### **RESEARCH ARTICLE**

# PCB contamination in soils of the Pearl River Delta, South China: levels, sources, and potential risks

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Abstract Polychlorinated biphenyls (PCBs) contamination in tropical and sub-tropical areas and the associated risks have attracted great concern. A total of 69 samples representing five distinct land types were collected to assess PCB concentrations in the Pearl River Delta (PRD), South China, including spatial distributions in soils of the area, the probable anthropogenic sources, and related potential risks. PCBs concentrations in soils of the PRD ranged from 0.3 to  $202 \text{ ngg}^{-1}$ . More severe PCBs contamination was presented in the western part than in the eastern part of the PRD region. The PCBs were dominated by low-chlorinated biphenyls; however, the proportion of higher-chlorinated biphenyls was elevated with the influence of industrial activities. Principal component analysis indicated that PCBs contamination in soils of the PRD region was mainly associated with 1#PCBs, while 2#PCB and ewaste emission in South China also accounted for it partly, especially to the industrial activity severely impacted areas. Toxic equivalent (TEQ) of the dioxin-like PCBs in the soils indicated that higher risk of PCB contamination was presented in the Dongjiang River Valley (55 ngTEQkg<sup>-1</sup>, on average) than in the Xijiang River Valley, and were mostly contributed by the congener of PCB126.

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Guangdong Institute of Eco-environment and Soil Science, Guangzhou 510650, China **Keywords** Dioxin-like PCBs · Anthropogenic sources · Contamination · Soil

## Introduction

Polychlorinated biphenyls (PCBs) have been used commercially since 1930 as dielectric and heat-exchange fluids in electronic products (capacitors, transformers, etc.) and a variety of other applications (Breivik et al. 2002). In China, approximately 10,000 t of PCBs were produced from 1965 to 1974 (production of PCBs was banned in 1974), with 9,000 t as trichlorobiphenyl and 1,000 t as pentachlorobiphenyl (Xing et al. 2005). Soil is an important reservoir for many persistent organic pollutants (POPs) including PCBs. About 93 % of the estimated UK environmental burden of PCBs was associated with soils (Harrad et al. 1994). Globally, approximately 21,000 t of PCBs have been discharged into surface soils (Meijer et al. 2003). Although the major PCB pollution is found between 30° and 60° north latitude, PCBs have been manufactured and used largely in tropical and sub-tropical zones (Erickson and Kaley 2011; Wilcke et al. 1999), and it is still being produced unintentionally by electronic waste processing in the developing nations such as China, Malaysia, India, Kenya, and various African countries (Wong et al. 2007). In tropical and sub-tropical zones, where temperatures and rainfall levels are higher than those in the temperate areas, the rapid dissipation of PCBs through air transport and water runoff may lead to a global scale environmental contamination (Thao et al. 1993). The spatial distribution of PCBs in soils is related with human activities and economic development as well (Meijer et al. 2003). It has been recognized that PCB concentrations in Chinese surface soils decreased from east to west (Ren et al. 2007; Xing et al. 2005), which corresponds to the higher level of economic development and population density in east than in west China. We have

investigated PCB distribution in soils of Hong Kong and observed higher PCBs concentrations coupled with diverse PCB congeners in urban areas than in rural areas (Zhang et al. 2007). The risks associated with PCB contamination, especially dioxin-like PCBs, have been discussed widely (Ahlborg et al. 1994; Hedley et al. 2006; Shen et al. 2009). It was assumed that the dioxin-like PCBs bind to the Ah-receptor and produce dioxin-like effects in organisms (Ahlborg et al. 1994). Therefore, the concept of toxic equivalent (TEQ) has been introduced to simplify risk assessment and regulatory control. The TEQ approach has been used to assess the toxic risk associated with mixtures of PCB congeners measured in environmental and biota samples and food stuff in big cities such as Beijing (Wu et al. 2011) and Hong Kong (Hedley et al. 2006) and e-waste recycling sites like Taizhou of Zhejiang province in China (Shen et al. 2009; Xing et al. 2011).

