Screening 31 endocrine-disrupting pesticides in water and surface sediment samples from Beijing Guanting reservoir

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Abstract

For screening 31 potential or suspected endocrine-disrupting pesticides in water and surface sediments, a multiresidue analysis method based on gas chromatography with electron capture detection (GC/ECD) was developed. Solid phase extraction (SPE) technology with Oasis[®] HLB cartridge was also applied in sample extraction. The relevant mean recoveries were 70–103% and 71–103% for water and sediment, respectively. Relative standard deviations (RSD) are 2.0–7.0%, 4.0–8.0% for water and sediment, respectively. Thirty one pesticides (α -HCH, β -HCH, γ -HCH, δ -HCH, hexachlorobenzene (HCB), aldrin, heptachlor, endosulfan I & II, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDE, endrin aldehyde, endosulfan sulphate, methoxychlor, heptachlor epoxide, α -chlordane, γ -chlordane, dieldrin, endrin, dicofol, acetochlor, alachlor, metolachlor, chlorpyrifos, nitrofen, trifluralin, cypermethrin, fenvalerate, deltamethrin) in water and surface sediment samples from Beijing Guanting reservoir were analyzed. Concentrations of pesticides ranged from 7.59 to 36.0 ng g⁻¹ on a dry wt. basis for sediment samples, from 279.3 to 2740 ng l⁻¹ for pore waters and from 48.8 to 890 ng l⁻¹ for water samples, respectively, with a mean concentration of 10.7 ng g⁻¹ in sediment, 735 ng l⁻¹ in pore water and 295 ng l⁻¹ in water, respectively. The data obtained provides information on the levels and sources of endocrine-disrupting pesticides in Guanting reservoir. These results underscore the need to improved environmental protection measures in order to reduce the exposure of the population and aquatic biota to these endocrine-disrupting compounds.

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1. Introduction

Endocrine disruptors are ubiquitous environmental contaminants found in a variety of products, such as pesticides, wood preservatives, paints and plastics as

well as occurring naturally in some plants. It is hypothesized that they can cause adverse effects by interfering in some way with the body's hormones or chemical messengers and may induce a broad spectrum of biochemical and toxic responses at low environmentally relevant dose (Colborn et al., 1996). Their potential health effects include reproductive disorders, cancer and impaired development (Hileman, 1994; Colborn and Smolen, 1996; Turusov et al., 2002; Zhou et al., 2004). Studies have suggested that some pesticides have been identified

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as potential or suspected endocrine disruptors. However, pesticide application safety was used to be internationally assessed by Maximum Residue Levels (MRL) based on the Acceptable Daily Intake (ADI) with a considerable safety margin. Safety assessments of pesticides do not take into account of possible endocrine disrupting properties of pesticides. Many MRLs may well be too high to exclude hormone disruption as a possible effect of being exposed to residues in food and drinking water. Studies have suggested that, unfortunately, there are no desirable methods to screen and test endocrine disruptors at present (Zhou et al., 2004). Pesticides not only can be concentrated in the environment through biogeochemical processes, but also often scavenged from the water through sorption onto suspended material and get deposited to become a part of the bottom substrate. The sediment component of aquatic ecosystems can be sunk for pesticides. Consequently, bottom sediments often become reservoirs of pesticides in the environment (Khan, 1977; Chau and Afgan, 1982). Therefore, the investigation of distribution of endocrine disrupting pesticides in water and sediment can provide a valuable record of contamination in aquatic environments (Doong et al., 2002).

Different pesticides pose varying degrees and types of risk to water quality. Some surveys of pesticide contamination in water have reported in coastal and estuarine sediments collected from Asian countries such as Vietnam, Turkey, Korea and China (Hong et al., 1999; Khim et al., 1999; Nhan et al., 1999; Doong et al., 2002; Bakan and Ariman, 2004; Zhang et al., 2004) indicating the presence of significant source of pesticides in these regions. China is the world's second largest producer of pesticides, and a pesticide production of 260 000 tonnes was recorded in 1994 (Zhang et al., 2002a). Several studies have reported, despite the ban and restriction on the usage of some organochlorine pesticides (OCPs) since 1983 in China, the presence of elevated levels of OCPs, such as DDTs and HCHs, in seawater and coastal sediments (e.g. Zhou et al., 2001) and some river/estuarine systems (Hong et al., 1995; Chen et al., 1996; Wu et al., 1999; Zhou et al., 2000). Furthermore, DDT concentrations in marine mussels collected from China were still high, one to two orders of greater than those of other Asian countries (Nakata et al., 2002; Monirith et al., 2003; Li et al., 2001). These results suggest significant pollution sources of pesticides are present in China. However, most studies examined pesticides (such as OCPs) levels in waters, sediments from the marine environment (Qiu et al., 2004; Nakata et al., 2005), and up to now, in China, very little field monitoring data is available for the presence of environmental endocrine disrupting pesticide residues in freshwater. An understanding of the impacts of endocrine disrupting pesticides on China's environment is therefore very limited.

The study focuses on developing a method based on a pesticide multi-residue analysis to screen endocrine disrupting pesticides in water and sediment. Some pesticides identified as potential or suspected endocrine disruptors such as α -HCH, β -HCH, γ -HCH, δ -HCH, hexachlorobenzene (HCB), aldrin, heptachlor, endosulfan, *p,p'*-DDD, *o,p'*-DDT, endrin aldehyde, endosulfan sulphate, *p,p'*-DDT, *p,p'*-DDE, methoxychlor, heptachlor epoxide, chlordane, dieldrin, endrin, dicofol, acetochlor, alachlor, metolachlor, chlorpyrifos, nitrofen, trifluralin (HEPO), cypermethrin, fenverate, deltamethrin were simultaneously determined. These pesticides were selected to be screened because they have been identified as potential pollutants in food or drinking water and also been listed as endocrine disrupting chemicals by EU or by the European Commission or US EPA (Kelce et al., 1995; US EPA, 1998; Ren and Jiang, 2001) or by the Federal Environment Agency in Germany (ENDS, 1999), and because they either are widely used in the studied area for agricultural and public purposes or are present as persistent residues of previous uses. The data would be useful to local government to renew Guanting reservoir, a Beijing municipal water supply source.

