

# Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in water and suspended particulate matter from the Xijiang River, China

Yanlin Liu<sup>a,b</sup>, Ping'an Peng<sup>a,\*</sup>, Xiaoming Li<sup>a,b</sup>, Sukun Zhang<sup>a,b</sup>, Man Ren<sup>a</sup>

<sup>a</sup> State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, People's Republic of China

<sup>b</sup> Graduate School of Chinese Academy of Sciences, Beijing 100080, People's Republic of China

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## Abstract

Concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in water and suspended particulate matter (SPM) collected from the Xijiang River, China, were measured by the quarter from September 2005 to June 2006. Total PCDD/F concentration ranged from 2.659 to 4.596 pg/L for water and from 562.4 to 3259.5 pg/g for SPM. Concentrations were high in summer and low in winter. I-TEQ values in water and SPM were low, ranging from 0.012 to 0.075 pg/L, with a mean value of 0.039 pg/L. Calculated annual loadings of total PCDD/Fs and I-TEQ were 8.55 kg and 0.026 kg, respectively. Composition and homologue distribution of PCDD/Fs were varied because of large seasonal differences in discharge from the Xijiang River into the South China Sea. Comparison of the PCDD/Fs homologue and congener profiles of atmospheric deposition, soil, and water revealed that soil was the dominant source of PCDD/Fs in the Xijiang River. Industrial effluents were also possible sources of PCDD/Fs. A good correlation between  $\log K_{oc}$  and  $\log K_{ow}$  was observed for 2,3,7,8-substituted PCDDs and PCDFs and correlation coefficients were 0.71 and 0.84, indicating organic matter in SPM played a dominant role in PCDD/Fs partition between SPM and water. Crown Copyright © 2007 Published by Elsevier B.V. All rights reserved.

**Keywords:** PCDD/Fs; SPM;  $K_{oc}$ ; PCDD/Fs loading; Xijiang River

## 1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are the most persistent and toxic pollutants in the natural environment, and they may cause serious human health and ecosystem problems. These compounds are unintentionally produced during solid waste incineration, chemical manufacturing, disposal of sewage sludge, vehicle exhaust, and domestic fires [1] and occur ubiquitously in many environmental compartments. Due to their low water solubility and semi-volatility, PCDD/Fs can be transported over long distance via various routes such as atmosphere and water, and thus affect regional environmental quality [2]. In the past few decades, researchers have conducted many studies on PCDD/Fs in ambient air, sediments, and soils [3–8].

However, PCDD/Fs in aquatic systems have received much less attention. Water, which acts as an intermediate for transfer PCDD/Fs from air to sediment, plays a very important role in the environmental behaviors of these compounds. Suspended particulate matter (SPM) in water is the predecessor of sediment. The PCDD/Fs in SPM, therefore, undergo less transformation than in sediments and may contain a strong signal indicative of their source. Studies focused on PCDD/Fs in SPM and partition between SPM and water will help elucidate the sources, transformation, and final fate of PCDD/Fs in the water and sediments.

The Xijiang River is the major tributary of the Pearl River that is the third largest river in China. It originates in Yunnan Province; flows through Guizhou, Guangxi, and Guangdong; and finally enters into the South China Sea (Fig. 1). The Xijiang River is 2214 km long and has a catchment area of  $3.53 \times 10^5 \text{ km}^2$ . The catchment is located in a tropical and semitropical area, and the river discharges  $2.38 \times 10^{11} \text{ m}^3$  of fresh water to the sea annually, which accounts for 70.8% of total runoff of the Pearl River. The Xijiang River is an important source of water for agricultural and industry activities and also

\* Corresponding author at: Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, People's Republic of China. Tel.: +86 20 85290126; fax: +86 20 85290117.

E-mail address: [pinganp@gig.ac.cn](mailto:pinganp@gig.ac.cn) (P. Peng).

serves as a major supplier of drinking water for 86 counties with a total population of 28.7 million. However, data that describe the concentration and distribution of PCDD/Fs in the Xijiang River do not exist.

This study focuses on water quality in Guangdong province, China. Our primary aim was to estimate the concentration and total loading of PCDD/Fs in the Xijiang River due to the increase of anthropogenic activities and fast economic development in China, especially in the Pearl River Delta. The results provide the basic information needed to assess the risk of exposure to PCDD/Fs in the Xijiang River. They also may be helpful in forming water protection strategies in this river.

## 2. Materials and methods

### 2.1. Sample collection and preparation

We collected the samples at Gaoyao Hydrological Station, which is located at the most downstream section of the Xijiang River (Fig. 1). It is far removed from the South China Sea, so this area is not influenced by tides. The discharge of the Xijiang River changes between the dry season (October–March)

and the wet period (June, July, and August). We collected the water samples in the different seasons, from September 2005 to June 2006, from the upper, middle, and lower layer of the water column. To obtain sufficient SPM for analysis of PCDD/Fs, we collected about 1000 L of water for each sample. Water depth, temperature, pH, and turbidity were measured and recorded in the Gaoyao Hydrological Station (Table 1). Water was pumped into 10 L pre-cleaned brown glass containers with a stainless-steel submersible pump that contained  $\text{NaN}_3$  (100 mg/L) (Damao Chemicals Co., Tianjin, China) to inhibit bacteria growth. We transported the water samples into the laboratory and filtered them as quickly as possible to avoid precipitation of SPM in containers. We used glass fiber filters (GF/F, 0.7  $\mu\text{m}$  pore size, 142 mm diameter; Whatman International Ltd., Maidstone, England) to collect SPM; they were pre-combusted at 450 °C for 5 h and weighed before use. After filtering, the glass fibers with SPM were wrapped with aluminum foil and stored in sealed bags at  $-20^\circ\text{C}$  until analysis. After filtration of a sample, the organic pollutants dissolved in the water phase were extracted by polyurethane foam (PUF). Prior to be used to extract, the PUF was purified with toluene, methanol, and dichloromethane for 24 h, respectively and was kept at sealed



Fig. 1. Sampling site and study area. The catchment area is shadowed in black.

