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Persistent organochlorine residues in sediments of Haihe River and Dagu Drainage River in Tianjin, China

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Abstract: Persistent organochlorine compounds were analyzed by means of GC-ECD in surface sediment samples from two selected rivers in Tianjin, Haihe River and Dagu Drainage River. A total of 16 surface sediment sites were selected along the both rivers. The frequency of detection of T-HCH and T-DDT in sediment samples both was up to 100%, which illustrated that the contamination of HCH and DDT was widespread in Haihe and Dagu Drainage Rivers. Results indicated that the concentrations of various pesticides in sediments from Haihe River were in the range of 3.30—75.96 ng/g dw for T-HCH and 1.57—211.57 ng/g dw for T-DDT. Compared with Haihe River, Dagu Drainage River was contaminated by HCHs and DDTs along the all locations and the values of T-HCH and T-DDT residues in sediments ranged from 2.30 to 124.61 ng/g dw and from 11.28 to 237.30 ng/g dw, respectively. The possible pollution sources were analyzed through monitoring results of organochlorine pesticides(OCPs) residues in sediments from the two rivers. The investigation also indicated that HCH was still used as pesticide in Tianjin partial area.

Keywords: Haihe River; Dagu Drainage River; sediment; OCPs; DDT; HCH

Introduction

Organochlorine pesticides (OCPs) such as hexachlorocyclohexane (HCH), dichloro diphenyltrichloroethane (DDT) have been of great concern due to their ubiquitous, persistent, highly bioaccumulative nature as well as toxic biological effects (Willett, 1998; Ciarelli, 1999; Goedkoop, 2003). Because of their strong lipophilic properties, these man-made compounds are often scavenged from water through sorption onto suspended material that later is deposited on the bottom to become part of the bottom substrate. Consequently, bottom sediments often become reservoirs of persistent organochlorine in the environment (Doong, 2002a; 2002b; Bakan, 2004). Although the production of HCH and DDT have been officially banned in China since 1983, some of organochlorine compounds are still being produced in Tianjin. Rivers have been severely polluted with high loads of persistent organic pollutants in Tianjin (Tao, 2003; Gong, 2004).

Tianjin, the third largest industrial city in China, is located in northern China near Beijing and adjacent to the Bohai Sea. Owning about 11200 km^2 of land and a population of 10 million, Tianjin is highly polluted with the development of industry and rapid urbanization. Water shortage has become a bottleneck to the further development of the economy and agriculture production. The Haihe River, the largest water system in north China, flows through Tianjin City and empties into the Bohai Sea. In 1958, to solve water shortage of Haihe River, regulating sluice was built to reserve water from upstream. So the Haihe River became an important water resource to Tianjin. At the same time, Dagu Drainage River, which is situated in the south of the Haihe River, was excavated to collect various domestic and industrial wastewater in order to reduce water pollution to the Haihe River (Tianjin Environmental Protection Bureau, 2001).

Due to lack of water resource, water has to be stored in both rivers for a long time, which aggravates the pollution especially to the sediments. Confronted with water shortage in agriculture, river water has been applied in this area for more than 40 years (Tianjin Environmental Protection Bureau, 2001). Besides wastewater irrigation, the sludge drudged from Haihe and Dagu Drainage rivers has also been used to fertilize farmlands in Tianjin suburban (Tianjin Environmental Protection Bureau, 1996; 2001). Therefore, the investigation of OCPs in sediments not only provides a valuable record of contamination in aquatic environment but also indicates ecological risk for farmland usage.

1 Materials and methods

1.1 Sampling

In order to understand the contamination and distribution of organochlrorine pesticides (OCPs) in sediments from the two typical rivers in Tianjin water system, sediment samples were collected from 16 sections along Haihe River and Dagu Drainage River. The sampling locations are showed in Fig.1. The sites of H1 and H9 are respectively the starting point and the end point, the entrance to the Bohai Sea, of the main branch of Haihe River. Sediment samples from Dagu Drainage River were marked from D1 to D7. With the assistance of Tianjin Environmental Protection Bureau, a sampling campaign was carried out in March 2002.