2. Materials and methods

2.1. Study area and sampling locations

Guanting reservoir located in the northwest of Beijing is one of two main water resources for agriculture, industry and living uses of Beijing. Since Guanting reservoir has suffered from extensive pollution over the last decades (particularly in 1980s) due to runoff from non-point sources, direct dumping of waste into rivers and pollutants carried by rivers (Wang et al., 2000; Zhang et al., 2002b), Guanting reservoir has not supplied with living water for Beijing city since 1997. Particularly, the economy of the coasts of these rivers that flow in Guanting reservoir is heavily based on agriculture, thus agrochemicals are used intensively to improve crop yields, and some pesticides were used heavily in the areas in past or at present time.

The locations of the sampling sites in Guanting reservoir are shown in Fig. 1. The sites were chosen based on hotspots of pollution around Guanting reservoir such as industrial region, domestic wastewater discharge areas or entrances of rivers. Throughout the survey a global positioning system (GPS) was used to locate the sampling locations. The top sediment samples (a mixture of sediment from the upper 10 cm) were collected by a grab sampler (Wildco 197c/s, Wildlife Supply Company, SAGINAW, Michigan, USA) in seven sampling sites. Samples were homogenized on site in clean glass containers. All samples were immediately sealed and stored

Fig. 1. Sampling sites in Guanting reservoir and its geographical location (1, 2, 3, 4, 5, 6 and 7 denote seven sampling sites in Beijing Guanting reservoir: 1, Yangqing; 2, Liushawang; 3, Erdaojian; 4, Baizhaihe; 5, Baohaoqiao; 6, Yanghekou; 7, Baqian).

at -20°C in pre-cleaned glass jars until analysis. Samples were collected in September and November 2003, June and August 2004. Site descriptions have been given in Table 2 indicating the possible load of pollutants through agricultural, industrial and domestic discharges. Surface water samples were collected in the same sites. Samples were taken using pre-cleaned glass bottles held in a weighted stainless-steel frame fitted with a spring-loaded PTFE (polytetrafluoroethylene) stopper with a subsurface trigger to avoid sampling the surface microlayer. Aliquots of the sample were added into internal standard (IS, $0.05\text{ }\mu\text{g l}^{-1}$ sample) and then filtered under vacuum to remove suspended particulate matter (SPM) after returning to the laboratory within one or two days.

2.2. Chemicals and materials

Chromatography analysis-grade acetonitrile (ACN) and methanol (Tianjing chemical plant, China), residue analysis-grade *n*-hexane, acetone, dichloromethane (DCM) and ethyl acetate (Merck, Darmstadt, Germany) were used for sample processing and extraction. Anhydrous sodium sulfate was supplied by Liu-Li chemical plant (Beijing, China) and treated at 140°C for 24 h before using. De-ionized water was purified with an Ultra-pure water system (Beijing Li-Yuan electronic Ltd., China). Some pesticide standards (α -HCH, β -HCH, γ -HCH, δ -HCH, HCB, aldrin, heptachlor, endosulfan, *p,p'*-DDD, *o,p'*-DDT, endrin aldehyde, endosulfan sulphate, *p,p'*-DDT, *p,p'*-DDE, methoxychlor, HEPO, chlordane, dieldrin, endrin) and internal standard (IS, 2,4,5,6-tetrachloro-*m*-xylene) used in this study from Dr. Ehrenstorfer (Augsburg, Germany) were purchased

from J&K CHEMICAL Ltd. (Table 1). Other pesticide standards (dicofol, acetochlor, alachlor, metolachlor, chlorpyrifos, nitrofen, trifluralin, cypermethrin, fenvalerate, deltamethrin) used in this study from Institute of Agricultural Environment Protection (Tianjing, China) were purchased from Yin Tian Yi standard Ltd. (Table 1). The purity of all compounds was more than 95%. Standard solutions of pesticides were prepared by dilution in acetone or alcohol and stored in freezer at -20°C . The stock standard solution of each pesticide was of 2 mg l^{-1} .

Intermediate standard solutions were prepared by dilution in acetone and subsequently dilution was made for GC analyses in the range $0.01\text{--}1.0\text{ ng l}^{-1}$ Florisil (60–100 mesh) from Supelco Inc. (Bellefonte, PA, USA) was used as sorbents in the clean-up columns. Florisil was activated at 130°C for 12 h and partially deactivated with 0.5% water prior to use. The columns were protected against water by adding a 1-cm layer of anhydrous sodium sulfate on top of the sorbent. The Oasis[®] HLB cartridge (6 cc, 500 mg) was purchased from Waters Corp. (Milford, MASS, USA) and Visiprep[™]-DL SPE Vacuum Manifold with disposable flow control valve liners, a solid-phase extraction (SPE) system, from Supelco Inc. (Bellefonte, PA, USA).

All glassware were treated with sulphochromic mixture at first and, then, washed with different solvents in the order of water, acetone and *n*-hexane prior to use.

