Safety assessment of the source water within the Pearl River Delta on the aspect of organochlorine pesticides contamination†

Meng Qiao,[ab] Taicheng An,*[a] Xiangying Zeng,[a] Delin Zhang,[ab] Guiying Li,[a] Guoying Sheng,[a] Jiamo Fu,[a] Guoxia Zhang[c] and Jun Guo[c]

The safety of source water is a noticeable problem in the Pearl River Delta, one of the densely populated areas in China. In this study, 20 individual organochlorine pesticides (OCPs) were investigated in 15 water sources within this area using gas chromatography-electron capture detector, and the hazard risks to human health were assessed in terms of individual OCPs based on daily water consumption according to the standard recommended by the United States Environmental Protection Agency. Results showed that the total OCP concentrations ranged from 2.42 ng l^{-1} to 39.52 ng l^{-1} during the years 2008 and 2009. The hazard ratios based on both non-cancer and cancer benchmarks were less than 1 for all the water samples, which indicated that individual OCPs posed no risk to human health. However, the risks caused by the combined toxicity of total OCPs in this area should not be ignored.

1. Introduction

Organochlorine pesticides (OCPs), considered as one of the most important groups of the persistent organic pollutants (POPs) defined by the United States Environmental Protection Agency (USEPA), are ubiquitous anthropogenic environmental contaminants. They are able to transport from soils and crops to the air and the waterways through evaporation. Finally, these compounds can accumulate in human bodies through food chains,[1,2] which can lead to various health problems in human beings.[3] Since the recognition of their toxicities including the three-induced effects (teratogenicity, carcinogenicity and mutagenicity) and neurotoxicity, the production and usage of hexachlorocyclohexanes (HCHs) and 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane (DDTs), the two kinds of the earliest and most widely used pesticides, have been banned in China since 1984.[4] The Chinese government also formally signed the Stockholm Convention in May, 2001. The convention, approved by the National People's Congress, formally became effective in China from November 11, 2004. China now strictly fulfils all her obligations under the convention.[5] Due to their persistence, chronic toxicity and bioaccumulation, OCPs are still detectable in the Pearl River Delta (PRD) area after being banned for nearly three decades. Therefore, it is significant for us to focus on the environmental pollution of OCPs.

The Pearl River Delta region, including nine cities and a population of 60 million, consists of four main rivers – Zhujiang River, Beijiang River, Xijiang River and Dongjiang River. Xijiang River and Beijiang River converge into Zhujiang River in Sanshui, while Dongjiang River directly runs into the Pearl River Estuary. The PRD region, an important agricultural area in the past few decades in China and one of the most industrial developed regions nowadays, may suffer from OCP pollution caused by both agricultural and industrial use. Several studies on the pollution levels of OCPs in fresh water have been documented within this area. Luo et al.[6] detected that the total OCP (17 targets) concentrations were 23.4 ng l^{-1}–61.7 ng l^{-1} in Baiertang water column, and 25.2 ng l^{-1}–67.8 ng l^{-1} in Macao column. Liu[7] found that the concentrations of the total OCPs (17 targets) varied from 2.28 ng l^{-1} to 10.21 ng l^{-1} in Xijiang River. In the Pearl River Estuary, the levels of HCHs and DDTs in water varied from 0.2 ng l^{-1} to 3.1 ng l^{-1} and 0.2 ng l^{-1} to 3.3 ng l^{-1}, respectively.[8] Nevertheless, all these studies were focused on the OCP concentrations in the water environment

[a]State Key Laboratory of Organic Geochemistry, Guangdong Key Laboratory of Environmental Resources Utilization and Protection, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China. E-mail: antc99@gig.ac.cn; Fax: +0086-20-85290706; Tel: +0086-20-85291501
[b]Graduate School of Chinese Academy of Sciences, Beijing, 100049, China
[c]Guangdong Institute of Microbiology, Guangzhou, 510070, China
† Electronic supplementary information (ESI) available: Fig. S1–S3 and Table S1–S3. See DOI: 10.1039/c002019b

Environmental impact

The Pearl River Delta region of China may suffer from organochlorine pesticides (OCPs) pollution caused by agricultural and industrial usage. Nevertheless, few studies have reported the levels of OCPs in the drinking water sources in this area. Additionally, the 2010 Asian Games will be held in Guangzhou which is the biggest city in this region. Thus, it is imperative to evaluate the safety of the drinking water sources. In the present study, the pollution levels of OCPs were examined in most of the drinking water sources, and the distribution characteristics and potential sources of OCP contaminants were analyzed. Furthermore, the potential hazard risks to human health caused by these contaminants were also assessed respectively.

in the PRD area. Few studies have reported the levels of OCPs in drinking water sources within this area.

In China, a great amount of attention has been paid to the safety of the drinking water sources nowadays. The Chinese government has formulated and promulgated a series of laws, regulations and standards for the safeguard of the drinking water sources, such as "Regulations on Administration of Pollution Prevention and Control for Protected Region of Drinking Water Source", "Water Quality Standard for Drinking Water Sources (CJ 3020-93)" and "Sanitary Standard for Drinking Water (GB 5749-85)". In 2010, the Asian Games will be held in Guangzhou which is the biggest city in the PRD region. Thus, it is imperative to evaluate the safety of the drinking water sources within the PRD region. However, few studies have been done on the potential health risks caused by OCPs through water consumption. There are some studies concerning the health risk induced by OCPs through food consumption[9–11] rather than water consumption. Therefore, it is also urgent for us to focus on the health risks caused by OCP contaminants in the drinking water sources.

In this study, the pollution levels of OCPs were examined in most of the drinking water sources within the PRD region. In addition, the characteristics and potential sources of OCP contaminants in this area were analyzed. Furthermore, the potential hazard risks to human health caused by these contaminants were assessed respectively.

2. Materials and methods

2.1. Materials

Twenty OCP standards (α-HCH, β-HCH, γ-HCH, δ-HCH, p,p'-DDD, p,p'-DDE, p,p'-DDT, α-chlordane, γ-chlordane,
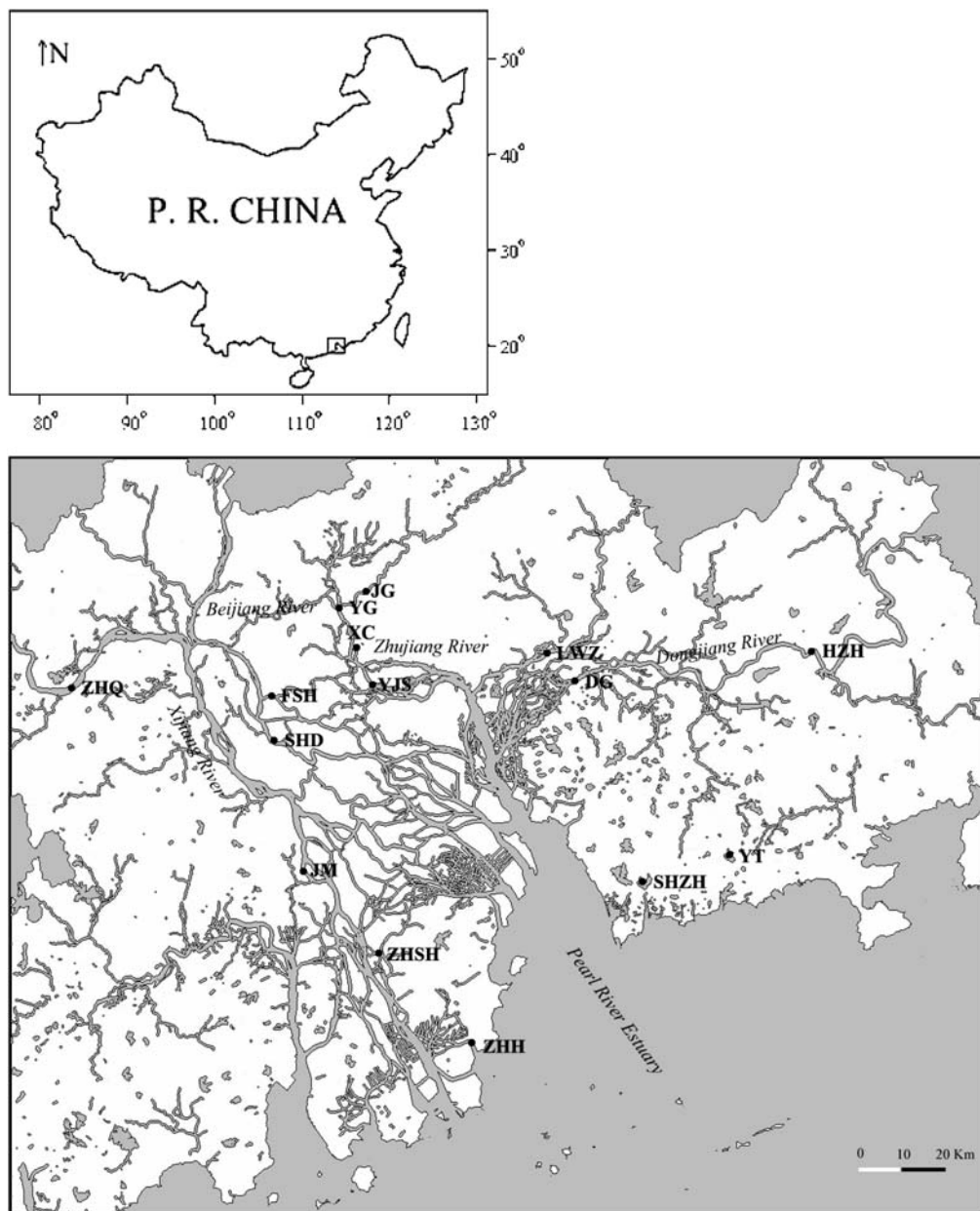

