Bull Environ Contam Toxicol (2009) 82:510–515
DOI 10.1007/s00128-008-9630-3

Vertical Fluxes and Accumulation of Organochlorine Pesticides in Sediments of Haihe River, Tianjin, China

Jie Chi

Received: 26 July 2008 / Accepted: 29 December 2008 / Published online: 9 January 2009

Abstract Organochlorine pesticides (OCPs) concentrations in sediments and sediment trap fluxes of particulate organic carbon and OCPs were measured from October 2006 to May 2008 in the urban reach of Haihe River, Tianjin, China, in order to investigate vertical fluxes and accumulation of OCPs in sediments. The concentrations of OCPs in sediments (dry weight basis) were in the range of 2.08–10.07 ng/g (mean 4.70 ng/g) for HCHs (α-, β-, γ-, δ-HCH), 5.82–43.39 ng/g (mean 17.43 ng/g) for DDTs (p,p′-DDE, p,p′-DDD, o,p′-DDT, p,p′-DDT). Compared with data reported in Haihe River 2003, the levels of OCPs showed a significant decrease between 2003 and 2008. This is mainly attributed to significant decrease of production and usage of HCHs and DDTs and biodegradation of HCHs and DDTs in sediment. Concentrations of HCHs and DDTs in sediments were well correlated with sediment organic carbon contents. Concentrations of OCPs in settling particles (dry weight basis) ranged from 21.2 to 138.4 ng/g (mean 52.6 ng/g) for HCHs, 30.0–245.7 ng/g (mean 87.1 ng/g) for DDTs, which were 2.2–48.2-fold higher than those associated with sediments. β-HCH was the dominant HCH isomer in both sediments and settling particles. Among DDTs, p,p′-DDE was found to be dominant in sediments, while p,p′-DDT was the predominant form in settling particles. This suggests that further biodegradation of OCPs occurred during the course of sedimentation and burial. The annual sediment trap flux of OCPs in Haihe River in the urban area of Tianjin was 177–211 μg/m^2 yr for HCHs and 213–341 μg/m^2 yr for DDTs, respectively.

Keywords Vertical fluxes · Sediments · HCHs · DDTs · Haihe river

Organochlorine pesticides (OCPs) are ubiquitous contaminants whose occurrence in the environment is of special concern because of their deleterious effect on non-target organism, bioaccumulation and persistence in the environment (Willett et al. 1998). Technical hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) were the most extensively used pesticides in China, resulting widespread contamination in various environmental compartments (Yang et al. 2006; Tang et al. 2008; Wang et al. 2008) although the production and use of technical HCH and DDT were banned in China in 1983. Because of their low water solubility, HCH isomers (HCHs), DDT and its metabolites (DDTs) tend to associate with soils and sediments which constitute long-term reservoirs and secondary sources.

Sediment trap fluxes are calculated as the total amount of matter or compounds obtained in the traps per unit of time. An estimation of down fluxes of settling particle associated compounds is of great interest for the general fate of organic pollutants, since sediments often serves as the final sink for these contaminants.

Tianjin is one of the most severely contaminated areas by HCHs and DDTs in China because of its long-term usage and wastewater discharge from local industries. As an important river in Tianjin, Haihe River receives input of industrial, domestic and agricultural effluents. It originates from the infall of Beiyun, Nanyun and Ziya rivers, flows through downtown of Tianjin and Tanggu, and finally enters into Bohai Sea. Because of the drought, there has been very little water from upriver branches since 1997 except during the flood season, and Haihe River is

J. Chi (✉)
School of Environmental Science and Engineering,
Tianjin University, Tianjin 300072, China
e-mail: cjiechi@yahoo.com

becoming a stagnant river. The amount of HCHs and DDTs in sediments from Haihe River remained at a high level in early 2000 (Yang et al. 2005) especially in the urban area of Tianjin because one of the major contributors was the upriver branches. Therefore, further analyses regarding the development of levels of HCHs and DDTs in Haihe River are still required.

In the present study, levels of OCPs in surface sediments from Haihe River in the urban area of Tianjin, China were measured from October 2006 to May 2008. Settling particles collected by sediment traps were analyzed for organic carbon and OCPs and the annual sediment trap flux of OCPs was calculated using the data obtained.

