Polychlorinated biphenyls (PCBs) in sediments/ soils of different wetlands along 100-year coastal reclamation chronosequence in the Pear River Estuary, China

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Abstract: PCBs (polychlorinated biphenyls) were determined in sediment/soil profiles to a depth of 30 cm from three different wetlands (i.e., ditch wetlands, riparian wetlands and reclaimed wetlands) of the Pearl River Estuary to elucidate their levels, distribution and toxic risks along a 100-year chronosequence of reclamation. All detected PCB congeners and the total 15 PCBs ($\Sigma 15$ PCBs) decreased with depth along sediment/soil profiles in these three wetlands. The $\Sigma 15$ PCBs concentrations ranged from 17.68 to 169.26 ng/g in surface sediments/soils. Generally, old wetlands tended to have higher PCB concentrations than younger ones. The dominant PCB congeners at all sampling sites were light PCB homologues (i.e., tetra-CBs and tri-CBs). According to the sediment quality guideline, the average PCB concentrations exceeded the threshold effects level (TEL, 21.6 ng/g) at most of the sampling sites, exhibiting possible adverse biological effects, which were dominantly caused by light PCB congeners. The total toxic equivalent (TEQ) concentrations of 10 dioxin-like PCBs (DL-PCBs) detected at all sampling sites ranged from 0.04 to 852.7 (10^{-3} ng/g), mainly affected by PCB126. Only DL-PCB concentrations in ditch and riparian wetland sediments with 40-year reclamation histories (i.e., D40 and Ri40) exhibited moderate adverse biological effects according to SQGQ values. Principal component analysis indicated that PCBs in three wetland sediments/soils mainly originated from Aroclor 1016, 1242, and 1248. Correlation analysis showed that sediment/soil organic carbon content had a significant correlation with the concentrations of several PCB congeners ($P < 0.05$), whereas no significant correlations were observed between any PCBs congeners and grain size or aggregate

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content ($P > 0.05$).

Capsule: Old wetlands tended to have higher PCB concentrations than younger wetlands and higher toxicity risks of PCBs were found in riparian wetlands.

Key words: PCB congeners; wetland sediments/soils; dioxin-like PCBs; total toxic equivalent; reclamation chronosequence

1. Introduction

Polychlorinated biphenyls (PCBs) are the mixtures of 209 congeners that have been produced through direct chlorination of biphenyls since 1920; and they have been widely used in electronic appliances, heat transfer systems and hydraulic fluids (USEPA, 1996; Khawaja, 2003; Takasuga *et al.*, 2006; Liu *et al.*, 2008; Barrs *et al.*, 2004). PCBs have high toxicity, which can be divided into “dioxin-like” toxicity and “non-dioxin-like” toxicity, depending on the chlorination pattern (Baars *et al.*, 2004). Moreover, they pose a high risk to the environment and human health as the persistent and hydrophobic nature of PCBs could give rise to bioconcentration and biomagnification effects through food chains in the environment (Ritter *et al.* 1995; Lallas, 2001). Therefore, many countries prohibited the use of PCBs in public applications starting in the 1970s, and similar measures were incorporated by the Stockholm Convention, which aimed at protecting the environment and human health from persistent organic pollutants (Stockholm Convention, 2011). However, PCBs are still routinely found in sediment/soil, water, air and even foodstuffs in many countries (e.g., America, China, the Netherlands, Brazil, Pakistan) (Baars *et al.*, 2004; Wu *et al.*, 2011; Colabuono *et al.*, 2010; Howell *et al.*, 2011; Eqani *et al.*, 2013). Disposal of e-waste and historical usage could contribute to higher PCBs concentrations in the environment (Wang *et al.*, 2011; Li *et al.*, 2012). A global level of PCBs (excluding China) ranging from 0.026 to 97 ng/g dry weight was reported in 2003 (Meijer *et al.*, 2003). In China, an average PCB concentration of 0.515 ng/g dry weight was found throughout the whole country (Ren *et al.*, 2007). Therefore, a better understanding of the distributions and toxic risks of PCBs can contribute to protecting ecosystems and human health.

Numerous researchers have focused on PCB levels in different environmental media (i.e.,

water/sediment, soil and air) (Xing et al., 2005; Nakata et al., 2005; Ren et al., 2007; Li et al., 2008; Chen et al., 2009; Wang et al., 2009; Colabuono et al., 2010). After a range of biochemical reactions, sediment/soil is the final deposition sink of PCBs (WHO, 1976), which is due in part to the hydrophobicity of PCBs (Simick et al, 1998). Simultaneously, emission from sediment/soil caused continual atmospheric transport of PCBs, leading to further pollution and ecological risks (Zheng et al., 2014). However, little information is available on PCB levels, distributions and risks in different wetland sediments/soils, though wetland sediments/soils have been recognized as sources, sinks or transfer media for chemical materials (Reddy and DeLaune, 2008).