Fig. 1 The location of the Pearl River Delta and sampling stations.

heptachlor, heptachlor epoxide, α-endosulfan, β-endosulfan, endosulfan sulfate, aldrin, dieldrin, endrin, endrin aldehyde, endrin ketone and methoxychlor) in a mixture solution of 2000 μg ml^{-1}, two surrogate standards (2,4,5,6-tetrachloro-m-xylene and 2,2′,3,3′,4,4′,5,5′,6,6′-decachlorobiphenyl) and one internal standard (pentachloronitrobenzene) were purchased from Supelco (Bellefonate, PA, USA).

Analytical-grade dichloromethane (Tianjin, China) was re-distilled using a glass system. Hexane and methanol were HPLC grade, purchased from Merck KGaA (Darmstadt, Germany). XAD-2 resins, purchased from Supelco (Bellefonate, PA, USA), needed a further cleaning with methanol and dichloromethane in a Soxhlet extractor system. Then, the pre-cleaned XAD-2 resins were soaked in methanol. Before using, the resin column was eluted with 500 ml deionized water. Neutral aluminium oxide (100–200 mesh, Shanghai, China) and neutral silica gel (80–100 mesh, Qingdao, China) were extracted with dichloromethane for 72 h using a Soxhlet extractor system. After dichloromethane on the particles volatilized completely, aluminium oxide and silica gel were activated at 250 °C and 180 °C for 12 h respectively, and deactivated with 3% deionized water 12 h later. After another 12 h, aluminium oxide and silica gel were soaked in hexane until use. Sodium chloride and anhydrous sodium sulfate (Tianjin, China) were baked at 450 °C before use.

All the glass containers were pre-cleaned by potassium dichromate–sulfuric acid solutions and kilned at 450 °C for 5 h.

2.2. Study site and sample collection

Fifteen water samples were collected using pre-cleaned amble glass bottles from fifteen stations located in the nine cities of the PRD region (shown in Fig. 1) during the wet season (from April to July, 2008) and dry season (from December, 2008 to February, 2009), respectively. The volume of each sample was 60 l. All the sampling stations are protected as the drinking water sources of the waterworks in each city, distributed among the four main rivers within the PRD region. Beijiang River mainly supplies water to Foshan and a small part of Guangzhou, and Zhujiang River to the main part of Guangzhou. Dongjiang River supplies water to Huizhou, Dongguan, Shenzhen and a small part of Guangzhou, while Xijiang River to Zhaoqing, Jiangmen, Zhongshan and Zhuhai area. The detailed description of sample locations and other physical-chemical parameters were listed in Table S1.

After returning to the laboratory, the samples added with analytical grade sodium azide (Tianjin, China) were stored at 4 °C and the pretreatment process was finished within one week. Suspended particular materials (SPMs) were collected by filtering the samples through glass microfiber filters (Whatman GF/F, 142 mm diameter, 0.7 μm pore size, pre-combusted at 450 °C for 5 h). Then the filters with SPMs were wrapped with aluminium foil and stored in a refrigerator at −20 °C until analysis. Dissolved organics were obtained by passing the filtered water through an XAD-2 resin glass column (25 mm diameter, 300 mm length).

2.3. Pretreatment procedure

The detailed procedures for extraction and purification have been described previously.[6] Briefly, for the dissolved phase, the XAD-2 resin columns, spiked with surrogated standards and absorbed with organics, were eluted with methane once and the mixture of methane and dichloromethane twice. The resins were then transferred into flasks and extracted with the mixture of methane and dichloromethane using an ultrasonic bath three times. The mixture of eluent was extracted with dichloromethane and saturated sodium chloride solution once, dichloromethane twice and deionized water three times. After that, the dichloromethane-phase extraction was concentrated using a rotary evaporator (Shanghai, China) and dehydrated with anhydrous sodium sulfate. Then the solvent of each extraction was exchanged into hexane. The hexane-phase extraction was concentrated to 1 ml and then fractionated with an alumina and silica gel (1 : 2) glass column (8 mm diameter, 180 mm height). The fraction of 10 ml hexane and the fraction of 75 ml hexane and dichloromethane were eluted consecutively. The second fraction containing OCPs was concentrated to 1 ml with a rotary evaporator and then to 0.2 ml under gentle nitrogen stream. Internal standard was added to each sample prior to instrument analysis.

As for the particulate phase, after frozen dried and weighted, the glass fibers were spiked with surrogate standards and extracted with 250 ml dichloromethane in a Soxhlet extractor system for 72 h. Activated copper were added into the dichloromethane before extraction to remove sulfur. Further treatment procedures of the dichloromethane-phase extractions were the same as described above .

2.4. Instrument analysis

An Agilent Technologies 6890N GC equipped with a ^{63}Ni electron capture detector (GC/ECD) and a HP-5 silica fused capillary column (30 m length × 0.32 mm diameter × 0.25 μm film thickness, J&W Scientific Inc., Folsom, CA) were used for the measurement of OCPs. Splitless injection of 1 μl of sample was conducted automatically. Ultra-high-purity nitrogen was used as the carrier gas at a speed of 1.2 ml min^{-1}. The injector temperature was 280 °C, and the detector 300 °C. The column temperature program was as follows: initially 80 °C for 1 min, and programmed to 140 °C at a rate of 15 °C min^{-1}, and then to 280 °C at a rate of 4 °C min^{-1} holding for 10 min. The peaks of individual OCPs was identified using an Agilent Technologies 7890A GC equipped with 5975C mass spectrometer detector (GC/MSD) on full-scan model on the same conditions as for the GC/ECD analysis.

2.5. Quality control and quality assurance

Quantification was performed using the external standard method based on a five-point calibration curve for individual components and the internal standard method based on normalizing. 2,4,5,6-tetrachloro-m-xylene and 2,2′,3,3′,4,4′,5,5′,6,6′-decachlorobiphenyl were used as surrogate standards for external standard method and penta-chloronitrobenzene was used for internal standard method. Measured individual OCP concentrations were normalized by the area of the internal standard, but not corrected with the recoveries of the individual OCPs. The correlation coefficients for all calibration curves for every target compound and

surrogate standard were greater than 0.995. The average recoveries of surrogate standards were shown in Table 1.