Materials and Methods

Haihe River in the urban area of Tianjin is 20 km long with an average width of 100 m and a mean depth of 4 m. Four sampling sites (S1–S4) were selected along the river in the urban area, as shown in Fig. 1. S1, from which Haihe River originates, is an important crossing point of Beiyun, Nanyun and Ziya rivers. S4 is about 16 km away from S1. Surface sediments (top 2 cm) were collected at all sampling sites, which was carried out seven times from October 2006 to May 2008. Sediment samples were sealed in polytetrafluoroethylene bags and stored at −20°C before analysis.

Settling particles were collected 1.2 m below the surface by sediment traps at sites S1 and S4. Sediment trap experiments were carried out eight times in 2007. The 15-cm-diameter trap is a plexiglas cylinder with a 3:1 height to diameter ratio (Blomqvist and Håkanson 1981). The trap has a funnel at the bottom connected to a 500-mL glass bottle. Formaldehyde was added to the bottle for preservation of the trapped settling matter and the entire trap filled with filtered river water prior to deployment to limit biological activity.

Settling particles and sediment samples were freeze-dried, ground and passed through an 80-mesh sieve. Dried samples (0.1–5 g) were sonically extracted with 20 mL hexane-dichloromethane (1:1). Each sample was extracted three times and each for 15 min. The extracts were combined and activated Cu was added to remove element sulfur. The extracts were concentrated to about 1–2 mL using a K-D concentrator, and further purified with a glass column (10 mm i.d. × 250 mm) packed with 7 g of activated silica gel. The elution was subsequently carried out using 50 mL of hexane-dichloromethane (3:1). The eluate was concentrated to 0.5 mL for GC-ECD analysis. Recovery studies were performed by spiking sediment samples (5 g) with 10 ng of composite OCPs standards (α-, β-, γ-, δ-HCH and p,p′-DDE, p,p′-DDD, o,p′-DDT, p,p′-DDT). A non-spiked sediment sample acted as a control and treated in the same manner as the spiked sediment samples with the method described above. The average recoveries of OCPs from spiked sediment samples were in the range of 86%–112% and the relative standard deviation (RSD) values ranged from 3% to 15%.

