Bull. Environ. Contam. Toxicol. (2003) 70:351–358
© 2003 Springer-Verlag New York Inc.
DOI: 10.1007/s00128-002-0198-z

Bulletin of Environmental Contamination and Toxicology

Organochlorine Pesticide Residues in Water from Guanting Reservoir and Yongding River, China

X. T. Wang, S. G. Chu, X. B. Xu

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, People's Republic of China

Received: 1 July 2002/Accepted: 27 November 2002

Organochlorine pesticides (OCPs) such as HCH and DDT were the most important insecticides and were extensively used throughout the world in agriculture, forestry and public health. Because of damage to wildlife and potential harm to human health, including environmental persistence, bioaccumulation and toxic action upon many non-target organisms, the use of DDT was banned in most developed countries in the 1970s, except for public health emergencies. However, these OCPs, characterized by cheapness, broad spectrum, very powerful effects, likely continue to be used in some developing countries (Goldberg 1991; Li 1999). Technical HCH is a mixture consisted of α-, β-, γ-, δ-isomer, and only γ-HCH exhibits significantly insecticidal activity, while all isomers are acutely and chroniclly toxic (Metcalf, 1955). The cumulative global usage of technical HCH has been estimated to be as high as 6 million tons (Huang, 1989), and the real figure may be even higher (Li et al, 1998). Most countries have banned the usage of technical HCH, but currently lindane, consisting of 90%-100% of the γ-HCH, is still registered for use in most countries. The global contamination caused by widespread and sometimes indiscriminate usage of these pesticides over the past four decades has been found to be a serious environmental problem. In China, the production and usage of HCH and DDT began in the 1950s, peaked in the 1970s and were banned in 1983. The total amounts of technical HCH and DDT produced in China are approximately 4.9×10^6 tons and 4.0×10^5 tons (Lin et al, 2000), respectively. As the main pesticides used in China in the past, and banned somewhat later than some developed countries, the potential contamination of HCH and DDT in food, water and soil has been concerned by the public.

Guanting Reservoir is a typical reservoir in the north China and used to be an important source of water for Beijing City mainly used for irrigation and potable water. It was contaminated seriously by the discharge of industrial and domestic sewage in the 1980s, so that it could not be used as potable water source. Compared to other contamination, such as heavy metals, there is limited information regarding historical usage of organochlorine pesticides in the nearby regions and present residues in this reservoir. Beijing is one of the most populous regions in China. Its annual water consumption reached 4 billion cubic meters. With economic development and continuous drought, Beijing is now facing a

---

Correspondence to: X. B. Xu

water shortage. The purposes of the study were to investigate the occurrence of HCH and DDT in Guanting Reservoir and Yongding River and their main contamination sources after the usage of the organochlorine pesticides was banned for about 20 years in the area. The information will be useful for the management and remediation for some water system.

MATERIALS AND METHODS

A composite stock standard solution of organochlorine pesticides including α-, β-, γ- and δ-HCH and *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT was obtained from National Research Center for Certified Reference Materials of China at a concentration of 100 mg/L and further diluted to obtain the desired concentration. Decachlorobiphenyl (PCB209) and Florisil (60-100 mesh) were from Supelco (Bellfonte, USA), the latter was activated in drying oven at 130°C for 16 hr. XAD-2 resin (20-60 mesh) was purchased from Rohm and Haas (Philadelphia, Pa., USA). The resin was Soxhlet extracted successively with methanol, acetonitrile and diethyl ether for 12 hr per solvent, and kept it in methanol for use. The resin was washed with distilled water before the adsorption process. All solvents used were of analytical grade and redistilled in all-glass system to remove impurities prior to use. Glass fiber filter (Gelman type A/E) was obtained from Gelman Sciences Inc.