The surface sediment samples were collected with a stainless steel grab sampler and frozen immediately and transported to the laboratory and then kept in the refrigerator at −18℃ before analysis. To eliminate randomicity, sediment samples were collected from three to five adjacent points for each site. After centrifuging (3000 r/min, Centrifuge TDL-5, China) and freeze drying (EYELA-FDU-830, Japan), every sediment sample was rubbed to granular powder to pass through a 70-mesh sieve and homogenized.

1.2 Extraction and cleanup

Glassware was washed with liquid soap and rinsed properly with distilled water, and then with pure acetone. They were then baked in the oven at 100℃ for 24 h. Florisil (60—100 mesh, Beijing Kanlin Chemical Regents Co. Ltd., China) was activated in the muffle at 650℃ for 6 h. The organic reagents including hexane, dichloromethane were redistilled before use. The standard solution of OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH, *p,p'*-DDT, *p,p'*-DDE,

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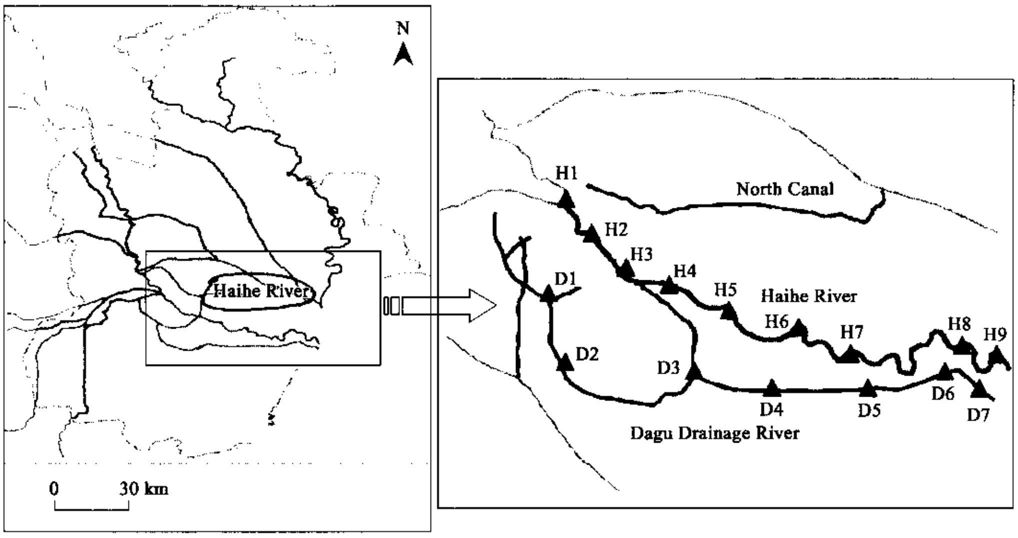

Fig.1 The study areas and sampling sites

p, *p*′-DDD) was purchased from National Research Center for Certified Reference Materials of China. These solutions were further diluted as required.

The OCPs were analyzed following the method reported by Wu *et al*.(Wu, 1999) with slight modification. Briefly, each sediment sample (10 g) was spiked with internal standard: 2, 4, 5-trichlorobiphenyl, which was used to quantify the overall recovery of the procedures. The samples were Soxhlet extracted for 10 h with 100 ml of *n*-hexane and acetone(1 : 1, v : v). The extracts were decanted, and concentrated down to a few millilitres using rotary evaporation and subsequently eluted through an anhydrous sodium sulfate column. Activated copper (1 g) was added to sediment fractions for removal of sulphur. After rotary vacuum evaporation to 1 ml again, the extract was purified on a 2 g silica gel and 1 g florisil column. The elution was eluted with 15 ml hexane as the first fraction, followed by 15 ml hexane: dichloromethane(7 : 3) as the second fraction. The two fractions were combined and concentrated to a final volume of about 0.5 ml were ready for analysis.

