Transport and fate of organochlorine pesticides in the River Wuchuan, Southeast China

Zulin Zhang,[a] Huashong Hong,[b] John L. Zhou,*[c] Gang Yu,[a] Weiqi Chen[b] and Xinghong Wang[b]

[a]*Department of Environmental Science and Engineering, Tsinghua POPs Research Centre, Tsinghua University, Beijing 100084, China*
[b]*Key Laboratory of Marine Environmental Science of Ministry of Education, Environmental Science Research Centre, Xiamen University, Xiamen 361005, China*
[c]*School of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, Brighton, UK BN1 9QJ. E-mail: J.Zhou@sussex.ac.uk; Fax: 44 1273 677196; Tel: 44 1273 877318*

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Persistent organic pollutants (POPs) such as chlorinated pesticides are of global concern due to their widespread occurrence, persistence, bioaccumulation and toxicity to animals and human. This paper summarises recent research on 18 chlorinated pesticides in an important catchment in China, by determining their concentrations and behaviour in water, sediment, soil and plants. The concentrations of the total pesticides were in the ranges 187–893 ng l^{-1} in river water, 8.53–210 ng g^{-1} dry weight in soil, 2.66–13.45 ng g^{-1} dry weight in river sediment, and 651–2823 ng g^{-1} dry weight in plants. The predominance of β-HCH as the major isomer of HCHs in all water, soil, sediment and plant samples was clearly observed, due to β-HCH's resistance to biodegradation. On average β-HCH accounted for 44%, 53%, 50%, and 46% of the total HCH concentration in water, soil, sediment and plant, respectively. Of the DDTs, DDE accounted for 48%, 43%, 53%, 55% of the total DDT, which suggested that DDT had been transformed to its metabolites, DDE and DDD, of which DDE was the more stable. The chlorinated pesticide levels in the River Wuchuan were generally below the guideline values in China, but some sites displayed levels in excess of EC Environmental Quality Standards for HCHs and DDTs. The results therefore provide important information on the current contamination status of a key agricultural watershed in China, and point to the need for urgent actions to evaluate the long-term fate and toxicity of such persistent compounds and an appropriate remediation strategy.

Aim of investigation

The first generation of pesticides, based on arsenic, copper and sulfur, were predominant in the late-1800s to the 1940s, but were not widely used and consequently never emerged as a global concern. However, the second generation of pesticides, namely the organochlorine (OCl) pesticides were used intensively over a large part of the globe including tropical regions, until the late 1980s.[1–4] Their widespread use was mainly due to their low cost and high efficacy in controlling pests and certain disease such as malaria.[3] The presence of chlorine in the OCl pesticides tends to enhance their persistence in the environment; in fact, many of them are now classified as the so-called persistent organic pollutants (POPs). Many POPs are semi-volatile; their vapour pressures are sufficiently high to cause appreciable evaporation over a period of weeks to years, enabling the compounds to cycle between gaseous and condensed phases in the environment and to travel long distances. In addition, POPs can also be transported through ocean circulation. As a result of their widespread use and persistence, many POPs (including OCl pesticides) have been dispersed on a global scale and have found their way to pristine environments, such as the Arctic and Antarctic.[1,4,5] While some use of these compounds continues, their production and use is in decline and international negotiations are underway to eliminate 12 persistent OCl compounds worldwide, 8 of which are OCl pesticides.[6]

Wuchuan agricultural catchment is a branch of the River Jiulong Watershed, which is located in the southeast of China. Wuchuan is one of the 1000 ecological model watersheds in China and covers an area of approximately 530 ha, which is mainly used for planting orchard. Although Wuchuan is a model watershed, it has never been studied for its environmental quality.[7] The aims of this paper are therefore to determine the levels of important OCl pesticides in the River Wuchuan, focusing on the main phases in which pollutants may accumulate including water, sediment, soil and plants, in order to identify the "hot spots" with toxic levels of the target compounds; and to evaluate the sources and transport pathways of OCl pesticides. It is hoped that by determining the levels of pollutants in various phases, a systematic assessment of the environmental quality and of the impact of OCl pesticide usage on the ecosystem can be made. In addition, the results will have implications for the classification of watersheds and the quality control of fruits and vegetables in relation to toxic chemicals.

Experimental

Chemicals

Reference OCl pesticides (18 compounds, each at 2000 μg ml^{-1}) and an internal standard (2,4,5,6-tetrachloro-*m*-xylene, at 200 μg ml^{-1}) were obtained from Supelco. The stock solutions were diluted with ethyl acetate to prepare working standards, which were then combined to prepare calibration solutions for capillary GC analyses in the range 0.01–1.0 ng μl^{-1}. All solvents used for sample processing and analyses (ethyl acetate, cyclohexane, methanol) were of HPLC grade. Ultrapure deionised water was taken from a Milli-Q system (Millipore,

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Watford, UK). Although 21 chlorinated biphenyl congeners were analysed simultaneously with the pesticides, they are not reported in this paper as the focus is on the OCl pesticides.

Sampling and sample processing

Water samples from the River Wuchuan were collected in September 2000. The locations of the sampling stations are shown in Fig. 1. Throughout the survey a global positioning system was used to locate the sampling positions. Samples were taken using precleaned glass bottles held in a weighted stainless-steel frame fitted with a spring-loaded PTFE stopper with a subsurface trigger to avoid the surface microlayer.[8] Aliquots of the sample (1.0 l) were filtered under vacuum through pre-ashed glass fibre filters (Whatman, GF/F). The filtrates were spiked with the internal standard at 100 ng l^{-1}.