Guanting Reservoir is located in the northwest of Beijing City, at a distance of approximately 90 km. The reservoir dammed the Sanggan River, Yang River and Guishui River and converged into Yongding River. Thirteen sampling sites, seven sites (GT1-GT7, among them GT1 and GT2 are two inlets situated in Yang River and Guishui River, respectively) were at Guanting Reservoir and six (YD1-YD6) at Yongding River, were selected in the areas for investigation. Water samples were collected during October to November 2000. The geographical location of Guanting Reservoir, Yongding River, and the sampling sites are shown in Figure1. 20 L of water from each site was collected and filtered by glass fiber filter. The filtered water was passed through the XAD-2 resin column (200 mm×10 mm id) by siphonage at a flow rate of less than 15 mL/min. After adsorption, the pollutants trapped on XAD-2 resin were eluted with 90 mL of diethyl ether. The eluate was divided into two parts, one for PAHs and other organic pollutant analyses, and the other for HCH and DDT analyses. In the latter, 1mL of PCB209 solution at a concentration of 100 μg/L was added as surrogate. The sample solution was dried with anhydrous sodium sulfate (purified previously at 400°C for 4 hr in a shallow tray) and concentrated to 2 mL, which was cleaned up by concentrated sulfuric acid and Florisil column chromatography. The sample was concentrated and reduced finally to 0.2 mL by a gentle nitrogen steam for GC analysis.

The identification and quantification of HCH and DDT were carried out with an Agilent 6890 gas chromatograph equipped with ^{63}Ni electron capture detector (μ-ECD). The separation was performed on a fused silica capillary column (HP-5, 30 m×0.25 mm id, and 0.25 μm film thickness) with nitrogen as carrier gas and make-up gas. The GC oven temperature was programmed as follows: initial temperature of 50 °C was held for 1 min, increased at a rate of 4 °C/min to 280 °C,

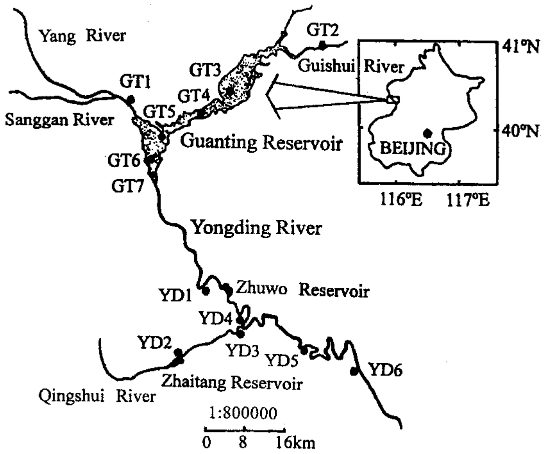


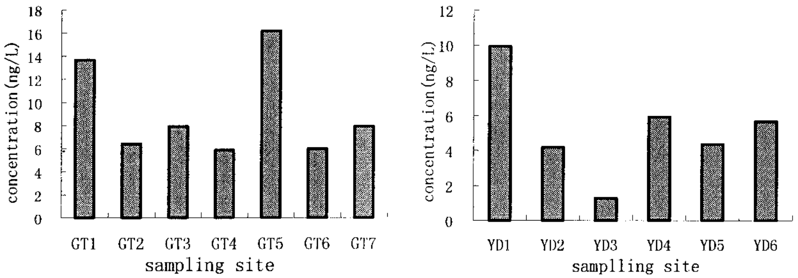
Figure 1. Geographical location of sampling sites

then held for 10 min. The injector and detector temperature were 280°C and 300°C, respectively. 1 μL of sample was injected in splitless mode and the purge time was 1 min. Peak identification of HCH including α-, β-, γ-, δ-HCH and DDT including *p,p′*-DDE, *p,p′*-DDD, *o,p′*-DDT, *p,p′*-DDT was made by comparison of retention times with corresponding standards.