2.3. Analytical procedures

Water samples collected from Guanting reservoir were pre-filtered using $0.45\text{ }\mu\text{m}$ PTFE fiberglass filters

Table 1

Average recoveries and relative standard deviations (RSDs, %) for 31 endocrine disrupting pesticides in water and sediment fortified at 0.05, 0.1, 0.5 ($\mu\text{g l}^{-1}$) in water and 0.5, 5.0, 50 ($\mu\text{g/kg}$) in sediment

Pesticides	Water		Sediment	
	Mean recoveries (%)	RSD (%)	Mean recoveries (%)	RSD (%)
IS ^a	97	± 2	92	± 5
Trifluralin	90	± 6	84	± 4
α -HCH	87	± 4	84	± 6
HCB ^b	90	± 3	95	± 5
β -HCH	78	± 4	73	± 7
γ -HCH	99	± 6	93	± 5
Dicofol	72	± 5	73	± 6
δ -HCH	77	± 7	81	± 5
Acetochlor	82	± 5	88	± 5
Heptachlor	96	± 7	93	± 5
Alachlor	75	± 7	74	± 8
Aldrin	101	± 3	93	± 7
Metolachlor	71	± 4	73	± 6
Chlorpyrifos	83	± 4	86	± 5
HEPO ^c	99	± 5	95	± 7
γ -chlordane	90	± 6	90	± 8
Endosulfan I	92	± 5	90	± 4
α -chlordane	93	± 6	87	± 7
Dieldrin	90	± 5	85	± 4
<i>p,p'</i> -DDE	96	± 3	98	± 5
Endrin	97	± 7	103	± 5
Nitrofen	83	± 4	85	± 6
Endosulfan II	103	± 6	97	± 6
<i>p,p'</i> -DDD	89	± 5	84	± 4
<i>o,p'</i> -DDT	73	± 7	73	± 7
Endrin aldehyde	89	± 4	98	± 6
Endosulfan sulfate	72	± 6	75	± 8
<i>p,p'</i> -DDT	73	± 7	71	± 7
Methoxychlor	84	± 5	85	± 8
Cypermethrin	76	± 4	76	± 8
Fenvalerate	89	± 5	83	± 5
Deltamethrin	70	± 7	71	± 7

^a IS = Internal Standard.

^b HCB = hexachlorobenzene.

^c HEPO = heptachlor epoxide.

(Millipore, Bedford, MA, USA) to eliminate particulate matter. Up to 1 l of water samples were extracted by SPE following the revised method after Nogueira et al. (2004). An IS was added to each water sample (0.05 μg IS per 1.0 l water). Each of Oasis[®] HLB cartridges was conditioned with 5 ml of methanol/ACN (50/50, v/v), 5 ml of methanol and 5 ml of ultra-pure water and slowly aspirated (-0.2 bar). Water samples were passed through the cartridges at a flow rate of 4 ml min⁻¹ under vacuum (-0.3 bar). The column was wash with 2 $\times$ 4 ml of ultra-pure water, followed by vacuum dry for 2 min. Subsequently, the elution took place with 3 $\times$ 4 ml of methanol/ACN (50/50, v/v). After water being removed from the extracts by anhydrous Na₂SO₄, the extract was reduced in volume to dryness under a gentle stream of nitrogen in a water bath. The dry residues obtained were

re-dissolved in 0.5 ml of acetone for GC determination. For blank assays the same procedure as above was performed using water samples with an IS spiked.

After returning the laboratory, routine wet sediment sample analyses were done as follows: the water content was determined by drying about 20 g of wet sediments for 12 h (or to constant weight) at 105 °C. The dried sediment was heated at 550 °C for 1 h in order to determine the organic matter (Golterman et al., 1983; Hakanson and Jansson, 1983). Silt and clay analyses of sediment samples were done by pipette analyses (Carver, 1971). pH values were determined by a pH meter (pHs-2, Shanghai 2nd Analytical Instrument Factory, China). Each sediment sample was centrifuged (4000 rpm, Q/1BL001-94, Beijing Centrifuge Instrument Factory, China) at 4 °C to obtain pore water in sediment. After

being pre-filtered using 0.45 μm PTFE fiberglass filters, the pore water (300 ml) was extracted and analyzed using the same procedure as described as water samples. Twenty grams (wet weight) of the centrifuged sediments (the wet-to-dry weight ratios of the sediments have been determined and spiked with IS to quantify the overall recovery of the procedures) was weighted into a glass vial and sonicated for 30 min with 2 $\times$ 40 ml of methanol/ACN (50/50, v/v) in an ultrasonic bath (Institute of acoustics, CAS, China). Because the centrifuged sediment still contains significant volume of water, the extraction efficiency of pesticides may be low. In the case, sediment samples were extracted twice by being sonicated with methanol/ACN and centrifuged. Extracts were transferred into glass flasks by careful decantation. The extracts were evaporated to about 25 ml under vacuum with a rotavapor (Büchi, Flawil, Switzerland) with a water bath (about 80 $^{\circ}\text{C}$). The concentrated extracts were re-extracted with hexane-ether (6:94, 15:85, 50:50, v:v) three times, with 10 ml quantities each time. The organic phase was evaporated to near dryness. The residues were cleaned up by a Florosil column (8 mm i.d. $\times$ 350 mm) containing 8 g of Florosil. Anhydrous sodium sulfate (2 cm) was added to the top of the column in order to remove water. The column was then eluted first with 4 ml of DCM/*n*-hexane (20/80, v/v) and the solution discarded. Further 25 ml of DCM/*n*-hexane (20/80, v/v) was needed to elute to obtain pesticides. After collection, the eluate was evaporated near dryness under a nitrogen flow. Subsequently, the sample was dissolved in 1 ml of acetone for GC determination. Sulfur was noted in many of the sediment samples, and copper powder was added to eliminate the sulfur interference in the chromatograms. However, no significant improvement was found in the later part of the chromatogram where the tested pesticide peaks dominated in current experiment. Therefore, copper was not used as a cleanup step.

Determination was done by a GC system with a micro cell electron capture detector ($\mu\text{-ECD}$) and split/splitless injector (Agilent Series 6890), equipped with ChemStation Software. A fused silica capillary column (HP-5, 30 m $\times$ 0.25 mm i.d. and 0.25 μm film thickness) was used. The oven temperature was programmed from 80 (equilibrium time 1 min) to 150 $^{\circ}\text{C}$ at a rate of 10 min^{-1} and held for 2 min, from 150 to 180 $^{\circ}\text{C}$ at a rate of 2 min^{-1} and held for 1 min then rising to 250 $^{\circ}\text{C}$ at a rate of 5 min^{-1} and held for 1 min. The temperature was finally increased to 290 $^{\circ}\text{C}$ at a rate of 8 min^{-1} and held for 5 min; with a total run of 50 min. Nitrogen (99.999%) was used as carrier gas and make-up gas. A split/splitless was used in the splitless mode. Injector temperature and the electron capture detector temperature were set at 230 and 310 $^{\circ}\text{C}$, respectively. The injection volume was of 1 μl .