Surface sediment samples were collected with a grab sampler, and the top 1 cm surface layer was carefully removed with a stainless-steel spoon and stored in pre-ashed glass bottles. After returning to the laboratory, the sediments were then stored at −20 °C until extraction. Soil samples were also collected by a stainless-steel spoon and stored in pre-ashed glass bottles at −20 °C until further processing. Plant samples were cut and collected by tweezers, then stored in pre-ashed glass bottles at −20 °C as well.

Sample extraction

Filtered water samples were processed using a solid-phase extraction (SPE) technique, following established procedures.[4,8,9] The Supelco SPE cartridges (ENVI-18) were first conditioned with 2 × 5 ml of methanol followed by 2 × 5 ml of Milli-Q water. Water samples (1.0 l) were passed through the cartridges at a flow rate of 6 ml min^{-1} under vacuum. Following extraction, the cartridges were eluted with 10 ml of ethyl acetate, which was combined with an ethyl acetate (10 ml) rinse from the extraction glassware. After water was removed from the extracts by ashed Na_2SO_4, the dried extracts were reduced in volume by N_2 blow-down in a water bath.

Soil, sediment and plant samples were extracted by ultrasonication. Briefly, soil and sediment samples were homogenised with a stainless-steel spatula, while plant samples were cut into small pieces. Sub-samples (approximately 30 g wet weight) of soil, sediment and plants were mixed with anhydrous Na_2SO_4, Cu granules, internal standard and 60 ml of ethyl acetate, which were extracted twice first for 30 min and then overnight. The extracts were concentrated to 0.5 ml by rotary evaporation and under a gentle stream of nitrogen. The concentrated extracts were fractionated by a silica gel column (4 mm id × 90 mm). The column was then eluted first with 3.5 ml of hexane and the solution discarded. Further elution was by ethyl acetate (2 × 5 ml) to obtain the OCl pesticides.[4,9] All the extracts were concentrated by gentle N_2 blow-down to about 100 μl. Good recovery was obtained using this procedure, as shown in Table 1.

Sample analyses

A Hewlett-Packard 6890 plus GC with a micro-cell electron capture detector (μECD), an autosampler, and Chemstation software was used for determining the levels of OCl pesticides in water, soil, sediment and plant samples. The capillary column used for the analyses was an HP5 (30 m × 0.32 mm id × 0.25 μm film thickness). The oven temperature programme was programmed from 60 °C (equilibrium time 1 min prior to the ramp) to 140 °C at 10 °C min^{-1}, 140 °C to 230 °C at 1 °C min^{-1}, 230 °C to 260 °C at 10 °C min^{-1}, and held at 260 °C for 10 min.

Before analysis, relevant standards were run to check column performance, peak height and resolution. With each set of samples to be analysed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. Compounds were identified mainly by their retention times. Selected samples were analysed by full scan GC-MS for confirmation. All results for soil, sediment and plant samples were reported on a dry weight basis. Typical GC-ECD chromatograms of a calibration standard and samples are shown in Fig. 2.

Analytical quality controls

All data were subject to strict quality control procedures, including the analysis of procedural blanks and spiked samples with each set of samples analysed. None of the target compounds were detected in the procedural blanks. Spiked water, soil and plant samples (n = 6, 100 ng l^{-1} or 100 ng g^{-1} of each target compound) were determined with good recoveries and precision (Table 1). In addition, an internal standard (2,4,5,6-tetrachloro-*m*-xylene) was used to compensate for losses involved in the sample extraction and work-up, to further improve the analytical quality.

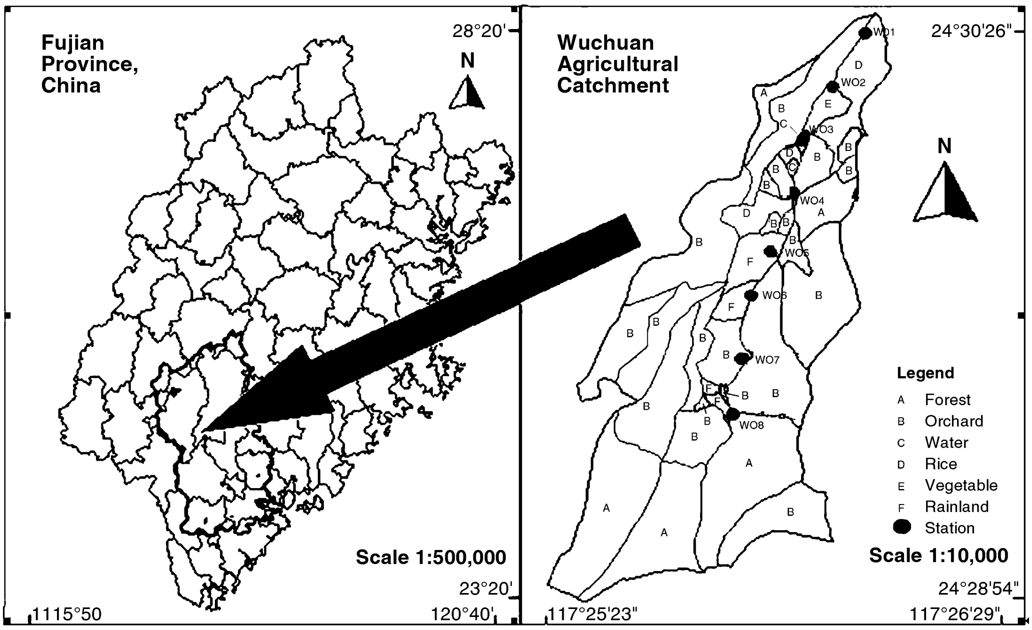

Fig. 1 A map of Wuchuan catchment showing the sampling stations.