For the procedure of chemical analysis, surrogate standards were added to all the analyzed samples including dissolved and particulate samples, procedural blanks and spiked blanks before extraction in order to quantify the procedural recovery. A procedural blank and a spiked blank were conducted for every ten samples. The detection limits of individual OCPs ranged from 0.003 ng l^{-1} to 0.014 ng l^{-1} with a sample size of 60 l.

2.6. Calculation of the hazard ratio

Risks of OCPs to human health *via* drinking water were assessed according to the standard recommended by the USEPA. Risk effects can be divided into two different parts. One is the non-carcinogenic effect which is calculated based on a coefficient called the reference dose (RfD), and the other is the carcinogenic effect based on the drinking water unit risk.[9]

The hazard ratio is an index used for assessing risks to the human body. It can be calculated in accordance with:

Hazard ratio (HR) = Average daily intake/Benchmark concentration.

where benchmark concentration is the reference dose for non-carcinogenic effect, benchmark concentration is equal to (risk × body weight)/(water consumption × slope factor) for carcinogenic effect, and average daily intake (ng kg^{-1} body weight) is equal to water consumption (l kg^{-1} body weight) × contaminant concentration (ng l^{-1}).

If the hazard ratio is greater than unity, it indicates that the water is posing hazard risks to humans.[12]

The benchmark concentration for carcinogenic effect is derived by setting the risk to one in one million due to a lifetime exposure. The reference dose and the slope factor which is considered as the drinking water unit risk can be obtained from the USEPA Integrated Risk Information System (IRIS) (http://www.epa.gov/iris). The average daily intake was calculated by setting 2 l as the daily water consumption and 60 kg as the body weight of an adult according to the Chinese habit.[13]

3. Results and discussion

3.1. Level of OCPs residues

Total OCPs. The concentration ranges of measured individual OCPs in the wet and dry season were listed in Table S2 and
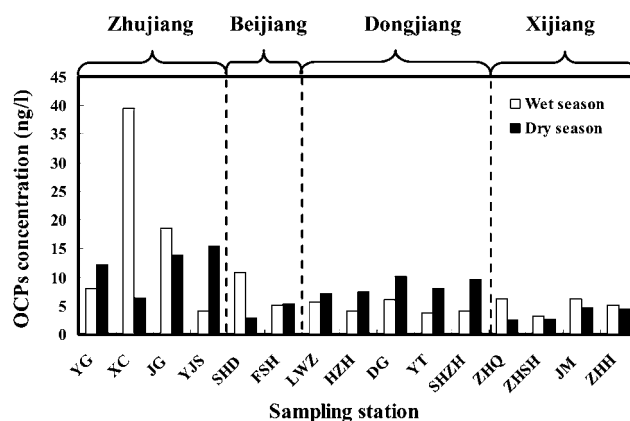

Fig. 2 Contrast of the total OCP concentrations between the wet and dry season.

Table 1 Surrogate recovery of samples

Surrogate standard	Wet season		Dry season	
	Dissolved (%)	Particulate (%)	Dissolved (%)	Particulate (%)
2,4,5,6-tetrachloro-*m*-xylene	83.3 ± 10.5	85.2 ± 8.9	98.5 ± 13.42	74.8 ± 16.6
decachlorobiphenyl	104.2 ± 11.7	101.7 ± 16.9	112.1 ± 15.0	103.4 ± 13.1

Table 2 Ranges of OCP concentrations in source water in the main areas of China

Location Target Number	The PRD Region 20	Guanting Reservoir 17	Qiantang River 13	Minjiang River 18	Yangtse River 18	Three Gorge Reservoir 28
Total OCPs/ng l^{-1}	2.42–39.52	10.06–87.37	7.68–269.4	214.4-1819	9.60–18.5	2.33–3.60
HCHs/ng l^{-1}	0.84–12.23	3.93–38.94	0.74–202.8	52.09–515.0	4.24–5.57	0.103–0.626
DDTs/ng l^{-1}	0.18–0.79	0.80–12.34	0.40–97.54	40.61–223.5	0.20–1.53	0.375–0.676
Chlordanes/ng l^{-1}	0.14–7.91	—	—	—	—	0.027–0.063
Heptachlor/ng l^{-1}	0.08–4.78	0.41–3.95	1.40–88.34	10.81–404.7	—	0.001–0.005
Heptachlor epoxide/ng l^{-1}	0.01–0.56	—	0.14–111.8	5.7–96.01	—	—
α-Endosulfan (ng l^{-1})	0.05–7.08	—	—	—	0.53–0.78	0.015–0.144
β–Endosulfan (ng l^{-1})	0.01–0.63	—	—	—	0.3–0.47	0.007–0.045
Aldrin/ng l^{-1}	0.01–0.05	0.37–6.24	0.23–103.9	5.25–53.17	0.67–2.44	0.006–0.025
Deldrin/ng l^{-1}	0.07–5.01	—	0.15–42.06	5.39–74.03	—	—
Endrin/ng l^{-1}	0.04–0.51	—	0.1–28.46	13.37–101.3	—	—
Endrin aldehydes/ng l^{-1}	0.02–0.51	—	—	1.84–33.52	—	—
Endrin ketone/ng l^{-1}	0.08–3.10	—	—	4.19–141.9	—	—
Methoxychlor/ng l^{-1}	0.03–0.17	10.06–87.37	—	20.12–150.1	0.2–1.18	0.003–0.008
Reference	This study	14	15	16	17	18

This journal is © The Royal Society of Chemistry 2010

J. Environ. Monit., 2010, **12**, 1666–1677 | 1669

Table S3, respectively.† The total OCP concentrations in water of the wet season varied from 2.37 ng l^{-1} (SHZH sample) to 15.79 ng l^{-1} (JG sample) with a mean value of 5.69 ng l^{-1} for the dissolved phase and from 0.39 ng l^{-1} (FSH sample) to 2.75 ng l^{-1} (JG sample) with a mean of 1.04 ng l^{-1} for the particulate phase except for XC sample with an especially high concentration of 30.51 ng l^{-1}. While during the dry season, the concentrations of the dissolved OCPs ranged from 1.99 ng l^{-1} (ZHQ sample) to

12.99 ng l^{-1} (YJS sample) with a mean value of 6.42 ng l^{-1} and of the particulate OCPs ranged from 0.38 ng l^{-1} (HZH sample) to 3.62 ng l^{-1} (XC sample) with a mean of 1.05 ng l^{-1}.

Compared with the contaminations of the drinking water sources in other areas of China, listed in Table 2, the total OCP concentrations in both the wet and dry season (20 targets, 2.42 ng l^{-1}–39.52 ng l^{-1}) of the drinking water sources in this study were much lower than those in Guanting Reservoir (17 targets 10.06 ng l^{-1}–87.37 ng l^{-1}) which was considered as a drinking water source before 1997 in Beijing[14] and might resume in 2010, those in Qiantang River (13 targets, 7.68 ng l^{-1}–269.4 ng l^{-1}), the main source of drinking water in Zhejiang province,[15] and those in Minjiang River (18 targets, 214.4 ng l^{-1}–1819 ng l^{-1}) recognized as the drinking water source of Fujian province in China.[16] Our results revealed that the total OCP concentrations were very near to those in the Yangtse River (18 targets, 9.60 ng l^{-1}–18.5 ng l^{-1}) deemed as the main source of drinking water for Nanjing city,[17] but were higher than those in the Three Gorges Reservoir (28 targets, 2.33 ng l^{-1}–3.60 ng l^{-1}) from the drinking water source of part of Sichuan province.[18] We could recognize from the comparison results that OCP contamination of source water in the PRD region was less severe than that in most areas of China, whereas the pollution was still more severe than that of the Three Gorges Reservoir.