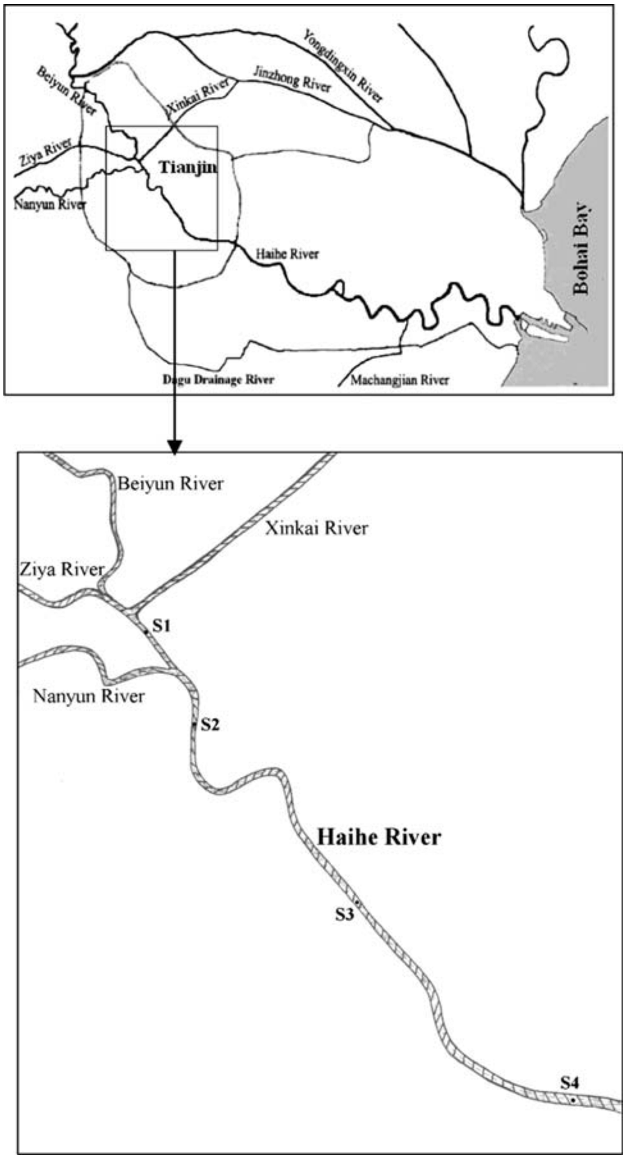


Fig. 1 Map of the study area and sampling sites

OCPs concentrations in settling particles and sediment samples were determined by an Agilent 6890N gas chromatograph equipped with a ^{63}Ni electron capture detector and a DB-35 ms capillary column (film thickness, 0.25 µm; inner diameter, 0.32 mm; length, 30 m). High pure nitrogen was used as both the carrier gas and make-up gas with a flow rate of 1.5 and 58.5 mL/min, respectively. The temperature of injector and detector was set at 250 and 300°C, respectively. Oven temperature was increased from 160°C (held for 0.5 min) to 230°C at 15°C/min, and then programmed to 275°C at 10°C/min, held for 3 min. The existence of these compounds was confirmed by the comparison of GC retention times and GC/MS spectra with those of the calibration standards. Determination of total organic carbon (TOC) was performed on a Shimadzu model VCPH TOC analyzer.

Results and Discussion

The variations of OCPs concentration in surface sediments on dry weight (dw) basis are shown in Figs. 2, 3. The detection rates of both HCHs and DDTs in sediments are up to 100%. Concentrations of OCPs ranged from 2.08 to 10.07 ng/g for HCHs, 5.82 to 43.39 ng/g for DDTs, respectively. The average concentration of OCPs decreased from upstream to downstream, and the decrease of DDT concentrations was more significant than that of HCH concentrations. High levels of OCPs at site S1 may be due to the pollution contribution from upstream branch rivers which were seriously polluted by OCPs (Yang et al. 2005). Levels of OCPs in sediments from Haihe River in the year 2003 were reported by Yang et al. (2005). High levels of HCHs and DDTs, which ranged from 18.76 to 19.03 ng/g and 61.71 to 80.18 ng/g, respectively, were found in sediments collected from Haihe River in the urban area of Tianjin. This study showed that, after about 4 years, levels of HCHs and DDTs in the same reach decreased significantly to a mean concentration of 4.70 and 17.43 ng/g, respectively. This can be supposed from the following two aspects: (1) significant decrease of production and usage of HCHs and DDTs, especially in the late 1990s; (2) biodegradation of HCHs and DDTs in sediment (Wu et al. 1997; Chiu et al. 2004; Huang et al. 2007).