Table 1  
Basic sampling data

| Sampling date                       | 09/2005        |                |                | 12/2005 |      |      | 04/2006 |      |      | 06/2006 |      |      |
|-------------------------------------|----------------|----------------|----------------|---------|------|------|---------|------|------|---------|------|------|
| Discharge ( $\text{m}^3/\text{s}$ ) | 4400           |                |                | 1800    |      |      | 4300    |      |      | 15300   |      |      |
| Layer                               | A <sup>a</sup> | B <sup>b</sup> | C <sup>c</sup> | A       | B    | C    | A       | B    | C    | A       | B    | C    |
| Depth (m)                           | 0.5            | 5.2            | 9.5            | 0.5     | 5.3  | 9    | 0.55    | 5    | 9    | 0.5     | 8.2  | 16   |
| $T$ ( $^\circ\text{C}$ )            | 28             | 28             | 28             | 16      | 16   | 16   | 16      | 16   | 16   | 25      | 25   | 25   |
| pH                                  | 8.10           | 8.08           | 8.05           | 7.93    | 7.94 | 7.93 | 7.93    | 7.90 | 7.90 | 7.88    | 7.89 | 7.90 |
| Turbidity                           | 12             | 22             | 23             | 30      | 25   | 25   | 17      | 18   | 19   | 233     | 236  | 238  |
| Salinity (mg/L)                     | 6.1            | 6.6            | 10.9           | 6.5     | 5.7  | 5.7  | 7.7     | 7.2  | 8.1  | 6.1     | 5.9  | 6.1  |
| SPM (mg/L)                          | 5              | 6              | 9              | 12      | 11   | 9    | 11      | 13   | 14   | 25      | 27   | 19   |
| DOC (mg/L)                          | 1.09           | 1.15           | 1.16           | 1.54    | 1.41 | 1.39 | 1.58    | 1.53 | 1.64 | 1.11    | 1.16 | 1.16 |
| POC (%)                             | 5.46           | 3.25           | 3.84           | 4.39    | 4.20 | 4.57 | 6.48    | 4.77 | 4.70 | 2.07    | 2.56 | 2.37 |

<sup>a</sup> The upper layer of the water column.

<sup>b</sup> The middle layer of the water column.

<sup>c</sup> The bottom layer of the water column.

bags after evaporation of the solvents at room temperature in a hood.

Concentration of SPM, particulate organic carbon (POC), and dissolved organic carbon (DOC) (Table 1) were determined by using 350–1200 mL samples of unfiltered water, which were passed through pre-combusted and pre-weighed glass fiber filters (GF/F, 0.7  $\mu\text{m}$  pore size, 47 mm diameter; Whatman). The glass fiber filters were then freeze-dried, re-weighed for SPM, and after acid (HCl) treatment to remove inorganic carbon, analyzed for POC with an elemental analyzer (Elementar, Vario, EL III, Germany). The filtrates were analyzed for DOC with a total organic carbon analyzer (Shimadzu TOC-VCPH, Kyoto, Japan).

## 2.2. Analysis of PCDD/Fs

The freeze-dried and re-weighed glass fiber filters containing SPM and the PUF samples were Soxhlet extracted with toluene for 72 h. Prior to extraction, the  $^{13}\text{C}_{12}$ -PCDD/F internal standards, which included  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD,  $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD,  $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDD,  $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD,  $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD,  $^{13}\text{C}_{12}$ -OCDD,  $^{13}\text{C}_{12}$ -2,3,7,8-TCDF,  $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF,  $^{13}\text{C}_{12}$ -2,3,4,7,8-PeCDF,  $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF,  $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDF,  $^{13}\text{C}_{12}$ -2,3,4,6,7,8-HxCDF,  $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDF,  $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF, and  $^{13}\text{C}_{12}$ -1,2,3,4,7,8,9-HpCDF, were spiked. During extraction, we added activated copper to remove sulfur from the samples. The extract of each sample was filtered through a funnel packed with a glass-wool plug and anhydrous sodium sulfate to remove copper chips and trace levels of water. The filtered extracts, to which we added 20  $\mu\text{L}$  *n*-tetradecane to avoid the loss of PCDD/Fs, were concentrated using a rotary evaporator.