Quality assurance criteria for these compound analyses were based on the measure of blank water sample including the complete analytical procedure. The detection limits for the analytes were defined as the lowest quantity of injected standard giving a 3:1 signal versus noise value in blank water sample. The detection limits of α-, β-, γ- and δ-HCH were 0.21, 0.25, 0.26, 0.33 ng/L, and those of *p,p′*-DDE, *p,p′*-DDD, *o,p′*-DDT, *p,p′*- DDT were 0.35, 0.14, 0.15 and 0.57 ng/L, respectively. The quantification of the analytes were performed by comparison to external standards. All results were corrected using individual surrogate recovery values. Matrix spike analyses were made by spiking standard solution into distilled water, and the samples sequentially underwent the whole process. The recoveries corrected using PCB209 as surrogate of α-, β-, γ- and δ-HCH were 55.7±4.2, 74.3±9.9, 67.2±2.8, 70.9±5.5%, respectively, and those of *p,p′*-DDE, *p,p′*-DDD, *o,p′*-DDT, *p,p′*-DDT were 79.0±16.3, 79.3±12.8, 81.1±15.2 and 95.8 ±14.6%.

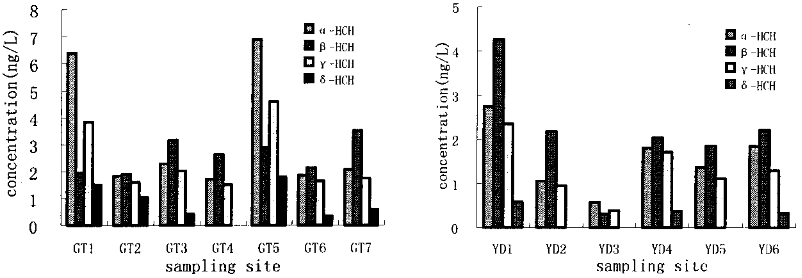
RESULTS AND DISCUSSION

The distributions of total HCH (sum of α-, β-, γ- and δ-HCH) residues in water from Guanting Reservoir (a) and Yongding River (b) are illustrated in Figure 2. Because the greater part of Guanting Reservoir was shallow (no more than 4 meters in depth), the main storage of the reservoir was in the sampling sites GT6 and GT7 (more than 10 meters in depth). The concentrations of total HCH in the water from Guanting Reservoir were about 5.9 to 16.2 ng/L. The concentrations of HCH in samples of GT2, GT3 and GT4 were low and similar to GT-6 and GT-7, and it means that the intake water from GT2 was not the pollution source. In the sampling



(a) (b)

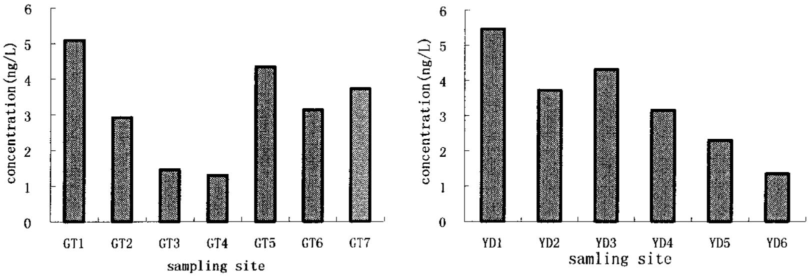
Figure 2. Concentrations of total HCH in water samples



(a) (b)

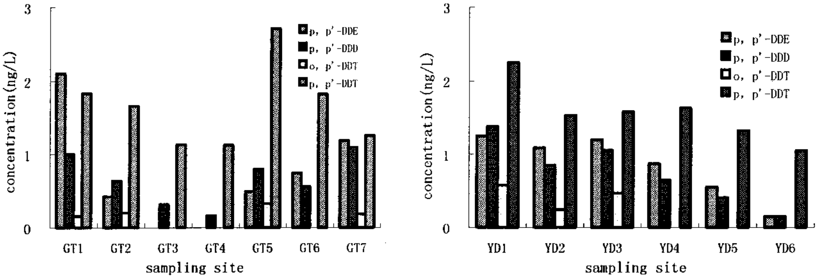
Figure 3. Concentrations of HCH isomers in water samples