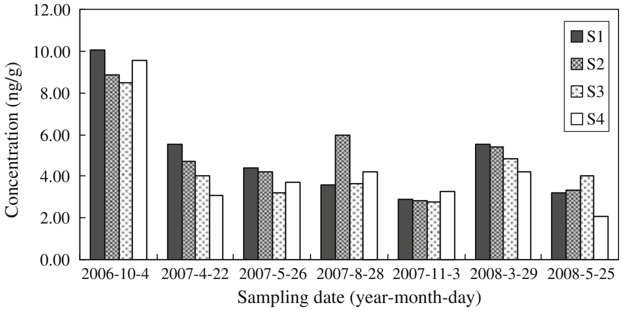


Fig. 2 Concentration of HCHs in sediments

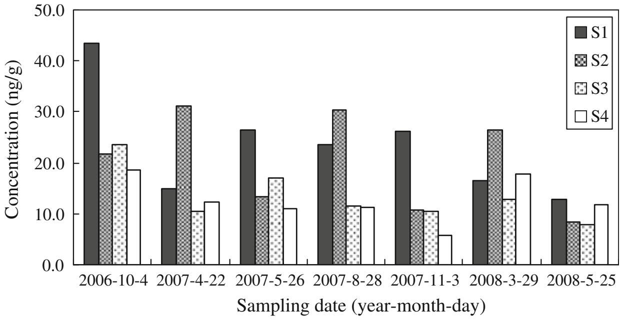
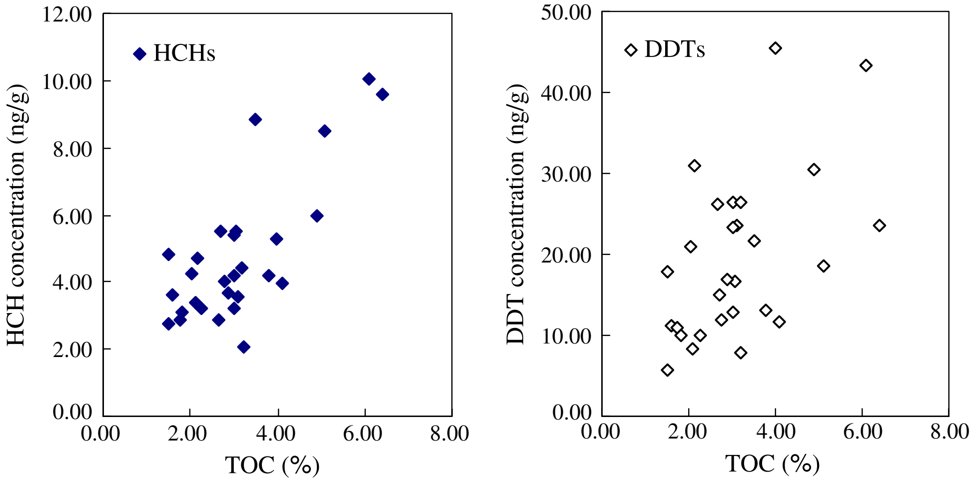


Fig. 3 Concentration of DDTs in sediments

The kinetic behavior of hydrophobic organic pollutants is significantly influenced by organic carbon contents in sediments and soils (Karickhoff 1981; Zhou and Rowland 1997). Figure 4 shows the relationship between TOC and OCPs concentrations in sediments along the river, and good correlations for HCHs ($R^2 = 0.7020$, n = 28, $p = 0.0000$) and DDTs ($R^2 = 0.5642$, n = 28, $p = 0.0000$) are observed. This is due to the lipophilic nature of OCPs which results in the high tendency of OCPs to associate with organic carbon in sediments.

Concentrations of OCPs in settling particles (dry weight basis) ranged from 21.2 to 138.4 ng/g (mean 52.6 ng/g) for HCHs, 30.0 to 245.7 ng/g (mean 87.1 ng/g) for DDTs. Concentrations of OCPs in upstream (S1) were higher than those in downstream (S4), which is related to OCPs

Fig. 4 Correlation between TOC and OCPs concentrations in sediments



pollution at the sampling sites, because OCPs pollution at site S1 was more seriously than that at site S4.

Concentrations of HCHs and DDTs in settling particles were 6.1 to 48.2-fold and 2.2 to 9.4-fold higher than those associated with sediments. Differences in concentration of OCPs can be due to the contaminant release during in situ organic matter degradation and the contaminant degradation processes in sediments (Wu et al. 1997; Skei et al. 2000; Chiu et al. 2004; Huang et al. 2007), which does not occur in the sediment traps, where formaldehyde preserves the settled material and prevents degradation.

Composition differences of HCH isomers in the environment can indicate different contamination sources (Iwata et al. 1995; Doong et al. 2002). The physical and chemical properties of the HCH isomers are quite different from one another. *β*-HCH has the lowest vapor pressure and water solubility, which is the most stable and relatively resistant to microbial degradation (Ramesh et al. 1991). Tianjin is one of the most severely contaminated regions by HCHs in China because of its long-term usage and wastewater discharge from local industries. The average compositions of HCHs were *α*: 24.9%, *β*: 48.8%, *γ*: 21.1%, and *δ*: 5.2% in sediments, *α*: 19.2%, *β*: 40.1%, *γ*: 23.1%, and *δ*: 17.6% in settling particles, respectively. Obviously, *β*-HCH was the dominant HCH isomer in both sediments and settling particles, which indicated that residues of HCHs were mainly from the large usage in the history. The average percentage of *β*-HCH in sediments was higher than that in settling particles because of further biodegradation occurring during the course of sedimentation and burial.