In this study, we applied the following steps to effectively remove impurities: (1) The concentrated extracts were pre-cleaned with 20 g  $\text{H}_2\text{SO}_4$ /silica gel (w/w, 40%) in 100 mL hexane and stirred for 2 h with a Teflon-coated magnetic stirring bar. The entire content of the flask was filtered through a funnel with glass wool covered with 10 g anhydrous sodium sulfate. Hundred millilitre hexane was used to rinse the flask and the slurry. (2) The filtrates were further cleaned with a multi-layer silica-gel column, which was packed from bottom to top with glass wool, silica gel (1 g), 33% (w/w) NaOH/silica-gel (4 g), silica gel (1 g), 40% (w/w)  $\text{H}_2\text{SO}_4$ /silica-gel (8 g), silica gel (2 g), and 4 g anhydrous sodium sulfate. The column was eluted consecutively with 20 mL hexane (to be discarded) and 100 mL 3% dichloromethane/hexane. The collected eluate was concentrated using a rotary evaporator. (3) For the final procedure, we used a basic alumina column (20 cm  $\times$  i.d. 8 mm) that was packed with glass-wool (bottom), activated basic alumina (10 g), and 1 cm anhydrous sodium sulfate (top). After pre-cleaning the column with hexane and applying the concentrated extract to the column, we sequentially eluted the column with 20 mL hexane and 80 mL 2% dichloromethane/hexane to remove background organic chemicals and then eluted the target chemicals with 50 mL 50% dichloromethane/hexane. The collected eluate was concentrated again to 1 mL and transferred

into a 1.5 mL teardrop vial. Finally, injection standards ( $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and  $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD) were spiked for the recovery and the final volume was adjusted to 20  $\mu\text{L}$  before analysis.

We purchased all  $^{13}\text{C}_{12}$ -PCDD/F standards from Cambridge Isotope Laboratories Inc., USA. The solvents, including methanol, acetone, dichloromethane, toluene, and hexane, were all pesticide grade or high grade and were purchased from Merck, Germany; the sulfuric acid and sodium hydroxide also were obtained from Merck. The silica gel (70–230 mesh, Aldrich, USA) was Soxhlet extracted for 24 h with dichloromethane and then vacuum dried. Before use, the silica gel was activated for 5 h at 170  $^\circ\text{C}$ . The basic alumina (70–230 mesh, Merck) was activated for 8 h at 500  $^\circ\text{C}$ .

## 2.3. Instrumental analysis

Gas chromatograms obtained from high-resolution gas chromatograph coupled with electrical conductivity detector (HRGC/ECD) showed that the background impurities in the extracts of our samples were efficiently removed. Identification and quantification of the PCDD/Fs in water and SPM samples were performed with high-resolution gas chromatograph coupled with high-resolution mass spectrometry (HRGC/HRMS), using a Trace GC 2000 and a Thermo Electron Finnigan MAT 95XP with a capillary column (CP-Sil 8 CB/MS, 60 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu\text{m}$  film thickness). Helium was used as the carrier gas at a flow rate of 0.8 mL/min. The sample (1  $\mu\text{L}$ ) was injected using the splitless injection mode. The GC temperature was programmed to change from 90  $^\circ\text{C}$  (1 min) to 220  $^\circ\text{C}$  (7 min) at 55  $^\circ\text{C}/\text{min}$ , then to 275  $^\circ\text{C}$  at 1.2  $^\circ\text{C}/\text{min}$ , and finally to 301  $^\circ\text{C}$  at 1.7  $^\circ\text{C}/\text{min}$ . The injector temperature was kept at 250  $^\circ\text{C}$  and the HRGC/HRMS interface temperature was held at 250  $^\circ\text{C}$ . The HRMS was operated in the EI positive (electric impact ionization) and LOCK MID mode with a mass resolution of 10000 (313.9839, perfluorotributylamine). The electron impact ionization energy was 55 eV with a source temperature of 250  $^\circ\text{C}$ .

## 2.4. Quality control and quality assurance

To generate field blanks, we carried two bottles (20 L) of deionized and contaminant-free water to the field and exposed them to the in situ environment during the course of each field sampling procedure. PCDD/Fs were not detected in any of the field blanks. Quality control and quality assurance (QA/QC) were conducted with the field blanks, the method blanks, the ongoing precise and recovery (OPR), the initial precise and recovery (IPR), the duplicate sample, and the standard reference material (SRM, EDF-2513). In this study, the detection limits of the method were ca. 0.1 pg for 2,3,7,8-TCDF, 0.2 pg for 2,3,7,8-TCDD, and 0.8 pg for OCDD. The calculated recovery efficiencies for the surrogate standards ranged from 65 to 88%, which met the recovery limit demand of US EPA Method 1613, and the relative standard deviation (R.S.D.) of the measurements was less than 10%. We calculated the toxic equivalent quantity

(TEQ) using the I-TEF method (International TEF). Concentrations that were lower than the method detection limits (MDL) were assigned a value of zero.

### 3. Results and discussion

#### 3.1. PCDD/F concentration in water and SPM

To calculate the total concentration of PCDD/Fs, unit of pg/g in SPM samples was converted to pg/L through multiplying by concentration of SPM (Table 1). The summation of concentration of water (pg/L) and of SPM (pg/L) yielded the total concentration of PCDD/Fs in water column (pg/L). As seen in Table 2, it varied from 20.4 to 72.6 pg/L (mean = 38.2 pg/L), which included the toxic 2,3,7,8-substituted congeners 16.4–67.5 pg/L. The corresponding I-TEQ values ranged from 0.012 pg/L to 0.075 pg/L (mean = 0.039 pg/L). The average concentration of 2,3,7,8-TCDD was 0.006 pg/L. The US EPA set a maximum allowable level for 2,3,7,8-TCDD in drinking water at 0.013 pg/L based on assessment of human cancer risks at  $10^{-6}$  [9]. Thus, the concentrations of 2,3,7,8-TCDD in the Xijiang River are below this limit. Compared with PCDD/Fs concentrations in other rivers of world, these in the Xijiang River were lower. For examples, Gifford et al. [10] reported the I-

TEQ of Lake Rotorua, New Zealand ranged from nd to 1.6 pg/L, and the I-TEQ of Utuhina upstream, Utuhina downstream and Puarenga Stream around Lake Rotorua was 1.2 pg/L, 1.3 pg/L and 5.4 pg/L, respectively.

