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Chlorobenzenes in waterweeds from the Xijiang River (Guangdong section) of the Pearl River

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Abstract

The Xijiang River is the major source of water for about 4.5 millions of urban population and 28.7 millions of rural population. The water quality is very important for the health of the rural population. The concentration and distribution of chlorobenzenes (CBs) in both water and waterweeds collected from 4 stations in the Xijiang River (Gangdong section) of the Pearl River in April and November were determined. The result showed that nearly every congener of CBs was detected. The total contents of CBs (∑CBs) in the river water ranged from 111.1 to 360.0 ng/L in April and from 151.9 to 481.7 ng/L in November, respectively. The pollution level of CBs in the water in April was higher than that in November. The contents of ∑CBs in waterweeds ranged from 13.53×10^2 μg/g to 38.27×10^2 μg/g dry weight (dw). There was no significant difference between April and November in waterweeds. The distribution of CBs in roots, caulis, and leaves of *Vallisneria spiralis* L. showed different patterns. The leaves mainly contained low-molecular-weight CBs (DCBs), whereas the roots accumulated more PCBs and HCBs. The average $\lg BCF_{lip}$ (bioconcentration factor) of CBs ranged from 0.64 to 3.57 in the waterweeds. The spatial distribution character of CBs in the Xijiang River was: Fengkai County < Yunan County < Yun'an County < Gaoyao County according to the ∑CBs, and the pollution deteriorated from the upstream to the downstream of the Xijiang River. Further analysis demonstrated that the discharge of waste containing CBs may be the main source of CBs pollution in the Xijiang River.

Key words: chlorobenzenes; pollution; water; water weeds; distribution; bioconcentration factor

Introduction

The Pearl River is one of the seven largest river systems in China, and the Xijiang River, which is the trunk stream of the Pearl River, serves over 50% of the total water source of the Pearl River (Deng *et al*., 2006; Chen, 2002). The Xijiang River flows throughout Yunnan, Guizhou, Guangxi, and Guangdong provinces, joins the other two major tributaries of the Pearl River at Sanshui in Guangdong Province, and enters the Pacific Ocean near Hong Kong. The Xijiang River provides convenience to the people in many ways, such as drinking purposes, water transportations, trade, and irrigation. Guangdong Province is the most developed province in the Pearl River Basin; however, during the past two decades, the economic boom and the continuous development of agriculture, industry, and city planning in the region have led to the accumulation of toxic organic compounds. This considerable environmental impact has been imposed on the Pearl River (Yang *et al*., 1998). The heavy metals and organochlorine pesticides' pollution in river sediment and estuary sediment have been reported (Kang *et al*., 2000). The water quality of the Pearl River has become questionable gradually, and some sections have worsened mainly owing to the organic discharge from the industries related to plastic, textile, dying, printing, tannery, electroplating, and paper production etc. (Yang *et al*., 1997). The chlorobenzene compounds were detected from the Pearl River water (Yang *et al*., 1996). Contamination of aquifers caused by halogenated organic compounds is a widespread problem owing to the extensive use of pesticides in agriculture and the irrational disposal of industrial chemical waste (Dewulf *et al*., 2006; Du *et al*., 2006). The potential human health risks of halogenated organic compounds in aquatic environments are the focus of the water quality research (Stahl, 1991; Jones *et al*., 2005). Nevertheless, at present, information on the distribution and the regularity of chlorobenzene compounds (CBs) in Pearl River waterweeds is still unavailable.

Very few studies have reported the CB levels in the waterweeds, especially, the distributions of organic chemicals in waterweeds. The *Potamogeton crispus* L. and *Vallisneria spiralis* L. were collected from the Xijiang River in our study. The main purpose of the present study is to investigate the concentrations and distributions of CB congeners in waters and waterweeds, and to elucidate

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the pollution level and bioaccumulations of CBs in the waterweeds of the Xijiang River.