The average compositions of DDTs were 46.1% p,p′-DDE, 34.1% p,p′-DDD, 4.3% o,p′-DDT, and 15.5% p,p′-DDT in sediments, 27.7% p,p′-DDE, 11.5% p,p′-DDD, 7.7% o,p′-DDT, and 53.1% p,p′-DDT in settling particles, respectively. p,p′-DDE was the most dominant compound in the sediments, while p,p′-DDT was the predominant form in settling particles. Studies showed that the ratio of (DDD + DDE)/DDTs > 0.5 can be thought to be subjected to a long-term weathering (Hites and Day 1992; Hong et al. 1999). Most values of (DDD + DDE)/DDTs in sediments were higher than 0.5, while values of (DDD + DDE)/DDTs in settling particles were no more than 0.5 in most samples of (Fig. 5). This revealed that further biodegradation of DDT occurred during the course of sedimentation and burial. DDT can be biodegraded to DDE under aerobic condition and to DDD under anaerobic condition (Kalantzi et al. 2001). Most values of DDD/DDE were < 1 in both sediments and settling particles (Fig. 5), indicating that biodegradation of DDT occurred mainly under aerobic condition.

OCPs settling fluxes obtained by sediment traps ranged from 0.121 to 1.578 μg/m^2 day for HCHs, 0.223 to 2.214 μg/m^2 day for DDTs, respectively (Figs. 6, 7), and the maximum values were observed after the spring bloom and autumn bloom. At the same time, organic carbon fluxes from the surface water were also high. Good correlation between them was obtained (for HCHs, $R^2 = 0.6281$, $n = 16$, $p = 0.0000$; for DDTs, $R^2 = 0.6894$, $n = 16$, $p = 0.0000$). This suggests that the variations of OCPs

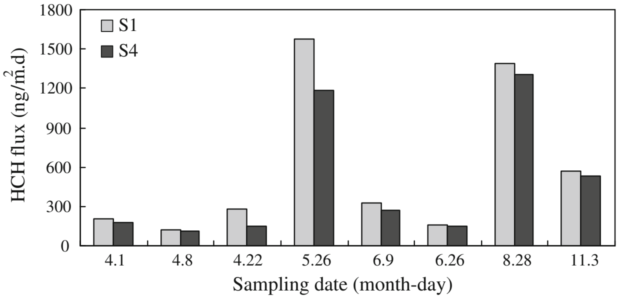


Fig. 6 Total HCH settling fluxes determined from sediment traps

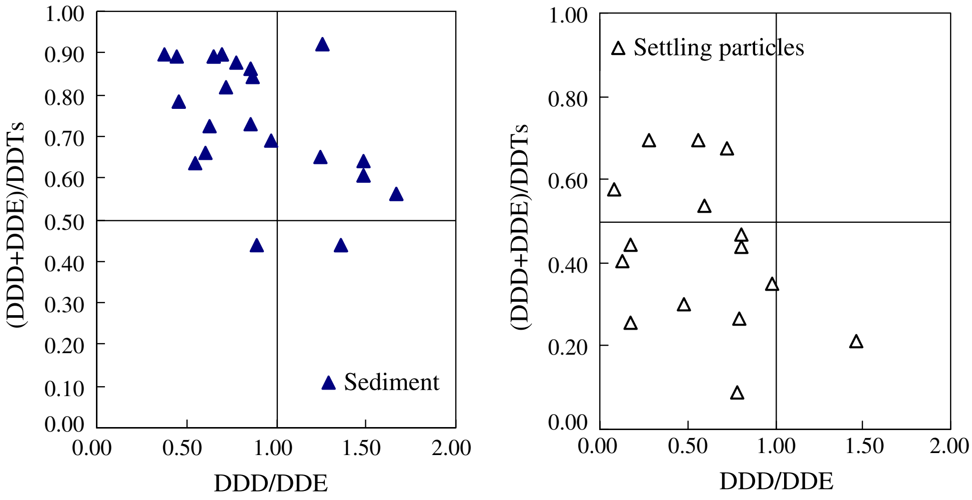


Fig. 5 The ratio of DDD/DDE and (DDD + DDE)/DDTs in sediments and settling particles