Table 2 provides the summary data for PCDD/Fs congeners and homologues found in water and SPM samples from the Xijiang River from September 2005 to June 2006. Concentrations of total PCDD/Fs in the water phase were low, ranging from 2.659 to 4.596 pg/L (mean = 3.691 pg/L); the 2,3,7,8-substituted congener concentrations ranged from 0.809 to 2.324 pg/L. The corresponding I-TEQ values varied from 0.009 to 0.050 pg/L (mean = 0.022 pg/L). We were able to detect such low concentrations because we used a very large volume of water (1000 L). However, these values were still several times higher than the total PCDD/Fs concentration in the water phase reported elsewhere (Table 3). For example, Broman et al. [11] reported an average dissolved PCDD/F concentration in the Baltic Sea of 0.12 pg/L. Total PCDD/Fs measured in Bunthaus and Blankenese Streams of the Elbe River were 0.211 pg/L and 0.275 pg/L, with 2,3,7,8-substituted I-TEQ values of 0.004 and 0.017 pg/L, respectively [12].

The concentration of total PCDD/Fs in SPM ranged from 611.8 to 3402.3 pg/g (mean = 2047.0 pg/g), including 2,3,7,8-substituted congeners (562.4–3259.5 pg/g). The corresponding

Table 2  
Summary PCDD/Fs congeners and homologues in water column from the Xijiang River, China

| Samples             | Water (pg/L) <sup>a</sup> |         |         |         | SPM (pg/g) <sup>a</sup> |         |          |          | Water + SPM (pg/L) <sup>b</sup> |         |         |         |
|---------------------|---------------------------|---------|---------|---------|-------------------------|---------|----------|----------|---------------------------------|---------|---------|---------|
|                     | 09/2005                   | 12/2005 | 04/2006 | 06/2006 | 09/2005                 | 12/2005 | 04/2006  | 06/2006  | 09/2005                         | 12/2005 | 04/2006 | 06/2006 |
| 2,3,7,8-TCDF        | 0.001                     | 0.002   | 0.021   | 0.034   | 2.504                   | 0.324   | 1.573    | 1.541    | 0.025                           | 0.011   | 0.045   | 0.064   |
| 1,2,3,7,8-PeCDF     | 0.002                     | 0.003   | 0.011   | 0.010   | 1.416                   | 0.228   | 1.476    | 2.071    | 0.015                           | 0.010   | 0.034   | 0.051   |
| 2,3,4,7,8-PeCDF     | 0.003                     | 0.004   | 0.006   | 0.011   | 2.245                   | 0.414   | 2.152    | 2.848    | 0.025                           | 0.017   | 0.039   | 0.068   |
| 1,2,3,4,7,8-HxCDF   | 0.022                     | 0.013   | 0.014   | 0.015   | 1.298                   | 0.539   | 2.484    | 3.578    | 0.034                           | 0.029   | 0.053   | 0.087   |
| 1,2,3,6,7,8-HxCDF   | 0.009                     | 0.006   | 0.007   | 0.006   | 0.987                   | 0.537   | 2.629    | 3.398    | 0.018                           | 0.021   | 0.048   | 0.074   |
| 2,3,4,6,7,8-HxCDF   | 0.009                     | 0.007   | 0.007   | 0.038   | 1.837                   | 0.534   | 3.978    | 3.396    | 0.026                           | 0.023   | 0.069   | 0.106   |
| 1,2,3,7,8,9-HxCDF   | 0.006                     | 0.008   | 0.005   | 0.006   | 0.750                   | 0.279   | 1.135    | 2.481    | 0.013                           | 0.016   | 0.022   | 0.055   |
| 1,2,3,4,6,7,8-HpCDF | 0.008                     | 0.010   | 0.024   | 0.039   | 5.878                   | 1.365   | 12.365   | 10.549   | 0.064                           | 0.050   | 0.217   | 0.250   |
| 1,2,3,4,7,8,9-HpCDF | 0.007                     | 0.005   | 0.005   | 0.009   | 0.000                   | 0.144   | 0.576    | 1.388    | 0.007                           | 0.009   | 0.014   | 0.037   |
| OCDF                | 0.010                     | 0.012   | 0.022   | 0.029   | 8.568                   | 3.018   | 28.062   | 22.085   | 0.091                           | 0.101   | 0.459   | 0.471   |
| 2,3,7,8-TCDD        | 0.000                     | 0.001   | 0.004   | 0.006   | 0.061                   | 0.053   | 0.000    | 0.390    | 0.001                           | 0.003   | 0.004   | 0.014   |
| 1,2,3,7,8-PeCDD     | 0.000                     | 0.000   | 0.008   | 0.029   | 0.467                   | 0.182   | 1.334    | 2.209    | 0.004                           | 0.005   | 0.029   | 0.073   |
| 1,2,3,4,7,8-HxCDD   | 0.003                     | 0.007   | 0.001   | 0.003   | 0.458                   | 0.114   | 0.750    | 2.304    | 0.008                           | 0.010   | 0.013   | 0.050   |
| 1,2,3,6,7,8-HxCDD   | 0.001                     | 0.004   | 0.004   | 0.036   | 0.380                   | 0.318   | 1.528    | 1.340    | 0.005                           | 0.013   | 0.028   | 0.063   |
| 1,2,3,7,8,9-HxCDD   | 0.006                     | 0.004   | 0.005   | 0.020   | 1.684                   | 0.276   | 0.981    | 3.599    | 0.022                           | 0.012   | 0.020   | 0.092   |
| 1,2,3,4,6,7,8-HpCDD | 0.077                     | 0.061   | 0.072   | 0.493   | 27.966                  | 10.314  | 41.685   | 46.422   | 0.343                           | 0.363   | 0.721   | 1.422   |
| OCDD                | 0.747                     | 0.662   | 1.521   | 1.539   | 1582.485                | 543.766 | 2032.866 | 3149.886 | 15.780                          | 16.603  | 33.189  | 64.537  |
| Σ2,3,7,8-PCDD/Fs    | 0.911                     | 0.809   | 1.737   | 2.324   | 1638.981                | 562.407 | 2135.575 | 3259.485 | 16.480                          | 17.296  | 35.005  | 67.514  |
| ΣI-TEQ              | 0.009                     | 0.009   | 0.020   | 0.050   | 4.411                   | 1.320   | 5.930    | 8.943    | 0.019                           | 0.012   | 0.050   | 0.075   |
| Total TCDF          | 0.211                     | 0.184   | 0.937   | 0.652   | 24.802                  | 6.829   | 29.887   | 18.617   | 0.446                           | 0.384   | 1.402   | 1.025   |
| Total PeCDF         | 0.072                     | 0.112   | 0.331   | 0.262   | 28.675                  | 8.475   | 51.538   | 23.158   | 0.344                           | 0.360   | 1.133   | 0.725   |
| Total HxCDF         | 0.359                     | 0.241   | 0.137   | 0.244   | 19.948                  | 4.580   | 18.832   | 17.744   | 0.549                           | 0.376   | 0.431   | 0.599   |
| Total HpCDF         | 0.151                     | 0.163   | 0.104   | 0.134   | 18.000                  | 3.095   | 21.443   | 17.732   | 0.322                           | 0.254   | 0.439   | 0.488   |
| OCDF                | 0.010                     | 0.012   | 0.022   | 0.029   | 8.568                   | 3.018   | 28.062   | 22.085   | 0.091                           | 0.101   | 0.459   | 0.471   |
| Total TCDD          | 0.040                     | 0.037   | 0.198   | 0.327   | 5.185                   | 2.060   | 9.959    | 3.973    | 0.089                           | 0.097   | 0.353   | 0.407   |
| Total PeCDD         | 0.088                     | 0.060   | 0.142   | 0.229   | 9.637                   | 2.808   | 11.616   | 6.659    | 0.180                           | 0.142   | 0.323   | 0.362   |
| Total HxCDD         | 0.091                     | 0.079   | 0.146   | 0.394   | 21.063                  | 5.465   | 39.848   | 28.757   | 0.291                           | 0.239   | 0.766   | 0.969   |
| Total HpCDD         | 1.546                     | 1.110   | 0.656   | 0.786   | 83.186                  | 31.687  | 128.285  | 113.703  | 2.336                           | 2.039   | 2.654   | 3.060   |
| OCDD                | 0.747                     | 0.662   | 1.521   | 1.539   | 1582.485                | 543.766 | 2032.866 | 3149.886 | 15.780                          | 16.603  | 33.189  | 64.537  |
| Σ PCDD/Fs           | 3.315                     | 2.659   | 4.193   | 4.596   | 1801.549                | 611.783 | 2372.337 | 3402.315 | 20.428                          | 20.594  | 41.150  | 72.642  |