1 Materials and methods

1.1 Chemicals and materials

Sodium sulfate (99% purity) was baked at 500°C for 6 h prior to use and then stored in an air and moisture tight container. Chlorobenzene (MeCB), 1,2-dichlorobenzene (1,2-DCB), 1,3-DCB, 1,4-DCB, hexachlorobenzene (HCB) were purchased from Standard Chemicals Office, Chinese Standard Technology Development Co. and 1,2,4-trichlorobenzene (1,2,4-TCB), 1,2,3-TCB, 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), 1,2,3,5-TeCB, 1,2,4,5-TeCB, and pentachlorobenzene (PeCB) were purchased from Chemservice Co. (Chester, England).

1.2 Sampling

The water and waterweed samples were collected at 4 stations of the Xijiang River (Guangdong section) in April and November, 2005, respectively (Fig.1). Sampling stations 1 and 2 are located at Fengkai County and Yunan County, the upper reach of the Xijiang River. Sampling stations 3 and 4 are located at Yun'an County and Gaoyao County, in the middle and lower reaches, respectively. The water samples (0.5 m below the surface) were collected using a stainless steel submersible pump and were stored in amber glass bottles. The waterweeds were collected using a weed collection device. The waterweeds were chosen and stored in freeze boxes. *P. crispus* and *V. spiralis* were the main kinds of water weeds. All the samples were stored at below 4°C and were transported to the lab in 2 d.

1.3 Sample pretreatments

Water samples: water samplings were centrifuged at 3000 r/min for 5 min to get rid of the suspensions. The water sample (500 ml) was extracted to 20 ml hexane in 1 L separating funnel and the organic extract was gathered. The extraction procedure was repeated with another 20 ml hexane. The organic extracts were then transferred into pretreatment columns, which contained anhydrous sodium sulfate. Prior to this filtration, the column must be prewashed by hexane. After the extracts had passed through the column, 10 ml of hexane was used to elute the columns. The eluate was then concentrated to approximately 1 ml with a rotating evaporator (Heidolph Laborota 4000, German) below 15°C prior to GC analysis.

Waterweed samples: the waterweeds were classified and washed by tap water and double distilled water in turn. These were frozen at –4°C and then freeze-dried for about 48 h (Freeze-dryer Edwards mod. 24). Then, these were weighed, ground using an Ultra-Turrax tissue grinder (Philip, Holand) and stored in glass jars in a desiccator. About 1.5 g of dried weeds was disrupted by an ultrasonic cell disruptor (500- and 750-W Ultrasonic Homogenizers with Temperature Controller, Cole-Parmer, America) with 50 ml hexane. The extracts were centrifuged and the upper organic extracts were collected. The extraction was repeated three times, and the organic extracts were concentrated to approximately 5 ml using a rotary evaporator at below 15°C. The hexane extracts were washed with concentrated Sulphuric acid to get colorless solutions. The organic extract was cleaned up by transferring into a 33-cm glass pretreatment column (φ 1 cm). The column contained (from bottom to top): 1 g anhydrous Na_2SO_4, 10 g Florisil, 5 g silica gel, and 2 g anhydrous Na_2SO_4. The columns were prewashed before clean up with 20 ml of hexane and were eluted after the extracts had passed through the column with 20 ml of hexane. The elute solution was concentrated to approximately 1 ml with a rotating evaporator at 15°C prior to GC analysis.

For quality assurance and quality control (QA/QC), two bottles of deionized water were carried to the field and exposed to the *in situ* environment during the course of the sampling procedure. The deionized water samples were used as the field blanks, which were extracted and prepared in the same manner as the water samples described above.

1.4 Instrumental analysis

Sample analysis was conducted on HP6890 Series II gas chromatography (GC) equipped with a 30-m DB-0.25 capillary column and an ^{63}Ni electron capture detector (ECD). The injector temperature was 250°C, and the detector temperature was 300°C. The column temperature

