; sediment; soil

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are two classes of persistent organic pollutants (POPs). Experimental and epidemiological studies have suggested that most OCPs and PCBs are highly toxic, and studies have suggested that they may cause cancer (Polanco Rodriguez et al. 2017; Paydar et al. 2019), endocrine disruption (Rossi et al. 2018), neurological damage (Medehouenou et al. 2019) and reproductive system disturbances (Martenies & Perry 2013), even at low concentrations. Since 1970, most of them have been banned under the Stockholm Convention and are no longer used. However, PCBs and OCPs have been detected in soils, air particles, water, food and biological tissues (Degrendele et al. 2016; Aerts et al. 2019; Makris et al. 2019; Tran et al. 2019).

Soils and sediments play an important role in the global storage and distribution of POPs. The logKow values of PCBs and OCPs ranged between 3 and 10 (Wang et al. 2017a). This means that they easily combine with organic matter and enter the soil and sediment through river inputs, surface erosion, and atmospheric deposition (Zhan et al. 2017). However, the accumulation of PCBs and OCPs in soils and sediment means that they could be re-emitted into water, the atmosphere, and crops, and could enter

Supported by Excellent Young Talents Fund Program of Higher Education Institutions of Anhui Province, Project No. gxyqZD2016162; the Natural Science Foundation for colleges and universities of Anhui Province, Project No. KJ2015A212, No. KJ2017A227, No. KJ2018A1021 and No. KJ2015B069by.

https://doi.org/10.17221/50/2019-SWR

the human body through the food chain. Therefore, studying PCBs and OCPs in sediments and soils is important when attempting to protect the environment. It is particularly important to reveal their source and transformation processes (Zhan et al. 2017; Nguyen et al. 2019).

The study area was located in the village of Qiugang, north of the city Bengbu near the Huaihe River in China. The village Qiugang was famous for a short environmental documentary entitled "The Warriors of Qiugang" which was nominated for the 83rd Academy Awards for the best Documentary Short film in 2011. Three chemical plants were built in this village during the 1970s. The pesticides and chemical products produced by these factories were: organophosphorus pesticides, organochlorine pesticides, dichlorvos, trimethyl esters, 3,4-dichloroaniline, p-chlorophenyl isocyanate, p-phenylenediamine, and other substances. Baojia is a ditch in the village of Qiugang. It was a drainage canal that discharged wastewater from the pesticide factories and chemical plants into the Huaihe River, and was also an irrigation canal for the nearby agricultural production. Serious environmental pollution led the local government to begin improving the water quality of the Baojia ditch in 2012. The measures taken by the local government included closing the factories and removing the upper silt, which are environmental protection measures that are currently being implemented across wide areas of China. However, there is no evaluation of their effectiveness. Therefore, five years later, we tested the upper silt from the Baojia ditch and the soil from the nearby villages in order to evaluate the local environment and provide data support for the environmental protection treatments in similar areas.

MATERIAL AND METHODS

Study area and sample collection. A total of 17 soil samples (0–20 cm layer) and 13 surface sediment samples (0–20 cm layer) were taken using a stainless-steel shovel or grab in winter in 2017 to evaluate the occurrence of PCBs and OCPs in the Baojia ditch irrigation area. The land-use types included farmland, vegetable fields, forests, uncultivated lands, and other agricultural uses. The sampling sites are shown in Figure 1. At each site, three samples, that were 2 m apart from each other, were combined to give a composite sample. The large stones and extraneous material were removed and about 1.0 kg of each soil sample was used for the analyses. The samples were air-dried and then milled through a 0.15 mm sieve. They were kept at –4 °C before the extraction process.

Sample extraction and clean-up. A focused ultrasound extraction method (FUSE) was used to extract 18 OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, g-chlordane, cis-chlordane, heptachlor, heptachlor epoxide B, heptachlor epoxide A, endosulfan I, endosulfan II, aldrin, dieldrin, endosulfan sulfate, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, and *p,p'*-DDT) and seven PCBs (PCB 28, 52, 101, 118, 138, 153, and 180) in the soil and sediment samples. In this study, 2,4,5,6-tetrachloro-m-xylene (TCMX) and PCB 209 were invoked as the surrogate standard and spiked before the extraction, which reached a concentration of 20 ng/g. A total of 2 g of the samples was sonicated in a 12 ml mixture of acetone: n-hexane (6.2 : 3.8, v/v) for 40 min using an ultrasonic device (Scientz-IIDM, Ningbo, China). The ultrasonic extraction was repeated three times. After each ultrasonic