PCB contamination in the Pearl River Delta (PRD) region was mainly concentrated in the sediment and water (Kang et al. 2000; Mai et al. 2005; Yang et al. 1997). However, no study has focused on soil contamination, although soil has been assumed to represent a major source of the PCB contamination of local water bodies (Mai et al. 2005). In addition, exposure of contaminated soil might cause toxic effects to humans and ecological systems. The main objectives of this paper are to cover an important gap in the literature regarding PCB contamination in soils of the PRD region, to identify the possible sources and make a risk assessment for PCB contamination in the soils.

#### Materials and methods

# Study area

The PRD is located on the southeast coast of China at the south edge of the subtropical area. With a total land area of 25,000 km<sup>2</sup> and a population of 42 million, it is the second most populous area in China and one of the most densely populated areas of the world. The PRD region is also one of the most economically prosperous regions in China, with an annual gross domestic product (GDP) increase rate of 16.9 % in comparison with 9.6 % for the nation in the past decade. Electronics, electrical machines, and petrochemicals dominate the local industrial structure, cumulatively accounting for over 50 % of the local industry (ISIC 2005). These industrial activities were assumed to be the main sources of environmental pollution (Kang et al. 2000; Mai et al. 2005; Nie et al. 2006).

The PRD region, which is formed by three major rivers, the Xijiang, Beijiang, and Dongjiang, is surrounded by highly developed, metropolitan cities including Guangzhou, Shenzhen, Dongguan, Foshan, Zhongshan, Zhuhai, Jiangmen, and parts of Huizhou and Zhaoqing. The climate of the area is characterized by high humidity and temperature, with annual average precipitation of 1,800 mm and annual average temperature of 22 °C. The soil is highly weathered in highland areas and waterlogged in flat terrain. Ferralsol and Anthrosols are the two dominant soil types based on the FAO World Reference Base for Soil Resources (IUSS Working Group WRB. 2006). As presented in Table 1, soils in the PRD region are acid to neutral, and the soil organic matter content is high in paddy fields and orchards but comparatively low in uncultivated land.

### Soil sampling and analysis

A total of 69 topsoil (0–20 cm) samples covering paddy fields, vegetable lands, orchards, woodland, and uncultivated land were taken from the whole territory (Fig. 1). Samples were collected using a clean stainless steel spade, placed in solvent-rinsed brown grass bottles with Teflon caps, and transported to laboratories at the Institute of Soil Science, Chinese Academy of Science in Nanjing where they were stored frozen (–20 °C) until analysis. The samples were freeze-dried, grounded, and sieved to less than 2 mm prior to extraction. Separate samples were analyzed for pH, soil organic matter (SOM) content, cation-exchange capacity (CEC), and soil particle-size composition. The analysis of these soil properties was based on the methods of Lu (2000).

#### Sample extraction and cleanup

Details of the method for sample extraction and cleanup can be found in Zhang et al. (2011). Briefly, 7.5 g of freeze-dried soil sample, together with 35 mL mixed solvent (20 mL nhexane, 10 mL methanol, and 5 mL deionized water) were added to the extraction vessel and extracted in an ultrasonic bath for 1 h. 2,4,5,6-Tetrachloro-m-xylene was spiked into the sample as a surrogate standard to examine the matrix effect prior to extraction. The extraction procedure was repeated once after adding an additional 20 mL n-hexane to the residue. The two collections were then combined, anhydrous sodium sulfate was added for drying, and then the extraction mixture was concentrated to around 1 mL by rotary evaporation. The concentrated extracts were purified through a silica gel column (6 g) with a layer of 0.5 g Na<sub>2</sub>SO<sub>4</sub> at the top. The silica gel had been activated at 135 °C for 16 h, and the Na<sub>2</sub>SO<sub>4</sub> had been oven-dried at 400 °C for 4 h before using. The silica gel column was eluted with 7 mL n-hexane, and the eluate was concentrated to 1 mL. The solution was finally concentrated to around 100 µL under a gentle stream of pure nitrogen. Ten microliters of the internal standard (pentachlorotoluene,  $1 \text{ mgL}^{-1}$ ) was added to the purified extract prior to transferring to a glass microvial for gas chromatographic (GC) analysis