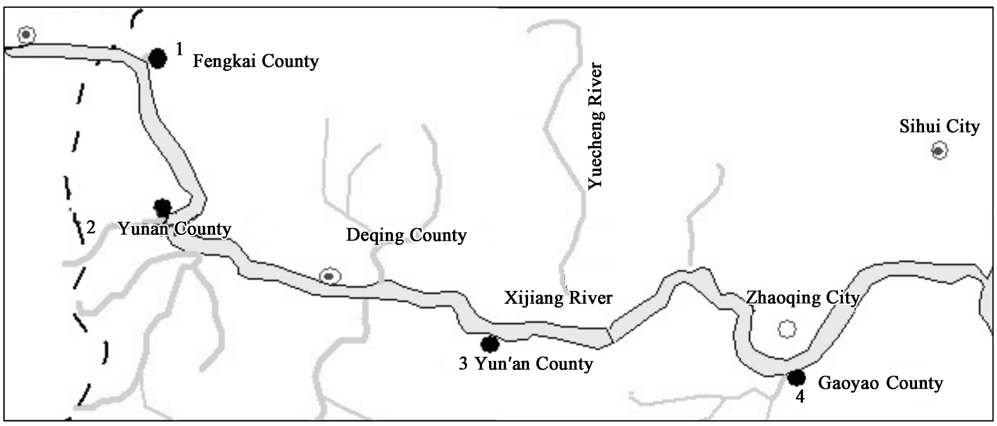

Fig. 1 Sampling stations in the Xijiang River of the Pearl River.

was set up as follows: held at 50°C for 3 min, raised to 80°C at the rate of 2°C/min, then raised to 250°C at the rate of 10°C/min, and held for 10 min. The injection sample volume was 2 μl. The samples were analyzed in triplicates in HW-2000 chromatography station 2.07.

1.5 Lipid content determination

Triplicate aliquots (5 ml) from each hexane extract (see above) were transferred to preweighed vials for a gravimetrical lipid determination. The hexane was blown off under a gentle stream of nitrogen. The vials were closed and reweighed after 2 d. From the difference in weights, the hexane-extractable lipid content was calculated (de Maagd *et al.*, 1997).

1.6 Quality assurance and quality control

Qualitative and quantitative determination of samples was done using a hexane-based mixture of 12 congeners of CB standards (Fig.2). The standards were repeated three times. Fig.2 shows that CB could not be detected in this condition. Further more 1,2,3,5-tetrachlorobenzene (1,2,3,5-TeCB) and 1,2,4,5-TeCB could not be effectively discriminated, and therefore their sum was regarded as 1,2,3,5-TeCB. The other 9 kinds of CBs were determined. Quantification was performed using a five-point calibration curve, which was established using an internal standard for each individual chlorobenzene.

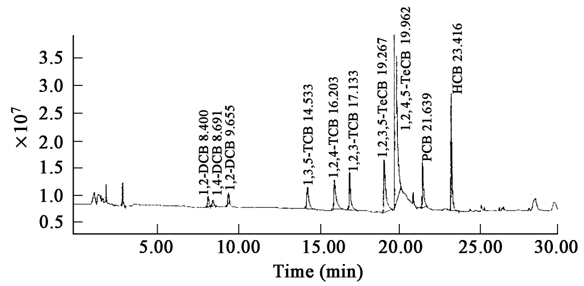

Fig. 2 Gas chromatogram of CBs in a standard mixture.

The sample recoveries of the standard chemicals in water and waterweeds were determined according to the above methods in the same chromatography conditions. The CBs recoveries in water and waterweeds were in the range of 85.2%–98.6% and 88.2%–105.3%, respectively. The results of the experimentation confirmed the applicability and reliability of the methods.

1.7 Statistical analysis

Data were shown as mean ± standard deviation (SD) and were analyzed by Independent-Samples *t*-test with the Statistical Package for Social Sciences (SPSS for Windows, version 10.1; SPSS Inc., Chicago, IL, USA).

2 Results

2.1 Concentrations and distributions of CBs in the water of the Xijiang River

CBs in the water samples collected from the Xijiang River of the Pearl River were analyzed in triplicates according to the method mentioned above. The concentrations of CBs in April and November are given in Tables 1 and 2.