The effects of land use on PCB concentrations in biota and sediments began to draw increasing attention a decade ago (Chevreuil et al, 1995; Munn, 1997; Black et al, 2000), because the distribution characteristics and contamination levels of PCBs were closely related to land use (Kinslow, 2012). King *et al.* (2004) indicated that land use was strongly linked to PCBs on the watershed scale in White Perch with compelling evidence. Recently, Shahbazi *et al.* (2012) reported that the concentrations of PCB residues in reclaimed wetland and urbanized soils were much higher than those in forest soils. However, the effects of wetland reclamation and reclamation history on PCBs in wetland sediments/soils are still unknown.

As one of the most prosperous regions in China, the Pearl River Estuary (PRE) has been undergoing rapid industrialization and urbanization, as well as enhanced agricultural development due to rapid population growth, which would further lead to the intensive reclamation of estuarine wetlands (Bai *et al.*, 2011). Large amounts of organic pollutants, including PCBs, are also generated and transported to these estuarine wetlands (Yang *et al.*, 1997; Zhang *et al.*, 1999; Luo *et al.*, 2004; Mai *et al.*, 2005;). Therefore, the primary objectives of this study were to investigate the distribution, levels and toxic risks of PCBs in sediments of both riparian and ditch wetlands and in reclaimed wetland soils along a 100-year chronosequence of reclamation in the Pearl River Estuary of China and to identify the relationship between PCBs and selected sediment/soil properties under different land uses and reclamation histories in this region.

2. Materials and methods

2.1 Study area

The study site is located at Wanqingsha region in the Pearl River Estuary of China ($22^{\circ}36' 39''$ to $22^{\circ}44' 36''$ N and $113^{\circ}23' 42''$ to $113^{\circ}38' 34''$ E). Impacted by the sub-tropical maritime climate, the annual mean temperature and rainfall of this region are 21.9°C and 1647.5 mm, respectively. The location of Wanqingsha was a shallow sea until one hundred years ago, when it began to be reclaimed as reclaimed wetland. To date, approximately 5200 ha of coastal wetlands have been reclaimed for urbanization, industrialization and agricultural development (Cui, 2010). Because coastal reclamation occurred in this region at different times (Xiao et al., 2015), in this study, we established three sampling belts based on wetland types along a 100-year chronosequence of reclamation to illustrate the impacts of coastal reclamation on PCB levels and distributions in the Pearl River Estuary. Based on the investigation from local residents and local government, 12 sampling sites with a reclamation history of approximately 100, 40, 30 and 10 years were selected in each type of wetland (Figure 1). The chronosequence was determined by reclamation history in this place (Cui, 2010; Xiao *et al.*, 2015). All sampling sites were grouped into riparian wetlands (Jiaomen waterway; Ri100, Ri40, Ri30 and Ri10), ditch wetlands (D100, D40, D30 and D10) and reclaimed wetlands (Re100, Re40, Re30 and Re10). The development of the electronic, shipping and metalwork industries, printing and dyeing mills both sides of the rivers and the increasing residents and heavy applications of agrochemicals on both sides of the ditches produced a large amount of industrial and domestic sewage, which were directly discharged into the Pearl River (Bai et al., 2011; Xiao et al., 2015). The dominant vegetation is

Cyperus Malaccensis and *Scripus triqueter* in ditch wetlands and riparian wetlands. The main crops in reclaimed wetlands are banana trees, longan trees and sugarcane.

2.2 Sediment/soil sample collection

During March 22- March 30, 2012, sediment cores in ditch and riparian wetlands and soil cores in reclaimed wetlands to a depth of 30 cm were randomly collected along a 100-year chronosequence of reclamation. Each sediment/soil core was collected with three replicates. The distances between sampling sites ranged from 40m to 120m. The sediment/soil cores were stratified into three layers at 10-cm intervals and mixed with the same layers from each wetland type. All samples were placed in polyethylene bags, brought to the laboratory and preserved in a refrigerator at 2-4°C before analysis. Some fresh samples were used to determine microbial biomass carbon and nitrogen. And other samples were air dried for three weeks at room temperature and sieved through a 2-mm nylon sieve to remove coarse debris and stones to determine the congeners and concentrations of PCBs in sediments/soils. One portion of the fresh samples was used to determine sediment/soil particle size. All of the air-dried subsamples were ground with a pestle and mortar until all particles passed a 0.149-mm nylon sieve to analyze selected sediment/soil properties.

2.3 Sediment/soil analyses

The accelerated solvent extraction method (ASE-300, Dionex, America) was adopted to extract PCBs in samples. A 20.00 g sub-sample was extracted with 30 mL of n-hexane/acetone solvent mixture at 100°C and 1500 psi in triplicate. Then, the extracts were mixed. Later, the combined extracts were evaporated to approximately 1 mL by a rotary evaporator (RE-52, Shanghai Yarong

Company, China) with a N₂ stream for cleanup.