# PCB analysis

PCB congeners (8, 18, 28, 44, 52, 66, 77, 101, 118, 126, 128, 138, 153, and 200) were analyzed using a Hewlett-Packard 6890 GC equipped with a <sup>63</sup>Ni electron capture detector-µECD (Agilent Technology Co., USA) under the splitless mode. The solution was chromatographed on a 30-m×0.32-mm i.d. HP-5 capillary column with a film thickness of 0.25 µm at a pressure of 50 kPa. High purity (99.99 %) helium was used as the carrier gas at 2.7 mLmin<sup>-1</sup> and nitrogen as the make-up gas at 54.4 mLmin<sup>-1</sup>. The oven temperature was set at 60 °C for 1 min, from 60 °C to 170 °C at 25 °Cmin<sup>-1</sup>, from 170 °C to 190 °C at 4 °Cmin<sup>-1</sup>, from 190 °C to 270 °C at 10 °Cmin<sup>-1</sup>, and then at 270 °C for 5 min. The injector and detector were set at 220 °C and 270 °C, respectively. The chromatographs were recorded and analyzed by using HP ChemStation software. The quantification was obtained using the internal standard calibration curve method according to the US-EPA method 8000b.

# Quality control

Method detection limits (MDLs) was calculated based on the US-EPA method for quality control. Briefly, seven replicate spikes containing the target PCB compounds at a concentration of five times estimated MDL were measured, and the standard deviation of the seven measured data was obtained. The MDL was then calculated by multiplying the appropriate one-sided 99 % *t*-statistic by the standard deviation. The MDLs of PCB congeners ranged from 0.02 to 0.10  $ngg^{-1}$ . Blank samples in each extraction batch of the samples were performed throughout all the experiments, and the target PCB compounds were not detected. The matrix spike recovery rates have been assessed by spiking the mixed standard with known amounts of the 14 PCB congeners into a soil before extraction as reported by Zhang et al. (2007). Three

Table 1 Soil properties of the Pearl River Delta region

replicates were measured for each PCB congener. Average percentage recovery and relative standard deviation for the individual selected PCB congeners ranged from 74.6 % to 102.3 % and from 2.9 % to 13.4 %, respectively. The recovery of 2,4,5,6-tetrachloro-*m*-xylene surrogate in all samples was within the range of 78.9–110.7 %.

Calculation of TEQ for dioxin-like PCBs

The TEQ values were calculated using the measured dioxinlike PCB concentrations and WHO 2005 TEF values (toxic equivalency factors) for human and mammals (Van den Berg et al. 2006). The calculation was carried out using Eq. 1:

$$TEQ = TEF \times C_i \tag{1}$$

in which  $C_i$  was the concentration (nanograms per gram) of the *i*th PCB congener in the soil, and *i* was the IUPAC No. of PCB congener.

# Statistical analysis and spatial interpolation

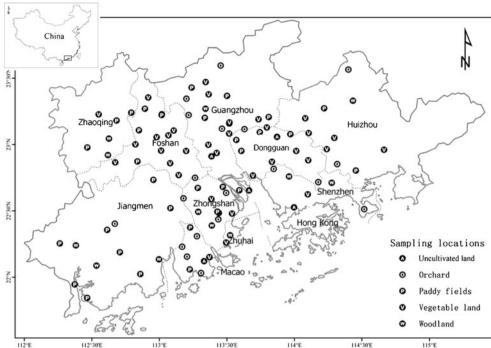
Principal component analysis (PCA) was performed using the SPSS 11.0 for Windows software package. All available data including the PCB concentration data, congener composition of Aroclor commercial mixtures (1016, 1242, 1248, and 1254), and PCB concentration of a reference soil from an e-waste burning site was firstly standardized by *Z*-score method prior to PCA analysis. The principal components were considered if their Eigenvalues were >1. The method of Varimax with Kaiser Normalization was selected for rotation in the PCA analysis, and five iterations were performed. The scores of principal factor 1 and 2 for each sample and Aroclor mixtures were plotted to identify the possible source. Spatial interpolation was conducted using Surfer 8.0 (Golden Software Inc., Golden, CO, USA) by the kriging method.