<sup>a</sup> Average concentrations of upper, middle and bottom layers of water; layer definitions see Table 1.

<sup>b</sup> Summation of concentration in water and SPM.

Table 3  
PCDD/Fs concentrations in waters, SPMs and sediments at different sites of the world

| Samples type         | Location                   | Concentration                                      | TEQ                      | References                               |      |
|----------------------|----------------------------|--|--------------------------|--|------|
| Water (pg/L)         | Baltic Sea                 | 0.12   | 0.001 <sup>a</sup>       | [11]                                     |      |
|                      | River Elbe, Germany        | Bunthaus Streams                                   | 0.211                    | 0.004 <sup>a</sup>                       | [12] |
|                      |                            | Blankenese Streams                                 | 0.275                    | 0.017 <sup>a</sup>                       |      |
|                      | Hudson River, NY           | 2.35   | 0.017 <sup>a</sup>       | [13]                                     |      |
|                      | Houston Ship Channel, TX   | 0.99–69.13   | 0.01–0.25 <sup>b</sup>   | [14]                                     |      |
|                      | Lake Rotorua, North Island | Lake zones   |                          | nd–1.6 <sup>a</sup>                      | [10] |
|                      |                            | Utuhina upstream and downstream<br>Puarenga Stream |                          | 1.2–1.3 <sup>a</sup><br>5.4 <sup>a</sup> |      |
| Xijiang River, China |                            | 2.659–4.596  | 0.009–0.050 <sup>a</sup> | This study                               |      |
| SPM (pg/g)           | Baltic Sea                 | 0.23 <sup>c</sup>                                  | 0.0018 <sup>a,c</sup>    | [11]                                     |      |
|                      | River Elbe, Germany        | Bunthaus Streams                                   | 6440                     | 73 <sup>a</sup>                          | [12] |
|                      |                            | Blankenese Streams                                 | 2970                     | 41 <sup>a</sup>                          |      |
|                      | Hudson River, NY           | 5430   | 33 <sup>a</sup>          | [13]                                     |      |
|                      | Houston Ship Channel, TX   | 11.28–392.74 <sup>c</sup>                          | 0.09–2.91 <sup>b,c</sup> | [14]                                     |      |
| Xijiang River, China | 611.8–3402.3               | 1.320–8.943 <sup>a</sup>                           | This study               |  |      |
| Sediment (pg/g)      | Taihu Lake, China          | 120.1–1315.1                                       | 2.0–16.6 <sup>b</sup>    | [15]                                     |      |
|                      | Hyeongsan River, Korea     | 4.8–1600   | 0.38–1037 <sup>b</sup>   | [16]                                     |      |
|                      | Detroit River, Canada      |  | 1.02–284 <sup>b</sup>    | [5]                                      |      |
|                      | Houston Ship Channel, TX   |  | 0.9–139.8 <sup>b</sup>   | [14]                                     |      |

<sup>a</sup> I-TEQ.