It could be noted from Fig. 2 that of the four sampling sites of Zhujiang River, the concentrations of the total OCPs in the wet season were much higher than those in the dry season in JG and especially XC station, but lower in YG and YJS station. At the two sampling sites of Beijiang River, the total OCP concentrations of SHD station in the wet season were much higher than those in the dry season, while there was no significant difference of the OCP concentrations between the wet and dry season in FSH station. At all the five sampling sites of Dongjiang River (LWZ, HZH, DG, TY and SHZH), the concentrations of OCPs in the wet season were lower to varying degrees than those in the dry season. In contrast, the concentrations in the wet season were all higher than those in the dry season at the four sampling sites of Xijiang River (ZHQ, JM, ZHSH and ZHH). Results indicated that there must be some new pollutants input to XC and JG
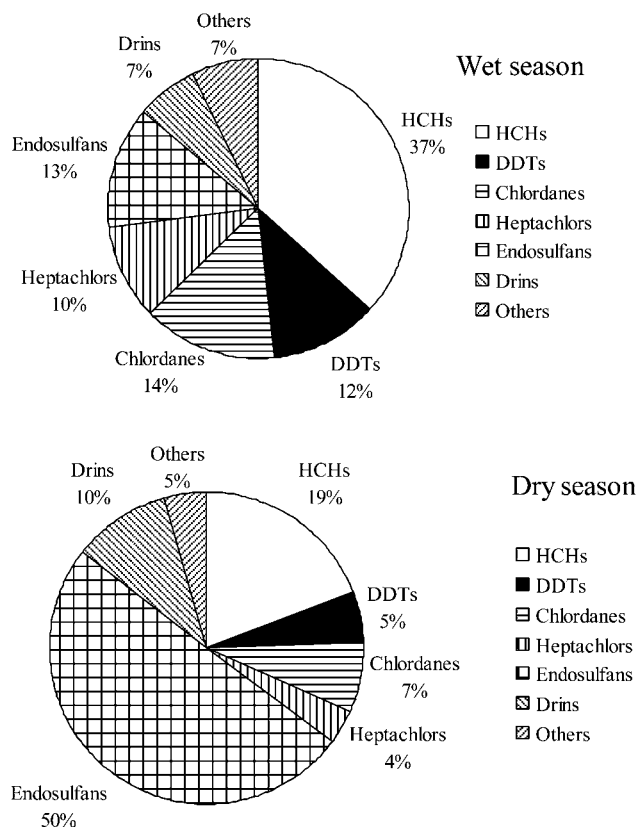

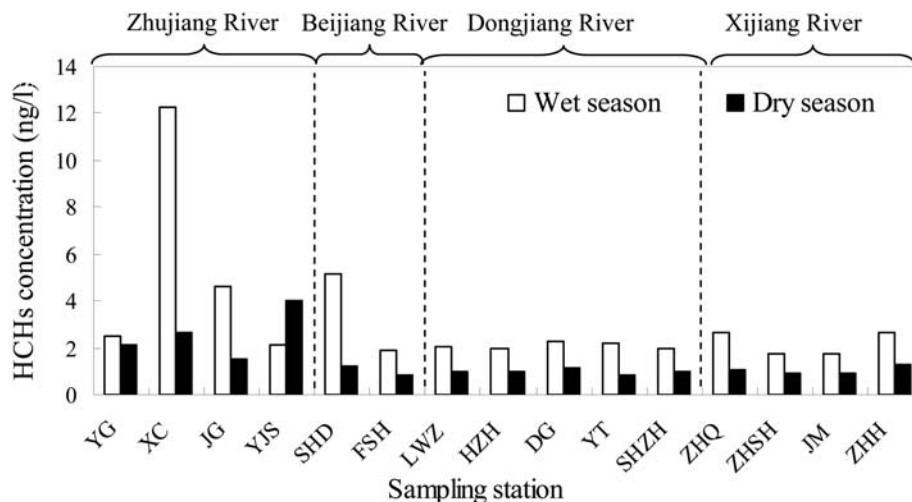Fig. 3 Contributions of the seven groups of OCPs.

Fig. 4 Contrast of HCHs concentrations between wet and dry season.

station in Zhujiang River, SHD station in Beijiang River and in all sampling stations in Xijiang River during the wet season.

Twenty individual OCPs were divided into seven groups, HCHs (α-HCH, β-HCH, γ-HCH and δ-HCH), DDTs (DDD, DDE and DDT), chlordanes (α-chlordane and γ-chlordane), heptachlors (heptachlor and heptachlor epoxide), endosulfans (α-endosulfan, β-endosulfan and endosulfan sulfate), drins (aldrin, dieldrin and endrin), and others (endrin aldehydes, endrin ketone and methoxychlor). Fig. 3 shows the percentages of different groups in the total OCPs. It could be indicated that in the wet season the largest part of the total OCPs was HCHs, while in the dry season endosulfans accounted for over 50% of the total and HCHs were also a large part.

Individual OCPs. During the wet season, the concentrations of HCHs varied from 1.70 ng l^{-1} to 12.23 ng l^{-1}, with a mean value of 3.18 ng l^{-1}, while in the dry season, the concentrations ranged from 0.84 ng l^{-1} to 4.00 ng l^{-1}, with a mean of 1.43 ng l^{-1} (Table S2†). Overall, the levels of HCHs in the wet season were higher than those in the dry season except YJS, implying the new inputs of contaminants (Fig. 4). However, the content of HCHs in the drinking water sources within the PRD region was far below the guideline (sum of α-HCH, β-HCH, γ-HCH and δ-HCH, 5000 ng l^{-1}), according to the Chinese Water Quality Standard for Drinking Water Sources (CJ 3020-93). The data listed in Table 2 indicated that the source water of the PRD region was less severely polluted by HCHs than other source waters in China except the Three Gorge Reservoir.

Of all the water samples collected in the wet season, the total concentrations of DDTs ranged from 0.20 ng l^{-1} to 5.93 ng l^{-1} with a mean value of 1.01 ng l^{-1}, while in the dry season, from 0.18 ng l^{-1} to 0.79 ng l^{-1} with a mean of 0.39 ng l^{-1} (Table S2†). The levels of DDTs both in the wet and dry season were also far below the guideline (CJ 3020-93) (sum of DDD, DDE and DDT,
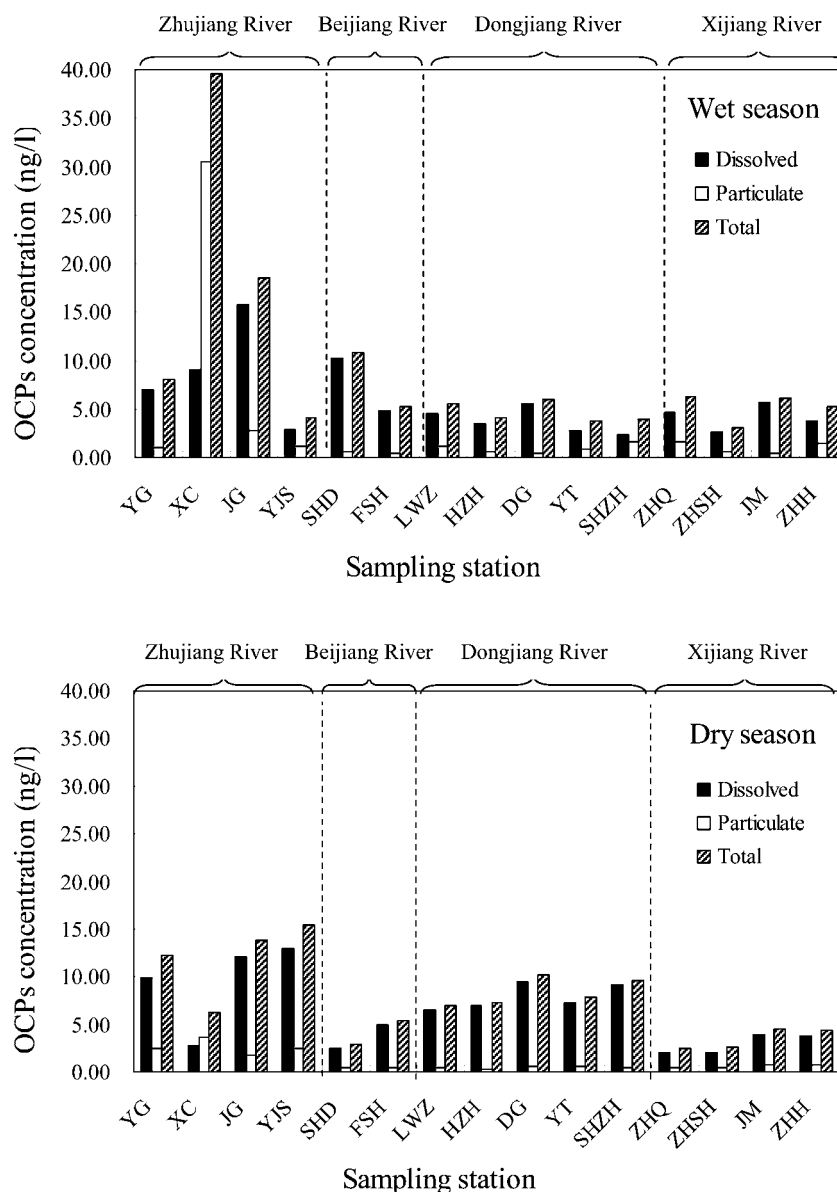

Fig. 5 Contrast of the OCPs concentrations between dissolved and particulate phase.