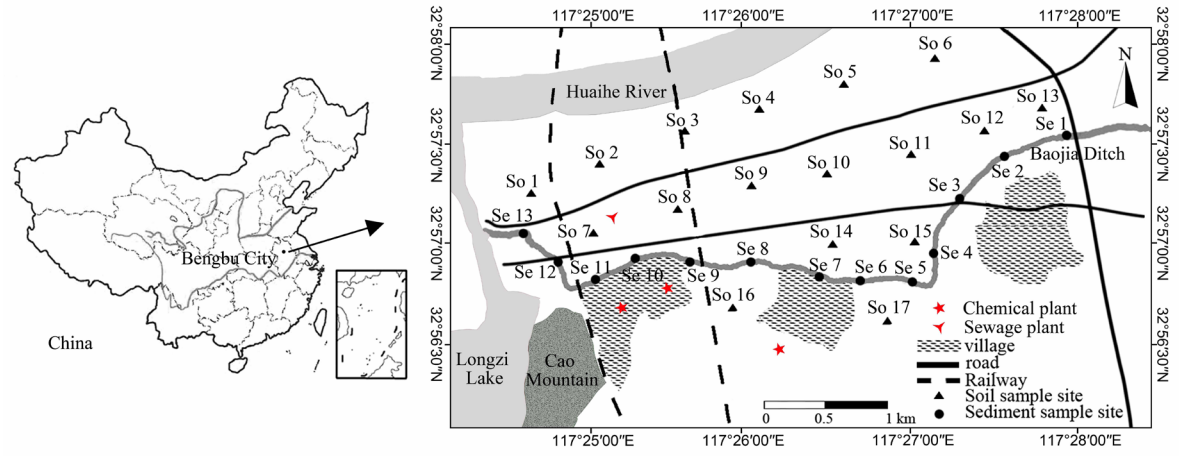

Figure 1. Location of the sampling points

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treatment, all of the extraction solvent was collected and evaporated to 1 ml under a mild nitrogen flow, and then the sample was subjected to soil phase extraction (SPE) clean-up.

Organochlorine pesticides and polychlorinated biphenyls analyses. The OCP and PCB analyses were undertaken using an Agilent 7890A GC-5975C MS. The analytes were separated by a HP-5 MS capillary column (30 m × 0.25 mm I.D., 5% phenyl-methylpolysiloxane, 0.25 μm). The column oven temperature was initially 50 °C for 1 min, ramped up at 30 °C/min to 150 °C for 1 min, 10 °C/min to 180 °C for 3 min, 3 °C/min to 210 °C for 1 min, 5 °C/min to 250 °C, and finally 15 °C/min to 290 °C for 3 min (the total acquisition programme time: 36 min). Then 1 μl of the extracted or standard solutions was injected into the analyser in the splitless mode.

Quality control procedure and data analysis. The sample concentrations were quantified by an external standard multipoint calibration. The correlation coefficients (r^2) of all the calibration curves were greater than 0.998. Laboratory blanks and fortified blanks were run once every 10 samples. All the samples were analysed in triplicate and the relative standard deviations (RSDs) were < 15%. The surrogate recoveries in all the samples were 76 ± 14% and 87 ± 15% for TCMX and PCB 209, respectively. The logarithm of the odds (LODs) estimated on the basis of a signal-to-noise ratio (S/N) of 3, were in the range 0.05–0.25 ng/g. The extraction recoveries were determined using the spiked samples (20 ng/g) and ranged from 88.1% to 102.1%. Their RSDs were less than 6% (n = 6).

The statistical analyses were undertaken using SPSS (Ver. 22.0, 2013). Samples below the detection limit were replaced by zero in the statistical analysis (Devi et al. 2015). Student's t-test was used to test for the significant differences by the least significant difference at a P < 5% significance level. A hierarchical cluster analysis (HCA) and a principal component analysis (PCA) were also carried out using SPSS 22.0, and the results are graphically displayed as loading plots.

RESULTS AND DISCUSSION

The OCP and PCB analytical results are summarised in Table 1. The results showed every sample contained organochlorine pollutants. The surface sediments contained higher concentrations of the total contaminants than the soils (t-test, P < 0.05). The highest concentration was at site Se 11, which was located beside the village of Qigang, and was close to the factory sewage outlet and the local sewage treatment facility. The highest concentration in the soil was at site So16, which was close to the closed chemical plant and showed higher concentrations of DDTs and PCBs.

Hierarchical cluster analysis. A hierarchical cluster analysis was conducted to classify the sampling sites into groups according to the persistent organochlorines in the samples and their concentration changes. The sites in the study area divided into four groups according to their contamination degree (Figure 2). Most of the soil and upstream sediment sampling sites were classified as being in category A, which represents an environment that is less affected by the pollution. Se 1, the most upstream sediment sampling site, fell into category B, which means it may have a pollution-free background value. Se 13 and Se 11, located in the downstream part of the river and near the villages and sewage treatment plants, were in category C, which means they may be exposed to more serious pollution. The D category contains sediment samples from the middle and lower reaches of the Baojia ditch. This suggests that these sites were moderately contaminated. The soil sample sites So 15, So 16 were in category D. They were close to the river and the original pesticide plant, respectively, and the results indicated that they had similar sediment pollution sources.

Composition and the levels of OCPs. The OCP pollution levels in the soil were less than in the sediment, with mean concentrations ranging from 12.20 ng/g (site So 11) to 66.47 ng/g (site So 16) and 18.09 ng/g (site Se 2) to 97.04 ng/g (site Se 11) for the soil and sediment samples, respectively. In both the soil and sediment samples, DDTs and HCHs were the major pollution components, and they accounted for 84.86% and 68.84% of the total OCPs in the soil and sediment, respectively. The other OCPs in the sediments with a detection rate from high to low, were aldrin, heptachlor, cis-chlordane, heptachlor epoxide B, endosulfan II, g-chlordane, heptachlor epoxide A, dieldrin, endosulfan I, and endosulfan sulfate. The detection rates of the other OCPs, except endosulfan II, were lower than 50% in the soil, which indicated that their historical usage was not large.

A comparison between this study and other areas is given in Table 2. The OCP residues (18.09–97.04 ng/g) in the sediments results for this study were greater than in those collected from the Huaihe River (4.16 to

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14.4 ng/g) (Da et al. 2017), and Lake Chaohu (0.03 to 86.27 ng/g) (Li et al. 2015). This can be attributed to the former chemical plants that discharged waste water into the Baojia ditch. Conversely, the OCP concentrations in the sediments taken in this study were lower than those collected from the Jiaomen River, which flows through a well-developed urban region (27.55–660.13 ng/g) (Wang et al. 2017b). This may have been due to the relatively earlier closure of the chemical factories, and to the efforts that the government has made to clean up the Baojia ditch.