sites of GT1 and GT5, the concentrations of HCH were significantly higher than those of other water samples in the reservoir. It is obvious that the discharge of heavily polluted water came from the upper reaches of Yang River was one of the main pollution source in the reservoir. The other pollution source located at the site GT5 with a large shoal and reed marshes, the concentration of HCH was higher at the sampling site than those of other sampling sites. This result can also be observed in the HCH isomer distribution of individual sampling site in Figure 3 (a). The ratio of α-HCH to γ-HCH can be used to provide evidences of formulation types, transport pathways, and current HCH application (Strandberg et al., 2000). HCH is available as either technical HCH, or lindane. The technical HCH produced in China consists of 65-70% for α-HCH, 5-6% for β-HCH, 13% for γ-HCH, and 6% for δ-HCH (Cai et al., 1992). The pattern of HCH isomers in Figure 3 (a) showed that at GT1 and GT5 the distributions of α-, β-, γ- and δ-HCH were different from other sampling sites. The dominant isomers at GT-1 and GT-5 were α-HCH and γ-HCH, while in other samples β-HCH was predominant. Nowadays, if HCH was the current pollution source, the ratios of α-HCH/ γ-HCH would be in the range of 5.0 to 5.4 for technical HCH and nearly zero for lindane. The ratios found in present study were in the ranges of 1.1 to 1.7 in Guanting Reservoir, suggesting that the HCH source arose from both the formulations. β-HCH is the least reactive and most persistent among HCH isomers. High concentration of β-HCH in collected samples also means an old pollution source. The different pattern of HCH isomers in the mouth of Yang River and Guanting Reservoir showed that the contaminated water and the old sediment in the reservoir were the main



(a) (b)

Figure 4. Concentrations of total DDT in water samples



(a) (b)

Figure 5. Concentrations of DDT and its metabolites in water samples

This different isomer distribution at GT1 can be explained as follows. It was drought season in October in the north China, the flow rate of the Yang River was low, after the water contaminated by HCH leached from agriculture area, in which α-HCH was dominant, and flowed into the reservoir and stored in it, the isomer distribution was changed in the store periods resulting from the different metabolism rate of HCH isomers. Because of the higher concentrations of total HCH and higher ratios of α-HCH/γ-HCH at GT1 and GT5, it can also be concluded there might be current influx of HCH into the waters .The concentrations of HCH in most sampling sites of Yongding River were lower than those of the mainstream. The isomer distributions in the samples from Yongding River were similar to those in Guanting Reservoir (Fig3 (b)). This means that the contamination of HCH in Yongding River originated mainly from Guanting Reservoir and other HCH pollution sources were negligible.

The sum of total DDT including *p,p′* -DDE, p,p′-DDD, *o,p′*-DDT and *p,p′*- DDT in different water samples from Guanting Reservoir (a) and Yongding River (b) are shown in Figure 4. The highest concentrations of total DDT were also found in the sampling sites of GT1 and GT5, and this result coincides with the distribution of HCH in the water system. The concentrations of total DDT in sampling sites of GT3 and GT4 were lower than those in sampling sites of GT6 and GT7, and also showed that site GT2 was not the main pollution source. In Yongding River, the concentration of total DDT decreased from upstream to downstream, except the sampling sites of YD2 and YD3, which located in branch of the river. All the sampling sites in Guanting Reservoir contribute to the contamination by HCH and DDT, without knowing the values of water entering at GT1 and GT2, no decision can be made regarding whether either is the principal source of low level contamination .

The concentrations of DDT and its metabolites in water from Guanting Reservoir (a) and Yongding River (b) are presented in Figure 5. The most abundant DDT was *p,p′*-DDT in all samples except for GT1 in which *p,p′*-DDE was predominant. The predominating presence of *p,p′*-DDT in most samples argues for recent usage, or release from a previously dormant source. In Guanting Reservoir, the concentration of *p,p′*-DDT ranged from 1.1 ng/L at GT3 to 2.7 ng/L at GT5. In sampling site GT5 the concentration of *p,p′*- DDT was significantly higher than those of other sampling sites, and this distribution of DDT and its metabolites was similar to typical pattern of soil contamination, in which the concentration of *p,p′*-DDT was higher. *p,p′*- DDT in air lasts only a short time and in surface water DDE is the predominant compound if there is no recent usage. It is clearly known that large amounts of *p,p′*-DDT were directly applied to soil. Once entering the environment, *p,p′*-DDT in soil lasts for a very long time. Some studies showed that half-life of *p,p′*-DDT in soil is more than 15 years (Aislabie et al.,1997). It means that the higher concentration of *p,p′*-DDT found in site GT5 may come from the release from contaminated soil or sediment. In Yongding River *p,p′*-DDT was also the predominant compound and decreased from upstream to downstream.