Land using	Ν	рН (H <sub>2</sub> O)	SOM	CEC	Soil texture (% volume)		
			g/kg	cmol/kg	Sand	Silt	Clay
Paddy fields	26	5.3 (3.5-8.1)	37.0 (16.5-65.3)	15.7 (7.5–24.8)	23.5 (15.3–38.3)	54.3 (51.7-64.3)	22.1 (14.7–31.2)
Vegetable land	20	6.3 (4.3-7.7)	21.2 (11.3–34.1)	13.8 (5.7–22.2)	35.1 (10.7–59.4)	45.5 (31.1-59.8)	19.6 (9.6-26.5)
Orchard	12	5.5 (4.1-7.4)	30.1 (20.3-43.9)	16.2 (9.0-22.9)	2.1	68.6	29.2
Woodland	6	4.7 (4.3–5.1)	24.7 (13.2-41.0)	11.0 (6.9–16.1)	80.9	13.6	5.5
Uncultivated land	5	7.1 (6.0-8.3)	13.9 (2–22.5)	12.3 (3.1–21.2)	86.0	10.6	3.4

Data are indicative of mean (minimum-maximum)

SOM soil organic matter, CEC cation exchange capacity

**Fig. 1** Map of soil sampling locations in the Pearl River Delta region. *Circled letters* in the graph means the sampling sites with various land using types



5153

# **Results and discussions**

Levels and spatial distributions of PCBs in soils of the PRD region

PCBs were detected ubiquitously in soils of the PRD region. Table 2 shows statistical summary of the PCB concentrations. Total concentrations of the 14 PCBs congeners ranged from 0.3 to 202  $ngg^{-1}$ , with an average of 18.4  $ngg^{-1}$ . Two maps with raw data of PCBs concentrations (Fig. 2a) and soil

organic matter (SOM) content normalized PCBs concentrations (Fig.2b) were used to show the spatial distribution of PCBs in soils of the PRD region, respectively.

As shown in Fig.2a, the highest PCBs concentration was found in the sample from Zhaoqing, and another sample with the total concentration higher than  $100 \text{ ngg}^{-1}$  was collected from Guangzhou, the largest industrial city in the PRD region. On average, relatively higher concentrations of PCBs were observed in the western part of the PRD region, especially at the borders between Foshan and Zhongshan and Jiangmen.

Table 2PCB concentration insoil of Pearl River Delta	PCBs	IUPAC number	MLD	Mean	Median	Minimum	Maximum	DR (%)
region (nanograms per gram)	Di-CBs	8	0.01	9.09	2.31	0.01	109.9	71.4
	Tri-CBs	18	0.05	3.54	2.30	0.08	10.2	37.1
		28	0.01	7.13	3.65	0.04	37.1	58.6
	Tetra-CBs	44	0.01	4.15	1.58	0.01	19.4	11.4
		52	0.01	4.25	1.84	0.01	24.1	47.1
		66	0.01	4.86	2.69	0.10	16.9	18.6
		77	0.01	1.36	0.60	0.05	8.55	22.9
	Penta-CBs	101	0.01	0.09	0.09	0.09	0.09	1.4
		118	0.02	2.32	1.22	0.03	18.3	18.6
$\Sigma$ 14PCBs indicates the total		126	0.02	0.90	1.00	0.06	2.33	11.4
concentration of all the 14 PCB	Hexa-CBs	128	0.02	3.56	0.81	0.10	12.5	5.7
congeners; $\Sigma$ 6PCBs indicates the sum concentration of PCB		138	0.10	2.72	0.70	0.16	9.75	25.7
28, 52, 101, 118, 138, and 153		153	0.05	0.28	0.27	0.14	0.41	5.7
congener that was detected by	Octa-CBs	200	0.02	0.73	0.33	0.03	3.73	30.0
European countries frequently	Σ14РСВ			18.4	9.25	0.30	202.0	94.3
<i>MLD</i> method limit of detection, <i>DR</i> detectable rate of PCB	Σ6PCBs			9.00	3.40	0.15	61.2	81.4