In China, HCHs in soils and sediments can be derived from technical HCH and lindane. Technical HCH contains α-HCH (60–70%), β-HCH (5–12%), γ-HCH (10–15%), and δ-HCH (6–10%), whereas lindane mainly contains γ-HCH (> 99%) (Bajwa et al. 2016). The ratio of α-HCH/γ-HCH ranged from 4 to 7 indicates the use of technical HCHs, and nearly zero indicates the use of lindane (Wang *et al.* 2017b). The α-HCH and γ-HCH can be transformed into β-HCH. Therefore, the β-HCH/(α-HCH + γ-HCH) ratio was used to determine whether the HCH levels were due the historical pollution (Wang et al. 2016a). In our samples, γ-HCH had the highest concentration out of the four HCH isomers in the soil and sediment samples and accounted for 43.01% and 41.02% of the

Table 1. The concentration of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in the samples around the Baojia ditch

Compounds	Sediment samples (n = 13)				Soil samples (n = 17)			
	range	mean	SD	detection frequency (%)	range	mean	SD	detection frequency (%)
	(ng/g)				(ng/g)			
α-HCH	0.89–4.76	2.76	1.26	100.00	0.00–4.37	2.02	1.53	88.24
β-HCH	0.99–3.67	2.19	0.93	100.00	1.34–4.86	3.04	1.09	100.00
γ-HCH	2.80–6.93	4.74	1.20	100.00	2.42–8.54	3.95	1.51	100.00
δ-HCH	0.00–5.32	1.33	1.84	53.85	0.00–2.64	0.75	1.05	41.18
p,p'-DDE	2.08–16.79	9.76	4.62	100.00	1.86–11.96	5.00	2.82	100.00
p,p'-DDD	1.32–10.77	5.46	2.84	100.00	1.62–6.31	3.07	1.19	100.00
o,p'-DDT	1.38–8.84	5.59	2.19	100.00	0.00–6.09	2.47	1.37	94.12
p,p'-DDT	0.70–13.72	8.93	4.20	100.00	1.24–11.78	3.99	2.63	100.00
Heptachlor epoxide B	0.00–5.21	1.90	1.50	84.62	0.00–1.60	0.23	0.52	17.65
Heptachlor epoxide A	0.00–5.41	3.12	2.03	76.92	0.00–2.34	0.41	0.92	17.65
Heptachlor	0.00–5.76	3.10	1.71	92.31	0.00–3.61	1.04	1.39	41.18
Aldrin	0.53–4.70	2.31	1.32	100.00	0.00–2.17	0.42	0.73	29.41
Dieldrin	0.00–5.62	1.49	1.90	61.54	0.00–2.34	0.14	0.57	5.88
g-Chlordane	0.00–4.09	1.64	1.23	84.62	0.00–1.24	0.27	0.44	29.41
cis-Chlordane	0.00–4.64	2.32	1.40	84.62	0.00–2.44	0.57	0.94	35.29
Endosulfan I	0.00–3.25	0.76	1.24	30.77	0.00–1.83	0.11	0.44	5.88
Endosulfan II	0.00–3.31	1.70	1.09	84.62	0.00–3.45	1.09	1.26	52.94
Endosulfan sulfate	0.00–0.89	0.12	0.30	15.38	0.00–0.39	0.02	0.09	5.88
∑ OCPs	18.09–97.04	59.22	22.78		12.20–66.47	28.60	14.56	
PCB 28	1.75–6.52	3.54	1.43	100.00	0.55–4.47	1.62	1.15	100.00
PCB 52	1.04–5.73	3.02	1.46	100.00	0.00–3.43	0.95	1.14	58.82
PCB 101	1.57–7.21	3.59	1.82	100.00	0.00–4.17	0.92	1.33	47.06
PCB 118	2.16–7.52	4.34	1.74	100.00	0.00–5.09	1.13	1.65	47.06
PCB 138	1.78–9.04	4.18	2.15	100.00	0.00–4.80	1.26	1.49	70.59
PCB 153	2.17–7.21	4.06	1.56	100.00	0.00–4.35	1.20	1.40	52.94
PCB 180	1.93–9.85	4.49	2.33	100.00	0.00–5.13	1.68	1.41	94.12
∑ PCBs	13.53–46.25	27.22	11.93		0.55–31.44	8.76	9.44	
∑ OCPs + ∑ PCBs	44.59–143.29	86.43	29.23		13.94–97.91	37.35	23.38	

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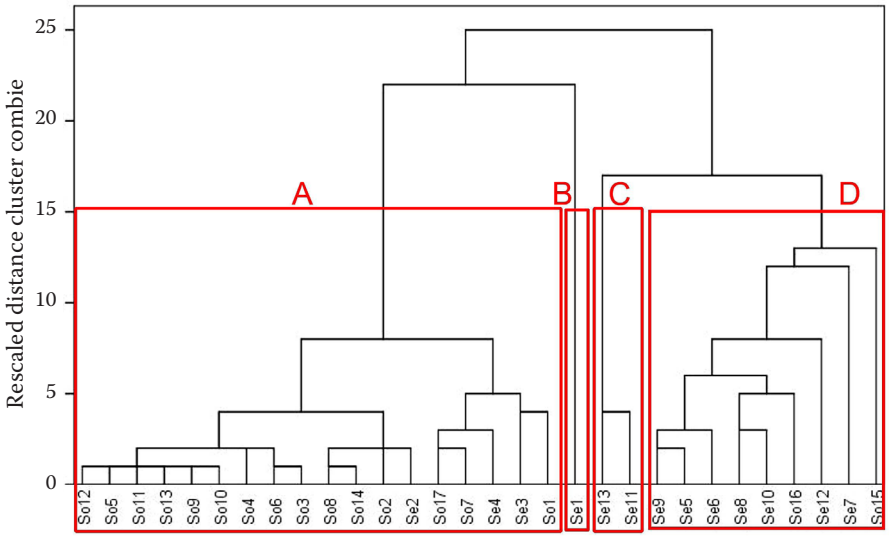