1.3 Analysis procedures

One microlitre of each extract was injected in a splitless model into a HP 6890 GC equipped with a 50 m × 0.32 mm × 0.25 μm HP1 fused-silica capillary column and a 63Ni electron capture elector(micro-ECD). The oven temperature was programmed for an initial temperature of 50℃ (2 min hold) to 180℃(3 min hold) at a rate 10℃/min, followed to 210℃ at the rate of 8℃/min and finally programmed to 260℃ at 10℃/min (10 min hold). Injector and detector temperatures were maintained at 210 and 300℃, respectively. Nitrogen was used both as the carrier(2 ml/min) and the make-up(60 ml/min) gas. Concentrations of individual organochlorines were quantified relative to the peak area of the respective external standards following calibration with standards. The correlation coefficients(*r*) of calibration curves of HCHs and DDTs were all higher than 0.998. T-HCH were expressed as a sum of α-HCH, β-HCH, γ-HCH, δ-HCH. T-DDT were defined as a sum of *p*, *p*′-DDT, *p*, *p*′-DDE, *p*, *p*′-DDD. The triplicate recovery tests of T-HCH and T-DDT yielded (98 ± 12)% and (92 ± 7)%, respectively. Detection limits of T-HCH and T-DDT were determined to (0.09 ± 0.08)% and (0.11 ± 0.07)%, respectively. All data presented here were corrected for each blank.

2 Results and discussion

2.1 Contamination level of OCPs in sediments

Table 1 shows the concentrations of OCP residues in surface sediments from both Haihe and Dagu Drainage Rivers, respectively. All the selected OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH; *p*, *p*′-DDT, *p*, *p*′- DDE, *p*, *p*′-DDD) were detected. Concentrations of OCPs in sediments from the Haihe River were 3.30—75.96 ng/g dw for T-HCH and 1.57—211.57 ng/g dw for T-DDT. The mean concentrations were 18.25 ng/g dw for T-HCH and 153.24 ng/g dw for T-DDT. Biological metabolites *p*, *p*′- DDE and *p*, *p*′-DDD of DDT were in the range of 0.73—113.95 ng/g dw and 0.69—452.52 ng/g dw, respectively.

Concentrations of HCH residues in surface sediments from the Dagu Drainage River were higher than those from the Haihe River. As illustrated in Table 1, concentrations of HCHs ranged from 0.77 ng/g dw to 69.98 ng/g dw(mean 20.59 ng/g dw) for α-HCH, 0.50 to 37.64 ng/g dw(mean 15.01 ng/g dw) for β-HCH, 0.65 to 19.38 ng/g dw(mean 6.21 ng/g dw) for γ-HCH, 0.06 to 19.02 ng/g dw(mean 6.13 ng/g dw) for δ-HCH. The mean concentrations of *p*, *p*′- DDE, *p*, *p*′-DDD and *p*, *p*′-DDT residues in sediments from the Haihe River were also lower than those from the Dagu Drainage River, except for the site of H2 with a high concentration(113.95 ng/g dw for *p*, *p*′- DDE, 452.52 ng/g dw for *p*, *p*′-DDD and 422.39 ng/g dw for *p*, *p*′-DDT). (High concentration of H2 is mostly due to random factor because there was no industry drainage resource around H2.)

The frequency of detection of T-HCH and T-DDT in sediment samples both were up to 100%, which illustrated that the contamination of HCH and DDT was widespread in the Haihe River water system. Recent studies also show that the contamination of OCPs is a serious problem in Tianjin area (Tao, 2003; Gong, 2004). The status of OCPs contamination in river sediments from other countries was compared with this study (Table 2). The highest concentration of T-HCH(mean 47.94 ng/g dw) was showed in sediments from the Dagu Drainage River. Compared with other rivers in the Table 2, T-HCH residue in sediments from the Haihe River was relatively higher except the most heavily polluted Dagu Drainage River. With respect to T-DDT concentrations for different sediments from listed rivers in Table 2, Haihe River and Dagu Drainage River also come out top as showed in Table 2.