p,p′-DDT undergoes slow degradation to *p,p′*-DDE and *p,p′*-DDD in natural environment by chemical and biological processes (Wedemeyer,1967; Baxtor, 1990). The ratio of (*p,p′*-DDE+*p,p′*-DDD)/*p,p′*-DDT provides an indication of how recently DDT has been released into the environment, with the ratio increasing over time as the DDT degraded. The ratio found in this study ranged from 0.2 at GT4 to 1.8 at GT7 in Guanting Reservoir, and 0.3 at YD6 to 1.4 at YD3 in Yongding River, respectively. It is clear that in 5 out of 7 water samples from Guanting reservoir and 3 out of 6 water samples from Yongding river the ratios were less than 1, which indicated that *p,p′*-DDT residue was recently introduced to the waters (Zhou et al., 2001).

To understand the status of organochlorine pesticide contamination in the area studied, the levels of total HCH and DDT determined in the present study were compared with other results in surface water from different places in China (Table1). Among the data the residue levels of total HCH and DDT in the earlier period were higher than those of the recent one, while among the recent reports the data in our study were lower than those of Baiyangdian Lake, Jiulong Rive Estuary and Liaohe River, and similar to those of Xiamen Harbour and Yangtze River (Nanjing section). We can conclude that the present contamination level of organochlorine pesticides in Guanting Reservoir and Yongding River is less serious than those in other lakes and rivers in China.

Our survey showed that the concentrations of total HCH and DDT in water from Guanting Reservoir and Yongding River were below the recommended maximum

Table 1. Comparison of HCH and DDT levels (ng/L) in surface water from other places in China

Locality	Survery year	HCH	DDT	Reference
Jiyun River	1979-1980	2443**	133.7**	IEC (1983)*
Second Songhua River	1982-1984	124	71	Li MX et al.(1989)
Yangtze River(Jiangyin section)	1987	52	19	Bao ZC et al (1990)
Pearl River Delta	1994	250	168	Yang YH et al (1996;)
Baiyangdian Lake	1994-1995	140	250	Dou W et al (1998)
Xiamen Harbour	1998	8.57	1.45	Zhang ZL et al (2000)
Jiulong River Estuary	1999	71.8	12.8	Zhang ZL et al (2001)
Liaohe River	1998	110.1	29.9	Zhang XF et al (2000)
Yangtze River (Nanjing section)	1998	9.81	1.67	Jiang X et al (2000)
Yongding River	2000	5.2	3.4	present study
Guanting Reservoir	2000	9.1	3.1	present study

*IEC: Institute of Enviromental Chemistry, Chinese Academy of Sciences (1983)
**: in ng/kg

residue levels in surface water established by the State Environment Protection Agency (GHZB1-1999) (500 ng/L for total HCH, 19 ng/L for lindane, and 100 ng/L for total DDT). This may be attributed to the banned usage of technical HCH and DDT in China for 20 years. There might be three possible main pollution sources of HCH and DDT for surface water, atmospheric deposition, contaminated water influx and release from the old sediment. The residues of HCH and DDT in the waters resulted primarily from the "old" pesticides which entered the waters mainly by surface runoff, soil erosion and release from sediment. Despite the low residue levels of HCH and DDT in water, new contamination sources may still be present in the area studied.

Acknowledgments. This study was financed by the Science and Technology Department of People's Republic China and KIP of CAS (RCEES 9902). We would like to thank Chemical Analysis Group of Agilent Technologies Co. Ltd. (China) for GC analysis support.