Figure 2. The dendrogram of the hierarchical cluster analysis of the samples

total HCHs, respectively (Figure 3A). The α-HCH/γ-HCH ratios were all below 1 (Figure 4A), and the β-HCH/(α-HCH + γ-HCH) ratio was greater than 0.5 in 64.17% of the soil samples, which suggests that the historical usage of lindane was the major source of the HCHs in the soil samples. Only 15.38% of the sediment samples had ratios over 0.5, which indicated that the contamination was due to recent lindane inputs.

The percentage compositions of the DDTs are given in Figure 3B. Among the DDTs, *p,p'*-DDE and *p,p'*-DDT were the major contaminants, with concentrations reaching 9.76 ng/g and 8.93 ng/g in the sediment, and 5.00 ng/g and 3.99 ng/g in the soil, respectively. *p,p'*-DDT can degrade to *p,p'*-DDE in aerobic environments or *p,p'*-DDD in anaerobic environments (Muzyed et al. 2017). Figure 3B shows that *p,p'*-DDE > *p,p'*-DDD in all the samples, which indicated that the dechlorinated DDTs in the study area were mostly exposed to oxic conditions with a small proportion of them exposed to anaerobic conditions. The *o,p'*-DDT/*p,p'*-DDT ratio was used

Table 2. The hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) concentrations in the soils and sediments from the other areas (ng/g)

Region	Σ HCHs	Σ DDTs	Type	Reference
Jinsha	0.006–0.096	0.034–0.904	soil	Zhan et al. (2017)
Changbai Mountain	3.1–25.6	0.95–19.4	soil	Wang et al. (2017c)
Yellow River Estuary	0.51–208.48	nd–109.16	soil	Perez-Palacios et al. (2012)
North-eastern part of Sao Paulo State	0.05–0.92	0.12–11.01	soil	Rissato et al. (2006)
Mexicali Valley	0.034–8.0	1.3–152	soil	Sanchez-Osorio et al. (2017)
Yaqui Valley	0.035–3.1	0.13–268	soil	Sanchez-Osorio et al. (2017)
Present study	4.80–20.31	6.74–31.84	soil	
Pearl River Delta	4.64–21.31	2.54–21.86	sediment	Wang et al. (2017b)
Yellow River Estuary	0.56–232.60	nd–52.03	sediment	Perez-Palacios et al. (2012)
Mexicali Valley	0.022–3.4	1.5–30	sediment	Sanchez-Osorio et al. (2017)
Yaqui Valley	0.032–5.6	0.21–55	sediment	Sanchez-Osorio et al. (2017)
Yellow River Estuary	0.56–232.60	nd–52.03	sediment	Perez-Palacios et al. (2012)
Huaihe River	2.54–13.91	0.016–2.54	sediment	Da et al. (2017)
Chaohu Lake	0.04–7.12	0.23–85.83	sediment	Li et al. (2015)
Present study	6.65–16.48	5.48–47.77	sediment	

nd – not detected

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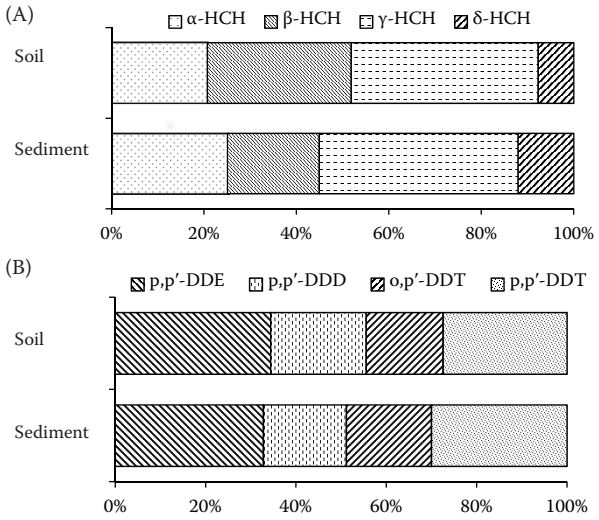

Figure 3. The percentages of the composition of hexachlorocyclohexanes (HCHs) (A) and dichlorodiphenyltrichloroethanes (DDTs) (B) in the soil and sediment samples

to determine whether the DDTs originated from a technical DDT or a dicofol (Degrendele et al. 2016). The technical DDTs generally contained *p,p'*-DDT (75%), *o,p'*-DDT (15%), *p,p'*-DDE (5%), and other trace impurities (< 5%). The results showed that the dicofol-type DDT had a higher *o,p'*-DDT/*p,p'*-DDT ratio (1.3–9.3) than the technical DDT (0.2–0.3) (Li et al. 2008). The *o,p'*-DDT/*p,p'*-DDT ratios shown in Figure 4B ranged from 0 to 1.97, with a mean of 0.74. All the sediment samples and 88.2% of the soil samples had a value of > 0.3, which suggested that the detectable DDTs were derived from both a technical DDT and a dicofol. A *p,p'*-DDT/(*p,p'*-DDE + *p,p'*-DDD) ratio that is higher or lower than 1 shows recent inputs of DDT or the long-term biodegradation of DDT, respectively (Zhang et al. 2015). In the studied region, the *p,p'*-DDT/(*p,p'*-DDE + *p,p'*-DDD) ratios were all < 1, which indicated that the historical usage of technical DDTs and dicofol were the main pollution sources.