2.4. Identification and quantification

Before analysis, relevant standards were run to check column performance, peak height, and resolution, and the limits of detection (LOD). With each set of samples analyzed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. None of the target compounds were detected in the procedural blanks for water and sediment. Spiked water and sediment samples (0.1 $\mu\text{g l}^{-1}$ of each target compound) were determined with good precision and high recoveries. Chromatograms are shown in Fig. 2(A) for a standard solution of pesticides with an IS spiked. The chromatogram of the spiked blank sample was free of interfering peaks and it showed a satisfactory overlay in terms of retention times with that of the standard solution. The recovery, LOD, and relative standard deviation (RSD) for water were as follows: LOD of target compounds (include IS) ranged from 5.0×10^{-4} to $1.5 \times 10^{-2} \text{ ng l}^{-1}$ for water, and 3.0×10^{-5} to $1.5 \times 10^{-3} \text{ ng g}^{-1}$ for sediment. The recovery study performed on blank samples spiked with known levels of the pesticides is summarized in Table 1. Three replicates for each sample have been carried out at three fortification levels (0.05, 0.1, 0.5 $\mu\text{g l}^{-1}$ for water and 0.5, 5.0, 50.0 $\mu\text{g kg}^{-1}$ for sediments, respectively), and the relevant recovery results, given as mean values, were 70–103% and 71–103% for water and sediment, respectively. RSD was 2.0–7.0% and 4.0–8.0% for water and sediment, respectively. The recoveries are satisfactory for all compounds apart for *o,p'*-DDT, endosulfan sulfate, *p,p'*-DDT and β -HCH (lower than 80%) and they were corrected for quantification. 2,4,5,6-tetrachloro-*m*-xylene was used as an IS to assess the losses involved in the sample extraction and analysis.

All data were subject to strict quality control procedures including the repeatability of GC/ECD determinations through the analysis of procedural blanks and spiked samples (100 ng g^{-1}) level. Identification was accomplished using relative retention time techniques while quantification was done by comparison of peak areas of samples to those of standards at known concentrations. Identification of those pesticides was confirmed on a number of samples with gas chromatography-mass spectrometry (Agilent 6890 with mass spectrometer Agilent 5973 MSD (Agilent Technologies, USA)). A capillary column (hp-35 ms, 30 m $\times$ 0.25 mm i.d. and 0.25 μm film thickness) was used. The oven temperature was programmed from 70 (initial time 2 min) to 150 $^{\circ}\text{C}$ at 25 min^{-1} , 150–200 $^{\circ}\text{C}$ at a rate of 3 min^{-1} , then 200–280 $^{\circ}\text{C}$ at a rate of 8 min^{-1} and held at 280 $^{\circ}\text{C}$ for 10 min. Injector temperature was set at 250 $^{\circ}\text{C}$. The constant pressure was of 20 psi and injection volume was of 2 μl .

Fig. 2. Chromatograms of a standard mixture of pesticides (at 0.1–0.5 $\mu\text{g g}^{-1}$ concentrations) with an IS spiked (A), and typical chromatogram of endocrine disrupting pesticides studied in water (B) and in sediment sample (C); Peaks: 1, IS (internal standard, 2,4,5,6-tetrachloro-*m*-xylene); 2, trifluralin; 3, α -HCH; 4, HCB; 5, β -HCH; 6, γ -HCH; 7, Dicofo; 8, δ -HCH; 9, acetochlor; 10, heptachlor; 11, alachlor; 12, aldrin; 13, metolachlor; 14, chlorpyrifos; 15, hepachlor epoxide; 16, γ -chlordane; 17, endosulfan I; 18, α -chlordane; 19, dieldrin; 20, *p,p'*-DDE; 21, endrin; 22, nitrofen; 23, endosulfan II; 24, *p,p'*-DDD; 25, *o,p'*-DDT; 26, endrin aldehyde; 27, endosulfan sulphate; 28, *p,p'*-DDT; 29, methoxychlor; 30, cypermethrin; 31, fenvalerate; 32, deltamethrin.

3. Results and discussion

3.1. Physicochemical characteristics of sediment and water samples

Table 2 provides the basic physicochemical parameters of sediment samples collected from the Guanting reservoir. The depth of the water column above the sediment layer was between 8.5 and 1.2 m. The water content of sediments ranged from 36.1% to 71.5%. The organic matter (denoted by loss on ignition, LOI%) of

sediments ranged from 3.98% to 8.49%. The maximum organic matter of the sediment samples was observed at the sampling site 7 that is located in front of a dam. Sediments with high organic carbon are more likely to adsorb lipophilic organochlorines than are those with lower organic carbon levels. pH Values of sediments ranged from 7.91 to 8.52 with an average of 8.06. The physicochemical properties of water samples were also analyzed. The range of COD_{Cr} in water samples was between 3.5 and 18.5 mg l^{-1} . The maximum value of COD_{Cr} was at site 7 and the minimum was at site 3. Silt

Table 2

The basic physicochemical properties of surface sediment samples collected from Guanting reservoir

Sampling sites/ geographic positions	Site description	Water depth (m)	Water content (g/kg)	Loss on ignition, LOI (%)	pH	Clay (%)	Silt (%)
1 (40°27'16"N, 115°59'34"E)	Yanqing	1.2	40.0	7.13	7.97	24.8	52.1
2 (40°16'08"N, 115°35'21"E)	Liushawang	1.5	42.8	4.58	8.12	18.5	37.7
3 (40°16'51"N, 115°35'08"E)	Erdaojian	1.5	69.7	3.98	8.52	8.9	28.2
4 (40°18'03"N, 115°36'58"E)	Baizhaihe	1.5	59.2	5.59	8.03	19.8	37.4
5 (40°16'11"N, 115°20'10"E)	Baohaoqiao	5.5	36.1	6.72	7.95	20.3	44.6
6 (40°16'11"N, 115°35'10"E)	Yanghekou	5.8	64.8	6.81	7.92	21.4	39.8
7 (40°15'07"N, 115°36'09"E)	Baqian	8.5	71.5	8.49	7.91	30.4	57.5

and clay analyses of sediment samples were done by pipette analyses method according to Carver (1971). Clay and silt content (%) denote the texture of sediment samples. The maximum value of sum of clay (%) and silt (%) was the sample from site 7 (87.9%).