This spatial distribution of PCBs in soil is generally in agreement with PCB concentrations in the riverine runoff outlets, with slightly higher PCBs concentrations in the western outlets than in the eastern outlets (Guan et al. 2009). The spatial distribution of SOM-normalized PCBs concentration does not change greatly as compared to that in Fig. 2a. However, the extent of high PCBs level was reduced obviously as shown in Fig. 2b, which implied that some areas with high PCBs level were mainly caused by the high content of SOM in the soil. Those sites that showed a high PCBs level in both figures were assumed to be influenced by anthropogenic sources. Six indicator PCBs (PCB28, 52, 101, 118, 138, and 153) of European norm were detected in most surface soil samples. The average total concentration of the indicator PCBs ranged from 0.15 to  $61.2 \text{ ngg}^{-1}$ , with a mean of 9.0 ngg<sup>-1</sup> (Table 2). The PCBs concentrations in soils of the PRD region are comparable to those of the Yangtze River Delta region, a subtropical area rapidly economically developing in the east of China (Table 3). However the concentrations are much higher than those reported in other tropical areas, including Hong Kong (Zhang et al. 2007), Bangkok of Thailand (Wilcke et al. 1999), and even Guiyu, a famous e-waste recycling site in the South of China (Leung et al.

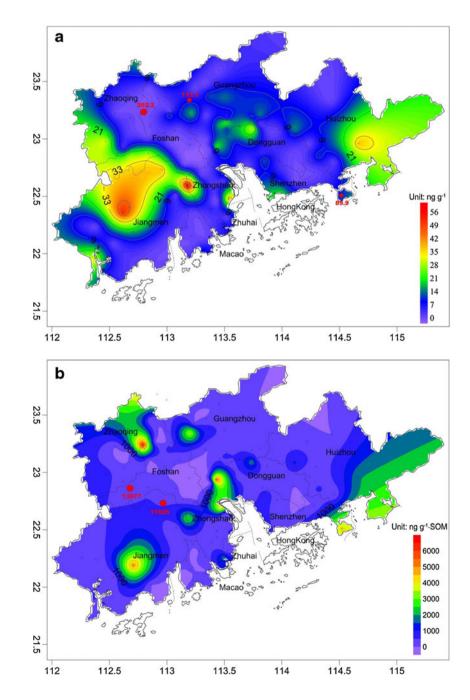


Fig. 2 Spatial distribution of total PCB concentrations (a) and SOM-normalized PCBs concentration (b) in the Pearl River Delta region. *Red solid circled and associated data* in the map represent the outlier values in the datasets, which have been excluded in spatial interpolation

2007). The PCBs concentration is also higher than those of the temperate regions (such as Beijing and Harbin; Ma et al. 2009; Wu et al. 2011) and the remote areas (such as Tibetan Plateau and Antarctic; Cabrerizo et al. 2012; Wang et al. 2012) that almost have not been influenced by industrial activities. This implied that the PRD region might still being a PCBs source to the temperate region and polar area regarding the global fractionation of POPs since the latter two regions tend to be accumulating POPs in the soils (Li et al. 2010; Meijer et al. 2003).

PCBs concentrations varied with land-use types. The highest mean concentration was found in paddy fields, followed by orchards and vegetable lands (Table 4). Woodland and uncultivated land had comparatively lower PCB concentrations in soils. Such a difference among the land types with respect to the PCB concentration was probably due to the impact of human activities (Zhang et al. 2007). On the other hand, soil properties might affect the distribution of PCBs in the soils. The variation in median value of the total PCB concentration with land type shows a similar trend with SOM content (Tables 1 and 4). However, statistically significant correlation between the total PCBs concentration and SOM content was not found.