Table 1 Concentrations of CBs in the water from the Xijiang River in April (ng/L)

CBs	Station 1	Station 2	Station 3	Station 4
1,2-DCB	14.9±4.0	28.7±7.7	67.9±30.3	85.3±34.6
1,3-DCB	14.7±2.7	17.8±4.6	17.2±1.1	42.9±0.6
1,4-DCB	26.7±8.4	54.0±6.5	105.5±1.7	129.2±7.6
1,2,3-TCB	1.3±0.2	0.2±0.1	2.4±0.5	2.2±1.1
1,2,4-TCB	44.8±8.4	80.4±20.1	40.1±1.6	75.4±44.3
1,3,5-TCB	1.2±0.1	0.3±0.2	1.1±1.0	0.6±0.2
1,2,3,4-TeCB	5.7±0.5	5.9±2.5	20.1±3.4	20.7±0.5
1,2,3,5-TeCB*	1.2±0.1	4.8±0.8	0.4±0.0	0.8±0.1
PCB	0.4±0.1	0.2±0.0	0.5±0.1	0.5±0.3
HCB	0.2±0.0	1.6±0.3	2.8±0.1	2.4±0.1
∑CBs	111.1±24.5	193.9±42.8	258.0±39.8	360.0±89.4

* Concentrations of 1,2,3,5-TeCB in the table were the sum of 1,2,4,5-TeCB and 1.2.3.5-TeCB.

Table 2 Concentrations of CBs in the water from the Xijiang River in November (ng/L)

CBs	Station 1	Station 2	Station 3	Station 4
1,2-DCB	16.3±1.5	58.6±0.8	122.8±29.2	108.1±38.1
1,3-DCB	15.9±2.6	61.3±1.2	62.5±1.6	81.0±1.9
1,4-DCB	32.3±1.9	122.9±12.7	131.5±31.1	157.7±37.9
1,2,3-TCB	2.5±2.6	0.7±0.5	3.4±0.5	3.3±0.1
1,2,4-TCB	47.8±10.5	100.4±47.9	93.1±21.6	89.5±79.7
1,3,5-TCB	2.9±1.2	0.4±0.1	1.9±0.3	1.5±0.3
1,2,3,4-TeCB	31.5±0.1	6.3±0.7	22.3±3.3	34.1±0.1
1,2,3,5-TeCB*	1.5±1.3	6.4±0.1	2.2±0.1	2.0±0.9
PCB	0.7±0.4	2.1±4.7	1.0±0.0	1.2±0.5
HCB	0.5±0.2	2.8±1.2	2.0±0.7	3.3±0.3
∑CBs	151.9±22.3	361.9±69.9	442.7±88.4	481.7±159.8

* Concentrations of 1,2,3,5-TeCB in the table were the sum of 1,2,4,5-TeCB and 1.2.3.5-TeCB.

Table 1 presents the mean concentration of each compound in April. All the 10 congeners were detected in the water of every station. The CB concentrations ranged from 0.2 to 129.2 ng/L. The concentrations of ∑CBs in station 1, 2, 3, and 4 were 111.1±24.5, 193.9±42.8, 258.0±39.8, 360.0±89.4 ng/L, respectively. Table 2 presents the mean concentration of each compound in November. The CB concentrations ranged from 0.4 to 157.7 ng/L. The ∑CBs in station 1, 2, 3, 4 were 151.9±22.3, 361.9±69.9, 442.7±88.4, 481.7±159.8 ng/L, respectively. Among the CB congeners measured, the low-molecular-weight CBs caused the dominant pollutions, especially 1,4-DCB and 1,2,4-TCB. The sums of 1,4-DCB and 1,2,4-TCB were 56.5%–69.3% and 51.3%–61.7% of the total CBs concentrations in April and in November. The sum of CBs measured in different stations in April and November in 2005 is shown in Fig.3.

Figure 3 shows that the concentrations of ∑CBs in different stations were different. The distribution character of CBs in the Xijiang River was as follows: Fengkai County < Yunan County < Yun'an County < Gaoyao County, which showed that the CBs concentrations gradually increased in water from the upstream to the downstream of the Xijiang River. Furthermore, the CBs concentrations in all the samples of November were generally higher than that of April. Some CB concentrations in November were 5 or

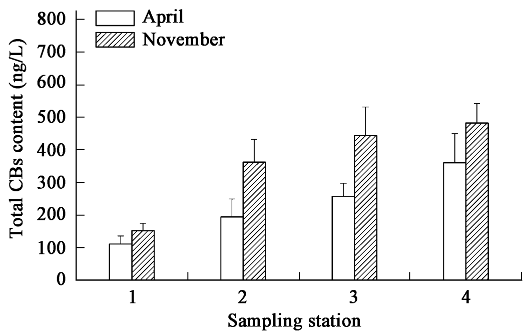

Fig. 3 Total CBs contents in river water in April and November in 2005.