3.2. Levels of pesticides residues in sediment and water samples

The analyzed samples showed the presence of pesticides in water and sediment at concentrations above the method of detection limits. Pesticides detected in water and sediment were listed in Table 3 including

p,p'-DDE, *p,p'*-DDD, *p,p'*-DDT, *o,p'*-DDT, α -, β -, γ - and δ -HCH, HCB, heptachlor, HEPO, α -chlordane, γ -chlordane, aldrin, endosulfan I & II, endosulphane sulphate, endrin aldehyde, endrin, methoxychlor, dicofol, acetochlor, alachlor, metolachlor, chlorpyrifos, nitrofen, trifluralin, cypermethrin, fenverate and deltamethrin. Typical chromatograms of pesticides studied in water and sediment samples were showed in Fig. 2(B) and (C), respectively.

The results of endocrine disrupting pesticide residues in sediment, pore water and water samples are shown in Table 3. Concentrations of pesticides ranged from 7590 to 36000 pg g^{-1} (dry weight) for sediment samples, from

Table 3

Range, Mean and Standard Deviations (SD) of pesticides concentrations in water (ng l^{-1}), pore water (ng l^{-1}) and sediment (pg g^{-1} , dry wt.) samples

Compounds	Water (ng l^{-1}) ^a			Pore water (ng l^{-1}) ^a			Sediment (pg g^{-1}) ^a		
	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD
Trifluralin	3.41–5.15	4.5	1.32	ND ^b –83.6	44.0	27.2	120–1010	127	311
α -HCH	1.32–17.8	7.62	3.57	2.20–66.4	24.8	22.6	56.2–159	149	30.4
HCB ^c	1.43–27.3	12.4	8.82	12.2–58.5	18.9	13.0	55.2–494	146	115
β -HCH	12.3–60.5	31.1	15.6	12.6–79.8	45.6	20.6	1530–6000	1730	1430
γ -HCH	ND–120	31.3	22.7	ND–13.7	1.32	11.5	1.32–140	104	35.8
Dicofol	ND–2.60	0.91	0.82	ND–28.5	4.00	8.42	ND–62.7	48.7	15.4
δ -HCH	0.39–4.62	1.24	0.73	ND–159	44.5	62.8	952–4670	1050	1770
Acetochlor	ND–1.50	0.55	0.41	ND–26.5	9.58	4.18	50.0–188	67.4	168
Heptachlor	0.66–8.50	0.98	3.14	ND–50.8	7.2	25.4	7.20–101	16.3	30.8
Alachlor	ND–5.68	1.72	2.08	ND–41.2	9.1	13.0	ND–219	87.2	61.4
Aldrin	1.65–32.4	23.0	8.05	132–798	146	130	132–1300	472	429
Metolachlor	15.5–27.2	22.7	5.21	42.5–138	45.3	29.5	65.8–297	74.2	145
Chlorpyrifos	0.30–1.89	1.5	0.44	1.90–8.77	3.3	2.81	52.9–165	65.9	60.0
HEPO ^d	0.49–12.0	4.10	2.86	ND–12.9	5.12	3.45	10.8–232	78.2	102.5
γ -chlordane	0.53–30.8	7.26	12.9	ND–10.2	1.86	2.04	46.6–398	76.4	78.1
Endosulfan I	0.07–13.8	1.48	11.9	5.05–38.3	16.6	7.03	15.1–58.0	38.5	12.7
α -chlordane	0.31–8.2	2.86	1.99	ND–34.9	17.8	7.82	ND–144	45.5	32.5
Dieldrin	ND–4.54	0.59	2.91	ND–12.9	8.52	4.04	17.2–219	48.7	40.8
<i>p,p'</i> -DDE	1.64–153	46.0	24.4	6.20–51.3	43.2	20.4	726–6400	854	1470
Endrin	ND–14.1	8.03	4.34	ND–6.11	4.58	1.47	43.8–513	61.4	148
Nitrofen	ND–2.28	1.30	0.35	ND–8.28	3.33	2.75	9.38–42.5	18.5	9.45
Endosulfan II	ND–12.2	0.67	2.24	ND–5.24	4.21	1.08	8.25–350	184	310
<i>p,p'</i> -ODD	ND–2.14	0.56	1.60	ND–6.89	3.19	1.95	ND–74.2	42.5	12.8
<i>o,p'</i> -DDT	4.14–161	35.2	29.0	ND–47.5	40.5	10.4	2920–9610	3310	1340
Endrin aldehyde	ND–5.00	1.45	0.71	6.6–24.5	18.6	6.61	36.6–147	68.4	38.4
Endosulfan	4.65–51.4	22.6	12.4	58.4–195	138.4	50.8	48.4–1050	458	108
<i>p,p'</i> -DDT	ND–30.0	11.4	5.16	ND–577	42.8	166	525–1180	1090	201
Methoxychlor	ND–21.6	4.07	3.65	ND–67.3	29.3	18.8	35.4–352	48.2	62.6
Cypermethrin	ND–1.89	1.25	0.20	ND–8.87	3.18	2.94	ND–8.77	3.48	1.94
Fenvalerate	ND–3.22	2.30	0.58	ND–26.3	6.32	5.54	45.4–158	70.3	31.9
Deltamethrin	ND–6.28	4.30	1.32	ND–54.2	31.8	14.5	78.6–301	81.4	108
$\sum$ OCPs ^e	29.6–795	253	179	235–2320	576	589	7170–33600	10200	7640
Total	48.8–890	295	191	279–2740	735	699	7590–36000	10700	8700

^a Values are mean of triplicate analyses for seven samples from different sampling sites.