# PCB sources as identified by congener patterns and PCA analysis

PCBs in soils of the PRD region were dominated by lowchlorinated biphenyls, such as di-, tri-, and tetrachlorobiphenyls in general. However, the relative proportions varied with sampling areas. PCB congener patterns in the different cities are summarized in Fig. 3. The sampling cities were divided into two groups based on the prevalence of industrial activity. The PCB patterns followed different trends in the two groups, especially for the highly chlorinated biphenyls (penta-, hexa-, and octa-chlorobiphenyls). Almost no highly chlorinated biphenyls were detected in the samples from areas only slightly influenced by industrial activity, while for the severely impacted cities such as Shenzhen, Guangzhou, and Zhongshan, the penta-, hexa-, and octa-chlorobiphenyls accounted for over 20 % of the total PCB concentration. It has been hypothesized that the more highly chlorinated congeners would remain closer to their source since they are less volatile, more strongly bound to soil particles, and therefore less readily susceptible to long-range atmospheric transport (LRAT) compared to their less highly chlorinated counterparts (Meijer et al. 2003). Therefore, the impact of local industrial activity on soil contamination by the PCBs was mainly displayed in a relatively high proportion of highly chlorinated PCB congeners.

The PCA method has been used widely to identify the sources of pollutant in soils and other environmental matrix (Hong et al. 2005; Zhang et al. 2007; Wu et al. 2011). Four principal components (PCs) with Eigenvalues >1 were extracted from the dataset, explaining 23.6 %, 17.4 %, 14.9 %, and 13.2 % of the total variance, respectively. Component 1 (PC1) contained the congeners of CB8, CB28, CB52, CB44, and CB66, all being recognized as low-chlorinated PCBs. While component 2 (PC2) contained the congeners of CB101, CB118, CB138, and CB153, characterized by highly chlorinated PCBs. As shown in Fig. 4, all the available samples can be classified into two groups generally. The first group locates in the bottom side of the plot, in which the most samples as well as Aroclor 1016, 1242, and 1248 are included. This implied that the source of the soil PCBs in this group were primarily associated with the above three Aroclor mixtures. Aroclor 1016 and 1242 were mainly dominated by tri-CB (54.67 % and 44.91 %, respectively; Frame et al. 1996), which was close to 1#PCB that had been produced and widely used in China. Guan et al. (2011) also identified that 1#PCB was the main source of PCBs contamination in riverine water of the outlets of the PRD region. The 1#PCB has been known to be mainly used

Study areas	Σ6PCBs of	conc. $(ngg^{-1})$	References		
	Mean	Median	Range		
PRD region, South China	9.00	3.40	0.15-61.2	This study	
Hong Kong, South China	2.5	0.5	0.07-9.9	Zhang et al. (2007)	
Guiyu, South China	-	-	6.0-31.5	Leung et al. (2007)	
Bangkok, Thailand	1.5	0.5	0.10-10.8	Wilcke et al. (1999)	
YRD region, East China	9.37	5.64	0.46-65.8	Zhang et al. (2011)	
Beijing, North China	3.10	3.15	n.d9.33	Wu et al. (2011)	
Harbin, North East China	0.42	0.36	0.11-1.19	Ma et al. (2009)	
Tibetan Plateau, North West China	0.14	0.137	0.024-0.31	Wang et al. (2012)	
Antarctic	0.031	0.017	0.003-0.22	Cabrerizo et al. (2012	
Dutch list, target value	20			VROM (2000)	

 Table 3
 Comparison of PCBs

 concentration in topsoil between
 the PRD region and other

 reported study areas
 the PRD region and other

PRD Pearl River Delta, YRD Yangtze River Delta **Table 4**PCB concentration(nanograms per gram) in thedifferent types of land use