Table 1 Concentrations of OCPs residues in surface sediments of the Haihe River and Dagu Drainage River(ng/g dry weight)

Sample	α-HCH	β-HCH	γ-HCH	δ-HCH	T-HCH	*p*,*p*′-DDE	*p*,*p*′-DDD	*p*,*p*′-DDT	T-DDT
H1	62.13	6.93	3.93	2.97	75.96	54.22	50.99	6.77	111.98
H2	5.29	5.79	3.11	1.99	16.18	113.95	452.52	422.39	988.86
H3	6.56	9.08	1.94	0.78	18.36	71.75	141.19	8.62	221.57
H4	10.58	8.14	2.81	0.87	22.40	5.93	17.99	5.08	29.00
H5	2.38	1.23	0.38	0.50	4.49	0.81	2.68	0.97	4.46
H6	2.42	5.53	0.49	0.27	8.71	0.73	0.69	0.15	1.57
H7	2.64	4.93	0.51	0.54	8.62	5.03	2.62	0.92	8.57
H8	1.16	0.79	3.05	1.25	6.24	1.54	1.43	2.74	5.70
H9	1.85	0.45	0.39	0.61	3.30	2.20	2.95	2.27	7.42
D1	5.35	8.47	1.50	2.01	17.33	68.85	33.28	19.84	121.96
D2	7.80	13.85	6.23	2.08	29.96	79.18	78.27	16.28	173.72
D3	1.49	6.16	5.45	0.06	13.16	15.93	56.19	165.18	237.30
D4	10.65	19.12	2.10	3.39	35.26	26.96	48.00	6.75	81.71
D5	0.77	0.50	0.65	0.39	2.30	5.87	11.99	7.19	25.04
D6	48.08	37.64	8.21	19.02	112.94	8.78	16.26	6.92	31.96
D7	69.98	19.33	19.38	15.93	124.61	1.17	1.03	9.08	11.28

Notes: H. Haihe River main branch; D. Dagu Drainage River

Table 2 Levels of T-HCH and T-DDT(ng/g dw) in the surface sediments from different rivers

River	T-HCH	T-DDT	References
Haihe River Main Branch, Tianjin, China	3.30—75.96(18.25)	1.57—211.57(48.78)	This study
Dagu Drainage River, Tianjin, China	2.30—124.61(47.94)	11.28—237.30(97.57)	This study
Daliaohe River, China	0.50—0.80 (0.65)	(0.20)	Wu, 1999
Yangtze River, China	0.40—0.70 (0.60)	0.10—0.20 (0.20)	Wu, 1999
Huanghe River, China	1.00—5.00 (3.00)	ND^{a}	Wu, 1999
Pearl River Estuary, China	0.28—1.23 (0.68)	1.36—8.99 (2.84)	Hong, 1999
Da-han River, Taiwan district, China	ND—2.08(0.39)^{b}	0.06—2.91(0.90)^{b}	Doong, 2002a
Erh-jen River, Taiwan district, China	ND—3.47(1.03)^{b}	ND-2.03(0.72)^{b}	Doong, 2002a
Wu-shi River, Taiwan district, China	0.99—14.5 (3.78)	ND—11.4 (2.51)	Doong, 2002b
Ebro River, Spain	0.038	51.8	Fernandez, 1998
Danube River, Ukraine	0.03—6.4	< 0.04—41	Fillmann, 2002
Mert Stream, Turkey^{c}	14—16	71	Bakan, 2004
Kizihrmak River, Turkey^{c}	5	ND^{a}	Bakan, 2004

Notes: ^{a} not detected; A-B (C) means that the range of concentration is A-B ng/g, while the mean value is C; ^{b} basis on ng/g total organic carbon; ^{c} basis on ng/g wet weight

2.2 Spatial distribution of OCPs

Fig.2 shows the distributions of T-DDT and T-HCH in sediments along Haihe and Dagu Drainage Rivers. Spatial distribution of T-HCH showed a ununiformity in sediment samples from the Haihe River(from H1 to H9) and the Dagu Drainage River (from D1 to D7). High concentrations of OCPs residues in sediments occur at reach from H1 to H4 of the Haihe River, which belongs to urban area of Tianjin. The site of H1 is the junction of four branches which are Beiyunhe, Nanyunhe, Xinkaihe and Ziyahe rivers. Because regulating sluice is built at the end of the Haihe River and there is little water from four branches recent years, water in mainstream often become nearly stagnant. Consequently, suspended sediment from upstream water gradually deposited in this reach, which may cause high OCPs residues in sediments. Relatively, the status of OCPs in sediments from downstream is less than those in upstream(Tao, 2003; Gong, 2004).