Table 1 The limit of detection (LoD), mean recovery and relative standard deviation (RSD) for OCl pesticides ($n = 6$)

	Soil			Plant			Water		
Compound	LoD/ pg g^{-1}	Recovery (%)	RSD (%)	LoD/ pg g^{-1}	Recovery (%)	RSD (%)	LoD/ pg l^{-1}	Recovery (%)	RSD (%)
α-HCH	0.11	92	10.6	0.82	84	16.1	1.31	73	13.8
β-HCH	0.47	98	5.9	3.66	89	15.5	5.82	80	22.4
γ-HCH	0.19	89	16.5	1.48	82	13.2	2.36	86	6.0
δ-HCH	0.28	82	11.7	2.18	88	18.8	3.47	104	6.3
Heptachlor	0.28	79	14.4	2.15	86	10.2	3.42	94	10.5
Aldrin	0.23	83	12.9	1.76	88	20.9	2.80	93	15.8
Heptachlor epoxide	0.18	91	14.3	1.37	84	12.1	2.18	98	12.9
Endosulfan I	0.10	83	14.0	0.76	93	17.5	1.21	86	11.2
Dieldrin	0.08	93	16.1	0.65	88	17.8	1.04	97	12.4
4,4′-DDE	0.09	88	17.2	0.73	86	19.6	1.16	78	12.5
Endrin	0.15	78	15.3	1.15	85	16.9	1.83	79	19.7
Endosulfan II	0.07	84	14.3	0.54	82	13.6	0.85	78	8.7
4,4′-DDD	0.24	85	19.3	1.86	84	18.1	2.96	66	11.3
Endrin aldehyde	0.28	89	21.1	2.14	86	20.9	3.42	92	7.9
Endosulfan sulfate	0.10	87	18.0	0.75	83	18.6	1.19	89	7.5
4,4′-DDT	0.50	99	14.3	3.88	89	19.2	6.19	78	22.8
Endrin ketone	0.09	96	12.5	0.70	73	5.9	1.11	65	7.1
Methoxychlor	0.53	88	20.3	4.07	94	20.6	6.49	91	15.7
Internal standard	0.03	88	22.2	0.24	88	17.4	0.39	85	25.0

Results and discussion

This paper reports the results obtained from a comprehensive study of the River Wuchuan for levels of organic contaminants and nutrients (not reported here), and represents an attempt to improve our understanding of pollution from non-point sources. As a result, the following interpretation and discussion will be focused on OCl pesticides in water, sediment, soil and plants. Concentration data for the level of 18 OCl pesticides in water, sediment, soil and plants is shown in Table 2.

OCl pesticide concentration in water, sediment, soil and plants

All 18 compounds were present in all samples (Table 2), indicating the widespread occurrence and persistence of such compounds in the environment. The total pesticide concentrations in the water ranged from 187 to 893 ng l^{-1} with a mean concentration of 571 ng l^{-1} (Fig. 3). The highest concentration was found at station 8, which is the outlet of the catchment. This could be due to the accumulation of leaching water from the upper catchment. In comparison to other locations in China, the levels of total OCl pesticides in the Wuchuan catchment water are similar to those detected in the Jiulong River Estuary (115–415 ng l^{-1}, with a mean value of 192 ng l^{-1}),[7] and higher than those found in the Pearl River Estuary (4.44–635 ng l^{-1}, with a mean value of 88.31 ng l^{-1})[7] and South China Sea (1.27–121.8 ng l^{-1}, with a mean value of 16.49 ng l^{-1}).[7] Even higher levels (up to 5100 ng l^{-1}) have been found in Daya Bay, China.[4] The results show that water in the River Wuchuan is moderately polluted by chlorinated pesticides.

The total OCl pesticide concentration in the sediment varied from 2.66 to 13.45 ng g^{-1} dry weight, with a mean concentration of 6.08 ng g^{-1} (Fig. 3). The highest concentration was found at station 4. Such levels are lower than those found in the sediments of the Pearl River Delta and Macao Harbour (11.9–158 ng g^{-1}), similar to those in the sediments of Daya Bay, China (2.43–86.25 ng g^{-1})[4] and Kingston Harbour (mean = 11.65 ng g^{-1}),[10] and higher than those in Xiamen Harbour sediments (<0.01–0.58 ng g^{-1}).[9]

The concentrations of total OCl pesticides in the soil varied from 18.53 to 210 ng g^{-1} dry weight with a mean concentration of 70.90 ng g^{-1} (Fig. 3). The highest concentration (210 ng g^{-1}) was found at station 5. The concentration of total OCl pesticides in the plants ranged from 651 to 2823 ng g^{-1} dry weight with a mean concentration of 1078 ng g^{-1} (Fig. 3). The highest concentration (2823 ng g^{-1}) was found at station 4, where the highest concentration in water was observed. It may be inferred that leaching and washing from plants are the main means of pesticide input to the surface water.