This journal is © The Royal Society of Chemistry 2010

J. Environ. Monit., 2010, **12**, 1666–1677 | 1671

1000 ng l^{-1}). Similar to the contamination levels of HCHs, the source water of the PRD region was also slightly polluted by DDTs. Although the levels of DDTs were not high, the bioaccumulation and biotransformation were more significant in organisms than those of other groups of OCPs.[19] Therefore, the low-level DDTs in drinking waters should not be overlooked.

The total concentrations of chlordanes ranged from 0.19 ng l^{-1} to 7.91 ng l^{-1} with a mean value of 1.26 ng l^{-1} in the wet season and from 0.14 ng l^{-1} to 0.95 ng l^{-1} with a mean of 0.54 ng l^{-1} in the dry season (Table S2†). Due to the few usages of chlordanes in the non-termite areas, few studies have reported the concentrations of chlordanes in drinking water sources except the Three Gorges Reservoir.[18] They ranged from 0.027 ng l^{-1} to 0.063 ng l^{-1}, which were much lower than those in this study. This phenomenon may reflect the wide use of chlordane to control termites in the southern part of China.

The total concentrations of endosulfans ranged from 0.13 ng l^{-1} to 8.13 ng l^{-1} with a mean value of 1.15 ng l^{-1} in the wet season, while from 0.55 ng l^{-1} to 10.42 ng l^{-1} with a mean of 3.75 ng l^{-1} in the dry season (Table S2†). Compared with other water sources, the concentrations of the total endosulfans in this study were higher than those of the Yangtse River[17] and the Three Gorges Reservoir,[18] indicating more severe endosulfan pollution in the PRD region.

The levels of drins and others were relatively low compared with other groups of OCPs. Hence, only a brief description was given here. The concentration of drins ranged from 0.07 ng l^{-1} to 5.12 ng l^{-1}, and others from nd to 3.25 ng l^{-1} (Table S2†).

3.2. Distribution and composition of OCPs

Distribution of OCPs between particulate and dissolved phase. Whether in the wet or dry season, the concentrations of the total dissolved OCPs were higher than those of particulate OCPs in all samples except XC, indicating that the OCPs in water mainly existed in dissolved phase (Fig. 5). As for XC, the difference from other samples might result from the high content of the total suspended solid (TSS).

Furthermore, the correlations were also studied both between the total OCPs concentrations of dissolved phase and dissolved organic carbons (DOC) and between the total OCPs concentrations of particulate phase and particulate organic carbons (POC). Results showed that the concentrations of OCPs in dissolved phase and DOC both in the wet season ($r^2 = 0.0716$) and dry season ($r^2 = 0.0157$) were not linear correlative, while the concentrations in particulate phase had significant linear correlations with POC both in the wet season ($r^2 = 0.8649$) and dry season ($r^2 = 0.5889$). Thus, it could be estimated that the ability of the particulates absorbing the hydrophobic organics was correlated with the organic carbons existed in the particulates.[20]

Composition of OCPs and possible sources. Composition of different HCH isomers in the environment can be used to identify the contamination sources. HCHs have been used in two ways. One is the industrial HCHs composed of α-HCH (65–70%), β-HCH (5–6%), γ-HCH (12–14%) and δ-HCH (6%). The other is lindane including γ-HCH (above 99%).[21] The source of the HCHs can be indicated by the ratio of α-HCH and γ-HCH, That is, if α-HCH/γ-HCH < 1, the main source is lindane and if 3 < α-HCH/γ-HCH < 7, industrial HCHs. Fig. S1 shows the profiles of α-HCH/γ-HCH in different sampling stations. It could be concluded that during the wet season, the new input of HCHs in XC, YJS, SHD and ZHQ station came from the use of both industrial HCHs and lindane. And during the dry season, HCHs came from the use of industrial HCHs and lindane in YJS station. In other stations, HCHs mainly came from the use of lindane. So we could propose that lindane was probably still used in the PRD region recently.
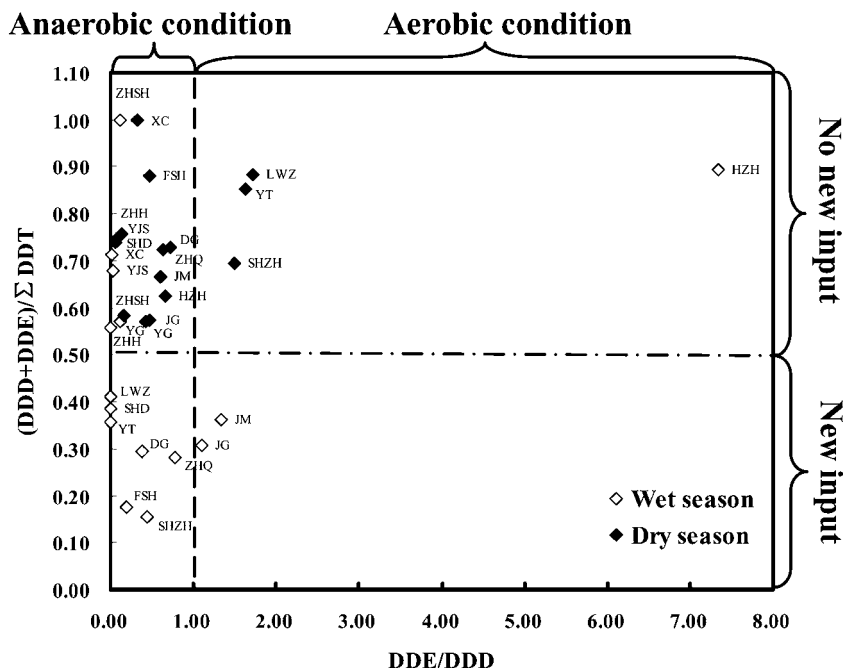

Fig. 6 Ratios of DDE/DDD and (DDD + DDE)/$\sum$DDT in different sampling stations.