Composition and levels of PCBs. Table 1 shows that the total PCB levels in the sediment (13.53–46.25 ng/g) exceeded those in the soil (0.55–31.44 ng/g). This might be because the PCBs have high logKow values and accumulate in matrices with high organic matter contents, such as sediments. The PCBs concentrations in the sediment were higher than those measured in the sediments from the Huangpu River, China (3.04–7.56 ng/g) (Wang et al. 2016b) and were similar to those recorded for Lake Baiyangdian, China (5.96–29.61 ng/g) (Zhang et al. 2011).

Figure 5 shows that PCB 180 was the major congener in both the sediment (4.49 ng/g, 16.50%) and the soil (1.68 ng/g, 19.18%) samples. The profiles of the PCBs in all the samples were dominated by hepta-, hexa- and penta-CB, which accounted for > 70% of the total PCB concentrations. These results suggest that Aroclor 1260 and 1262 had been used or produced in the past. The high chlorine components in the study area PCBs were considerably higher than in the domestic PCB products, which may be due to the input of foreign PCBs and the enrichment of high chlorine components. It may also be related to the linear distance between the research site and the local refuse incineration plant, which is less than 7 km. Studies have shown that PCB homologues are mainly substituted by high chlorine monomers in fly ash from refuse incineration (Zhao 2015). PCB 28 was

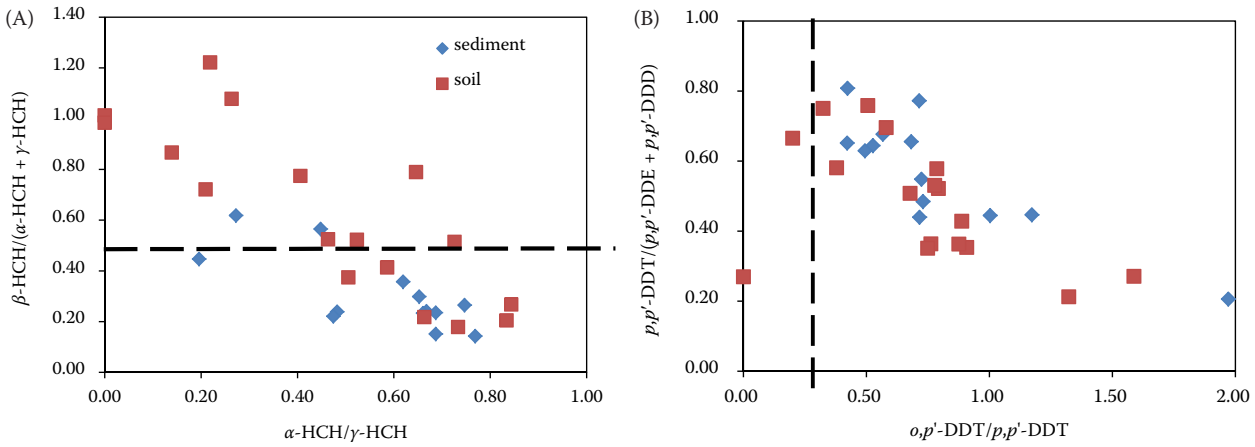

Figure 4. The composition of hexachlorocyclohexanes (HCHs) (A) and dichlorodiphenyltrichloroethanes (DDTs) (B) in the study area

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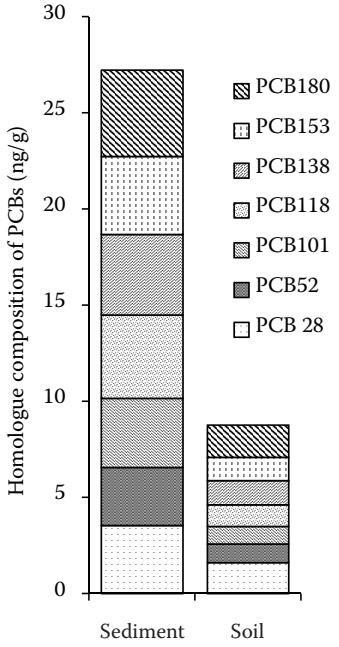
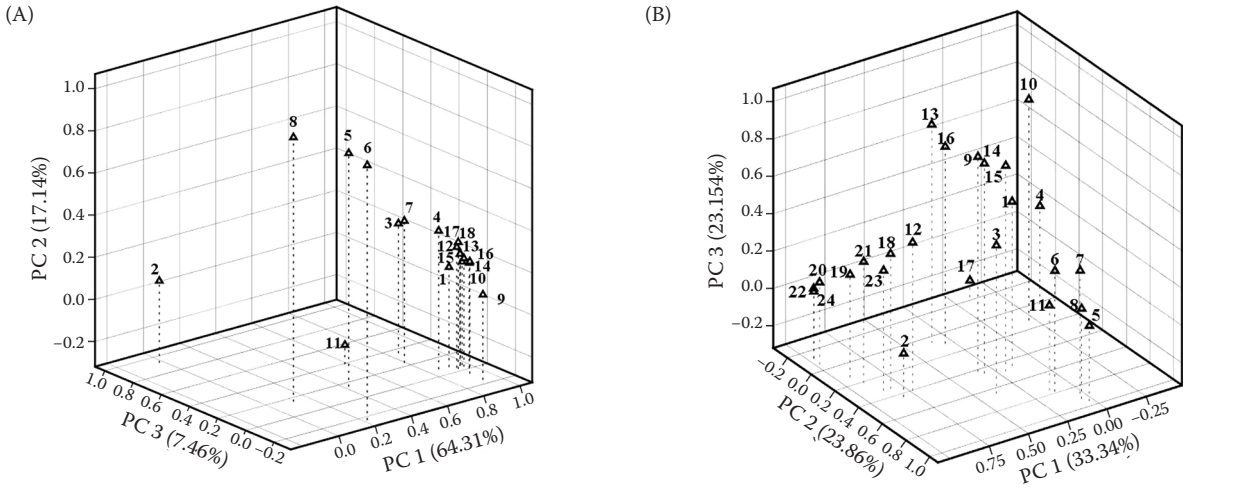