After OCl pesticides ceased to be used in China in 1983, it was thought that they would disappear from the environment. But the results of our study show that this was not the case, on the contrary, they were present in various matrices of the agricultural area, at high levels at some sites. They mainly come from the residues from former applications in agriculture. Due to their resistance to degradation in the environment, they can still be found many years later. The results of OCl pesticide concentration in various matrices showed that their concentrations in plants are higher than those in the soil and sediment. This could be due to the initial application of OCl pesticide on plants and subsequent accumulation in them. It is therefore necessary to take action to establish a program to routinely monitor these pesticides in the various matrices in order to improve the environmental quality in the area.

HCHs in water, sediment, soil and plants

Total HCHs in water ranged from 15.46 to 111 ng l^{-1}, with a mean concentration of 49.53 ng l^{-1}. Such levels are two to three orders lower than those detected in Giza, Egypt (20700–86200 ng l^{-1}),[11] but higher than those found in the Humber catchments, UK (5.78–61.58 ng l^{-1})[12] and on the coast of Alicante, Spain (1.3–2.3 ng l^{-1}).[13] Similar levels have also been found in Mar Menor Lagoon, Spain (30–300 ng l^{-1}).[14] According to the Chinese water quality guideline (GHZB1-1999), in grade 1–3 surface water, which is considered to pose no hazard to aquatic or human health, the concentration of HCHs should be less than 5000 ng l^{-1}. Although the levels of HCHs in Wuchuan water are significantly below the guideline value, there are sites where the HCH levels (111 ng l^{-1}) have exceeded the EC Environmental Quality Standard (EQS) for HCHs in water, which is 100 ng l^{-1}.[12] There is therefore a potential risk to aquatic organisms and human health.

Further analysis was made of the distribution of HCH isomers. As shown in Fig. 4, all 4 HCH isomers were present in all water samples. The predominance of β-HCH in the water samples was clearly observed. On average β-HCH accounted for 44% of the total HCH concentration in the water. This could be due to the fact that the β-isomer is very resistant to biodegradation.[15] HCHs have been used as a technical mixture and as high purity γ-HCH (lindane). The technical mixture consists of 65–70% α-HCH, 14–15% γ-HCH, and 7–10%