Land use	Di-CBs	Tri-CBs	Tetra-CBs	Penta-CBs	Hexa-CBs	Octa-CBs	Σ14PCB
Paddy fields	( <i>n</i> =26)						
Mean	8.47	10.5	6.98	0.07	0.18	0.10	26.3
Median	2.75	10.5	1.76	0	0	0	16.6
Minimum	0	0	0	0	0	0	0.87
Maximum	104.5	37.1	60.4	1.56	4.58	0.63	202.0
SD	21.2	9.13	12.4	0.31	0.92	0.18	39.4
Vegetable la	nd ( <i>n</i> =20)						
Mean	7.69	1.21	1.79	0.49	1.01	0.22	12.4
Median	0.82	0	0.24	0	0	0	2.99
Minimum	0	0	0	0	0	0	0.30
Maximum	109.9	13.5	12.3	3.93	10.3	1.83	113.0
SD	24.3	3.11	3.61	1.21	2.56	0.48	24.7
Orchards (n=	=12)						
Mean	1.85	5.84	3.54	0.51	1.30	0.21	13.3
Median	1.12	3.70	0.91	0	0	0	9.64
Minimum	0	0	0	0	0	0	0.40
Maximum	6.66	29.7	29.19	3.12	8.28	1.24	59.0
SD	2.13	8.87	8.56	1.15	2.78	0.40	16.2
Woodland (n	<i>i</i> =6)						
Mean	0.04	0.03	0.06	0.44	7.00	1.94	9.50
Median	0	0	0.01	0.09	0.29	2.08	3.73
Minimum	0	0	0	0	0	0	0.64
Maximum	0.11	0.08	0.18	1.22	20.7	3.73	24.1
SD	0.06	0.05	0.10	0.68	11.9	1.87	12.8
Uncultivated	land $(n=5)$						
Mean	0.38	2.60	0.51	0.16	0.63	0	4.28
Median	0.07	2.38	0.10	0	0.29	0	3.74
Minimum	0	0	0	0	0	0	0.78
Maximum	1.39	5.63	1.84	0.63	1.95	0	8.86
SD	0.67	2.42	0.89	0.32	0.92	0	3.37

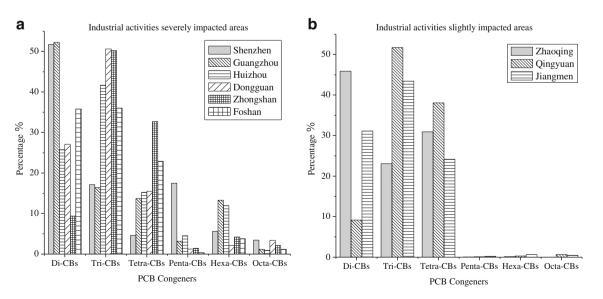
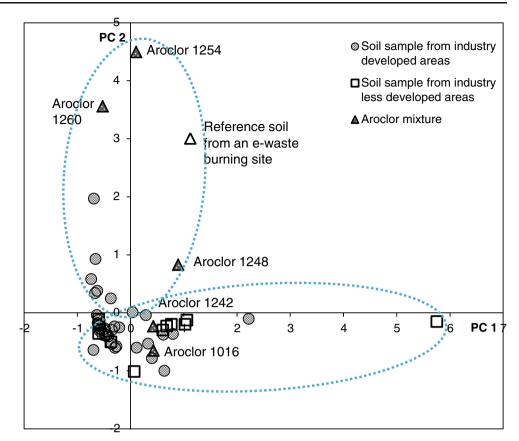


Fig. 3 Difference of soil PCBs patterns between the slight and strong industrial activities-influenced cities

**Fig. 4** Factor score scatter plot in soils of the PRD region, Aroclor mixture, and a reference soil sample from an e-waste recycling site. PC1 and PC2 account for 23.6 % and 17.4 % of the total variance, respectively



as Chinese transformer oil in China (Ren et al. 2007). The second group locates in the upper left side of the plot. Seven samples from Guangzhou, Shenzhen, and Huizhou that located in the northern and eastern parts of the PRD, as well as Aroclor 1248, 1254, and 1260, and the reference soil from an e-waste recycling site were included in this group. Aroclor 1248 and 1254 were dominated by penta-CB (42.3 % and 71.4 %, respectively; Frame et al. 1996), which was close to 2#PCB in China, which were used as an additive in paint, carbonless copy paper, cable insulation, etc. (Xing et al. 2005). In addition, unintentional emission of e-waste recycling in Qingyuan and Guiyu, Guangdong province also contributed to the PCBs contamination in the PRD region. Li et al.