Figure 5. The homologue composition of polychlorinated biphenyls (PCBs)

the second major congener in the soils and accounted for 1.62 ng/g (18.50%) of the total PCB concentration. Generally, the PCB mobility increases as the number of chlorine atoms decreases. Lighter PCBs may get transported over longer distances in the atmosphere (Wang et al. 2016b). Therefore, the origin of the PCBs in surface soil may be attributed to the historical application of commercial PCBs and the combustion sources from the atmospheric deposition.

Principal component analysis. The PCA was used to identify the possible sources of the OCPs and PCBs in the soil and sediment. In this study, the detection rates for heptachlor epoxide B, heptachlor epoxide A, aldrin, dieldrin, g-chlordane, endosulfan I, and endosulfan sulfate in the soil samples and endosulfan sulfate in the sediment samples were low (all < 30%), and less residual (all the mean concentrations were < 0.5 ng/g). Therefore, these OCPs were not included in the PCA.

Figures 6A, B show the PCA loading plots for the soil and sediment, respectively. The soil analysis showed that three factors explained 88.91% of the data variance in the chlorinated compounds. The first principal component (PC 1) explained 64.31% of the total variance, and was highly loaded by PCB 101 (0.969), PCB 138 (0.969), PCB 52 (0.968), PCB 118 (0.963), PCB 180 (0.954), PCB 28 (0.930), and PCB 153 (0.925). The results implied that the PCBs were the major pollutants in the soil and that they had originated from similar sources. Cis-chlordane (0.927) and heptachlor (0.922) also had high loadings on PC 1. This might be explained by the fact that these compounds and PCBs have high logKow values, which means that they may both have come from the deposition of the particulate matter in the



1– α-HCH; 2 – β-HCH; 3 – γ-HCH; 4 – δ-HCH; 5 – *p,p'*-DDE; 6 – *p,p'*-DDD; 7 – *o,p'*-DDT; 8 – *p,p'*-DDT; 9 – heptachlor; 10 – cis-chlordane; 11 – endosulfan II; 12 – PCB28; 13 – PCB52; 14 – PCB101; 15 – PCB118; 16 – PCB 138; 17 – PCB153; 18 – PCB180

1– α-HCH; 2 – β-HCH; 3 – γ-HCH; 4 – δ-HCH; 5 – *p,p'*-DDE; 6 – *p,p'*-DDD; 7 – *o,p'*-DDT; 8 – *p,p'*-DDT; 9 – heptachlor epoxide B; 10 – heptachlor epoxide A; 11 – heptachlor; 12 – aldrin; 13 – dieldrin; 14 – g-chlorane; 15 – cis-chlordane; 16 – endosulfan I; 17 – endosulfan II; 18 – PCB28; 19 – PCB52; 20 – PCB101; 21 – PCB118; 22 – PCB 138; 23 – PCB153; 24 – PCB180

Figure 6. The principal component analysis (PCA) for the organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in the soil (A) and the sediment (B)

https://doi.org/10.17221/50/2019-SWR

Table 3. The comparison between the persistent organochlorine residues in the sediment samples and the guideline values

Chemical	Range (ng/g)	ISQG	PEL	≤ ISQG (%)	ISQG–PEL (%)	≥ PEL (%)
γ-HCH	2.8–6.93	0.94	1.38	0	0.00	100
p,p'-DDE	2.08–16.79	1.42	6.75	0	30.77	69.23
p,p'-DDD	1.32–10.77	3.54	8.51	30.77	53.85	15.38
DDT[1]	2.08–20.95	1.19	4.77	0	7.69	92.31
heptachlor epoxide	0–10.26	0.6	2.74	15.38	7.69	76.92
dieldrin	0–5.62	2.85	6.67	84.62	15.38	0
chlordane	0–8.73	4.5	8.87	69.23	30.77	0
Total PCBs	13.53–46.25	34.1	277	69.23	30.77	0

ISQG – Interim Sediment Quality Guideline; PEL – Probable Effects Level; [1]the sum of the *o,p'* and *p,p'* isomers

atmosphere. The second factor (PC 2) was clustered with *p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE. The mean technical DDTs was another major component. PC 3 consisted of β-HCH. Unlike other HCH isomers, β-HCH is highly persistent, whereas α-HCH and γ-HCH are slowly transformed into β-HCH.

The distribution pattern of the sediment was similar to the soil, which verifies the results shown in Figure 6B. Principle component 1 (33.34%) was mainly associated with PCBs, whereas DDTs and their isomers were associated with PC 2 (23.86%). Finally, PC 3 explained 23.15% of the data variance. It was highly loaded by heptachlor epoxide A, heptachlor epoxide B, dieldrin, g-chlordane, cis-chlordane, and endosulfan I. The cluster can be defined as containing OCPs with lower logKow values (logKow = 3.5–6.26) and these pollutant compounds were probably derived from the same sources.

The results from Figures 6A, B show that the PCB and DDT data followed the aggregation trends in the soil and sediment samples. Combined with the previous analysis, the PCBs and DDTs were the major components of pollution in the study region. In addition, the sources of the OCPs in the sediments were more complex and may have been contaminated by various industrial wastewaters.

