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Polychlorinated biphenyls in agricultural soils from the Yangtze River Delta of China: Regional contamination characteristics, combined ecological effects and human health risks

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ABSTRACT

The current contamination status of polychlorinated biphenyls (PCBs) was studied in the agricultural soils of the Yangtze River Delta (YRD), one of the largest economic zones in China. The concentrations of PCBs ranged from <0.1 to 130 ng/g dry weight. Higher concentrations of PCBs were observed in the 0 e30 cm surface layers relative to the subsurface soils. A distinct spatial distribution was observed with a declining concentration gradient from the northwest to the southeast of the region. The composition of PCBs in the soils was consistent with the Chinese commercial PCB mixtures, but different from the compositions in global background soil. Local sources including large-scale use and disposal of PCB- containing products were the main potential sources to soil. The ecological effects and human health risks associated with combined persistent organic pollutants, including PCBs, organochlorine pesticides (OCPs), phthalate esters (PAEs) and polybrominated diphenyl ethers (PBDEs), were further estimated. The four toxic organic compounds and seven physicochemical parameters together could only explain 12.7% of the variation in microbial community composition, suggesting the soil ecosystem function was not strongly influenced by the combined pollution at low concentrations. However, the potential health risks to residents via multiple pathways were notably higher for PCBs than other chemicals. The potential risks were mainly derived from PCB-126, 81, and 169.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a well-known class of persistent organic pollutants (POPs), and have been used as dielectric and heat-exchange fluids, flame-retardants, plasticizers, and pesticide additives (Breivik et al., 2007). Despite being banned for several decades, the widespread production and use of PCBs before their legal restriction has led to ubiquitous contamination of the environment, presenting potential ecological and human health risks especially for metabolites upon PCBs transformation (Gutleb et al., 2010; Su et al., 2012; Sun et al., 2016a).

Soil is an important reservoir for many POPs including PCBs (Doick et al., 2005; Zhang et al., 2011; Zhong and Zhu, 2013), and is a secondary emission source to air (Bidleman and Leone, 2004; Cabrerizo et al., 2011) and water (Zhang et al., 2003). Even rela- tively low concentrations of PCBs in soils can be bioaccumulated gradually via food chains with potentially adverse effects on humans (Sirot et al., 2012). Globally, nearly 21,000 tons of PCBs have been discharged into soils (Meijer et al., 2003). In China, about 10,000 tons of commercial PCB were produced in the past (Zhang et al., 2013), which have polluted soils and other environmental components across the country (Bao et al., 2012; Ren et al., 2007; Zheng et al., 2016).

The Yangtze River Delta (YRD) is one of the three largest regional economic zones in China. A large number of industrial and commercial enterprises contribute to regional economic development, but also pose a serious threat to the environment quality. Our recent study found that the agricultural soil in the YRD is contaminated with organochlorine pesticides (OCPs), phthalate esters (PAEs) and polybrominated diphenyl ethers (PBDEs) (Sun et al., 2016b). It is important to investigate the regional-scale distribution and the associated risks of PCBs to manage environmental risks and facilitate sustainable industrial and economic development. Environmental pollution has been found to cause drastic changes in microbial community activity and affect the functions of soil ecosystems (Brantner and Senko, 2014; Turpeinen et al., 2004). Yet there are limited studies on the responses of soil microbiota to the combined pollution and its ecological consequences (Liu et al., 2015). The potential risks of combined pollution (including PCBs, OCPs, PAEs, and PBDEs) to human health via multiple pathways have not been well understood. Although an individual pollutant cannot impose significant health risk to human, a long-term chronic exposure to a mixture of contaminants could potentially cause serious carcinogenic and non-cancer effects (Sumpter and Johnson, 2005).

The aims of this work are (i) to investigate the concentration, composition and spatial distributions of PCBs in soils of the YRD region; and (ii) to assess the ecological effect and human health risk of combined pollution in soils and to provide a basis for assessing soil quality in the YRD during the course of rapid economic development.