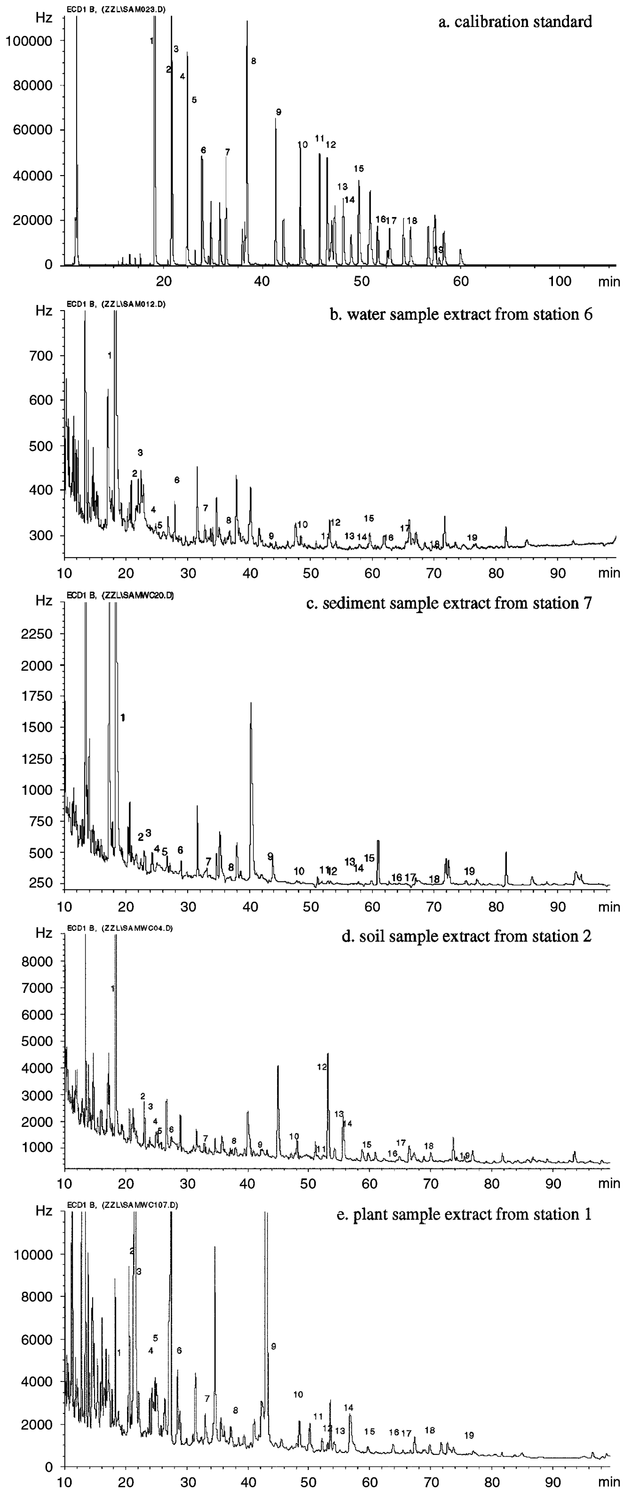

Fig. 2 GC-ECD chromatogram of (a) a standard mixture of OCl pesticides, (b) water sample extract from station 6, (c) sediment sample extract from station 7, (d) soil sample extract from station 2, and (e) plant sample extract from station 1. Peak numbers correspond to: (1) internal standard, (2) α-HCH, (3) β-HCH, (4) γ-HCH, (5) δ-HCH, (6) heptachlor, (7) aldrin, (8) heptachlor epoxide, (9) endosulfan I, (10) dieldrin, (11) 4,4′-DDE, (12) endrin, (13) endosulfan II, (14) 4,4′-DDD, (15) endrin aldehyde, (16) endosulfan sulfate, (17) 4,4′-DDT, (18) endrin ketone, and (19) methoxychlor.

β-HCH, while γ-HCH is above 99% in pesticide lindane.[12] The ratio of α-HCH/γ-HCH is therefore 4.3–5.0 for industrial HCHs and nearly 0 for lindane. In the current study, this ratio varied from 1.51 to 3.76 in water, which indicated that the early usage pattern of HCHs might be characterised by mixtures of technical HCHs and lindane.[2] The observed findings of component distribution dominated by β-HCH are consistent with previously published data on the Jiulong River Estuary,[7,9] where β-HCH accounted for over 40% of the total HCHs in the water. Similar contaminant distribution characteristics between the Jiulong River Estuary and one of its freshwater sources, the River Wuchuan, indicates that pesticide runoffs from agricultural land in Wuchuan represents an important source of the pollutants to the estuary.

The concentration of total HCHs in the sediment (0.29–4.94 ng g^{-1}) was higher than that observed in Lake Simbrirzzi, Italy (0.26 ng g^{-1})[16] and the River Ebro, Spain (0.007 ng g^{-1}),[17] similar to that in Daya Bay (0.32–4.16 ng g^{-1}),[4] but lower than that in the sediment of the River Mataniko, Solomon Islands (140 ng g^{-1}).[1] Similarly to the water samples, the distribution of the individual compounds is dominated by β-HCH in the sediment (Fig. 4). On average β-HCH accounted for 50% of the total HCHs in the sediment. It indicated again that β-HCH is more stable than the other isomers of the HCHs.[15,18] The observed finding of component dominance by the β-isomer is consistent with the distribution profile in water and sediments from other geographical locations.[7,15,18]

The levels of total HCHs in the soil (4.44–60.89 ng g^{-1}) were lower than those detected in Huhehaote, China (40–830 ng g^{-1}),[19] but higher than those detected in Alabama, USA (0.04–3.23 ng g^{-1})[20] and Korea (0.39–2.97 ng g^{-1}).[21] In comparison, the levels of total HCHs in the plants (22.03–342 ng g^{-1}) were higher than those detected in vegetables in Middle America (4.0 ng g^{-1}),[22] but lower than those in plants from Nanjing (16.7–2841 ng g^{-1}).[23]

According to Chinese food standard guidelines, in order to prevent a food hazard to human health, the maximum allowable residue in food for individual OCl pesticides is 200 ng g^{-1} for HCHs. The excess of HCHs in plants is clearly evident. There is therefore a potential human risk from exposure to these pesticides in food. There are no guidelines on OCl pesticide levels in soils and sediments, so no assessment can be made of the quality of the soils and sediments under investigation.

Further analysis was made of the individual component HCHs in the soil and plants (Fig. 4). On average β-HCH accounted for 53% and 46% of the total HCHs in the soil and plants, respectively. The predominance of β-HCHs is similar to that in water and sediments. The results therefore support the interpretation that the β-isomer is the most stable and the most difficult to degrade further in the environment.

DDTs in water, sediment, soil and plants

Total DDTs in water varied from 53.45 to 163 ng l^{-1}, with a mean concentration of 95.95 ng l^{-1}. The concentrations in the water are lower than those detected in El-Haram, Giza (2300–61000 ng l^{-1})[11] and Kingston harbour (ND–7020 ng l^{-1}),[10] but higher than those found in Humber catchments (0.22–1.75 ng l^{-1})[12] and on the coast of Alicante, Spain (<0.02 ng l^{-1}).[13] According to the Chinese water quality guideline (GHZB1-1999), for grade 1–3 surface water, which is considered to pose no hazard to aquatic or human health, the concentration of DDT should be less than 1000 ng l^{-1}. None of the sites have DDT levels above the guideline value, however there are some sites where the levels of DDTs (163 ng l^{-1}) have exceeded the EC EQS for DDTs in water (25 ng l^{-1}), the results therefore raise concerns over potential animal and human exposure to such chemicals.