Ecological risk assessment. There are no relevant standards for freshwater sediments in China. Therefore, the ecological risk was assessed by comparing the concentrations to the Interim Sediment Quality Guideline (ISQG) and the Probable Effects Level (PEL), which are found in the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. When the concentration is below the ISQG, the compounds are rarely associated with adverse biological effects. When the concentration is above the PEL, then they are frequently associated with adverse biological effects (Smith et al. 1996). Table 3 shows that the γ-HCH, *p,p'*-DDE, and total DDT concentrations in all the sediment samples exceeded the ISQG, which suggested that they were occasionally associated with adverse biological effects. Furthermore, the γ-HCH concentrations were all above the PEL, which suggests that γ-HCH exposure may represent a high ecological risk to the neighbouring benthic organisms. The dieldrin, chlordane, and total PCB levels were not above the PEL values. However, 15.38% of the sites in the study area were higher than the ISQG value, which indicated that the aquatic organisms living in the area may be negatively affected by dieldrin, chlordane, and the total PCBs.

CONCLUSIONS

In this study, 18 OCPs and seven PCBs congeners in the surface sediments and soils around the Baojia ditch (a previously seriously polluted river) drainage area were investigated. The PCBs and OCPs were ubiquitously distributed in the samples. The sample of contamination order from high to low was downstream sediment samples > midstream sediment samples > upstream sediment samples and the soil samples > the most upstream points of the Baojia ditch. The OCP and PCB residue levels in the study area were moderate compared to other studies. However, the PCBs and DDTs were the main pollutants in the study area. The proportions of the different pollutants in the soils and sediments were similar, which suggested that the pollutants may have originated from the same source. The risk assessment indicated that γ-HCH could pose the highest risks for benthic organisms, followed by DDTs and heptachlor epoxide. However, the ecological risks from PCBs are potentially low.

https://doi.org/10.17221/50/2019-SWR

In summary, although the government has cleaned up the polluted Baojia ditch and shut down the polluting enterprises, the accumulation of previous pollutants continues to affect the current environment, and may cause lasting damage to the environment and human health via the food chain. Therefore, routine monitoring of persistent organochlorine residues in the area is needed and the health risks to local residents should be assessed.

REFERENCES

Aerts R., Van Overmeire I., Colles A., Andjelkovic M., Malarvannan G., Poma G., Den Hond E., Van de Mieroop E., Dewolf M.C., Charlet F., Van Nieuwenhuyse A., Van Loco J., Covaci A. (2019): Determinants of persistent organic pollutant (POP) concentrations in human breast milk of a cross-sectional sample of primiparous mothers in Belgium. Environment International, 131: 104979.

Bajwa A., Ali U., Mahmood A., Chaudhry M.J., Syed J.H., Li J., Zhang G., Jones K.C., Malik R.N. (2016): Organochlorine pesticides (OCPs) in the Indus River catchment area, Pakistan: Status, soil-air exchange and black carbon mediated distribution. Chemosphere, 152: 292–300.

Da C., Wu K., Jin J., Yu M. (2017): Levels and sources of organochlorine pesticides in surface sediment from Anhui Reach of Huaihe River, China. Bulletin of Environmental Contamination and Toxicology, 98: 784–790.

Degrendele C., Audy O., Hofman J., Kucerik J., Kukucka P., Mulder M.D., Pribylova P., Prokes R., Sanka M., Schaumann G.E., Lammel G. (2016): Diurnal variations of air-soil exchange of semivolatile organic compounds (PAHs, PCBs, OCPs, and PBDEs) in a Central European receptor area. Environmental Science & Technology, 50: 4278–4288.

Devi N.L., Yadav I.C., Raha P., Shihua Q., Dan Y. (2015): Spatial distribution, source apportionment and ecological risk assessment of residual organochlorine pesticides (OCPs) in the Himalayas. Environmental Science and Pollution Research, 22: 20154–20166.

Li C.-C., Huo S.-L., Xi B.-D., Yu Z.-Q., Zeng X.-Y., Zhang J.-T., Wu F.-C., Liu H.-L. (2015): Historical deposition behaviors of organochlorine pesticides (OCPs) in the sediments of a shallow eutrophic lake in Eastern China: Roles of the sources and sedimentological conditions. Ecological Indicators, 53: 1–10.

Li X.H., Wang W., Wang J., Cao X.L., Wang X.F., Liu J.C., Liu X.F., Xu X.B., Jiang X.N. (2008): Contamination of soils with organochlorine pesticides in urban parks in Beijing, China. Chemosphere, 70: 1660–1668.

Makris G., Chrousos G.P., Anesiadou S., Sabico S., Abd-Alrahman S.H., Al-Daghri N.M., Chouliaras G., Pervanidou P. (2019): Serum concentrations and detection rates of selected organochlorine pesticides in a sample of Greek school-aged children with neurodevelopmental disorders. Environmental Science and Pollution Research, 26: 23739–23753.

Martenies S.E., Perry M.J. (2013): Environmental and occupational pesticide exposure and human sperm parameters: a systematic review. Toxicology, 307: 66–73.

Medehouenou T.C.M., Ayotte P., Carmichael P.H., Kroger E., Verreault R., Lindsay J., Dewailly E., Tyas S.L., Bureau A., Laurin D. (2019): Exposure to polychlorinated biphenyls and organochlorine pesticides and risk of dementia, Alzheimer's disease and cognitive decline in an older population: a prospective analysis from the Canadian Study of Health and Aging. Environmental Health, 18: 57.