<sup>b</sup> WHO-TEQ (1998).

<sup>c</sup> pg/L.

I-TEQ values were 1.320–8.943 pg/g (mean = 5.151 pg/g). Thus, the concentrations in SPM were much higher than those in the water samples. However, the PCDD/Fs concentrations in SPM from the Xijiang River were lower than those from Bunthaus and Blankenese Streams. Their total PCDD/Fs were 6440 pg/g and 2970 pg/g, with I-TEQ values of 73 pg/g and 41 pg/g, respectively [12]. They were also much lower than those from Hudson River, NY with 5430 pg/g (33 pg I-TEQ/g) [13]. Compared with PCDD/Fs in the sediments, I-TEQ values of SPM in the Xijiang River were also lower (Table 3).

### 3.2. Seasonal variation of PCDD/Fs in the Xijiang River

Both in water and SPM, the highest concentration of total PCDD/Fs occurred in wet season (06/2006) samples and the lowest in dry season (12/2005) samples, which indicates that pollution is more serious in the wet season in the Xijiang River (Fig. 2). Heavy wet deposition and runoff in the summer may be the best explanation for this seasonal change.

Fig. 3a illustrates that the water samples collected in the dry season were characterized by a high percentage of HpCDD and OCDD, which accounted for 46.63–41.73% and 22.55–24.89% of the total PCDD/Fs. The relative abundances of these two homologues in wet season samples were reversed: OCDD and HpCDD composed 36.27–33.49% and 15.64–17.69% of the total PCDD/Fs, respectively. For PCDFs, HxCDF and HpCDF in wet season samples were lower than that in the dry season. The changes of contribution of sources may bring this variation.

In contrast to water samples, SPM samples did not exhibit this seasonal variation. OCDD was the most prevalent compound in the samples from all seasons (Fig. 3b), constituting

85.69–92.58% of total PCDD/Fs. HpCDD was the second most prevalent homologue, making up 5% of total PCDD/Fs.

Fig. 4 shows the relative I-TEQ contributions of 2,3,7,8-substituted PCDD/F congeners to the total I-TEQ in water and SPM samples. Seasonal changes are obvious in water (Fig. 4a). In September 2005 (dry season), 1,2,3,4,7,8-HxCDF and 2,3,4,7,8-PeCDF were the dominant I-TEQ contributors, which accounted for 22.38% and 18.19%, respectively. And the prevalent contributors were 2,3,4,7,8-PeCDF (26.98%)

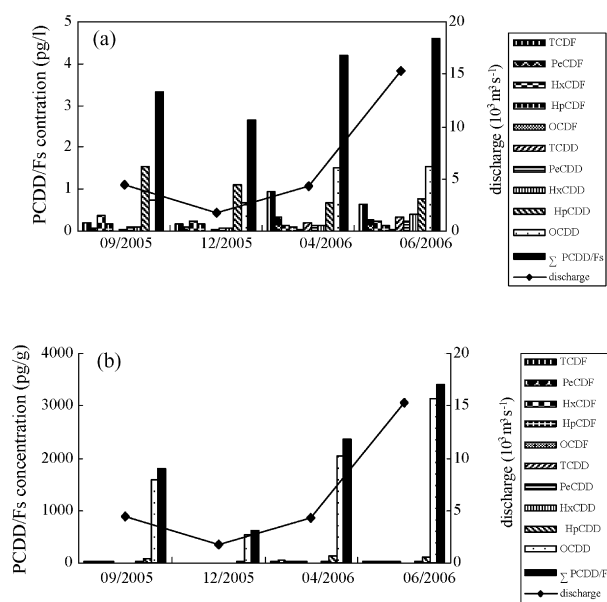


Fig. 2. The concentration of PCDD/Fs in water (a), SPM (b). Seasonal discharges of the Xijiang River are labeled with closed diamonds.

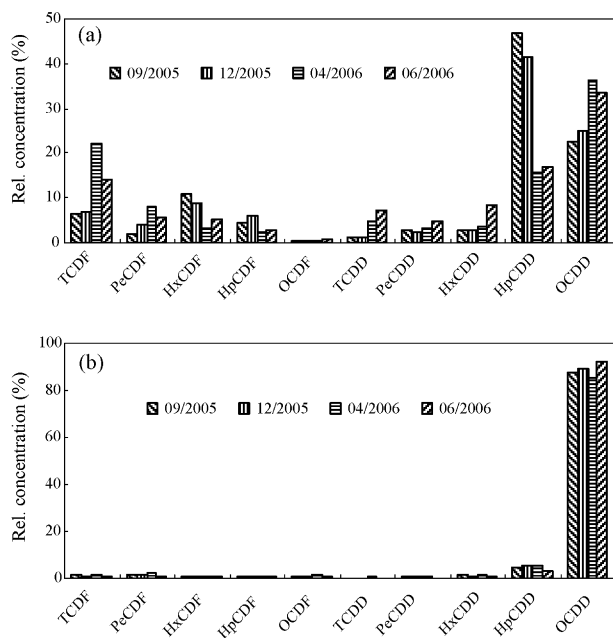


Fig. 3. Relative abundances of PCDD/F homologues in water (a) and SPM (b) of the Xijiang River.