As to the individual DDTs, they were detected at all stations, and their concentrations decreased in the order: DDE > DDT > DDD. On average DDE accounted for 48% of the total DDT concentration in the water. The results tend to suggest that such DDTs are from historical rather than more recent applications, as a result, a large proportion of DDT has been degraded to metabolites such as DDE, which is difficult to

Table 2 Concentrations of OCl pesticides in water, soil, sediment and plant from the River Wuchuan

	Water/ng l^{-1}			Soil/ng g^{-1} dry weight			Sediment/ng g^{-1} dry weight			Plant/ng g^{-1} dry weight		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
α-HCH	2.37–21.25	9.20	6.77	0.90–8.79	2.83	3.08	0.06–0.91	0.27	0.28	25.02–152	73.01	46.51
β-HCH	7.21–46.96	21.72	14.01	1.93–34.65	9.42	11.90	0.12–2.49	0.78	0.74	67.01–367	170	88.06
γ-HCH	0.78–12.34	5.38	4.28	0.38–4.76	1.79	1.71	0.03–0.45	0.16	0.13	11.94–79.95	33.19	21.29
δ-HCH	4.54–30.55	13.24	9.17	1.13–12.69	3.79	4.29	0.04–1.09	0.35	0.35	27.50–178	90.49	56.78
Heptachlor	8.43–77.75	25.39	22.98	0.28–85.53	13.17	29.45	0.08–3.77	0.79	1.21	11.46–189	63.29	54.72
Aldrin	5.38–49.62	15.32	15.10	0.04–2.94	0.82	0.97	0.02–0.87	0.23	0.31	3.43–924	153	314
Heptachlor epoxide	1.26–26.82	5.80	8.71	0.14–10.09	2.40	3.40	0.01–0.19	0.07	0.06	24.31–244	79.89	73.32
Endosulfan I	4.99–35.71	17.94	13.47	0.25–3.69	1.68	1.27	0.05–1.38	0.28	0.45	6.99–55.53	21.94	17.31
Dieldrin	1.78–21.14	6.98	7.01	0.10–5.29	1.21	1.71	0.03–0.24	0.06	0.07	5.81–44.42	18.64	15.17
4,4′-DDE	25.14–81.40	45.90	22.08	0.93–10.28	5.74	3.22	0.26–1.32	0.74	0.44	34.92–102	57.11	24.76
Endrin	1.90–26.38	7.15	8.37	0.25–4.57	1.62	1.38	0.02–0.13	0.06	0.04	6.23–74.50	21.88	22.12
Endosulfan II	2.43–20.55	6.41	6.34	0.02–2.32	0.90	0.85	0.03–0.15	0.06	0.04	3.70–16.12	9.10	4.32
4,4′-DDD	5.10–37.63	19.49	11.33	0.55–7.38	3.08	2.26	0.07–0.37	0.23	0.11	6.94–25.88	14.61	6.97
Endrin aldehyde	10.55–56.41	28.15	17.42	0.84–5.83	2.97	2.11	0.04–0.30	0.14	0.09	7.51–85.48	26.14	26.09
Endosulfan sulf	5.10–66.25	23.33	21.83	0.25–9.54	1.96	3.11	0.05–0.77	0.21	0.25	3.71–653	95.38	226
4,4′-DDT	14.86–52.12	30.56	13.86	0.88–6.88	4.45	2.67	0.14–0.72	0.41	0.21	17.57–95.83	32.52	25.93
Endrin ketone	4.37–24.66	12.58	7.74	0.41–6.38	2.84	2.14	0.02–0.43	0.19	0.13	2.56–69.26	26.00	23.15
Methoxychlor	22.40–505	276	182	4.52–21.74	10.25	5.51	0.34–2.45	1.06	0.78	18.48–205	91.26	65.14

degrade further.[15,18] The observed findings of component distribution dominated by DDE are consistent with previously published data on the Jiulong River Estuary,[7,9] where DDE accounted for about 45% of the total DDT concentration in the water. The similar contaminant distribution characteristics between Jiulong River Estuary and one of its freshwater sources, the River Wuchuan, indicate that pesticide runoffs from agricultural land in Wuchuan represents an important source of the pollutants to the estuary.

The total concentration of DDTs in the sediment (0.53–2.30 ng g^{-1}) was higher than that detected in the sediment on the coast of Alicante, Spain (<0.01–0.35 ng g^{-1})[13] and lower than that in Parramata River, Australia (26 ng g^{-1}).[1] Because of a lack of previous studies in the River Wuchuan and other watersheds in China, it is difficult to assess the temporal variation of water quality in the River Wuchuan during recent years. In order to develop and maintain an adequate level of environmental protection, there is an urgent need to develop a robust monitoring program for the continued surveillance of OCl pesticides and other organic pollutants in the region, and subsequently to adopt an efficient risk assessment strategy to determine the likely impacts these compounds may have on the local ecosystems.