After entering the environment, DDT can be biodegraded to DDE by dehydrochlorination, whereas to DDD by reductive dechlorination.[22] Therefore, the ratio of DDE and DDD can be used for distinguishing the possible pollution sources, and the ratio of the sum of DDD and DDE and the total DDTs can be used for indicating whether new DDT entered the environment or not.[6] If DDE/DDD > 1, the investigated water is in aerobic condition, and if DDE/DDD < 1, in anaerobic condition. If $(DDD + DDE)/\sum DDT > 0.5$, no new DDT has entered the water body recently, while if $(DDD + DDE)/\sum DDT < 0.5$, new DDT has entered the water body recently.[23] The relationships between DDE/DDD and $(DDD + DDE)/\sum DDT$ of all the samples were shown in Fig. 6. The water environments of LWZ, YT and SHZH in the dry season and HZH, JM and JG in the wet season were aerobic conditions, whereas others were anaerobic conditions. The water in aerobic conditions might originate from the flow of the surface water, while in anaerobic conditions might result from the turbulence of the sediments. In the dry season, there was no new DDT input to all the water sources

investigated, and in the wet season of most sampling stations except YG, XC, YJS, ZHSH, ZHH and HZH, there was new DDT input. However, the use of DDT has been banned since 1984, so new DDT input might result from the recent usage of dicofol.[5]

Technical chlordane is a mixture of over 140 different compounds, including γ-chlordane (13%), α-chlordane (11%) and heptachlor (5%) as the dominant parts of the compounds.[24,25] The ratio of α-chlordane and γ-chlordane in technical mixtures is 0.77 or so.[26] In the environment, γ-chlordane is easier to degrade than α-chlordane.[27] At the sampling stations of YG, SHZH, ZHQ and ZHH in the wet season, the ratios of α-chlordane to γ-chlordane > 0.77 (Fig. S2†). Thus the chlordane residues in these sites were from long-term accumulation. While in other samples in the wet season and all samples in the dry season were just attributed from new usage.

Heptachlor has been grouped out of technical chlordane since 1946, and in the environment it can be metabolized to heptachlor epoxide which is considered as a more stable and toxic
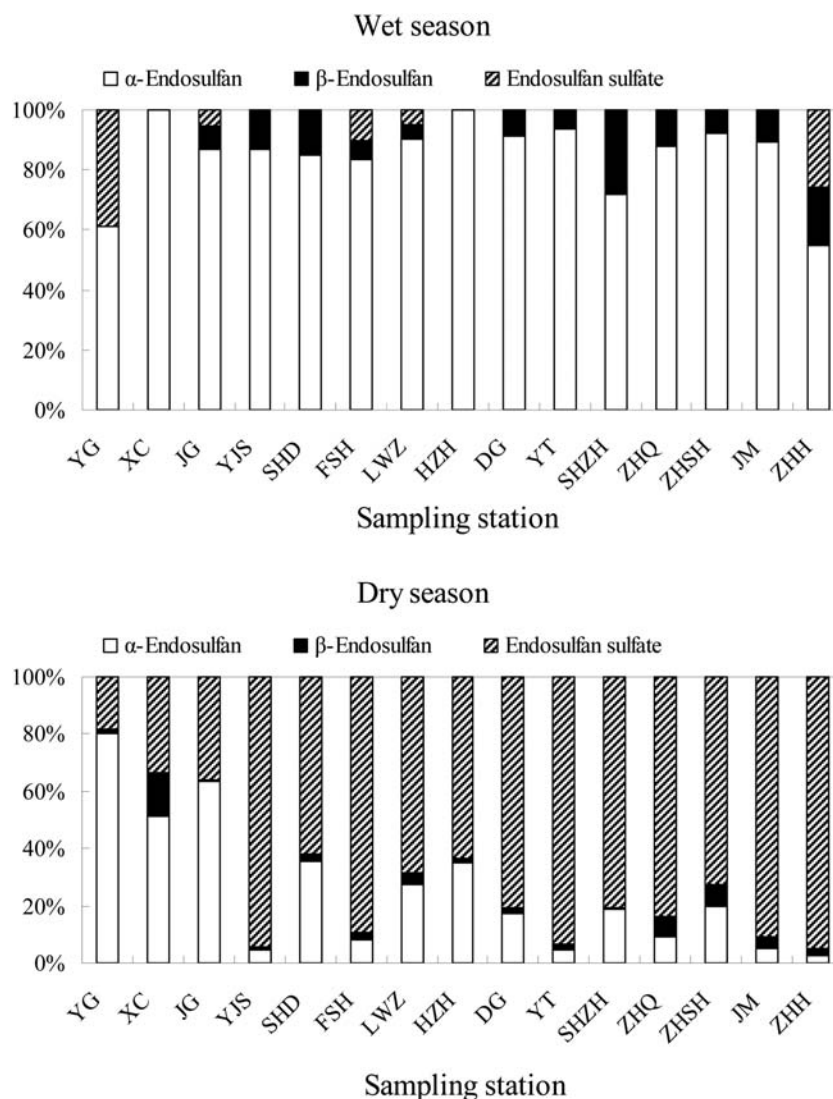

Fig. 7 Percentage of every endosulfan component in the wet and dry season at different sampling station.

This journal is © The Royal Society of Chemistry 2010

J. Environ. Monit., 2010, 12, 1666–1677 | 1673

compound.[24] Hence, according to the ratio of heptachlor epoxide and the total heptachlors, it could be concluded that there was no new heptachlor input during the wet season at ZHQ station, whereas new input appeared to all other stations whatever during the wet or dry season (Fig. S3†).

Technical endosulfan consists of α-endosulfan and β-endosulfan, and the ratio of the two components was 7 : 3. Also, a small amount of endosulfan sulfate existed in the technical endosulfan.[25] Endosulfan can be biologically and photochemically degraded into endosulfan sulfate, which is not susceptible to photolysis in the environment.[4] During the wet season, α-endosulfan was the dominant part of endosulfans in every sample, while during the dry season endosulfan sulfate was the dominant part of endosulfans in almost every sample in this study (Fig. 7). This phenomenon indicated that new input of technical endosulfan existed in the investigated areas in the wet season, whereas there was no input in the dry season.

In this study, aldrin in the dry season was undetectable in any of the samples, while dieldrin was the dominant part of the drins (Fig. 8). It could be interpreted that aldrin was able to rapidly transfer into dieldrin in the environment,[24] which might lead to the extremely high concentrations of dieldrin in the wet season at XC station.

3.3. Assessment of risk to human health

The reference dose, drinking water unit risk and their benchmark concentrations for individual OCPs were summarized in Table 3. The oral RfDs and drinking water unit risks were derived from USEPA's IRIS. The benchmark concentration was obtained from the formula mentioned in section 2.6. With these data, we calculated both the non-cancer hazard ratios and the cancer hazard ratios as follows.

Non-cancer hazard ratios. Fig. 9 showed the health risk of non-cancer both in the wet and dry season caused by ten individual OCPs. The non-cancer hazard ratios ranged from 2.00×10^{-7} to 3.34×10^{-3} far below unity during both wet and dry season. During the wet season, γ-HCH, chlordane, heptachlor epoxide and dieldrin were the dominant part in almost every sample caused the non-cancer risk to human health. The hazard ratio of XC was approximately 5 times higher than that of other samples. While during the dry season, dieldrin was the main cause of non-cancer risk in all of the samples especially those in Dongjiang River including LWZ, DG, YT and SHZH.

It also could be noted that of all the samples whatever in the wet or dry season, the non-cancer hazard ratios were below
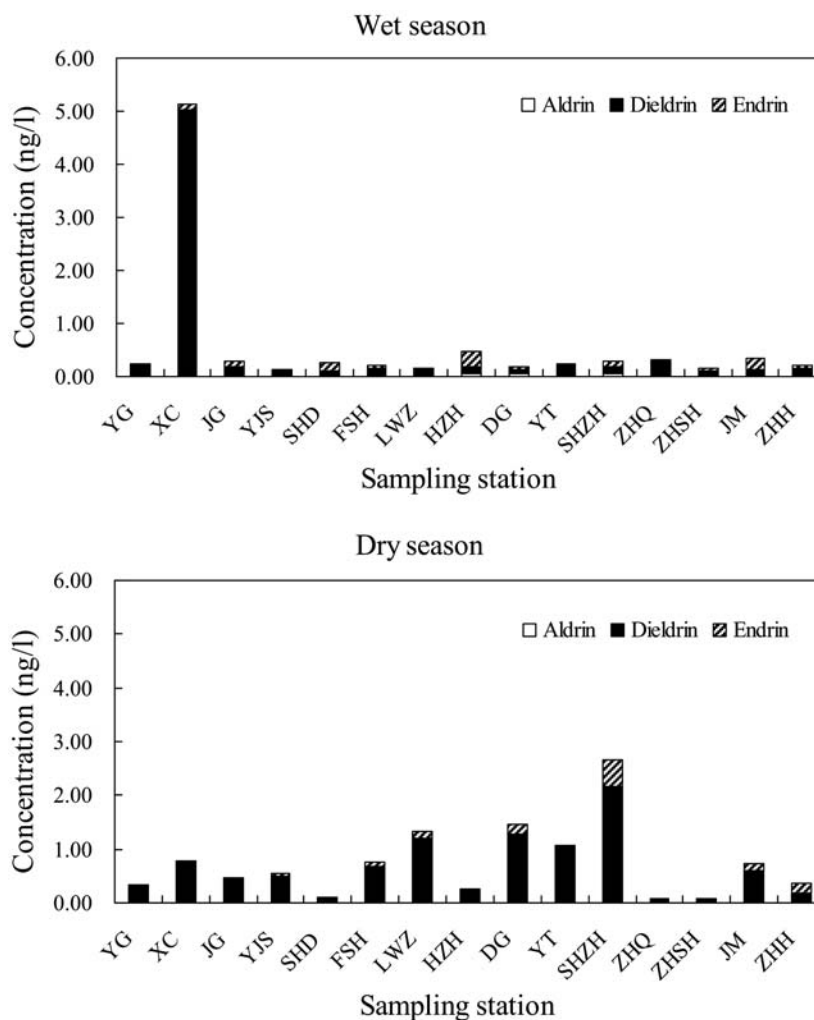