A chromatography column (30 cm ×10 mm i.d.) with 2 g of silver nitrate silica (10% concentrated silver nitrate, wt/wt), 1 g of activated silica gel, 3 g of basic silica gel, 1 g of activated silica gel, 4 g of acid silica gel (22% concentrated sulfuric acid, wt/wt), 1 g of activated silica gel and 2 g of anhydrous sodium sulfate was utilized to clean the concentrated extracts. The PCB fraction was eluted with 100 mL of hexane. The collected eluent was concentrated by a rotary evaporator and then reduced to 1 mL under a gentle N₂ stream for analysis.

An Agilent 6890 gas chromatograph (Wilmington, DE, USA) equipped with a micro-electron-capture detector (micro-ECD) was used to quantitatively analyze PCBs in all samples. Separation was carried out using an HP-5 capillary column (30 m×0.25mm×0.25 μm). Highly pure helium (99.9999%) was used as the carrier gas. A sample volume of 1 μl was injected in automatic splitless mode. The column oven temperature was initially maintained at 60°C for 1 min, increased to 140°C at a rate of 10°C/min (1 min), then increased to 230°C at a rate of 1.0°C/min (15 min) followed by an increase to 280°C at a rate of 10°C/min, which was maintained for 21 min. The injector, transfer line and ion source temperatures were maintained at 260°C, 280°C and 250°C, respectively. According to the retention time of individual authentic standards (±0.3%), GC peaks could be identified, and then, the concentrations of PCBs were quantified using the internal standard method.

The pH and EC were measured in the supernatant of 1:5 sediment/soil -water mixtures using a Hach pH meter (Hach Company, Loveland, CO, USA) and a conductivity meter (Mettler Toledo, USA). Sediment/soil organic carbon (SOC) was measured using dichromate oxidation (Nelson and Sommers, 1982). Particle size analysis was conducted on a laser particle size analyzer

(Microtrac S3500, America) after a series of pretreatment. First, 0.3-0.5g fresh samples were weighed and placed into meter glasses with 30 ml 10% H₂O₂. Then, 2-3 ml 10% HCl was added into the meter glasses to remove carbonate until no air bubbles appeared. After that, the samples were cleaned with deionized water to make sure the solution was neutral. Finally, 10 ml 4% sodium hexametaphosphate solution was added to each meter glass as dispersing agent. After Ultrasonic treatment for 3 minutes, the particles could be tested by the laser analyzer. Microbial biomass carbon (MBC) and microbial biomass nitrogen (MBN) were measured using the chloroform-fumigation extraction method (Vance et al. 1987). The size fractionations of the water-stable aggregates in the samples were determined using the wet sieving method (Yamashita et al., 2006). The water-stable aggregates were expressed as the percentages of four size fractions as follows: > 2 mm (large aggregates), 0.25-2 mm (medium aggregates), 0.053-0.25 mm (small aggregates) and < 0.053 mm (ultra-small aggregates) for each sample.

2.4 Quality assurance and quality control

Strict quality assurances and controls were implemented throughout the whole analysis process. One method blank was included in each batch of 15 samples. Additionally, duplicates and a certified reference material (PCB Mix77 from Dr. Ehrenstorfer GmbH) were included in each extraction batch of 15 samples throughout all of the experiments. The estimated analytical detection limit for individual PCB congeners was 0.005 ng/g. The recoveries of surrogate PCBs (PCB 204 and PCB 209) ranged from 80.3 to 112.5%, which met the requirements of EPA 1668A and 1614 draft protocol (USEPA, 1999). Before each batch of samples were analyzed, the calibration curves of PCBs were drawn with the correlation coefficients larger than 0.99.

2.5 Statistical analysis

Statistical analyses were carried out using the Microsoft Excel (Microsoft Inc., USA) and SPSS 16.0 (SPSS Inc.) software packages. All figures were created by Origin 8.0 (Origin Lab Corporation). Correlation analysis was conducted to reveal the relationships between PCBs and selected sediment/soil properties. To identify the possible source of PCBs in three wetland sediments/soils, Principle Component Analysis (PCA) was carried out for collected samples and five commercial mixtures (Aroclor 1016, 1242, 1248, 1254, 1260). By rotating the component matrix with a varimax rotation to the axes, the variance of the components was maximized. The percent composition of PCB congener for each Aroclor mixtures was obtained from USEPA (1996).

3. Results and Discussion

3.1 Concentration and composition of PCBs in surface sediments/soils of three types of wetlands

A total of 15 PCB congeners in sediments/soils were detected at all sampling sites from three types of wetlands, with the IUPAC numbers: 28, 52, 101, 77, 123, 118, 114, 153, 105, 138, 126, 167, 156, 169 and 189 (Figure 2a). PCB concentrations in the surface sediments/soils of the three types of wetlands ranged from 17.68 to 169.26 ng/g, which partly fell within the range of background values (0.026 to 97 ng/g) of global soils (Meijer *et al.*, 2003) and were higher than the mean PCB concentration (0.515 ng/g) in China (Ren *et al.*, 2007) and background mountain soils (0.510 ng/g for O- horizon samples and 0.227 ng/g for A-horizon samples) (Zheng *et al.*, 2015). Moreover, the mean PCB concentrations in these three wetland sediments/soils were similar to