^b ND means not detected.

^c HCB = hexachlorobenzene.

^d HEPO = heptachlor epoxide.

^e OCPs = organochlorine pesticides.

279 to 2740 ng l⁻¹ for pore waters and from 48.8 to 890 ng l⁻¹ for water samples respectively, with a mean concentration of 10 700 pg g⁻¹ (dry weight) in sediment, 1360 ng l⁻¹ in pore water, 295 ng l⁻¹ in water respectively. Because of limited research data on these total 31 pesticides in sediment, in pore water, and in water, it could not be compared with others. When comparing OCPs in water and in sediment, it was found that, the levels of total OCPs both in water (29.6–795 ng l⁻¹, with a mean of 253 ng l⁻¹) and in sediment (7170–33 600 pg g⁻¹, with a mean of 10 200 pg g⁻¹) from Guanting reservoir are lower than that from Beijing Tonghui River (Zhang et al., 2004). However the level in water is higher than that of several other locations on the east coast of China such as the Jiulong River Estuary (115.4–414.7 ng l⁻¹, with a mean of 191.5 ng l⁻¹; Zhang et al., 2002d), Pearl River Estuary (4.44–634.6 ng l⁻¹, with a mean of 88.31 ng l⁻¹; Zhang et al., 2002c), and South China Sea (1.27–121.8 ng l⁻¹, with a mean of 16.49 ng l⁻¹; Zhang et al., 2002c).

The data show that water in Guanting reservoir is moderately polluted by pesticides. The levels of endocrine disrupting pesticides in sediment samples recorded in this study are compared with those of other countries. HCH concentrations were found to be in the range of 0.24–10.8 ng g⁻¹ dry wt. (Table 3). Concentrations of γ -HCH (commercial name Lindane) in sediment samples (0.0013–0.12 ng g⁻¹) is lower than that reported from the Romania coastline by Fillmann et al. (2002) and from Indian cities by Sarkar and Sen Gupta

(1991) and Iwata et al. (1994a). Our results also showed lower mean concentrations of total DDTs in sediments than concentrations found in Turkey coastline and rivers (7–71 ng g⁻¹) (Bakan et al., 1999; Bakan and Ariman, 2004) and in the Ukrainian coastline of the Black Sea in the past (Fillmann et al., 2002) but similar to that in cities in Japan (2.5–12 ng g⁻¹) (Iwata et al., 1994a). Table 4 showed the comparison of the results of OCPs (DDTs, HCHs and CHLs) residues in sediment samples from the studied sites with those in the sediments in rivers, lakes or estuaries from other locations.

The total DDT (sum of *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT and *o,p'*-DDT) and γ -HCH in sediment samples were 3.25–17.6 ng g⁻¹ and 0.0013–0.12 ng g⁻¹, respectively. And levels of all detected pesticides were below the New York sediment quality criteria and guidelines to protect wildlife from adverse effect associated with bioaccumulation of persistent substance in aquatic biota (total DDT 100 and γ -HCH 1500 ng g⁻¹ dry wt.) (Mac Doanld, 1994). The concentrations of pesticides in water (Table 3) are generally lower than the Chinese standards for surface water (0.5 μ g l⁻¹ for OCPs) and tap water (0.5 μ g l⁻¹ for the sum of pesticides and 0.1 μ g l⁻¹ for individual pesticide). According to Chinese guideline (SEPA, 1999), in the grade 1–3 surface water, the concentration of HCHs should be less than 5000 ng l⁻¹, DDTs should be less than 1000 ng l⁻¹. (According to USEPA guideline, the critical value for DDT is 1000 ng l⁻¹ too.) However, values in a few sites are considerably high for use as a drinking water. Among the

Table 4

Comparison of organochlorine pesticides (DDTs, HCHs and CHLs) concentrations (ng g⁻¹ dry wt.) in the sediments in rivers, lakes or estuaries from other locations

Locations	Year	DDTs ^a	CHLs ^b	HCHs ^c	References
Washington, DC, USA	1991	7–160	5–153	NA ^d	Wade et al. (1994)
Rhone Prodelta, France	1990	73–704	NA	NA	Tanabe et al. (1994)
Ebro Prodelta, Spain	1990	0.8–93	NA	NA	Tanabe et al. (1994)
Ebro River, Spain	1995–1996	0.4–52	NA	0.001–0.038	Fernandez et al. (1999)
Lake Baikal, Russia	1992	0.014–2.7	n.d. ^e –0.003	0.019–0.12	Iwata et al. (1994b)
Ulsan Bay, Korea	1999	0.01–41.9	0.01–3.96	0.02–4.55	Khim et al. (2001)
Masan Bay, Korea	1998	0.07–7.83	n.d.–0.18	0.01–0.59	Khim et al. (1999)
Northern Coast, Vietnam	1998	6.2–10.4	NA	1.2–33.7	Nhan et al. (1999)
Yesilirmak river, Turkey (wet wt.)	1998–2000	71	NA	14–16	Bakan and Ariman (2004)
Wu-Shi estuary, Taiwan	1997–1998	n.d.–11.4	0.46–27.2	0.99–14.5	Doong et al. (2002)
Hong Kong, China	1997–1998	0.27–14.8	n.d.–11.3	0.1–16.7	Richardson and Zheng (1999)
Daya Bay, China	2000	0.14–20.3	NA	0.32–4.16	Zhou et al. (2001)
Yangtze river estuaries, China	2001	n.d.–0.57	NA	n.d.–30.4	Liu et al. (2003)
Minjiang river estuaries, China	1999	1.57–13.6	NA	2.99–16.2	Zhang et al. (2003).
Beijing Guanting reservoir, China	2003–2004	2.85–16.6	0.087–0.64	0.24–10.8	This study

^a DDTs = $\sum(o,p,p'$ -DDT + *p,p'*-DDT + *p,p'*-DDE + *p,p'*-DDD).