The concentrations of HCH residues in sediments from upstream(from D1 to D4) of the Dagu Drainage River were lower than those in downstream. The fact is consistent with discharging wastewater into the river directly from many chemical industrial factories, which located in the

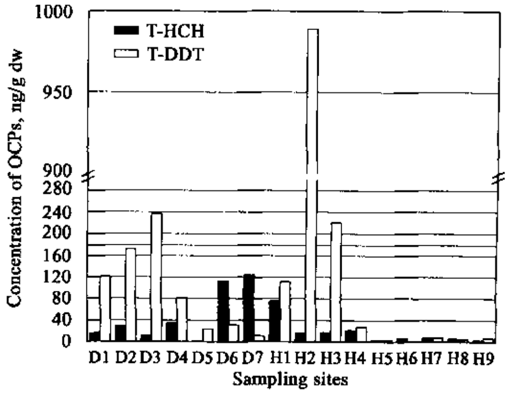

Fig. 2 Distribution of the mean T-HCH and T-DDT concentrations(ng/g dw) in sediments from Haihe and Dagu Drainage rivers

downstream of the Dagu Drainage River. For a long period, a large amount of HCH has been absorbed onto sediment due to less hydrodynamic conditions of river water. Conversely, the levels of DDT in sediments from upstream of the Dagu Drainage River were higher than those in downstream sediments. It is easy to find the answer. Dicofol is still permitted to use for fruit and garden to kill red spiders at present in urban area. Because dicofol mixture contained about 3.5%—10.8% DDT(Luo, 2000), DDT has been released into the environment due to extensive use of dicofol mixture. In fact, distributions of T-DDT and T-HCH in sediments from both rivers are well coincident with the investigations of OCPs residues in Tianjin's soil (Gong, 2004).

2.3 Compositions analyses

The relative concentration of the parent p, p'-DDT compound and its biological metabolites, p,p'-DDE and p, p'-DDD, can be used as indicator to assess the possible pollution sources. Since DDT can be biodegraded under aerobic condition to p, p'-DDE and under anaerobic condition to p,p'-DDD, ratio of(DDE + DDD)/T-DDT > 0.5 can be thought to be subjected to a long-term weathering (Hites, 1992; Hong, 1999; Doong, 2002a). Fig. 3 illustrates the relationship between(DDE + DDD)/T-DDT and DDD/DDE in surface sediments collected from the Haihe and Dagu Drainage Rivers. Ratios of (DDE + DDD)/T-DDT ranged from 0.52 to 0.96 and from 0.19 to 0.91 for the Haihe River and the Dagu Drainage River, respectively. All ratios of sites from the Haihe River are greater than 0.5. This means no recent input of technical DDT. That is to say, DDT compounds in sediments from the Haihe River may be mainly derived from DDT-treated aged and weathered agricultural soils (Doong, 2002b). However, for the Dagu Drainage River, the p,p'-DDT residues in sediments of D3 and D7 occupied 70% and 81%, respectively, which were very close to technical-grade DDT product(containing 75% p,p'-DDT). This indicates that the sites of D3 and D7 are in the vicinity of the discharging source. Most ratios of DDD/DDE were greater than unity for the Dagu Drainage River and near upon half of ratios less than unity for the Haihe River, which indicated that sediments was dominated by p,p'-DDD, the product of anaerobic degradation of p,p'-DDT, for the Dagu Drainage River. This result is in good agreement with the fact that anoxic conditions more often occur to the Dagu Drainage River than to the Haihe River, because lots of industrial and municipal wastewater was discharged to the former.