EXPERIMENTAL METHODS

Sample collection

The YRD economic region comprises the Shanghai Municipality, southern Jiangsu and northern Zhejiang Provinces in eastern China, covers 100,000 km^2 and has a population of about 100 million (China Today, 2013). An evenly distributed sampling network composed of 241 sites was schemed to cover an area of approximately 45,800 km^2 (Fig. 1). Detailed information was described in a previous publication (Sun et al., 2016b). During June 2014, a total of 241 topsoil samples (0e15 cm depth) and six soil profiles were collected from various farmlands in the YRD region. The land-use types included paddy fields, vegetable fields, forests, uncultivated lands, and other agricultural uses. The soil profiles were excavated to a depth of 80 cm. Soils were taken from the front of the soil trenches at 10 cm intervals, each interval provides approximately 500 g soil samples. The soil samples were collected using a stainless steel scoop, packed in aluminum foil, sealed in Kraft bags, and freeze-dried in the laboratory.

Extraction and analysis of PCBs

The extraction and cleanup procedures for PCBs were adapted from the reported methods (Wang et al., 2013). All freeze-dried samples were ground and sieved through a stainless steel 75- mesh sieve and stored at 20 C before analysis. A portion of soil samples (5 g) were spiked with recovery surrogate PCB-65, followed by ultrasonic extraction using hexane/dichloromethane (1:1 v/v, 40 mL) for 30 min. The procedure was repeated two more times. The extracts were combined and concentrated to 1 mL, and then subjected to cleanup by a multilayer silica column as follows (from bottom to top): 1 g silica, 4 g basic silica (1.2%, w/w), 1 g silica, 8 g acidic silica (30%, w/w), 2 g silica, and 4 g anhydrous sodium sulfate. The column was pre-washed with 80 mL of hexane. The extract was eluted with 100 mL of hexane, and was thereafter concentrated by rotary evaporation to a final volume of 200 μL prior to instrumental analysis.

The target compounds measured in all samples include 12 dioxin-like PCBs (DL-PCBs) (including PCB-77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189), and six indicator PCBs (including PCB-28, 52, 101, 138, 153, and 180). Determination of PCBs was performed on gas chromatography/mass spectrometry (GC/MS) (7890B/5977A, Agilent Technologies, Santa Clara, CA, USA) with an electron ionization source. A DB-5 MS capillary column was used (30 m 0.25 mm i.d. with 0.25 μm film thickness). All data were obtained in the selective ion monitoring (SIM) mode. High purity helium was used as carrier gas with a flow rate of 1.0 mL/min. Oven temperature program was as follows: initial column temperature at 80℃ for 3 min, ramp to 150℃ at 15℃/min and hold for 2 min, increase to 270℃ at 2.5 ℃/min and hold for 3 min, increase to 300℃ at 15 ℃ /min and hold for 5 min.

Quality assurance and quality control

A procedural blank, a spiked blank, and a sample duplicate were processed in parallel with each batch of ten samples. No targeted compound was found in the blanks. The recovery rates of PCBs in the spiked samples ranged from 86.1% to 94.4%. The variations in concentrations of PCBs in duplicates were lower than 20% (n = 3). Five-point standard calibration curves were employed for quantitative analysis. The recovery rates of surrogate standards were 81.7% - 103%. The concentrations were not corrected with recovery rate. The limit of detection (LOD) of PCBs was defined on a signal- to-noise ratio of three using the lowest concentration standard and ranged between 0.03 and 0.10 ng/g.

Microbiological analysis

Microbiological analysis was conducted for all the 241 topsoil samples. Extraction and analysis of microbial phospholipid fatty acids (PLFA) were performed with reference to the reported method (He et al., 2013). Briefly, PLFAs were extracted from soil sample using a mixture of chloroform-methanol-citrate buffer and then separated by solid-phase extraction cartridges. PLFAs were analyzed by GC fitted with MIDI Sherlock microbial identification system. The microbial biomass of bacteria, fungi, actinomycetes, gram-positive bacteria, and gram-negative bacteria were separately quantified on the basis of the detected 42 fatty acids.