^b HCHs = $\sum(\alpha$ -HCH + β -HCH + γ -HCH + δ -HCH).

^c CHLs = $\sum(\gamma$ -chlordan + α -chlordan).

^d NA = no data available.

^e n.d. = not detected.

analyzed pesticides, *p,p'*-DDE, *o,p'*-DDT, β -HCH, γ -HCH, endosulfan sulfate and aldrin were the most abundant pesticides in water while *p,p'*-DDT, δ -HCH, β -HCH, *p,p'*-DDE, *p,p'*-DDT and endosulfan sulfate were the most abundant in sediment, and *p,p'*-DDT, aldrin, endosulfan sulfate, δ -HCH, β -HCH and *p,p'*-DDE were the most abundant in pore water. In comparison with results from the Beijing Tonghui River (Zhang et al., 2004) alpha-HCH, δ -HCH, heptachlor, endosulfan II and DDT were the major pesticides in water while heptachlor, dieldrin and DDE composed of 95% of total pesticides in sediment in Tonghui River. It was reported that *o,p'*-DDT is contained in technical dicofol as impurity and that a possible cause of *o,p'*-DDT at relatively high concentrations in environment may be present application of dicofol in China (Qiu et al., 2004). Relatively high concentrations of *o,p'*-DDT was found in water, pore water and sediment samples in this study (Table 3), which suggested the possibility of present use of dicofol, a nonsystemic acaricide used extensively for the control of mites, in China even though more studies are needed to confirm.

Other pesticides considered in this work (metolachlor, trifluralin, nitrofen acetochlor, alachlor, chlorpyrifos, cypermethrin, deltamethrin and fenvalerate) are compounds frequently used in this region and are associated with health risks as endocrine disrupting pesticides. However, the data for their residues in water or in sediments were scarce, which can be attributed to their lesser persistence. But these currently used pesticides were monitored in Central American river ecosystems (Castillo et al., 2000; Castilho et al., 2000; Volker Laabs et al., 2002.) demonstrated that these substances are also relevant contaminants in the aquatic environment.

Metolachlor, deltamethrin, trifluralin, nitrofen and acetochlor were the pesticides most frequently found in water and sediments from Guanting reservoir. This reflects the abundant current use of them in the area and the river watersheds. These results also suggest that the use of the pesticides in the agricultural system should be minimized. The levels of metolachlor, trifluralin, nitrofen acetochlor, alachlor and chlorpyrifos in surface water and sediment samples recorded in this study are compared with those of the Northeastern Pantanal Basin, Brazil. Total concentrations of metolachlor, trifluralin, nitrofen acetochlor, alachlor and chlorpyrifos in water samples (in the range of 19.2–52.7 ng l⁻¹, with a mean value 36.5 ng l⁻¹), in sediment samples (in the range of 707–3410 pg g⁻¹, with a mean value 1510 pg g⁻¹) is lower than that reported from the Northeastern Pantanal Basin, Brazil, by Volker Laabs et al. (2002), where total concentrations were found in the range of 31–56 ng l⁻¹, with a mean value 55 ng l⁻¹.

Cypermethrin, deltamethrin and fenvalerate are in the class of synthetic pyrethroids that have been intro-

duced over the past two decades for a variety of insecticidal uses. Each of these chemicals is highly lipophilic and in aquatic environments trend to strongly adsorb to sediments (USEPA, 1999). They were frequently found in water and sediments from Guanting reservoir. This reflects the abundant current use of them in the area and the river watersheds. Among cypermethrin, deltamethrin and fenvalerate, deltamethrin had the highest concentration but cypermethrin was most frequently found in the water and sediment samples from Guanting reservoir.

Once entering water bodies, pesticides will partition between water, pore water and sediments. Although sediments may act a reservoir for these contaminations, they can also release the contaminations back into the overlying water under certain conditions. The investigation of pesticides in sediments and water column is therefore an important approach to assess the fate of these contaminations. The results showed that the concentrations of pesticides in sediment were higher than those in surface water and pore water in Guanting reservoir. It may be due to the fact that organic hydrophobic pollutants tend to stay in the sediments (Zhang et al., 2004). In order to estimate environmental distribution and fate of the pesticides, the flux composition of pesticides in surface water, pore water and sediments were calculated as

$$P_w^{\%} = C_w / \sum P \times 100\% \quad (1)$$

$$P_p^{\%} = C_p / \sum P \times 100\% \quad (2)$$

$$P_s^{\%} = C_s / \sum P \times 100\% \quad (3)$$

$$\sum P = C_w + C_p + C_s \quad (4)$$

where P_w , P_p and P_s denote the flux composition of individual pesticide in surface water, in pore water and in sediments, respectively; C_w , C_p and C_s denote flux of individual pesticide in surface water, in pore water and in sediments, respectively. P denote the total flux of individual pesticide in surface water, in pore water and in sediments.

For all 31 pesticides, the flux composition of pesticides in sediment, pore water and in surface water were showed in Fig. 3. From Fig. 3, the flux compositions (%) of individual pesticides were generally in the same order of magnitude as in sediment, pore water and in surface water with an exception of γ -HCH. The results indicate a distribution model of pesticides in the reservoir though more studies need be done to understand why there are high ratios about γ -HCH.