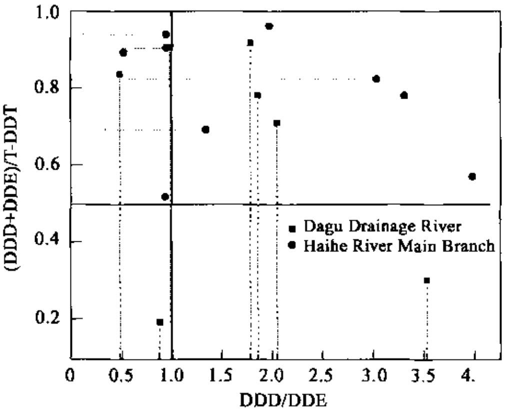

Fig. 3 The relationship between DDD/DDE and (DDE + DDD)/T-DDT in sediments from Haihe and Dagu Drainage rivers

As a cheap broad-spectrum insecticide, amounts of HCH had been used in Tianjin until 1983. Technical HCH consists principally of five isomers, α-HCH(60%—70%), β-HCH (5%—12%), γ-HCH (10%—15%), δ-HCH (6%—10%) and ε-HCH(3%—4%) (Walker, 1999). Regarding the composition of HCH isomers, α-, β-, γ- and δ-HCH were detected(Fig.4) in all samples from the Haihe River and the Dagu Drainage River. The isomers of α-, β-, γ- and δ-HCH were observed to contribute about 43%, 31%, 13% and 13% for the Dagu Drainage River and 58%, 26%, 10% and 6% for the Haihe River, respectively. The predominant species of HCHs in the selected two rivers were α- and β-HCH, suggesting that the contamination of HCH in both rivers may be attributed to the long-range transport and the erosion of the weathered agricultural soils containing HCH compounds. Nevertheless, high HCH residues in sediments from rivers in Tianjin also indicated their intense use in this area in history. The higher mean value of β-HCH found in the Haihe River than that in the Dagu Drainage River would be a consequence of its high persistence to microbial degradation under relatively aerobic conditions. Moreover, β-HCH is also the more lipophilic than the other isomers, enhancing the adsorption on sediment particles (Walker, 1999). The above observed result corresponded well with that in the residues of HCH in soils of Tianjin area(Gong, 2004) and can be explained by the fact that β-HCH is the most stable and persistent HCH-isomers in the environment. In addition, some β-HCH can be converted to γ-HCH(Wu, 1997). γ-HCH has higher water solubility and Henry' Law constant value than β-HCH(Lee, 2001). The results of investigation show that mean levels of γ-HCH in sediments from both rivers are near to ingredient of technical-grade HCH, which indicates that HCH be still used as pesticide in Tianjin area.

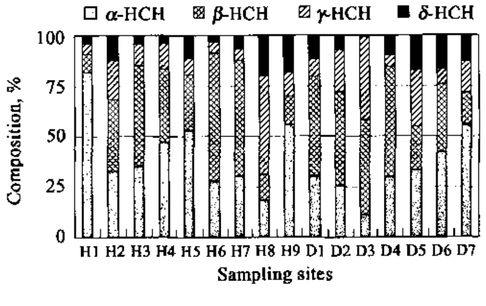

Fig.4 Composition of HCHs in sediments from the Haihe and Dagu Drainage rivers

3 Conclusions

This results obtained in this study documented the composition and distribution of OCPs in sediments collected from the Haihe River and the Dagu Drainage River. There exist a variety of OCP residues in both rivers, especially for the Dagu Drainage River. All the DDT and HCH isomers residues in sediments were detected in both rivers. The total concentrations of OCPs in sediments ranged from 8.95 to 1005.04(mean 171.49) and 27.35 to 250.46 ng/g dw(mean 145.50) for the Haihe River and the Dagu Drainage River, respectively. OCP concentrations of sediments from the

Haiher River and the Dagu Drainage River were higher than those from other rivers. While urban reach of the Haihe River was heavily contaminated with DDT and HCH, the downstream was relatively less polluted. The Dagu Drainage River were seriously polluted which reflects the fact that the contamination of the sediments was weathered agricultural soil and recent input of HCH and DDT into the Dagu Drainage River.

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