those in sediments of the Pearl River (83.1 ng/g), Dalian Bay (36.8 ng/g) and the Songhua River (58.1 ng/g) in China (Xing *et al.*, 2005). Generally, total PCB concentrations were much higher in riparian wetland sediments than in ditch wetland sediments and reclaimed wetland soils, which might be associated with increased PCB inputs from adjacent industrial sources (i.e. electronic, shipping and metalwork industries, printing and dyeing mills) of the riparian wetlands (Li *et al.*, 2013). Meanwhile, the e-waste recycling processes can also cause PCBs releasing or leaching into sediments/soils nearby or volatilizing to the atmosphere, followed by deposition to sediment/soil surface later (Wang *et al.*, 2011). The old wetland sediments/soils contained higher PCB concentrations than the younger ones, indicating that a longer reclamation history would contribute to PCB accumulation. The maximum PCB levels were observed in D40 and Ri30 in ditch and riparian wetlands, respectively. Generally, PCB levels in three wetland sediments/soils exhibited a decreasing tendency with a 100-year chronosequence of reclamation. This might be associated with PCBs deposition along time (Mai *et al.*, 2005). Besides, previous studies have shown that PCB concentrations continued to increase or flattened in top increments from the 1980s to the time research was conducted (Latimer and Quinn, 1996; Oliver *et al.*, 1989), which further explained why old sediments/soils generally contained higher PCBs concentrations.

The PCB congeners were grouped into tri-CB (PCB28), tetra-CBs (PCB52 and PCB77), penta-CBs (PCB101, PCB105, PCB114, PCB118, PCB123 and PCB126), hexa-CBs (PCB138, PCB153, PCB156, PCB167 and PCB169) and hepta-CB (PCB189) (Figure 2a). The light PCBs (i.e., tri-CBs, tetra-CBs and penta-CBs) were dominant PCB congeners in all of these wetland sediments/soils, occupying more than 90 % of the total PCBs (Figure 2b). PCB52 (a tetra-CB) in Ri30 sediments showed the highest concentration among all PCB congeners, followed by PCB28

(a tri-CB). This was consistent with the results of Ren *et al.* (2003), who reported that the richest PCB congeners in Chinese background/rural soils were tri-PCBs. Gao *et al.* (2013) also reported that light PCBs (with 2-3 chlorine atoms) predominate in sediments of the Yangtze River Estuary. Moreover, Li *et al.* (2012) reported that tri-CBs, tetra-CBs and penta-CBs were the dominant PCB congeners in surface water of the Yangtze River Delta. This was associated with the fact that PCBs produced in China mainly consisted of tri-CBs and penta-CBs (Jiang *et al.* 2011). Moreover, the light PCBs have higher volatility and thus can be much more easily transported for long distances (Bi *et al.*, 2002).

Comparatively, the heavy PCBs (hexa-CBs and hepta-CBs) accounted for a small percentage of the PCB composition of three wetland sediments/soils. Hepta-CB (PCB189) was only detected in Ri40 sediments, with a concentration of 0.50 ng/g. Hexa-CBs were observed with low concentrations in all samples except for D40 sediments. Although the dominant PCB congeners were hexa-PCBs and penta-PCBs in sediments near the cities of Guangzhou and Macao in 1997 (Kang *et al.*, 2000), the manufacturers (i.e. electronic, shipping and metalwork industries, printing and dyeing mills) and industrial production in Nansha District after wetland reclamation (especially in the older reclaimed region) and the disposal of e-waste (Li *et al.*, 2012) could contribute to PCB accumulation and the recalcitrance to degradation of penta-CBs, leading to the dominant percentage of light PCB congeners (i.e., tri-CBs, tetra-CBs and penta-CBs) in wetland sediments/soils of this region. The hexa-CB concentration was much higher in ditch wetland sediments than in riparian wetland sediments and reclaimed wetland soils. Old wetland sediments/soils contained higher hexa-CB concentrations than the younger ones, as heavier PCBs tend to deposit near the source and thus old wetland sediments/soils accumulated more heavy

PCBs (Chu *et al.*, 1995; Breivik *et al.*, 2002; Hong *et al.*, 2003; Meijer *et al.*, 2003).

Among these PCB congeners, there existed 10 “dioxin-like” PCBs (non-ortho DL-PCBs: PCB77, PCB126, PCB169; and mono-ortho DL-PCBs: PCB123, PCB118, PCB114, PCB105, PCB167, PCB156 and PCB189) and five “non-dioxin-like” ones (Figure 2a). Figure 2c shows the proportions accounted by non-dioxin-like PCBs, non-ortho DL-PCBs and mono-ortho DL-PCBs in the total PCB concentrations in the three types of wetlands. In surface sediments/soils of these three wetlands, the non-dioxin-like PCBs contributed more (> 50 %) to the total PCB concentrations, except for D30 and Ri10 sediments. Compared with the non-ortho DL-PCBs, mono-ortho DL-PCBs had a much higher concentration. The highest concentration of non-dioxin-like PCBs, non-ortho DL-PCBs and mono-ortho DL-PCBs were observed in surface sediments of D10, Ri10 and D30, respectively. Only the mono-ortho DL-PCBs were detected in surface sediments/soils of all sampling sites.