Physicochemical analysis

The water content in the soil samples was determined by weighing samples before and after oven-drying at 105°C for 24 h. The sieved and freeze-dried samples were used for subsequent analyses. The soil pH was measured using a pH meter (Mettlertoledo Instruments, Shanghai, China) with a soil/water ratio of 1: 2.5.The total organic carbon (TOC) (using Vavio EL III elemental analyzer, Elementar, Hanau, Germany), total nitrogen (using Rapid N cube, Elementar, Hanau, Germany), and total phosphorus (using UV-1800, Shimadzu Instruments, Suzhou, China) were analyzed according to standard methods (Page et al., 1982). The concentra- tions of zinc and copper were measured by inductively coupled plasma mass spectrometry (ICP-MS; NexION 300x , PerkinElmer, MA, USA) after acid digestion.

Health risk assessment

The non-cancer and carcinogenic risks of selected pollutants to human were evaluated with the methods recommended by the United States Environmental Protection Agency (USEPA, 1997). The average daily intake dose (ADD, mg kg-1 day-1) via non-dietary (including soil ingestion, inhalation and dermal contact) and di- etary (i.e., intake of agricultural products harvested from the soils) exposure routes (Niu et al., 2013) were estimated using the equations presented in Supporting Information (SI). The non-cancer risks of pollutants via non-dietary and dietary pathways were represented with the hazard index (HI). It is suggested that when HI < 1 the non-cancer risk is negligible. In the carcinogenic risk evaluation, the carcinogenic risk of a pollutant was classified as “very low” when the risk value was lower than 10^{-6}, “relatively low” in the range of 10^{-6} and 10^{-4}, “moderate” in the range of 10^{-4} and 10^{-3}, “high” between 10^{-3} and 10^{-1}, and “very high” when exceeding 10^{-1} (USEPA, 2009; Niu et al., 2013). This is a standard approach as a part of tiered risk assessment, which could help to identify contaminant hotspots and provide a good reference for site-specific, detailed assessment if needed in the future.

Statistical analysis

Statistical analyses were performed using SPSS 18.0, Origin 8.0, and R (http://www.r-project.org). Statistical significance was considered as $p < 0.05$. Spatial distributions of PCBs were predicted using universal Kriging in ArcGIS 10.2. Canonical correspondence analysis and partial canonical correspondence analysis were used to determine the contribution of selected variables to the variations of microbial community composition.

RESULTS AND DISCUSSION

Concentrations and composition of PCBs

A summary of the concentrations (ng/g dw) of PCB homologue groups and the sum of quantified PCBs in 241 topsoil samples is presented in Table SI-1. The concentrations of total PCBs in the YRD agricultural soils ranged from <0.1 to 130 ng/g, with a mean of 20.2 ng/g and a detection rate of 76.8%, indicating that PCBs were widely dispersed in the YRD soils. The total PCBs levels in the present study were higher than those in soil of Qinghai-Tibet Plateau (0.22e1.96 ng/g) (Gai et al., 2014), Hong Kong (0.07e9.87 ng/g) (Zhang et al., 2007), and Germany (0.95e3.84 ng/ g) (Manz et al., 2001), while they were lower than those in the soils of the Pearl River Delta in South China (0.3e202 ng/g) (Zhang et al., 2013), the Iowa State in USA (3e1200 ng/g) (Martinez et al., 2012), and the Greater London in the UK (9e2600 ng/g) (Vane et al., 2014). The levels of PCBs in these soils were similar to those found in the soils of Mongolia (0.53e114 ng/g) (Mamontova et al., 2013) and European cities (0.15e86 ng/g) (Cachada et al., 2009). According to the commonly used screening levels for resident soil (USEPA, 2016), PCB-77, PCB-81, PCB-126, and PCB-169 in 2, 11, 34, and 10 sampling sites, respectively, exceeded the allowable concentrations.