(2011) have reported the transport behavior of PCBs released from an e-waste recycling site in South China.

Risk assessment for the soil contaminated by PCBs with TEQ method

Dioxin-like PCB congeners (CB77, 118, and 126) were identified in 22 of the 69 soil samples. In order to quantify the potential toxicity of PCBs in soils of the PRD, the TEQ method was adopted to estimate the human exposure and health risk via dietary intake of three dioxin-like congeners, which accounted for an average of 27.7 % of the total PCBs concentration. We compared the TEQ concentrations between

Congener	TEFs <sup>a</sup>	Dongjiang F	Dongjiang River basin (13) <sup>b</sup>			Xijiang River basin (9) <sup>b</sup>			
		Mean	Minimum	Maximum	Mean	Minimum	Maximum		
PCB77	0.0001	0.098	0.0	0.855	0.085	0.005	0.293		
PCB118	0.0001	0.220	0.0	1.825	0.018	0.000	0.156		
PCB126	0.1	54.6	0.0	232.8	0.000	0.000	0.000		
Σ3PCBs <sup>c</sup>		55.0	0.008	232.9	0.103	0.005	0.293		

Table 5 TEQ concentrations (nanograms per kilogram) of dioxin-like PCBs

<sup>a</sup> The source TEFs data was from Van den Berg et al. (2006)

<sup>b</sup> Data in parenthesis indicate sample numbers

<sup>c</sup> ∑3PCBs means the total TEQ concentration of PCB77, PCB118, and PCB126

the Dongjiang River Valley (including the cities of Guangzhou, Dongguan, Shenzhen, and Huizhou) and the Xijiang River Valley (including the cities of Foshan, Zhongshan, and Zaoqing; Table 5). The total TEQ concentrations ranged from 0.008 to 232.9  $ngkg^{-1}$ , with an average of 55  $ngkg^{-1}$  in soils of the Dongjiang River Valley. This concentration is much higher than that in the Xijiang River Valley, where total TEQ concentrations in the soils ranged from 0.005 to 0.293  $ngkg^{-1}$ , with an average of 0.103  $ngkg^{-1}$ . The mean total TEQ concentrations in soils of the Dongjiang River Valley were higher than the Canadian soil quality guideline of polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs; 4 ngTEQkg<sup>-1</sup>; CCME 2007). The TEQ concentration is relatively high when compared with the data reported in other study areas, such as Beijing (0.35  $ngkg^{-1}$ ; Wu et al. 2011) and Dalian  $(1.372 \text{ ngkg}^{-1}; \text{Wang et al. 2008})$ , and even an area near e-waste recycling sites from Taizhou, China  $(0.42-11 \text{ ngkg}^{-1}; \text{Shen et al. } 2009)$ . The high risk posed by soils of the Dongjiang River Valley was mainly contributed by the congener PCB126, which accounted for 99 % of the total TEQ concentration. In contrast, no soil sample was detected with PCB126 contamination in the Xijiang River Valley.

# Conclusion

PCBs contamination in soils of the PRD was relatively serious compared with other studied areas. A relatively higher PCBs level was found in the western part than the eastern part of the PRD region. The main source of PCBs was assumed to be primarily associated with 1#PCB that had been produced and widely used in China. Other sources such as 2#PCB and e-waste recycling emission also accounted for the PCBs contamination in the PRD region, especially to the industrial activity severely impacted areas. Calculation of TEQ for the dioxin-like PCBs in the soils showed that higher risk of PCBs contamination was presented in the Dongjiang River Valley (55 ngTEQkg<sup>-1</sup> on average) than in the Xijiang River Valley, and the congener of PCB126 was the predominant dioxin-like contaminant. A detailed risk assessment was suggested to be carried out on the contaminated soil in this region.

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