3.2 Profile distribution of $\Sigma 15$ PCBs in three wetland sediments/soils

As shown in Figure 3, $\Sigma 15$ PCBs concentrations rapidly decreased with depth along sediment/soil profiles in the three types of wetlands with different reclamation histories, indicating a considerable accumulation of PCBs in surface sediments/soils. The result was consistent with the profile distributions of PCBs in Tibetan forest soils (Wang *et al.*, 2013). The light and heavy PCB congeners also exhibited a decreasing tendency with depth. This could be associated with recent heavy pollution sources (i.e. electronic, shipping and metalwork industries, printing and dyeing mills) after wetland reclamation in this region (Bai *et al.*, 2011), which led to high PCBs concentrations in surface sediments/soils. Additionally, PCBs in sediments/soils are mainly

derived from anthropogenic emission (Zhang *et al.*, 2011), thus surface sediments/soils contained higher PCBs concentrations than deeper ones. Light PCB congeners, especially tetra-CBs and penta-CBs, were dominant in the PCB composition in deeper sediments/soils of these three types of wetlands. This might be explained by their leaching and deposition of light PCB congeners, as tri-CBs and tetra-CBs could move downward, leading to the high proportion of light PCB homologues in deeper sediment increments (Mai *et al.*, 2005). Moreover, the anaerobic biodegradation of PCBs could cause the transformation of heavy PCBs to light PCBs because anaerobic microorganisms can dechlorinate PCBs from heavier congeners in an oxygen-free environment (Denny, 2004). Compared to deeper sediments/soils, higher tri-CB concentrations in surface sediments/soils were closely related to photolysis and biodegradation in aerobic environments (Denny, 2004). However, tri-CBs accounted for a smaller percentage than other congeners, which might be due to the easier degradation of PCB congeners containing no more than three chlorines (Bopp, 1986). However, Zhang *et al.* (2011) reported that the proportion of low-chlorinated PCBs (i.e. tri-CBs and tetra-CBs) increased with depth in Udic Luvisols and Stagnic Anthrosols of the Yangtze River Delta.

Higher PCB concentrations in deeper sediments were observed in older riparian wetlands (i.e., Ri30, Ri40 and Ri100) and in older ditch wetlands (i.e., D100), implying that a longer reclamation history could result in PCB accumulation in deeper sediments in both types of wetlands. In contrast, reclaimed wetlands showed similar PCB levels and patterns in deeper soils along the 100-year chronosequence of reclamation, which might be attributed to the consistent cultivation management in these reclaimed wetlands, not the reclamation history.

3.3 Source analysis

As a multivariate statistical technique, principal component analysis (PCA) could simplify large datasets and identify the factors determining the variation of variables. It has been an important tool to identify the source of pollutants in the environment (Cachada et al., 2009; Wang et al., 2011). In this study, three principal components (PCs) with eigenvalues > 1 were extracted by PCA, explaining 58.785%, 23.023% and 13.91% of the total variance, respectively. Lowly and highly chlorinated congeners characterized component 1 (PC1) and component 2 (PC2), respectively. Figure 4 exhibited that compositions of PCBs in most samples were similar and might originate from the same source. 31 samples and three commercial mixtures (Aroclor 1016, 1242 and 1248) could be classified into one group which was dominated by tri- and tetra-CBs. Five samples and Aroclor 1254 were grouped into another group which is comprised of 15% tetra-CBs, 53% penta-CBs and 26% hexa-CBs. Only Aroclor 1260 which mainly contains hexa-CBs and hepta-CBs was clearly separated from the samples indicating no effect from this mixture on PCBs levels in three wetlands. Therefore, it could be concluded that the PCBs in this study mainly originated from local sources such as Aroclor 1016, 1242, and 1248, partly influenced by Aroclor 1254. Simultaneously, uncontrolled recycling and disposal of e-waste (dumping, dismantling and burning) has become new sources of PCBs entering the environment (Wang et al., 2011; Li et al., 2012).

Additionally, the dominant proportion of tri-CBs, tetra-CBs and penta-CBs indicated that the major source of PCBs in reclaimed wetlands was atmospheric transportation because atmospheric transportation leads to the deposition of less-chlorinated PCB congeners (3-5 chlorines) in reclaimed wetlands (Shang *et al.*, 2013; Li et al., 2012). In D30 sediments, more than 90% of the

PCB congeners in sediment profiles were penta-CBs, which indicated that PCB concentrations at this sampling site were affected by industrial pollution because penta-CBs are mainly used in paint additives (Ren *et al.* 2007).