From Fig. 3, high flux composition (more than 10%) of individual pesticides in water for γ -HCH, metolachlor and cypermethrin and relatively high flux composition (more than 20%) of individual pesticides in pore water

Fig. 3. The composition of pesticides in surface water, pore water and sediments; P_w , P_p and P_s denote the flux composition of individual pesticide in surface water, in pore water and in sediments, respectively (1, trifluralin; 2, α -HCH; 3, HCB; 4, β -HCH; 5, γ -HCH; 6, dicofol; 7, δ -HCH; 8, acetochlor; 9, heptachlor; 10, alachlor; 11, aldrin; 12, metolachlor; 13, chlorpyrifos; 14, heptachlor epoxide; 15, γ -chlordane; 16, endosulfan I; 17 α -chlordane; 18, dieldrin; 19, p,p' -DDE; 20, endrin; 21, nitrofen; 22, endosulfan II; 23, p,p' -DDD; 24, o,p' -DDT; 25, endrin aldehyde; 26, endosulfan sulphate; 27, p,p' -DDT; 28, methoxychlor; 29, cypermethrin; 30, fenvalerate; 31, deltamethrin; 32, OCPs; 33, total pesticides).

for cypermethrin, trifluralin, methoxychlor, metolachlor, heptachlor, endosulfan I, α -chlordane, endrin aldehyde, endosulfan sulphate and deltamethrin though there were low concentrations of γ -HCH and heptachlor, α -chlordane, endrin aldehyde in the reservoir. However, though high fluxes of β -HCH, δ -HCH, aldrin, p,p' -DDE, o,p' -DDT and p,p' -DDT were found, low flux composition (%) in surface water were found. The difference of flux composition for pesticides in sediment, pore water and surface water may be mainly caused from different pesticide's properties such as degradation, migration and adsorption of pesticides in environmental media. The values of octanol–water partition coefficient (K_{ow}) and sediment–pore water equilibrium partitioning coefficient (K_{oc}), the main parameters of degradation, migration and adsorption of pesticides, play an important role in distribution of pesticides in water body (Khim et al., 2001). The flux composition were 92.8% in sediment, 5.0% in pore water and 2.2% in surface water, respectively, for total OCPs and 91.6% in sediment, 6.0% in pore water and 2.4% in surface water, respectively for total 31 pesticides. Therefore, sediments, as a sink of most pesticides, are the potential pesticide sources of surface water. The degree of sediment–water partitioning of a substance therefore plays a key role in the development of sediment quality criteria (Frank et al., 2003). It was possible to examine the relationship between sediment and water flux of pesticides. The flux of pesticides between water and sediment, water and pore water were calculated when predicting the degree of sediment–water partitioning in order to estimate environmental distribution and fate of the contaminants.

Sediment–water partition coefficient (K_{sw}) was derived as

$$K_{sw} = C_s / C_w \quad (5)$$

where C_s is the flux in sediment, C_w is the flux in water. K_{sw} can be therefore calculated though the values C_s and C_w for each individual pesticide in Guanting reservoir. The results showed that values of K_{sw} vary with different pesticides and different sampling sites. There are higher K_{sw} values for some pesticides such as δ -HCH (847) and endosulfan II (275), and there are lower K_{sw} values for other pesticides such as cypermethrin (2.8), metolachlor (3.3) and γ -HCH (3.3). The larger discrepancy of values are possibly correlated with some factors such as different physicochemical characteristics of individual pesticide, the current status of individual pesticide used and different organic matter content in sampling sites.

Among all sampling sites, there were the higher pesticide level in site 1, site 5, site 6, site 7 than others in Guanting reservoir whether in water, pore water or in sediment. The data from water samples are in agreement with the results about HCH and DDT in Guanting reservoir from Wang et al. (2000). Considering to higher values of organic matter (LOI, %), Clay (%) plus Silt (%) in site 1, site 2, site 6, site 7 than in other sites, we can conclude that pesticides in the reservoir sediment are correlated with some factors such as organic matter LOI (%), Clay (%) and silt (%). Particularly organic matter, which influences microbial activities and variation, plays a most important role in accumulation, enrichment or degradation to pesticides. It may be due to

the fact that organic hydrophobic pollutants tend to stay in the sediments.

4. Summary

A method based on a pesticide multi-residue analysis to screen potential or suspected endocrine-disrupting pesticides in water and sediment was developed. The analyzed samples showed the presence of 31 pesticides in water and sediments from Beijing Guanting reservoir. The concentrations of pesticides in water are generally lower than the Chinese standards (in the grade 1–3 surface water) for surface water. However, values in a few sites are considerably high considering to being used as a drinking water source. Due to the analytical restrictions, ionic and thermally unstable pesticides could not be covered by our monitoring study, although some of them were also frequently used in the study area and they were also identified as potential or suspected endocrine disruptors such as atrazine, 2,4-D, diazinon, malathion (Dutta et al., 1993; Crain and Guillelte, 1998; Ren and Jiang, 2001; Laura and Dutta, 2005). Further monitoring method study, which can screen more endocrine-disrupting pesticides, is also needed to understand and assess fully the contamination status about endocrine-disrupting pesticides in the studied area.

Pesticides were expected to be caused from several pathways such as contaminants through the rivers and drainage of contaminated water from the surrounding agricultural fields into Guanting reservoir, the diffusion of contaminants in sediment through the pores, agricultural operations. The concentration of pesticides in sediment was higher than those in surface water. It may be due to the fact that organic hydrophobic pollutants tend to stay in the sediments. And considering to higher values of pesticides in the sites with higher values of organic matter (LOI, %), we can conclude that organic matter, which influences microbial activities and variation, play a most important role in accumulation, enrichment or degradation to pesticides.

Among the analyzed pesticides, *p,p'*-DDE, *o,p'*-DDT, β -HCH, γ -HCH, endosulfan sulfate, aldrin were the most abundant pesticides in water while *o,p'*-DDT, δ -HCH, β -HCH, *p,p'*-DDE, *p,p'*-DDT, endosulfan sulfate were the most abundant in sediment. These results underscore the need to improved environmental protection measures in order to reduce the exposure of the population and aquatic biota to these endocrine-disrupting compounds. And the abundant current use of the pesticides in the area and the river watersheds should be minimized. Furthermore, regular monitoring is needed to evolve a strategy to manage the environmental hazards due to these pesticides. Further measures, such as dredging sediment, need be taken for using as a municipal water supply source.

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