and 2,3,7,8-TCDD (15.72%) in December 2005 (dry season). Whereas 1,2,3,7,8-PeCDD (20.24% and 25.17%) and 2,3,7,8-TCDD (18.83% and 14.06%) were major I-TEQ providers in April and June 2006 (wet season). For the SPM samples (Fig. 4b), in both wet and dry seasons, OCDD was the most prevalent I-TEQ contributor, constituting 37.24%, 41.58%, 34.93% and 35.94% of total I-TEQ. 2,3,4,7,8-PeCDF was the

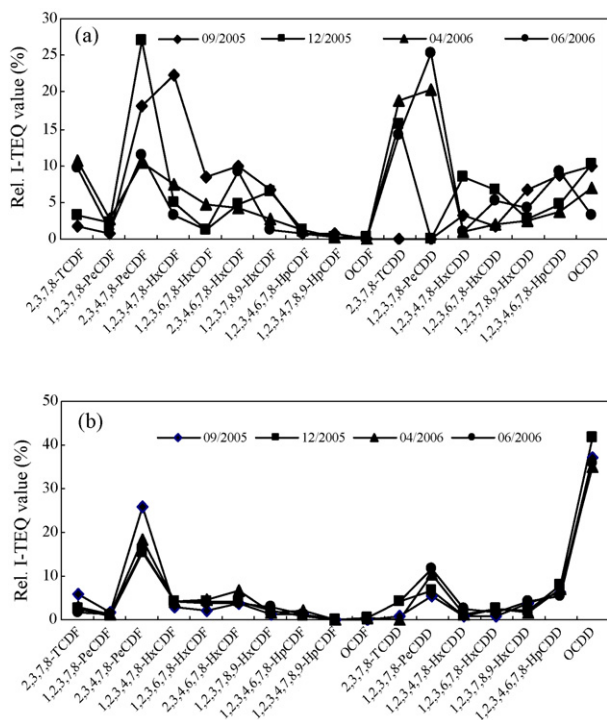


Fig. 4. The contribution of 2,3,7,8-substituted congeners to the total I-TEQ in the Xijiang River. (a) Water and (b) SPM.

second major I-TEQ contributors which accounted for 25.91%, 15.59%, 18.27% and 15.76% of total I-TEQ, respectively.

### 3.3. Possible sources of PCDD/Fs in the Xijiang River

PCDD/Fs in rivers mainly derive from industrial effluents, soil runoff, and atmospheric deposition of combustion products. The Xijiang River covers a large area with many cities in southern China, thus all three of these sources are potential contributors to the PCDD/Fs in the samples.

The homologue and congener profiles of PCDD/Fs often are characteristic of pollutant sources and can be used to identify them [1,17–20]. In the Xijiang River, the most obvious features are the high contribution of OCDD to the total PCDD/F concentration and the relatively low levels of PCDFs. Sediments and soils are sinks of PCDD/Fs. OCDD is the most resistant congener against degradation. Therefore, most of soils and sediments show similar pattern. Similar congener profiles were reported for sediment samples from Mississippi, USA [21] and from Hong Kong [22]. Similarly, soil samples from Guangzhou [23] and Hong Kong's New Territories [4] also contained this "OCDD abnormality". Therefore, high OCDD concentrations in the Xijiang River may be attributable to the input of soil runoff. It was a dominant source of PCDD/Fs in Xijiang River. The high percent of OCDD in soil was described to derive from the photolysis and biodegradation of PCDD/Fs deposition in soil [24,25] or from the impurities of sodium pentachlorophenate (PCP-Na) and PCPs [26] which were widely used as pesticides of wood preservatives in China. The photochemical synthesis from PCP may also give rise to the high concentration OCDD in soil [20].

The homologue profiles of PCDD/Fs in atmospheric deposition reported by Ren et al. [23] in Guangzhou are characterized by increasing concentrations of PCDDs with an increasing degree of chlorination and decreasing concentrations of PCDFs with an increasing degree of chlorination. The profile shape looks like a letter "V", and 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were the important contributors to the total I-TEQ. In our study of the Xijiang River, Figs. 3 and 4 show strong similarities between atmospheric deposition [23] and water during the wet season for tetra to hepta CDD/Fs, indicating that atmosphere deposition may be a source for low chlorinated PCDD/Fs. PCDD/Fs in atmospheric depositions were reported to originate from general combustion of fossil fuels, for examples, coal and gasoline [23].

Industrial effluents, especially those from paper pulp mills, contain PCDD/Fs with a high ratio of PCDDs over PCDFs. For example, Zheng et al. [27] reported that HpCDD was the most abundant homologue in chlorine bleaching waste water. There are many paper mills in cities of Liuzhou and Nanning in Guangxi province where Xijiang River flows through. For example, Liujiang paper mill is the greatest paper factory in Guangxi province, and annual product of paper pulp was 0.4 million ton which will reach 1 million ton in 2010 [28]. The high concentration of HpCDD in our water samples collected during the dry season might be attributable to industrial input (Fig. 3).