3.4 Toxicity and risk assessment of $\Sigma 15$ PCBs in three types of wetlands

We adopted the sediment quality guidelines for total PCBs, including the threshold effects level (TEL) and probable effects level (PEL) (Table 1, Long *et al.*; 1995) to assess the toxicity and risks of PCBs at the sampling sites. TEL and PEL guidelines could divide the adverse biological effects of PCBs into rarely, occasionally and frequently observed ones. From Figure 3, we could conclude that most sampling sites of the three land uses, especially reclaimed wetland soils, have possible adverse biological effects that occasionally occur. This also indicated that reclaimed wetlands were more severely polluted by PCBs than ditch and riparian wetlands. Only PCBs in D30 and Ri10 sediments have rare adverse biological effects. The levels of all light PCB congeners were in excess of the TEL value, which indicated that the adverse biological effects in these three wetlands mainly resulted from light PCB congeners.

Table 1 shows the average concentrations of $\Sigma 15$ PCBs, light PCB congeners (3-5 chlorines), heavy PCB congeners (6-7 chlorines), dioxin-like PCBs and non-dioxin-like PCBs in the top 30 cm of sediments/soils from the three types of wetlands. The mean levels of $\Sigma 15$ PCBs, light PCBs and non-dioxin-like PCBs in the three types of wetlands were grouped into TEL-PEL. However, the average levels of heavy PCBs and dioxin-like PCBs in the three types of wetlands were all below the TEL value. This indicated that occasional adverse biological effects could occur in these three wetlands, with higher contribution ratios of light PCBs or non-dioxin-like PCBs to the

adverse biological effects in the top 30 cm sediments/soils. Generally, no significant differences in $\Sigma 15$ PCBs, heavy PCBs, dioxin-like PCBs and non-dioxin-like PCBs were observed among the three types of wetlands ($P > 0.05$). Although there were not statistically significant differences in light PCBs concentrations between reclaimed wetlands and ditch wetlands ($P > 0.05$), a higher average level of light PCBs was observed in reclaimed wetlands. However, riparian wetland sediments exhibited significantly higher levels of light PCBs than ditch wetland sediments, indicating higher toxicity risks of PCBs in riparian wetlands compared to ditch wetlands ($P < 0.05$).

3.5 Toxicity and risk assessment of DL-PCBs in three types of wetlands

Figure 5 illustrates the profile distributions of DL-PCBs in the three types of wetlands. Generally, DL-PCBs decreased with depth along sediment/soil profiles in these three wetlands. The concentrations of DL-PCBs in surface sediments of D40, Ri10, Ri40, Ri100 and deeper sediments (20-30 cm) of D100, and in Re100 surface soils exceeded the TEL value. However, DL-PCB values in all sediments/soils were below the PEL value. PCB123 represented the highest proportion of the detected DL-PCBs in three wetland sediments/soils, and held the highest concentration in riparian wetlands and reclaimed wetlands among all DL-PCB congeners. Additionally, PCB167 in D40 surface sediments exhibited the highest concentration among the detected DL-PCBs in ditch wetlands.

Owing to the dioxin-like biological and toxic effects of DL-PCBs, risk assessments of DL-PCBs have gained increasing attention. The total toxic equivalent (TEQ) was developed to assess the toxicity of PCBs; TEQ could be calculated with the PCB congener concentration and TEF

(toxic equivalency factor) values for human and mammals provided by WHO (2005).

The magnitudes of the TEQs of the detected DL-PCBs varied greatly in sediment/soil profiles of the sampling sites. The TEQs of DL-PCBs were much higher in surface sediments/soils than those in deeper ones in the three types of wetlands. Moreover, PCB126 contributed more to the TEQs of DL-PCBs compared with other DL-PCB congeners.

The average TEQs of PCBs in these three wetlands ranged from 0.04×10^{-3} to 852.70×10^{-3} ng/g. Ri40 sediments contained the highest TEQ_{PCB} (852.70×10^{-3} ng/g), whereas D10 sediments exhibited the lowest TEQ_{PCB} level (0.04×10^{-3} ng/g). The mean percentages of TEQ_i for various DL-PCB congeners followed the order PCB126 (66.25%) > PCB123 (20.88%) > PCB167 (6.52%) > PCB77 (5.52%) > PCB114 (0.60%) > PCB169 (0.22%) > PCB118 (0.0055%) > PCB156 (0.0037%) > PCB189 (0.0004%) > PCB105 (0.0002%). The high TEF value of PCB126 represented the highest contribution to the TEQ of DL-PCBs, which suggested that penta-CBs were the dominant pollutants in these sampling sites. The mean TEQ concentrations of DL-PCBs in ditch, riparian and reclaimed wetlands were 94.07×10^{-3} ng/g, 266.69×10^{-3} ng/g and 143.36×10^{-3} ng/g, respectively. The toxicity of DL-PCBs was higher in riparian wetlands than those in ditch and reclaimed wetlands. According to the Canadian soil quality guidelines for polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) (4×10^{-3} ng/g), the TEQ concentrations of DL-PCBs at seven sampling sites (i.e. D100, D30, F40, F10, R100, R30 and R10) exceeded the Canadian standard (CCME, 2007) due to higher PCB126 concentrations.