Fig. 8 Concentrations composition of drins at different sampling station.

Table 3 National average exposures and benchmark concentrations for individual OCPs in water[a]

Contaminants	Oral RfD (mg kg⁻¹ day⁻¹)	Non-cancer benchmark concentration (mg kg⁻¹ day⁻¹)	Drinking water unit risk [per µg l⁻¹]	Cancer benchmark concentration (mg kg⁻¹ day⁻¹)
α-HCH	—	—	1.8×10^{-4}	1.67×10^{-4}
β-HCH	—	—	5.3×10^{-5}	5.66×10^{-4}
γ-HCH	3×10^{-4}	3×10^{-4}	—	—
δ-HCH	—	—	—	—
p,p'-DDD	—	—	6.9×10^{-6}	4.35×10^{-3}
p,p'-DDE	—	—	9.7×10^{-6}	3.09×10^{-3}
p,p'-DDT	5×10^{-4}	5×10^{-4}	9.7×10^{-6}	3.09×10^{-3}
Chlordane	5×10^{-4}	5×10^{-4}	1×10^{-5}	3.00×10^{-3}
Heptachlor	5×10^{-4}	5×10^{-4}	1.3×10^{-4}	2.31×10^{-4}
Heptachlor epoxide	1.3×10^{-5}	1.3×10^{-5}	2.6×10^{-4}	1.15×10^{-4}
Endosulfan	6×10^{-3}	6×10^{-3}	—	—
Endosulfan sulfate	—	—	—	—
Aldrin	3×10^{-5}	3×10^{-5}	4.9×10^{-4}	6.12×10^{-5}
Dieldrin	5×10^{-5}	5×10^{-5}	4.6×10^{-4}	6.52×10^{-5}
Endrin	3×10^{-4}	3×10^{-4}	—	—
Endrin aldehyde	—	—	—	—
Endrin ketone	—	—	—	—
Methoxychlor	5×10^{-3}	5×10^{-3}	—	—

[a] Oral RfDs and drinking water unit risk were obtained from USEPA's Integrated Risk Information System (IRIS).
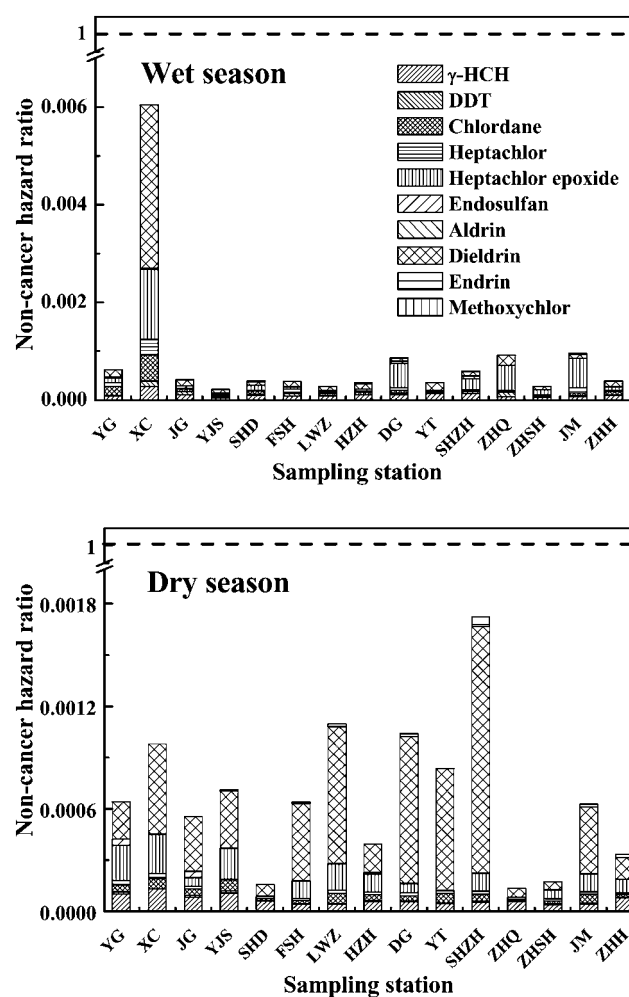

Fig. 9 Non-cancer hazard risks caused by individual OCPs through daily water consumption by people in the PRD region.

5×10^{-3}, far lower than 1. So it could be concluded that the individual OCPs might not induce non-cancer hazard risk in all source water samples in this study. Nevertheless, we could not ensure the non-cancer risk caused by the total OCPs in that the combined effects[28] (including additional joint action, synergistic joint action, potentiation, antagonistic joint action and independent joint action) of individual OCPs were not considered. Therefore, the non-cancer hazard risk caused by the total OCPs should not be ignored.

Cancer hazard ratios. The cancer hazard ratios ranged from 1.08×10^{-7} to 2.56×10^{-3}. The health risk of cancer could be caused by ten kinds of individual OCPs determined in this study (Fig. 10). α-HCH, β-HCH, heptachlor and dieldrin were the dominant part of the individual OCPs which might cause cancer risk to human health in the wet season. The same as the non-cancer hazard ratio in the wet season, cancer hazard ratio of XC sample was about 10 times as high as that of other samples. Dieldrin and α-HCH were the dominant parts in the dry season. The risk caused by dieldrin was more severe than that caused by α-HCH in almost every sample except for YJS. Overall, in the dry season, the cancer hazard ratios of dieldrin in Dongjiang
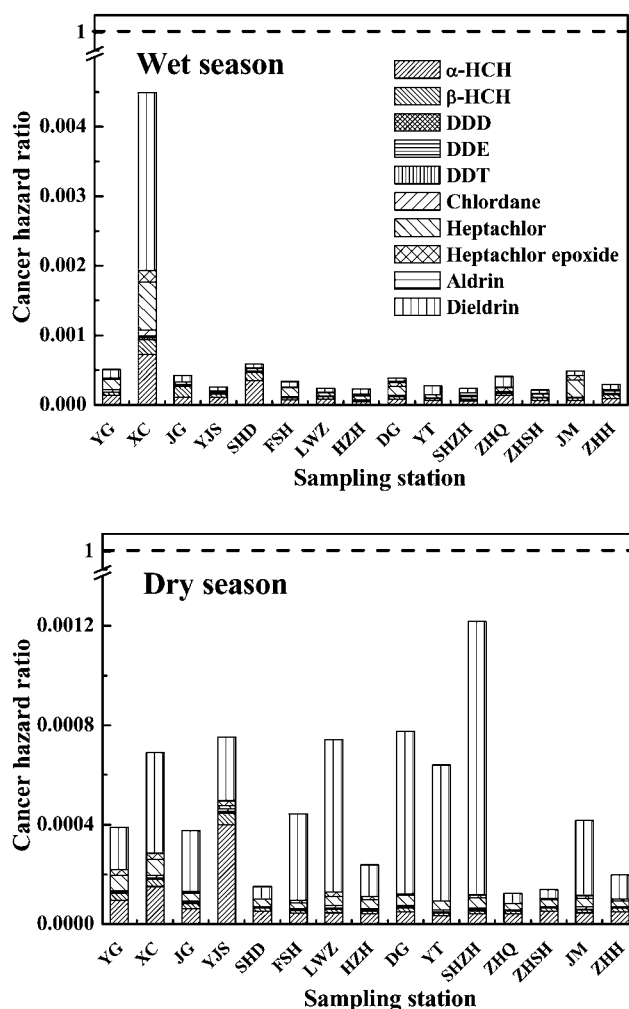
Fig. 10 Cancer hazard risks caused by individual OCPs through daily water consumption by people in the PRD region.