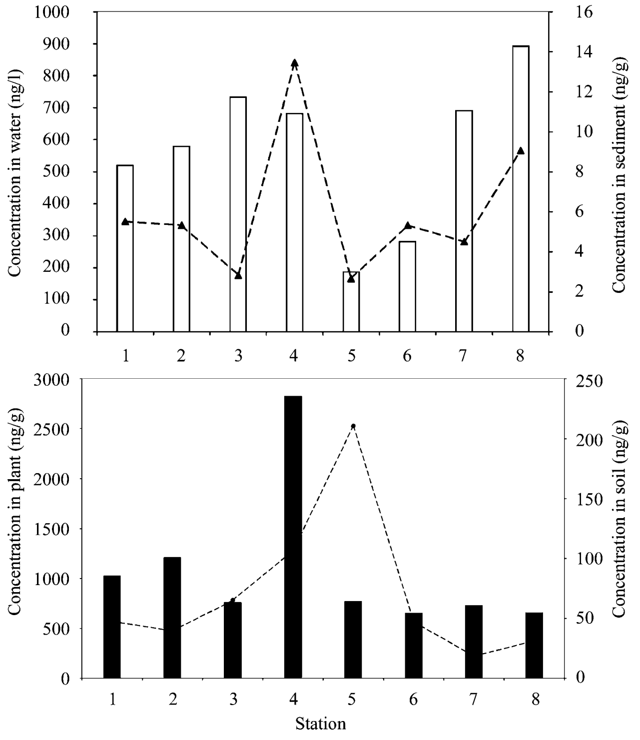

Fig. 3 Concentrations of total OCl pesticides in water (□), sediment (▲), plant (■) and soil (●) at different stations.

The distribution of individual compounds in the sediment is shown in Fig. 5, and as was similar to the water samples, the DDTs were dominated by DDE. On average, DDE accounted for about 53% of the total DDTs in the sediment. This indicated again that DDE is the major metabolite of DDT and that it is difficult to degrade DDE further. The observed finding is consistent with the distribution profiles in the water and sediments from other geographical locations.[7,15,18]

The total DDT levels in soil (2.36–26.28 ng g^{-1}) were lower than those detected in the Jiansu Province (534–2118 ng g^{-1})[24] and in Nanjing, China (32.0–517 ng g^{-1}),[23] however, they were higher than those detected in the agricultural land in Korea (0.34–0.48 ng g^{-1}).[21] Total DDT levels in the plant samples (10.39–56.65 ng g^{-1}) were similar to those detected in Nigeria (ND–47.2 ng g^{-1}),[25] but lower than those found in Nanjing, China (42–1821 ng g^{-1}).[23]

According to Chinese food standard guidelines, in order to prevent a food hazard to human health, the maximum allowable residue in food for individual OCl pesticides is 100 ng g^{-1} for DDTs. The levels of DDTs in plants from River Wuchuan are below the guideline value. There are no guidelines for OCl pesticide levels in soils and sediments, so no assessment can be made of the quality of the soils and sediments under investigation.

Further analysis was made of the individual components of DDTs in soils and plants (Fig. 5). On average, DDE contributed 43% and 55% of the total DDTs in the soils and plants, respectively. The predominance of DDE is similar to the results for the water and sediments. The results therefore support the interpretation that DDE is stable and is difficult to degrade further in the environment.

Inter-relation between individual OCl pesticides

As all 18 OCl pesticides may come from the same sources and have similar environmental behaviour, they may therefore display some correlations between themselves. Detailed analysis of the data set showed that although there were some significant correlations existing between a few compounds in the soil, sediment and plants, the extent and significance of such correlations was most evident in the water samples. The

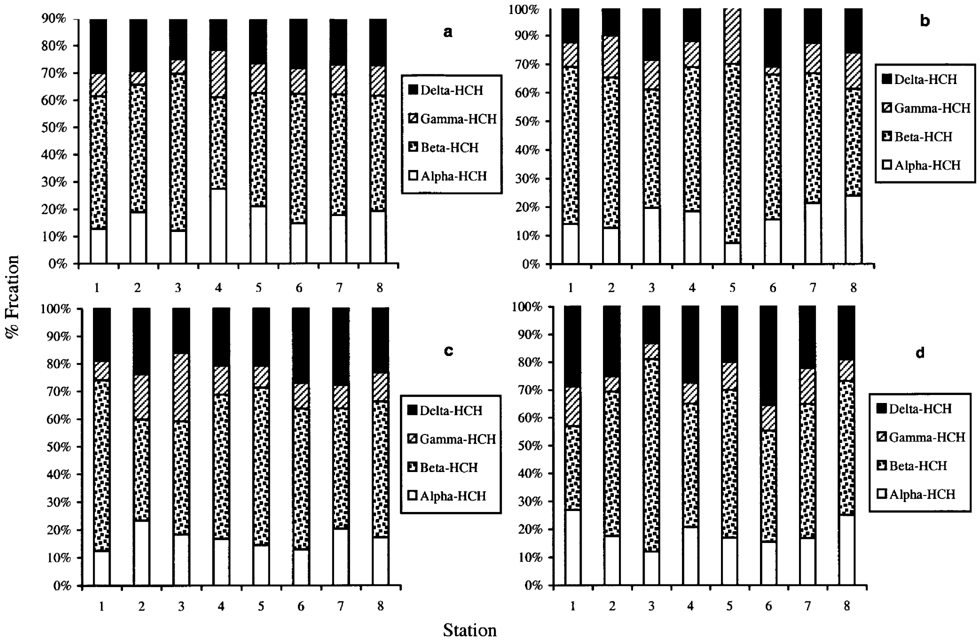

Fig. 4 HCH isomer distribution in (a) water, (b) sediment, (c) soil and (d) plants.

correlation values for the 18 pesticides in the water are shown in Table 3. It is clear that most compounds showed strong correlations with each other, with correlation coefficients frequently greater than 0.8. The only exception is methoxychlor which displayed low *r* values.