The detection rates of all the 18 PCB congeners ranged from 4.1% (PCB-153) to 45.2% (PCB-81). The concentration of the sum of six indicator PCBs (PCB-28, 52, 101, 138, 153 and 180) among the 241 sites varied from <0.1 to 119 ng/g, with a mean value of 17.1 ng/g, accounting for 80.2% of the total PCBs concentrations. The concentrations of these six indicator PCBs were significantly correlated with the concentrations of total PCBs ($R = 0.916$, $p < 0.01$, $n = 241$), thus they could be used to represent the extent of PCBs contamination in the soil environment.

The major PCB homologue group residing in the YRD topsoil was tetra-PCB, followed by tri-PCB and penta-PCB, which was consistent with the fact that 70% of the PCBs technical mixtures produced globally were tri-, tetra- and penta-PCBs (Breivik et al., 2002). The detected composition of PCBs was dominated by the low- chlorinated PCBs, while the high-chlorinated congeners, such as hepta-PCBs, were detected at significantly lower concentrations in the YRD soil samples. Although the global background soil was dominated by hexa-PCBs and penta-PCBs (Ren et al., 2007), this study showed that the PCBs homologue compositions of the YRD agricultural soils were different and hexa-PCBs were mainly found in the top 10e30 cm surface soil only (Fig. SI-1).

The concentration of the sum of 12 dioxin-like PCBs among the 241 sites ranged from <0.1 to 78.9 ng/g, with a mean value of 7.5 ng/g. The World Health Organization toxic equivalency factors (Van den Berg et al., 2006) were used to calculate the toxicity equivalents (TEQs) of the DL-PCBs.

The TEQ values ranged from below LOD to 379 ng-TEQ/kg, with the mean values of 9.5 ng-TEQ/kg. The non ortho-PCB congeners, PCB-126 and PCB-169, presented the highest TEQ values (i.e., highest toxic potency) among PCB homologous, accounting for >90% of the total TEQ. The TEQ concentration was notably higher than the data reported in other Chinese cities, such as Beijing (0.35 ng/kg) (Wu et al., 2011) and Dalian (1.37 ng/kg) (Wang et al., 2008).

The vertical concentrations and distributions of PCBs at different depths in six selected agricultural soil profiles collected from the YRD are shown in Fig. SI-1. The higher concentrations of PCBs were observed in the 0 - 30 cm surface layers relatively to the subsurface soils, because the upper 30 cm of the soil was a plow layer formed through frequent cultivation and plowing activities with regular irrigation. A rapid decline of PCB concentrations to marginal level or even below the detection limit was observed when the soil depth was greater than 30 cm, which was consistent with previous findings (Cousins et al., 1999; Wang et al., 2006). This indicated that PCBs in agricultural soils were less likely to contaminate the groundwater and subsurface environment.

Spatial distributions and potential sources

Distinct spatial distribution patterns of PCBs were observed (Fig. 1), where the concentrations of PCBs were much higher in Jiangsu Province than those in Zhejiang Province and Shanghai Municipality. A declining concentration gradient from the north- west direction was identified. The highest concentrations of PCBs were found in Danyang, Jurong, and Changzhou cities, at the longitude range between 119° and 120°, latitude range between 31° and 32°.

The composition of PCBs in the YRD soils was consistent with the Chinese commercial PCB mixtures, which contained more low- molecular-weight PCBs (tri-CBs 40.4%, tetra-CBs 31.1%)

than global PCB products (tri-CBs 25.2%, tetra-CBs 24.7%) (Ren et al., 2007). The soil PCB concentrations were strongly influenced by proximity to the sources. The large-scale use and disposal of PCB-containing products, such as lubricants, dielectric fluids, transformers, capacitors, and plasticizers by the industries in these areas were potential sources for the high PCB levels in soils (Breivik et al., 2002; Ren et al., 2007). Moreover, PCBs in building materials such as joint sealing materials, plaster and paint might enter surrounding soils (Herrick et al., 2007). On the other hand, long-range atmospheric transport and deposition of PCBs could not be excluded, especially for low-molecular-weight PCBs (Meijer et al., 2003). Some micro- organisms might also degrade highly chlorinated PCBs via dechlorination reaction into lower chlorinated PCBs as residues in soils (Abraham et al., 2002).