6-fold of that in April.

2.2 Contents of CBs in waterweeds

CBs in water weed samples (mainly including the *P. crispus*, *V. spiralis*) collected from the Xijiang River of the Pearl River were analyzed in triplicates according to the method mentioned above. The average contents of CBs in waterweeds in April and November are given in Tables 3 and 4.

As seen from Tables 3 and 4, all the 10 congeners analyzed were almost detected in the waterweeds samples of every station. The mean contents of each compound ranging from 10 to 18.79×10^2 μg/g dw in waterweeds in April are given in Table 3. The ∑CBs contents in station 1, 2, 3, and 4 in waterweeds were $(13.53\pm8.91)\times10^2$, $(26.55\pm8.29)\times10^2$, $(30.69\pm3.42)\times10^2$, and $(38.27\pm7.24)\times10^2$ μg/g dw, respectively. Table 4 presents the average content of each compound in waterweeds in November. The ∑CBs contents in station 1, 2, 3, and 4 in waterweeds in November were $(13.56\pm2.28)\times10^2$, $(26.71\pm9.36)\times10^2$, $(30.87\pm4.07)\times10^2$, and $(37.36\pm4.57)\times10^2$ μg/g dw, respectively. The dominating congeners of CBs in waterweeds were DCBs, 1,2,4-TCB, and TeCBs. There was no significant difference among the ∑CBs contents of 10 CBs measured in waterweeds in April and November as shown in Fig.4. The spacial distribution character of ∑CBs in waterweeds was as follows: Fengkai County < Yunan County < Yun'an County < Gaoyao County. The character of spacial distribution was the same as that in water. When compared with the water samples, the CBs contents in waterweeds were considerably higher than that in water.

Table 3 Contents of CBs in waterweeds from the Xijiang River ($\times10^2$ μg/g dw) in April

CBs	Station 1	Station 2	Station 3	Station 4
1,2-DCB	1.55±1.27	4.46±3.80	8.21±1.82	7.51±3.70
1,3-DCB	0.64±0.08	1.40±0.72	6.07±0.55	6.02±1.64
1,4-DCB	9.42±7.21	16.49±3.25	11.82±0.91	18.79±1.76
1,2,3-TCB	0.10±0.00	0.61±0.00	0.30±0.02	0.30±0.00
1,2,4-TCB	0.48±0.01	1.04±0.03	1.42±0.01	1.92±0.01
1,3,5-TCB	0.11±0.00	0.60±0.00	0.41±0.00	0.30±0.00
1,2,3,4-TeCB	0.59±0.17	1.16±0.33	1.22±0.05	1.93±0.05
1,2,3,5-TeCB*	0.22±0.11	0.20±0.02	0.82±0.05	0.95±0.05
PCB	0.14±0.02	0.14±0.01	0.21±0.01	0.29±0.00
HCB	0.28±0.04	0.45±0.13	0.21±0.00	0.26±0.03
∑CBs	13.53±8.91	26.55±8.29	30.69±3.42	38.27±7.24

*Contents of 1,2,3,5-TeCB in the table were the sum of 1,2,4,5-TeCB and 1.2.3.5-TeCB.

Table 4 Contents of CBs in waterweeds from the Xijiang River ($\times10^2$ μg/g dw) in November

CBs	Station 1	Station 2	Station 3	Station 4
1,2-DCB	1.72±0.16	5.04±2.02	6.99±0.72	7.27±1.99
1,3-DCB	0.77±0.09	2.09±1.08	5.48±1.37	7.72±0.68
1,4-DCB	9.01±1.85	15.46±5.75	13.09±1.84	16.80±1.83
1,2,3-TCB	0.11±0.00	0.61±0.00	0.51±0.00	0.60±0.00
1,2,4-TCB	0.56±0.01	1.03±0.01	1.83±0.01	1.92±0.01
1,3,5-TCB	0.11±0.00	0.40±0.00	0.31±0.00	0.30±0.00
1,2,3,4-TeCB	0.62±0.10	1.33±0.42	1.38±0.07	1.47±0.02
1,2,3,5-TeCB*	0.28±0.01	0.22±0.06	0.80±0.02	0.81±0.00
PCB	0.11±0.00	0.13±0.01	0.21±0.01	0.22±0.00
HCB	0.27±0.06	0.40±0.01	0.27± 0.03	0.25±0.04
∑CBs	13.56±2.28	26.71±9.36	30.87±4.07	37.36±4.57

*Contents of 1,2,3,5-TeCB in the table were the sum of 1,2,4,5-TeCB and 1.2.3.5-TeCB.