in dissolved phase, except XC sample. HCHs concentrations varied from 0.84 ng l^{-1} to 12.23 ng l^{-1} and DDTs from 0.17 ng l^{-1} to 5.92 ng l^{-1}, which were below Chinese guidelines (CJ 3020-93). Compared with other drinking water sources, the source water in this study was slightly polluted by the OCPs. So the quality of the source water within the PRD region as on the OCPs aspect was reasonably good.

Individual OCPs, whether concerning non-cancer or cancer hazard risk, were all not posing health threats to the local residents *via* daily water consumption. However, the combined effects were not taken into consideration in this study. So the hazard risk caused by the total OCPs should not be overlooked. Further study is needed, with the methods of toxicology, to determine the hazard risk concerning the combined effects among the individual OCPs.

Acknowledgements

References

1 J. M. Fu, B. X. Mai, G. Y. Sheng, G. Zhang, X. M. Wang, P. A. Peng, X. M. Xiao, R. Ran, F. Z. Cheng, X. Z. Peng, Z. S. Wang and U. W. Tang, *Chemosphere*, 2003, **52**, 1411–1422.
2 H. Iwata, S. Tanabe, N. Sakal and R. Tatsukawa, *Environ. Sci. Technol.*, 1993, **27**, 1080–1098.
3 S. A. Lee, Q. Dai, W. Zheng, Y. T. Gao, A. Blair, J. D. Tessari, B. T. Ji and X. O. Shu, *Environ. Int.*, 2007, **33**, 157–163.
4 W. H. Li, Y. H. Zhang, Q. Y. Fan, H. Nakada, T. Kitano, S. Abe and X. C. Ding, *J. Environ. Occup. Med.*, 2005, **22**, 14–16.
5 T. C. An, J. X. Chen, J. M. Fu, G. Y. Sheng, G. Y. Li, Z. Y. Hu and Y. Q. Kuang, *Ecol. Environ.*, 2005, **14**, 981–986.
6 X. J. Luo, B. X. Mai, Q. S. Yang, J. M. Fu, G. Y. Sheng and Z. S. Wang, *Mar. Pollut. Bull.*, 2004, **48**, 1102–1115.
7 Y. L. Liu, *J. Shenzhen Inst. Inf. Technol.*, 2008, **6**, 76–80.
8 M. Yu, X. J. Luo, S. J. Chen, B. X. Mai and E. Y. Zeng, *Environ. Toxicol. Chem.*, 2007, **27**, 10–17.
9 Q. T. Jiang, T. K. M. Lee, K. Chen, H. L. Wong, J. S. Zheng, J. P. Giesy, K. K. W. Lo, N. Yamashita and P. K. S. Lam, *Environ. Pollut.*, 2005, **136**, 155–165.
10 J. Y. Guo, E. Y. Zeng, F. C. Wu, X. Z. Meng, B. X. Mai and X. J. Luo, *Environ. Toxicol. Chem.*, 2007, **26**, 1109–1115.
11 G. F. Zhao, Y. Xu, W. Li, G. G. Han and B. Ling, *Sci. Total Environ.*, 2007, **378**, 281–292.
12 C. P. Dougherty, S. H. Holtz, J. C. Reinert, L. Panyacosit, D. A. Axelrad and T. J. Woodruff, *Environ. Res.*, 2000, **84**, 170–185.
13 H. Zhang, J. Zhang and Y. Zhu, *Environ. Toxicol.*, 2008, **24**, 82–86.
14 Y. W. Wan, T. F. Kang, Z. L. Zhou and Y. Zhang, *J. Agro-Environ. Sci.*, 2009, **28**, 803–807.
15 R. B. Zhou, L. Z. Zhu, K. Yang and Y. Y. Chen, *J. Hazard. Mater.*, 2006, **137**, 68–75.
16 Z. L. Zhang, H. S. Hong, J. L. Zhou, J. Huang and G. Yu, *Chemosphere*, 2003, **52**, 1423–1430.
17 C. Sun, Y. Dong, S. Xu, S. Yao, J. Dai, S. Han and L. Wang, *Environ. Pollut.*, 2002, **117**, 9–14.
18 J. X. Wang, Y. H. Bi, G. Pfister, B. Henkelmann, K. X. Zhu and K. W. Schramm, *Chemosphere*, 2009, **75**, 1119–1127.
19 R. W. M. Kwong, P. K. N. Yu, P. K. S. Lam and W. X. Wang, *Environ. Toxicol. Chem.*, 2008, **27**, 2053–2063.
20 S. W. Karickhoff, D. S. Brown and T. A. Scott, *Water Res.*, 1979, **13**, 241–248.
21 A. Ramesh, S. Tanabe, H. Murase, A. N. Subramanian and R. Tatsukawa, *Environ. Pollut.*, 1991, **74**, 293–307.
22 R. L. Metcalf, *J. Agric. Food Chem.*, 1973, **21**, 511–519.

River were the highest, and in Zhujiang River were higher than those in Beijiang and Xijiang River, which was similar to the non-cancer hazard.

Furthermore, we noticed that both in the wet and dry season, the cancer hazard ratios of individual OCPs in all samples were below unity, which demonstrated that no cancer hazard risks to human health were caused by individual OCPs detected. But we still could not ensure the cancer risk caused by the combined effects of the total OCPs for the same reason as non-cancer risk. Thus, the cancer hazard risk also should not be overlooked.

4. Conclusions

This study has provided data on the levels of OCPs in drinking water sources including the dissolved phase and particulate phase within the PRD region and estimated the hazard risks to human health caused by individual OCPs through daily water consumption with the standard recommended by the USEPA.

The concentrations of the total OCPs ranged from 3.13 ng l^{-1} to 39.52 ng l^{-1} in the wet season and from 2.42 ng l^{-1} to 15.42 ng l^{-1} in the dry season. The OCPs in water mainly existed

1676 | *J. Environ. Monit.*, 2010, **12**, 1666–1677

This journal is © The Royal Society of Chemistry 2010

23 R. Q. Yang, G. B. Jiang, Q. F. Zhou, C. G. Yuan and J. B. Shi, *Environ. Int.*, 2005, **31**, 799–804.
24 X. F. Wang, X. H. Li, H. X. Cheng, X. B. Xu, G. M. Zhuang and C. D. Zhao, *J. Hazard. Mater.*, 2008, **155**, 350–357.
25 Y. F. Jiang, X. T. Wang, Y. Jia, F. Wang, M. H. Wu, G. Y. Sheng and J. M. Fu, *J. Hazard. Mater.*, 2009, **170**, 989–997.

26 W. Sovocoo, R. G. Lewis, R. L. Harless, N. K. Wilson and R. D. Zehr, *Anal. Chem.*, 1977, **49**, 734–740.
27 B. D. Eitzer, M. I. Mattina and W. Iannucci-Berger, *Environ. Toxicol. Chem.*, 2001, **20**, 2198–2204.
28 Z. Q. Meng, *Environ. Toxicol.*, 2000, China Environmental Science Press, Beijing, pp. 38–57.

This journal is © The Royal Society of Chemistry 2010

J. Environ. Monit., 2010, **12**, 1666–1677 | 1677