The results also showed that the concentration of PCBs was positively correlated with pH ($R = 0.149$, $p < 0.05$, $n = 241$), while there was no significant correlation with TOC ($R = -0.099$, $p = 0.126$, $n = 241$). The mean concentrations of total PCBs categorized with respect to land uses ranked as follows: paddy fields (19.2 ng/g, $n = 44$) $>$ vegetable fields (15.7 ng/g, $n = 48$) $>$ uncultivated lands (13.5 ng/g, $n = 26$) $>$ forests (11.6 ng/g, $n = 52$). The anaerobic condition in paddy fields was likely to hinder possible degradation of PCBs, though no statistically significant difference was observed between different land-use types ($p > 0.05$). The relationship was also analyzed between population density of sampling sites and the concentrations of PCBs. Positive correlation was observed between PCBs and population density ($R = 0.140$, $p < 0.05$, $n = 241$), suggesting that dense population, associated with high urbanization and industrialization, was partly responsible for the elevated levels of PCBs in soils.

Combined effects on microbial communities

In the microbial communities of the studied soils, bacteria were predominant and made up 63.9 ± 13.7% of the total biomass. There was no significant difference between overall microbial diversity in the collected agricultural soils ($p > 0.05$). As shown in Fig. 2, both fungi and actinomycete were positively correlated with the concentrations of PBDEs and total phosphorus, and negatively correlated with the concentrations of PAEs, PCBs and copper, whereas bacteria were positively correlated with the pH, and the concentrations of PCBs, PAEs, and copper. Compared to gram-positive bacteria, gram-negative bacteria were more correlated with pH and water.

Canonical correspondence analysis was applied to identify the combination of environmental variables that could best fit the community composition patterns. The subset of 11 variables was identified (i.e., seven soil physicochemical parameters including water content, pH, TOC, total nitrogen, total phosphorus, copper, and zinc, and four kinds of toxic organic compounds including PCBs, PBDEs, OCPs, and PAEs) to explain the variations in microbial community composition in the soils. The results showed that the 11 selected variables together could explain 12.7% of the observed variation in the community composition (Fig. 2). The subsequent partial canonical correspondence analysis revealed that the seven physicochemical parameters, the four kinds of toxic organic com- pounds, and the interaction effect of all these variables explained 11.4%, 0.86% and 0.44% of the variation, respectively (Fig. 2). Thus, soil physicochemical parameters played a more important role in regulating microbial communities than the combination of selected organic pollutants in the YRD soils. Water content and pH were the primary factors, displaying 5.03% and 2.06% explanation among the predicator variables.

Liu et al. (2015) found significant differences in microbial composition between the contaminated soils and reference soils due to the ecotoxicological effects of combined pollution associated with crude e-waste processing. In comparison, the soils of this study were collected from farmland that had not been severely polluted by point pollution sources. As the 241 sampling sites were evenly distributed in the YRD region, these results suggested that the microbial communities in agricultural soils were not strongly influenced by the combined pollution at low concentrations. Other factors might have higher impact on soil microbial communities. It has been reported that soil type, vegetation, climate, and land management practice also contribute to the diversity of microbial communities (Fisk et al., 2003; Liu et al., 2000; Lupwayi et al., 2001). Such information should be obtained and considered in future studies to capture more of the variation.