2.3 Bioconcentration factors of CBs in waterweeds

CBs as hydrophobic organic contaminants entered the plants and accumulated mainly in the fat tissues of the plants (Chessells *et al*., 1992), therefore, the lipid contents were used to calculate the BCF of CBs in waterweeds in this study. The bioconcentration factor (BCF_{lip}) was denoted as:

$$BCF_{lip} = C_{organism}/C_{water} \quad (1)$$

where, $C_{organism}$ is the content of pollution in organism; and C_{water} is the content of pollution in water.

The $lgBCF_{lip}$ of CBs in tested waterweeds is shown in Table 5.

Table 5 presents the mean $lgBCF_{lip}$ of each CB detected in April and November. The average $lgBCF_{lip}$ ranged from 0.64 to 3.57. The BCF rank order of CBs in waterweeds was PCB > HCB > 1,4-DCB > 1,2,3,5-TeCB > 1,2,3-TCB > 1,2-DCB > 1,3-DCB > 1,2,3,4-TeCB > 1,2,4-TCB > 1,3,5-TCB. The $lgBCF_{lip}$ values of high-molecular-weight CBs, such as PCB and HCB were relatively higher than that of the low-molecular-weight CBs. However, the rule was not clear for DCBs, TCBs, and TeCBs. The BCF values of the same CB in different stations were different.

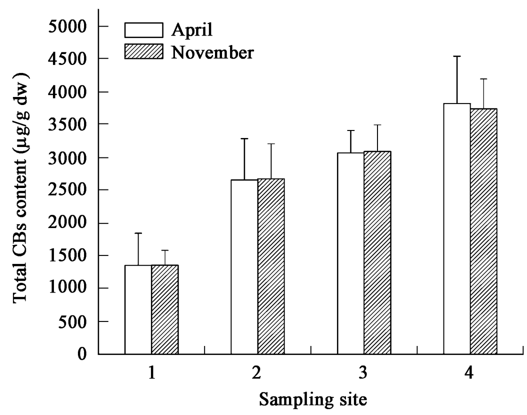

Fig. 4 Total CBs contents in waterweeds in April and November, 2005.

Table 5 The $lgBCF_{lip}$ of CBs in waterweeds

CBs	$lgBCF_{lip}$				
	Station 1	Station 2	Station 3	Station 4	Average
1,2-DCB	2.62	2.66	2.52	2.49	2.57
1,3-DCB	2.26	2.32	2.84	2.67	2.52
1,4-DCB	3.09	2.89	2.62	2.69	2.82
1,2,3-TCB	2.37	2.75	2.63	2.66	2.61
1,2,4-TCB	1.65	1.66	2.02	1.97	1.83
1,3,5-TCB	1.11	1.39	1.34	0.64	1.12
1,2,3,4-TeCB	2.25	2.91	1.73	2.41	2.32
1,2,3,5-TeCB*	2.88	2.17	2.85	3.13	2.76
PCB	2.99	2.89	3.09	3.14	3.03
HCB	3.57	2.91	2.62	2.55	2.91

*Contents of 1,2,3,5-TeCB in the table were the sum of 1,2,4,5-TeCB and 1.2.3.5-TeCB.

2.4 Distribution of CBs in different parts of waterweeds

As an example of the distribution of CBs in different parts of water weeds, the contents of CBs in different parts of *V.spiralis* were determined. *V. spiralis* collected from 4 different sampling stations in November was put together and divided into 4 groups randomly. The leaves, caulis, and roots were then separated and lyophilized in Freeze-dryer. The contents of CBs in roots, caulis, and leaves of V. spiralis were determined and the average values are given in Table 6.