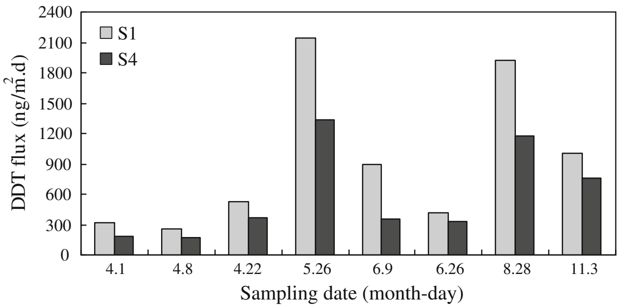


Fig. 7 Total DDT settling fluxes determined from sediment traps

settling fluxes are mainly controlled by differences in fluxes of organic matter and biological production.

The magnitude of vertical fluxes of OCPs depends on concentrations in settling particles and on total mass fluxes. The mass sedimentation and OCPs concentrations in settling particles were both higher in site S1 than those in site S4, which resulted in higher OCPs fluxes in site S1 (with mean value of 578.9 ng/m^2 day for HCHs, 935.1 ng/m^2 day for DDTs) as compared to site S4 (with mean value of 486.3 ng/m^2 day for HCHs, 583.7 ng/m^2 day for DDTs).

The annual sediment trap flux of OCPs in Haihe River in the urban area of Tianjin, which was estimated using data obtained in the area, was 177–211 μg/m^2 yr for HCHs and 213–341 μg/m^2 yr for DDTs, respectively. The annual sediment trap flux of OCPs in Haihe River was higher than that in the northern part of the Baltic Sea (9.8–20 μg/m^2 yr for HCHs, 2.2–11 μg/m^2 yr for DDTs; Strandberg et al. 1998) and comparable to that in a eutrophic lake in Tianjin, China (117 μg/m^2 yr for HCHs; Chi et al. 2008). The high sedimentation fluxes of OCPs in Haihe River are related to severe local contamination.

Conclusions

Wide occurrence of HCHs and DDTs in both sediments and settling particles has been found in the study area. The levels of OCPs in sediments decreased significantly between 2003 and 2008, which is due to significant decrease of production and usage of OCPs and biodegradation of OCPs in sediment. Concentrations of HCHs and DDTs in sediments were well correlated with sediment organic carbon contents. Levels of OCPs in settling particles were higher than those in sediments, which is due to the contaminant release during in situ organic matter degradation and the contaminant degradation processes in sediments. β-HCH was the dominant HCH isomer in both sediments and settling particles. Among DDTs, p,p′-DDE was found to be dominant in sediments, while p,p′-DDT was the predominant form in settling particles. This suggests that further biodegradation of OCPs occurred during the course of sedimentation and burial. Sediment traps deployed in the study area revealed large sediment fluxes of OCPs and the maximum values were observed after the spring bloom and autumn bloom. The high sedimentation fluxes of OCPs in the investigation area are related to severe local contamination.

Acknowledgments The authors are grateful to National Natural Sciences Foundation of China (Contract/grant number: 20677042 and 20777052).

References

Blomqvist S, Håkanson L (1981) A review on sediment traps in aquatic environments. Arch Hydrobiol 91:101–132

Chi J, Wang QY, Huang JJ, Huang GL (2008) Sedimentation and seasonal variation of hexachlorocyclohexanes in sediments in a eutrophic lake, China. J Environ Sci Health Part B 43:611–616. doi:10.1080/03601230802234724

Chiu TC, Yen JH, Liu TL, Wang YS (2004) Anaerobic degradation of the organochlorine pesticides DDT and heptachlor in river sediment of Taiwan. Bull Environ Contam Toxicol 72:821–828. doi:10.1007/s00128-004-0318-z