Seasonal variation in PCDD/F concentrations provides evidence for above PCDD/Fs sources in the Xijiang River. In the wet

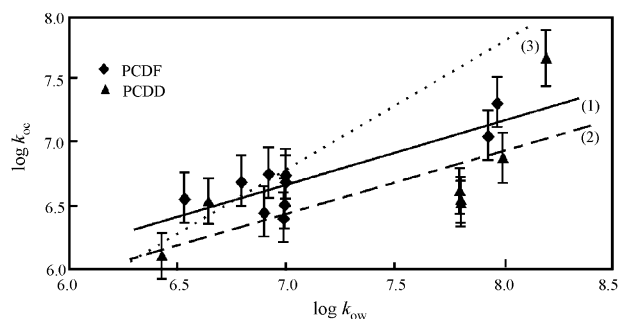


Fig. 5. Relationship between  $\log K_{oc}$  and  $K_{ow}$  for 2,3,7,8-substituted PCDD/Fs. The values of  $\log K_{ow}$  from Doucette and Andren [31]; Shiu et al. [32]; Sijm et al. [33]; Broman et al. [11]; Mackay et al. [34]; and Rantalainen et al. [35]. (1) Ten 2,3,7,8-substituted PCDFs; (2) seven 2,3,7,8-substituted PCDDs; (3) the predicted value of the equation reported by Karickhoff et al. [30].

season, large amount of runoff brings soil PCDD/Fs and atmospheric depositional PCDD/Fs into the river, and the PCDD/Fs in the water phase are dominated by OCDD and a normal V-type distribution (Fig. 3). In the dry season, less runoff occurs and the homologue profiles in the water phase show mixed features of industrial effluent, atmospheric deposition, and soil (e.g., a complicated homologue distribution and higher HpCDD (Fig. 3)). These results show that PCDD/Fs in water are mixtures of three sources but that the proportion contributed by each source changes seasonally.

### 3.4. Partition between SPM and water

Table 1 lists the basic data from the samples collected in this study. The DOC concentrations of water collected during the dry season were a little higher than those collected during the wet season. DOC did not correlate well with total PCDD/Fs concentration, possibly due to the relatively constant DOC concentration in the samples (1.09–1.64 mg/L). The same phenomenon was observed in the Baltic Sea [11]. However, POC concentrations were much higher than DOC concentrations and showed a better correlation with the total PCDD/F concentration ( $R^2 = 0.6$ ). This finding is consistent with the explanation that the capacity of particles to sorb hydrophobic organic chemicals (HOCs) in water is related to their fraction of organic carbon [29].

We calculated particulate-water partition coefficients ( $K_p$ ) and particulate organic carbon partition coefficients ( $K_{oc}$ ) from the data in Tables 1 and 2. As shown in Fig. 5, a sufficiently good correlation exists between  $\log K_{oc}$  and  $\log K_{ow}$  for the 2,3,7,8-substituted congeners, with the correlation equations  $\log K_{oc} = 0.498 \log K_{ow} + 2.948$  ( $R^2 = 0.51$ ) (line 2) and  $\log K_{oc} = 0.503 \log K_{ow} + 3.137$  ( $R^2 = 0.70$ ) (line 1) for PCDDs and PCDFs, respectively. Clearly,  $\log K_{oc}$  from our study is not consistent with the predicted value of the equation,  $\log K_{oc} = \log K_{ow} - 0.21$  (line 3) [29]. Compared with the  $K_{oc}$  values for Bunthaus and Blankenese Streams of the Elbe River and the Baltic Sea,  $K_{oc}$  in the Xijiang River is lower. Recent studies showed that nature organic matter is very complex and may differ locally [35]. This may explain  $K_{oc}$  differences in the rivers.

### 3.5. Annual loading of PCDD/Fs

Daily loadings for each PCDD/Fs were estimated by multiplying the chemical concentrations by the measured daily river flow [36]:

$$L_i = Q \times C_i \times n$$

where  $L_i$  is the calculated load for PCDD/F  $i$  (g/day),  $Q$  is the daily average river discharge rate ( $m^3/s$ ),  $C_i$  is the concentration of PCDD/F  $i$  (pg/L), and  $n$  is the constant conversion factor ( $0.0864 L s g/m^3 day ng$ ). The data for daily water discharge rate were collected from Gaoyao Hydrological Station.  $C_i$  included PCDD/F concentrations in water and SPM. For each season, the concentrations for each day were assumed to be equal to the concentrations measured on the sampling day. According to this assumption, daily loading were tentatively calculated. The annual loading was the sum of the daily loading.

Based on the calculation, the annual loading for total PCDD/Fs, 2,3,7,8-chlorine substituted PCDD/F, and I-TEQ are 8.55 kg, 7.74 kg, and 0.026 kg, respectively.

## 4. Conclusions

The composition and distribution of PCDD/Fs in the Xijiang River varied seasonally. Higher PCDD/F concentrations occurred in summer; lower in winter. Compared with PCDD/F concentrations in other rivers of the world, the Xijiang River exhibited lower concentrations.

The PCDD/Fs in the Xijiang River derived from soil runoff, atmospheric deposition, and industry sewage, although those from soil were dominant. The proportion contributed by the three sources varied temporally due to large seasonal differences in water discharge.

A sufficiently good correlation existed between  $\log K_{oc}$  and  $\log K_{ow}$  for 2,3,7,8-substituted PCDD/F congeners, indicating organic matter in SPM played a dominant role in PCDD/Fs partition between SPM and water.

The annual loadings for total PCDD/Fs, 2,3,7,8-chlorine substituted PCDD/Fs, and I-TEQ were 8.55 kg, 7.74 kg and 0.026 kg, respectively.

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