Table 6 Contents of CBs in different parts of *Vallisneria spiralis* L. ($\times 10^2$ μg/g dw)

CBs	Root	Caulis	Leaf
DCBs	5.64±0.42	5.99±0.29	9.56±0.34
TCBs	0.64±0.11	0.63±0.12	0.68±0.07
TeCBs	0.80± 0.12	0.74±0.05	0.81± 0.07
PCB	0.28±0.03	0.12± 0.02	0.15±0.02
HCB	0.41± 0.03	0.21±0.03	0.22±0.04
∑CBs	7.77±0.71	7.69±0.51	11.42±0.54

Table 6 shows that the distribution of CBs in three parts of *V. spiralis* was universal. Furthermore, the roots, caulis, and leaves of *V. spiralis* showed different patterns of CBs accumulation. DCBs in leaves were higher than that in roots and caulis, but the contents of PCBs and HCBs in the roots were higher than that in leaves and caulis. DCBs and TCBs in the three parts had no clear difference. The leaves contained the highest contents of ∑CBs, the roots were intermediate, and the caulis had the lowest contents. The results showed that the low-molecular-weight CBs were mainly accumulated in the leaves, whereas the roots contained the high-molecular-weight CBs.

3 Discussion

In the present study, the concentration and distribution of CBs were investigated in the water and waterweeds in the Xijiang River of the Pearl River. The results showed that CBs pollutions are ubiquitous in the water and waterweeds in the Xijiang River. All the 10 congeners were detected in every sample. The ∑CBs ranged from 111.1 to 481.7 ng/L in water, and the contents of ∑CBs in waterweeds ranged from 13.53×10^2 to 38.27×10^2 μg/g dw. When compared with the water samples, the CBs content in waterweeds was higher than that in water, which showed obvious bioaccumulations. The average $lgBCF_{lip}$ ranged from 0.64 to 3.57. The distributions of CBs in three parts of *V. spiralis* were universal, and the roots, caulis, and leaves of *V. spiralis* showed different patterns of CBs accumulation. The low-molecular-weight CBs were mainly accumulated in the leaves, whereas the roots contained the high-molecular-weight CBs.

Waterweeds are a particular kind of plant. Some are annual plants, while some are perennial plants. Thus, the contents of CBs in plants of different growth stages were different. In this study, the plants of the same growth stage were sampled in the experiments to decrease the errors of samples. The predominant pollutants of CBs were DCBs, 1,2,4-TCB, and TeCBs in waterweeds, which were different from that in water. The difference of dominating congeners of CBs among water and waterweeds, or the different parts of the roots, caulis, and leaves was perhaps mainly attributed to the results of biotransformation and biotransport of waterweeds. The bioconcentration factor (BCF) was determined to describe the concentration trend of compounds in the waterweeds. The BCF values of the same CB in different stations were different, which may be attributed to the simultaneous operations of several factors, such as the octanol-water partition coefficient ($K_{o/w}$) of the chemical, the other chemical-physical characteristics of CBs, the concentrations of CBs in water, the absorbance sites and ways of CBs in the waterweeds, etc. The BCF values of CBs in waterweeds were considerably higher, which suggested that CBs in the Xijiang River will exhibit potential danger to the organisms which use the waterweeds as food.

As seen from the ∑CBs, there were clear time and spatial distribution characters. The spatial distribution character of CBs in the Xijiang River was that Fengkai County < Yunan County < Yun'an County< Gaoyao County. The contents of ∑CBs were gradually increscent from upriver to downriver of the Xijiang River. Furthermore, the concentrations of ∑CBs in water in November were higher than those in April. Some CB concentrations in November were 5- or 6-fold of that in April, which was perhaps attributed to monsoon prevailing in April in the South China. The amount of water in April in Pearl River was more than that in November, and all compounds were diluted. Moreover, the contaminations in water in November could not be transferred to other waters for the decrease of the rate of flow.

The organochlorinated compounds were determined by Yang *et al*. (1996) in water systems in the three cities of the Pearl River delta area about 10 years ago. In their study, the ∑CBs contents ranged from 10 to 120 ng/L, which was lower than that determined in our study. Although the sampling stations were different, the comparison of data could reflect the changes of ∑CBs pollutions in the whole Pearl River in nearly 10 years. The concentrations of 1,2-DCB (14–108 ng/L), 1,4-DCB (26–157 ng/L) in the present study were considerably higher than the data 10 years ago (3–22 ng/L of 1,2-DCB, 29 ng/L of 1,4-DCB).