Furthermore, sediment quality guideline quotient (SQGQ) was used to evaluate the potential adverse biological effects of contaminant mixtures (Long *et al.*, 1995). In this study, SQGQ was used to assess the potential biological effects of DL-PCBs at sampling sites. To calculate the

SQGQ of DL-PCBs, the PELQ (PEL quotient) should first be determined by using the formula below (MacDonald et al. 1996; MacDonald et al. 2004):

$$PELQ_i = \frac{C_i}{PEL} \quad (2)$$

where PEL is the guideline value for contaminant I, and C_i is the measured concentration of the same contaminant. Then, the SQGQ was calculated for each site as:

$$SQGQ = \frac{\sum_{i=1}^n PELQ_i}{n} \quad (3)$$

where n is the quantity of analyzed contaminants for which sediment quality guidelines can be acquired. According to Costa et al. (2011), the potential adverse biological effects of sediment contamination could be categorized into three groups according to SQGQ value: no effects ($SQGQ < 0.1$), moderate effects ($0.1 \leq SQGQ < 1$) and high adverse biological effects ($SQGQ \geq 1$).

Table 2 shows the profile distributions of the PELQs and SQGQs of DL-PCBs in the three types of wetlands. From Table 2, we can see that the SQGQs for most sampling sites were below 0.1, except for D40 and Ri40 sediments. This indicates that DL-PCBs in D40 and Ri40 sediments would cause moderate adverse biological effects. Thus, it is critical to take steps to monitor and control DL-PCBs in D40 and Ri40 sediments. The PELQ of PCB123 was the highest among the 10 DL-PCBs due to its high concentrations in three wetland sediments/soils.

3.6 Relationships between PCB congeners and selected sediment/soil properties

Most previous studies have shown that sediment/soil properties (e.g., organic carbon content, clay fraction, and grain size) could impact the distribution and contamination levels of PCBs in wetland sediments/soils (Burgess *et al.*, 2001; Edgar *et al.*, 2003; Meijer *et al.*, 2003; Yang *et al.*,

2011). Generally, higher PCBs were related with smaller grain size (Chiou et al. 1998 and Warren et al. 2003). And Yuan et al. (2014) found clay contents could positively impact $\sum$ PCBs in soils of the central Tibetan Plateau. However, no significant correlations were observed between PCBs concentrations and clay contents and grain size in this study ($P > 0.05$) (Table 3), which is consistent with the result by Gao et al. (2013). The influence of sediment/soil organic carbon content (SOC) on PCBs concentrations has been controversial. In the studies of Backe et al. (2004) and Meijer et al. (2003), sampling sites with higher SOC content showed higher PCBs concentrations. In this study, we also observed that the concentrations of PCB 28, 105, 114, 123, 126, 138 and 189 were significantly related to SOM contents ($P < 0.05$). However, no significant correlations were observed between other PCB congeners and SOC contents ($P > 0.05$) (Table 3). Gao et al. (2013) and Yuan et al. (2014) reported that a weak liner relationship existed between PCBs concentrations and total organic carbon content in sediment. This might be possibly explained by the fact that the impact of anthropogenic activities in estuarine regions could overshadow the effects of total organic carbon content and grain size under some circumstances (Gao et al. 2013).

4. Conclusions

We observed higher PCB concentrations in older wetlands than those in younger ones. Surface sediments/soils tended to contain more PCBs than deeper sediments/soils. Higher organic carbon contents and exogenous pollution from different sources should take a big responsibility for higher PCBs in surface sediments/soils. The dominant PCB homologues are tetra-CBs, tri-CBs and penta-CBs in these three types of wetlands. PCA analysis indicated that most of the PCBs in all

samples might originate from local sources such as Aroclor 1016, 1242 and 1248 in addition to long distance atmospheric transportation. However, the PCB concentrations in all reclaimed wetland soils were in excess of the TEL value, indicating occasional adverse biological effects would occur in reclaimed wetlands. Therefore, it is very important to carry out a long-term monitoring of PCB dynamics in this region. Moreover, some potential sources (i.e. electronic, shipping and metalwork industries, printing and dyeing mills) should be further identified and some steps should be taken to control PCBs in reclaimed wetlands to protect food security and human health. The management of PCB126 should particularly be examined because PCB126 represented the highest contribution to TEQ_{PCB} in this study area.