Conclusions

This study has provided the first set of data on the levels of 18 persistent chlorinated pesticides in water, soil, sediment and plants of the River Wuchuan. Due to their extensive previous applications in agriculture and resistance to degradation, all 18 OCl pesticides were found in the various matrices. Of all the HCH isomers, β-HCH was the most important, accounting for over 40% of the total HCHs in all the samples, whilst DDE dominated the distribution of DDTs contributing over 40% of the total DDT budget in the water, soil, sediment and plant samples. The concentrations of OCl pesticides at most sites did not exceed the Chinese guideline values for water and plants. For HCHs and DDT, a number of samples exceeded the EQS values proposed by the EC. The findings point to the urgent need to establish a reliable monitoring program for POPs including OCl pesticides, so that any exceedance in concentration over the EQS values can be detected and appropriate action taken. Further work is needed, through regular sampling of terrestrial and aquatic biota, to determine the bioaccumulation of POPs in the food web and the associated risks to the ecosystems and human health.

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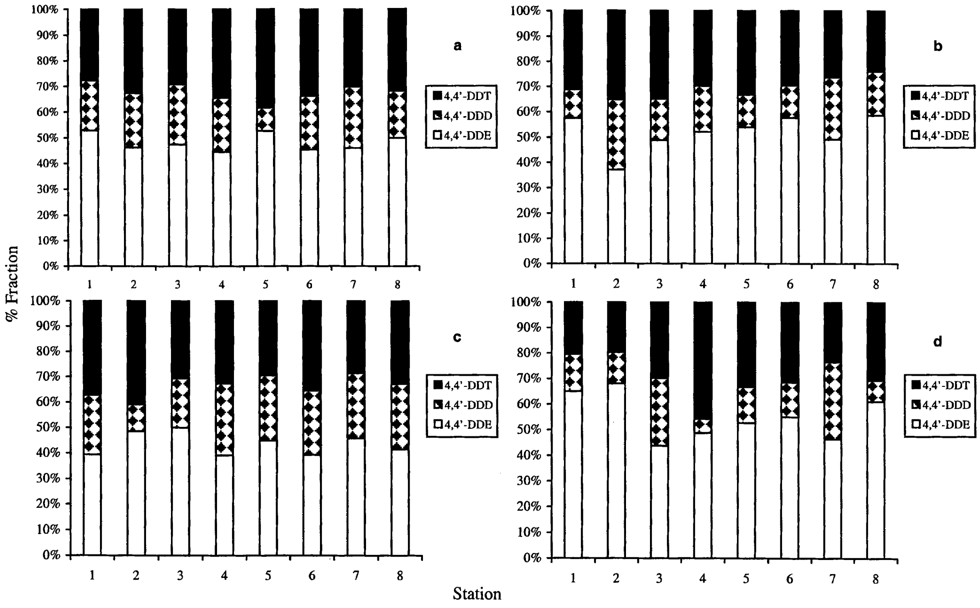

Fig. 5 Distribution of DDT and its degradation products in (a) water, (b) sediment, (c) soil and (d) plants.

Table 3 Correlation value (r) between individual OCl pesticide compounds[a] in water

Compound	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
A	1.000																	
B	0.760	1.000																
C	0.987	0.745	1.000															
D	0.818	0.983	0.800	1.000														
E	0.849	0.776	0.797	0.841	1.000													
F	0.622	0.725	0.540	0.746	0.847	1.000												
G	0.574	0.559	0.486	0.623	0.841	0.834	1.000											
H	0.552	0.754	0.545	0.774	0.471	0.438	0.408	1.000										
I	0.759	0.784	0.699	0.822	0.834	0.922	0.722	0.591	1.000									
J	0.262	0.416	0.201	0.391	0.378	0.748	0.446	0.283	0.707	1.000								
K	0.731	0.720	0.651	0.774	0.918	0.968	0.890	0.482	0.943	0.638	1.000							
L	0.754	0.797	0.692	0.848	0.927	0.952	0.844	0.561	0.961	0.609	0.983	1.000						
M	0.152	0.301	0.125	0.251	0.170	0.466	0.128	0.161	0.493	0.840	0.347	0.350	1.000					
N	0.590	0.738	0.541	0.718	0.588	0.801	0.493	0.595	0.902	0.833	0.756	0.783	0.727	1.000				
O	0.527	0.673	0.471	0.678	0.691	0.922	0.657	0.458	0.927	0.854	0.874	0.890	0.640	0.902	1.000			
P	0.317	0.435	0.246	0.418	0.385	0.730	0.435	0.331	0.726	0.970	0.639	0.602	0.822	0.857	0.805	1.000		
Q	0.826	0.707	0.850	0.766	0.740	0.608	0.442	0.537	0.810	0.338	0.694	0.770	0.270	0.669	0.664	0.353	1.000	
R	0.061	0.150	0.063	0.175	0.041	0.011	0.075	0.526	0.033	0.003	0.026	0.045	0.049	0.023	0.004	<0.001	0.028	1.000

[a] A: α-HCH; B: β-HCH; C: γ-HCH; D: δ-HCH; E: heptachlor; F: aldrin; G: heptachlor epoxide; H: endosulfan I; I: dieldrin; J: 4,4′-DDE; K: endrin; L: endosulfan II; M: 4,4′-DDD; N: endrin aldehyde; O: endosulfan sulfate; P: 4,4′-DDT; Q: endrin ketone; R: methoxychlor.

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