The results suggested that although HCB had been banned for use for several years and the input pollutants were less than that earlier, there were still higher concentrations of HCB remaining in the river water (0.2–3.3 ng/L). Some low-molecular-weight CBs, such as DCB and TCB, were still in production and in use, furthermore, the discharge of ∑CBs was gradually higher than that earlier. Low-molecular-weight CB congeners were the predominant pollutants of CBs.

When compared with the data reported from other water systems in China, the detailed information of organochlorinated pollutants in the Xijiang River was scarce. For instance, higher PAH concentrations were reported for the Minjiang River Estuary of Fujian (Zhang *et al*., 2004), the Hang Zhou Rivers of Zhejiang (Chen *et al*., 2004), and the Daya Bay, the mainstream of the Pearl River and the Macao Harbor of Guangdong (Zhou and Maskaoui, 2003; Luo *et al*., 2004). These rivers flow through well-industrialized and greatly urbanized areas and are likely polluted severely. In contrast, the Xijiang River flows through relatively undeveloped rural areas and smaller cities such as Liuzhou, Wuzhou, Nanning and Zhaoqing. The contamination levels are likely not as high as in the surface water systems mentioned above. However, in our study, the concentrations of the ∑CBs, especially some low-molecular-weight CB compounds such as DCB and TCB, were relatively higher. The higher concentrations of CBs in water and waterweeds in Xijiang River will be attributed to the use of CB productions or the wastewater discharged from local inhabitant's life or the production of agriculture and industry at the present stage. On one hand, the Pearl River Delta is in a highly industrialized and urbanized area and is the important base of China's chemical industry, which stimulates the fast growth of economy in the Xijiang drainage area, and more and more productions of CBs and organochlorinated compounds appear in our life. Relatively high-level pollutants of PCBs and PAH were found in some locations in the Pearl River, most of which are harbors and industrial areas (Luo *et al*., 2006; Chau, 2005). CBs as important chemical products are widely used in various fields of medicine, pesticides, dyes, and so on. The uses or the wastewater discharge of CB productions were gradually increased. On the other hand, the transfer of some factories from big cities to rural cities and the foundation of some new chemical industries were increased gradually with the limit of chemical plants in the big cities. For example, there were 11 big chemical factories founded in a town of Gaoyao County between the years 1999 and 2005. Thus, the amounts of the waste materials and the outputs of chemical pollutants increased. The main sources of CB pollutants in the river water of the Xijiang River were wastewater discharged from households in the urban and rural areas, industrial facilities, non-point sources from agricultural areas, or the point source pollution where improper disposal and leakage of CBs productions.

The Xijiang River is currently the major source of water for several major cities with a total urban population of about 4.5 millions. It also serves as the major drinking water supply and source water for agricultural and industrial activities in 86 counties with a total population of 28.7 millions (Chen *et al*., 2006). The results of our research program will provide important information on the water quality of the Xijiang River and will help the future plan of protecting the Xijiang River of the Pearl River.

4 Conclusions

CBs were measured in river water and waterweeds in the Xijiang River of the Pearl River to elucidate the pollution level and the distribution and bioaccumulations of CBs in the water environment of the Xijiang River. The concentrations of ∑CBs in water ranged from 111.1 to 360.0 ng/L in April and from 151.9 to 481.7 ng/L in November. The contents of ∑CBs in waterweeds ranged from 13.53×10^2 to 38.27×10^2 μg/g dw. There was no obvious difference in the data of waterweeds between April and November. The average $\lg BCF_{lip}$ of CBs ranged from 0.64 to 3.57 for the waterweeds measured. The roots, caulis, and leaves of *V. spiralis* showed different patterns of CBs accumulation. The leaves had the highest contents of ∑CBs, the roots were intermediate, and the caulis had the lowest contents. The predominant pollutants were DCBs, 1,2,4-TCB, and TeCBs in water and in waterweeds. The CBs pollutions were more severe from the upstream to the downstream of the Xijiang River.

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