Doong RA, Peng CK, Sun YC, Liao PL (2002) Composition and distribution of organochlorine pesticide residues in surface sediments from the Wu-Shi River estuary. Taiwan Mar Pollut Bull 45:246–253. doi:10.1016/S0025-326X(02)00102-9

Hites RK, Day HR (1992) Unusual persistent of DDT in some western USA soils. Bull Environ Contam Toxicol 48:259–264

Hong H, Chen W, Xu L, Wang X, Zhang L (1999) Distribution and fate of organochlorine pollutants in the Pearl River Estuary. Mar Pollut Bull 39:376–382. doi:10.1016/S0025-326X(99)00081-8

Huang Y, Zhao X, Luan SJ (2007) Uptake and biodegradation of DDT by 4 ectomycorrhizal fungi. Sci Total Environ 385:235–241. doi:10.1016/j.scitotenv.2007.04.023

Iwata H, Tanabe S, Ueda K, Tatsukawa R (1995) Persistent organochlorine residues in air, water, sediments, and soils from the lake Baikal region, Russia. Environ Sci Technol 29:792–801. doi:10.1021/es00003a030

Kalantzi QI, Alcock RE, Joneston PA, Santillo D, Stringer RL, Thomas GO, Jones KC (2001) The global distribution of PCBs and organochlorine pesticides in butter. Environ Sci Technol 35:1013–1018. doi:10.1021/es0002464

Karickhoff SW (1981) Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere 10:833–846. doi:10.1016/0045-6535(81)90083-7

Ramesh A, Tanabe S, Murase H, Subramanian AN, Tatsukawa R (1991) Distribution and behavior of persistent organochlorine insecticides in paddy soil and sediments in the tropical environment: a case study in South India. Environ Pollut 74:293–307. doi:10.1016/0269-7491(91)90077-A

Skei J, Larsson P, Rosenberg R, Jonsson P, Olsson M, Broman D (2000) Eutrophication and contaminants in aquatic ecosystems. AMBIO 29:184–194. doi:10.1639/0044-7447(2000)029[0184:EACIAE]2.0.CO;2

Strandberg B, Bavel BV, Bergqvist PA, Broman D, Ishaq R, Naf C, Pettersen H, Rappe C (1998) Occurrence, sedimentation, and spatial variations of organochlorine contaminants in settling particulate matter and sediments in the northern part of the Baltic Sea. Environ Sci Technol 32:1754–1759. doi:10.1021/es970789m

Tang ZW, Yang ZF, Shen ZY, Niu JF, Cai YP (2008) Residues of organochlorine pesticides in water and suspended particulate matter from the Yangtze River catchment of Wuhan, China. Environ Monit Assess 137:427–439. doi:10.1007/s10661-007-9778-z

Wang XF, Li XH, Cheng HX, Xu XB, Zhuang GM, Zhao CD (2008) Organochlorine pesticides in particulate matter of Beijing, China. J Hazard Mater 155:350–357. doi:10.1016/j.jhazmat.2007.11.116

Willett KL, Ulrich EM, Hites SA (1998) Differential toxicity and environmental fates of hexachlorocyclohexane isomers. Environ Sci Technol 32:2197–2207. doi:10.1021/es9708530

Wu W, Xu Y, Schramm KW, Kettrup A (1997) Study of sorption, biodegradation and isomerization of HCH in simulated sediments/water system. Chemosphere 35:1887–1894. doi:10.1016/S0045-6535(97)00266-X

Yang NQ, Matsuda M, Kawano M, Wakimoto T (2006) PCBs and organochlorine pesticides (OCPs) in edible fish and shellfish from China. Chemosphere 63:1342–1352. doi:10.1016/j.chemosphere.2005.09.029

Yang RQ, Lv AH, Shi JB, Jiang GB (2005) The levels and distribution of organochlorine pesticides (OCPs) in sediments from the Haihe River, China. Chemosphere 61:347–354. doi:10.1016/j.chemosphere.2005.02.091

Zhou JL, Rowland SJ (1997) Evaluation of the interactions between hydrophobic organic pollutants and suspended particles in estuarine waters. Water Res 31:1708–1718. doi:10.1016/S0043-1354(96)00323-5