Muzyed S.K.I., Kucuksezgin F., Tuzmen N. (2017): Persistent organochlorine residues in fish and sediments collected from Eastern Aegean coast: Levels, occurrence and ecological risk. Marine Pollution Bulletin, 119: 247–252.

Nguyen T.X., Nguyen B.T., Tran H.T.T., Mai H., Duong T.T., Bach Q.V. (2019): Seasonal, spatial variation, and potential sources of organochlorine pesticides in water and sediment in the lower reaches of the Dong Nai river system in Vietnam. Archives of Environmental Contamination and Toxicology, 77: 514–526.

Paydar P., Asadikaram G., Fallah H., Zeynali Nejad H., Akbari H., Abolhassani M., Moazed V., Khazaeli P., Heidari M.R. (2019): Serum levels of organochlorine pesticides and breast cancer risk in Iranian women. Archives of Environmental Contamination and Toxicology, 77: 480–489.

Perez-Palacios D., Fernandez-Recio M.A., Moreta C., Tena M.T. (2012): Determination of bisphenol-type endocrine disrupting compounds in food-contact recycled-paper materials by focused ultrasonic solid-liquid extraction and ultra performance liquid chromatography-high resolution mass spectrometry. Talanta, 99: 167–174.

Polanco Rodriguez A.G., Riba Lopez M.I., DelValls Casillas T.A., Araujo Leon J.A., Mahjoub O., Prusty A.K. (2017): Monitoring of organochlorine pesticides in blood of women with uterine cervix cancer. Environmental Pollution, 220: 853–862.

Rissato S.R., Galhiane M.S., Ximenes V.F., de Andrade R.M., Talamoni J.L., Libanio M., de Almeida M.V., Apon B.M., Cavalari A.A. (2006): Organochlorine pesticides and polychlorinated biphenyls in soil and water samples in the Northeastern part of Sao Paulo State, Brazil. Chemosphere, 65: 1949–1958.

Rossi M., Taddei A.R., Fasciani I., Maggio R., Giorgi F. (2018): The cell biology of the thyroid-disrupting mecha-

https://doi.org/10.17221/50/2019-SWR

nism of dichlorodiphenyltrichloroethane (DDT). Journal of Endocrinoligical Investigation, 41: 67–73.

Sanchez-Osorio J.L., Macias-Zamora J.V., Ramirez-Alvarez N., Bidleman T.F. (2017): Organochlorine pesticides in residential soils and sediments within two main agricultural areas of northwest Mexico: Concentrations, enantiomer compositions and potential sources. Chemosphere, 173: 275–287.

Smith S.L., Macdonald D.D., Keenleyside K.A., Ingersoll C.G., Field L.J. (1996): A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. Journal of Great Lakes Research, 22: 624–638.

Tran T.A.M., Malarvannan G., Hoang T.L., Nguyen V.H., Covaci A., Elskens M. (2019): Occurrence of organochlorine pesticides and polychlorinated biphenyls in sediment and fish in Cau Hai lagoon of Central Vietnam: Human health risk assessment. Marine Pollution Bulletin, 141: 521–528.

Wang B., Wu C., Liu W., Teng Y., Luo Y., Christie P., Guo D. (2016a): Levels and patterns of organochlorine pesticides in agricultural soils in an area of extensive historical cotton cultivation in Henan province, China. Environmental Science and Pollution Research, 23: 6680–6689.

Wang X., Han J., Bi C., Huang X., Jia J., Chen Z. (2016b): Distribution, sources, and risk assessment of polychlorinated biphenyls in surface waters and sediments of rivers in Shanghai, China. Frontiers of Earth Science, 11: 283–296.

Wang G., Liu Q., Feng L., Qi J., Li X. (2017a): Typical persistent organic pollutants (POPs) in sediments from the Yellow and East China Seas and adjacent coastal areas, China. Science China-Chemistry, 47: 1284–1297.

Wang W., Bai J., Xi M., Zhao Q., Zhang G., Wen X., Xiao R. (2017b): Occurrence, sources, and risk assessment of OCPs in surface sediments from urban, rural, and reclamation-affected rivers of the Pearl River Delta, China. Environmental Science and Pollution Research, 24: 2535–2548.

Wang X., Chen S., Wan K., Yin X., Zhu X., Pan J., Yang Y. (2017c): Altitude distributions and source analysis of OCPs and PCBs in surface soils of Changbai Mountain, Northeast China. Bulletin of Environmental Contamination and Toxicology, 98: 798–804.

Zhao X., Li J., Lu K., Huang X. (2015): Characterization of particle/gas partition, congener patterns, and TEQ of PCBs and PCNs released from a municipal solid waste incinerator (MSWI) in South China. Environmental Chemistry, 34: 1268–1274.

Zhan L., Lin T., Wang Z., Cheng Z., Zhang G., Lyu X., Cheng H. (2017): Occurrence and air-soil exchange of organochlorine pesticides and polychlorinated biphenyls at a CAWNET background site in central China: Implications for influencing factors and fate. Chemosphere, 186: 475–487.

Zhang J., Liu J., Yu R., Liu Q., Wang Y. (2015): Pollution assessment of organochlorine pesticides in urban agricultural soils of Jilin City, China. Human and Ecological Risk Assessment: An International Journal, 22: 792–801.

Zhang J., Qi S., Xing X., Tan L., Gong X., Zhang Y., Zhang J. (2011): Organochlorine pesticides (OCPs) in soils and sediments, southeast China: A case study in Xinghua Bay. Marine Pollution Bulletin, 62: 1270–1275.

Received: May 8, 2019
Accepted: October 15, 2019
Published online: December 6, 2019