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Figure 1 Location map of sampling sites in the Pearl River Estuary

Figure 2 PCB Concentrations (a), composition of heavy- and light- PCBs (b) and DL- and non-DL-PCBs of PCBs (c) in surface sediments/soils of three types of wetlands

Figure 3 Profile distributions of $\Sigma 15$ PCBs concentrations in ditch wetland sediments (a), riparian wetland sediments (b) and reclaimed wetland (c) soils

Figure 4 Principal component plot of PCBs in three types of wetland sediments/soils

Figure 5 Congener profiles of 10 DL-PCBs types in ditch wetland sediments (a), riparian wetland sediments (b) and reclaimed wetland (c) soils

Table 1 PCB concentrations in the top 30 cm of sediments/soils in three types of wetlands

ng/g	Ditch wetlands	Riparian wetlands	Reclaimed wetlands	The Pearl River sediments	Dalian Bay	Songhua River	TEL	PEL
Σ15PCBs	34.10±38.05	67.05±56.73	54.73±25.82	83.1	36.8	58.1		
Light PCBs	29.88±28.77	65.15±55.08	54.69±25.76					
Heavy PCBs	4.22±14.25	1.90±3.76	0.05±0.17					
Dioxin-like PCBs	11.23±16.46	19.42±20.35	11.61±8.15				21.6	189
Non-dioxin-like PCBs	22.87±24.79	47.63±47.10	43.13±19.20					

Note: the PCBs concentrations in the Pearl River sediments, Dalian Bay and Songhua River were cited from *Xing et al., 2005*.

Table 2 Average PELQs (PEL quotients), TEQ (total toxic equivalent) and SQGQs (sediment quality guideline quotients) of 10 DL-PCBs in the top 30 cm of sediments/soils in three types of wetlands

Sites	PELQs										TEQ	SQGQ
	PCB77	PCB105	PCB114	PCB118	PCB123	PCB126	PCB156	PCB167	PCB169	PCB189		
D10	--	--	--	--	0.01	--	--	--	--	--	0.04	0.01
D30	--	--	0.03	0.01	0.01	--	--	--	--	--	60.31	0.05
D40	--	--	0.01	--	0.02	--	--	0.09	--	--	0.63	0.11
D100	0.01	--	--	--	0.05	0.02	--	--	--	--	315.30	0.07
Ri10	0.02	--	0.01	--	0.05	0.01	--	--	--	--	113.20	0.08
Ri30	--	--	--	--	0.06	--	--	--	--	--	0.35	0.06
Ri40	--	--	0.01	--	0.14	0.05	--	--	--	0.01	852.70	0.20
Ri100	--	--	--	--	0.05	0.01	0.01	--	--	--	100.51	0.06
Re10	0.01	--	--	--	0.05	0.01	--	--	--	--	152.12	0.06
Re30	0.01	--	--	--	0.04	0.01	--	--	--	--	118.75	0.06
Re40	0.02	--	--	--	0.03	--	--	--	--	--	0.46	0.04
Re100	--	--	--	--	0.07	0.02	--	--	--	--	302.13	0.08

Note: -- means the value is zero.

Table 3 Correlation between PCB congeners and selected soil properties

	SOC	MBC	MBN	Clay	Silt	Sand	Large aggregates	Medium aggregates	Small aggregates	Ultra-small aggregates
PCB28	0.35*	0.17	-0.16	-0.05	-0.13	0.13	0.12	0.09	-0.13	0.01
PCB52	-0.16	-0.06	-0.03	-0.12	-0.15	0.15	0.07	-0.09	0.14	-0.14
PCB77	-0.09	0.09	0.07	-0.06	0.04	-0.04	0.11	0.14	-0.16	-0.02
PCB101	0.22	0.17	0.10	-0.14	-0.19	0.19	-0.12	0.02	-0.07	0.16
PCB105	0.66**	0.27	0.04	-0.13	-0.16	0.16	0.11	0.19	-0.18	-0.07
PCB114	0.29*	0.55**	0.48**	-0.11	-0.20	0.20	0.31*	0.12	-0.22	0.03
PCB118	0.01	0.24	0.24	-0.11	-0.01	0.02	0.13	0.24	-0.19	-0.14
PCB123	0.51**	0.25	-0.02	-0.16	-0.18	0.18	0.13	0.24	-0.24	-0.06
PCB126	0.74**	0.41**	0.03	-0.24	-0.19	0.20	0.14	0.36**	-0.33*	-0.10
PCB138	0.80**	0.29*	0.08	-0.20	-0.19	0.20	0.11	0.26	-0.23	-0.10
PCB153	0.46**	0.05	0.02	-0.15	-0.13	0.13	-0.02	0.08	-0.06	-0.01
PCB156	0.07	0.11	0.07	-0.14	-0.11	0.12	0.11	0.28*	-0.22	-0.142
PCB167	0.14	0.13	0.04	-0.12	-0.05	0.052	0.78**	0.03	-0.21	-0.10
PCB169	0.17	0.25	-0.04	-0.11	0.01	-0.03	0.02	0.25	-0.18	-0.12
PCB189	0.55**	0.10	0.02	-0.14	-0.14	0.14	0.01	0.12	-0.10	-0.04
PCBs	-0.01	0.18	-0.02	-0.20	-0.23	0.23	0.28	0.10	-0.10	-0.13

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).