REFERENCES

Aislabie JM, Richards NK, Boul HL (1997) Microbial degradation of DDT and its residues, New Zeal. J Agr Res 40:269-282

Baxtor RM (1990) Reductive dechlorination of certain chlorinated organic compounds by reduced haematin compared with their behavior in the environment. Chemosphere 21:451-458

Bao ZC, Zhang Z (1990) Identification and analysis of organics in Yangtze River (Jiangyin Section). Environ Chem 9:1-8

Cai DJ, Sun LJ, Tang GC (1992) Pesticide usage in China. Report prepared for Environment Canada, Downsview, Ontario, Canada

Dou W, Zhao ZX (1989) Contamination of DDT and BHC in water, sediments and fish *(carassius auratus*) muscle from Baiyangdian lake. Acta Scientiae Circumstantiae 18(3):308-312

Goldberg ED (1991) Halogenated hydrocarbons: past, present and near-future problems. Sci Total Environ 100:17-28

Huang HX(1989) Discussion on environmental contamination and related problems caused by organochlorine pesticides. Sci Man Pest 2:26-29

Institute of Environmental Chemistry, Chinese Academy of Sciences (1983) Distribution of chlorinated pesticides in Jiyun River. Huanjing Kexue 4:12-158

Jiang X, Xu SF, Martens D, Wang LS (2000) Polychlorinated organic contaminants in waters, suspended solids and sediments of the Nanjing section, Yangtze River. China Environ Sci 20:193-197

Li MX, Yue GC, Gao FM, Du YG (1989) Transport and distribution of PCBs and organochlorine pesticides in the Second Songhua River. Huanjing Huaxue 8:49-54

Lin YS, Gong RZ, Zhu ZL (2000) Pesticides and eco-environmental protection. Chemical Industry Press, Beijing

Li YF, Cai DJ, Singh A (1998) Technical hexachlorocyclohexane use trends in China and their impact on the environment. Arch Environ Contam Toxicol 35:688 -697

Li YF (1999) Global technical hexchlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997. Sci Total Environ 232:121-158

Metcalf RL (1955) Organic insecticides, their chemistry and mode of action. New York: Interscience

Strandberg B, Bandh C., Bavel BV, Bergqvist PA, Broman D, Ishaq R, Naf C, Rappe C (2000) Organochlorine compounds in the Gulf of Bothnia: sediment and benthic species. Chemosphere 40:1205-1211

The State Environment Protection Agency (1999) Environmental quality standard for surface water, GHZB1-1999. China Environmental Science Press, Beijing

Wedemeyer G (1967) Dechlorination of 1.1.1-trichloro-2.2-bis (*p*-chlorophenyl) ethane by *aerobactor aerogenes.* Appl Microbiol 15:569-574

Yang YH, Sheng GY, Fu JM (1996) Organochlorinated compounds in water systems in three cities of the Pearl River delta area, Guangdong China. Acta Scientiae Circumstantiae 16:59-65

Zhang XF, Quan X, Chen JW, Zhao YZ, Chen S, Xue DM, Yang FL (2000) Investigation of polychlorinated organic compounds (PCOCs) in middle and lower reaches of Liaohe River. China Environ Sci 20:31-35

Zhang ZL, Chen WQ, Khalid M, Zhou JL, Xu L, Hong HS (2001) Evaluation and fate of the organic chlorine pesticides at the waters in Jiulong River Estuary. Environ Sci 22:88-92

Zhang ZL, Hong HS, Khalid M, Zhou JL, Chen WQ, Hong HS (2000) Study on organochlorine pesticides and PCBs at surface water in Xiamen Harbour. Mar Environ Sci 19:48-51

Zhou JL, Maskaou K, Qiu YW, Hong HS, Wang ZD, (2001) Polychlorinated biphenyl congeners and organochlorine insecticides in the water column and sediments of Daya Bay, China. Environ Pollut 113:373-384