Human health risk assessments

The non-cancer risks and carcinogenic risk of chemicals to res- idents via multiple pathways were assessed. The non-cancer risks to children were higher than those to adults (Fig. 3). The average non-cancer risk of PCBs (HI = 44.0 for children, and 24.7 for adults) was overwhelmingly high, followed by much lower risk due to OCPs (HI = 0.048 for children, and 0.026 for adults), PAEs (HI = 0.036 for children, and 0.020 for adults) and PBDEs (HI = 0.017 for children, and 0.009 for adults). Among the measured PCB congeners, the average HI of individual congeners in arable soils was the highest for PCB-126 (HI = 37.1 for children, and 20.8 for adults), followed by PCB-81 (HI = 5.74 for children, and 3.23 for adults), and PCB-169 (HI = 0.506 for children, and 0.280 for adults). The HI of other chemicals descended in the order of bis (2-ethylhexyl) phthalate (DEHP) (HI = 0.028 for children, and 0.016 for adults) > γ-hexachlorocyclohexane (γ -HCH) (HI 0.016 for children, and 0.009 for adults) > BDE-47 (HI = 0.015 for children, and 0.008 for adults). The estimated intake doses of PCBs exceeded the acceptable levels (HI > 1) for children and adults in 55% and 52% of the soil samples, respectively. The estimated intake doses of PBDEs exceeded the acceptable levels for children and adults in 0.83% and 0.42% of the soil samples, respectively. None of the samples pose non-cancer risk from PAEs and OCPs.

On the contrary, the carcinogenic risks to adults were higher than those to children (Fig. SI-2). The average carcinogenic risk of PCBs (3.42×10^{-4} for children and 8.32×10^{-4} for adults) to residents was also the highest, followed by OCPs (2.30×10^{-6} for children and 5.53×10^{-6} for adults), PAEs (6.78×10^{-7} for children and 1.63×10^{-6} for adults), and PBDEs (2.49×10^{-10} for children and 5.96×10^{-10} for adults). The high risks were mainly derived from PCB-126, PCB-81, and PCB-169, respectively. Approximately 36% and 33% of the samples showed very low carcinogenic risks ($<10^{-6}$) of PCBs to children and adults, respectively. The carcinogenic risks of PCBs in a large number of samples (40% for children and 29% for adults) were between 10^{-6} and 10^{-4}, implying relatively low carcinogenic risks to residents. Moderate cancer risks (10^{-4} - 10^{-3}) of PCBs to children and adults were found in 15% and 22% of the samples, respectively. Notably, 9% and 16% of the samples posed high cancer risks (10^{-3} - 10^{-1}) to children and adults, respectively. In contrast, the carcinogenic risks posed by other chemical in the soils via non-dietary and dietary routes were all on the low side ($<10^{-6}$).

The combined risks were estimated by summing the risks of all individual compounds in an additive manner, which was implicitly assumed in the standard risk assessment of USEPA (Niu et al., 2013). This may be a limitation of the cumulative risk interpretation. As shown by the findings of this study, the combined risks of pollut- ants were dominated by PCBs. Human health risks through intake of agricultural products contributed for over 99% of the total risks, suggesting that the food consumption would be the primary contributor. A large number of soil samples in this study were collected from farmlands inside villages or around farmers' houses. People living in rural areas may frequently contact with these soils. The health risks of coexisting chemicals to residents via multiple pathways should arouse more concern.

CONCLUSION

In this study, 241 topsoil samples and six soil profiles from agricultural fields in the YRD region (approximately 45,800 km^2) were collected and analyzed to reveal the status of PCB contamination in one of regional economic zones of China. PCBs were found widespread contaminants in the YRD region. The higher PCBs concentrations were observed in the 0 - 30 cm surface soils. PCBs compositions in the YRD agricultural soils were consistent with the Chinese commercial PCB mixtures, suggesting that local sources were potentially the main input of PCBs to soil. The mean concentrations of PCBs measured in different land uses were in the following order: paddy field > vegetable fields > uncultivated lands > forests. The subset of selected soil physicochemical parameters better explained the variation in microbial community composition than the combination of selected organic pollutants in soil. The risks of chemicals to residents via multiple pathways ranked as PCBs > OCPs > PAEs > PBDEs, of which PCB-126, 81, and 169 showed much higher risks than other compounds. Notably, PCBs in 9% and 16% of the samples posed potential cancer risks (10^{-3} - 10^{-1}) to children and adults, respectively. The non-cancer risks of PCBs exceeded acceptable levels (HI > 1) for children and adults in 55% and 52% of the soil samples, respectively. Ubiquitous occurrence of coexisting organic compounds and their health risks to residents should warrant more studies in the future.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2016.08.038

LIST OF FIGURES

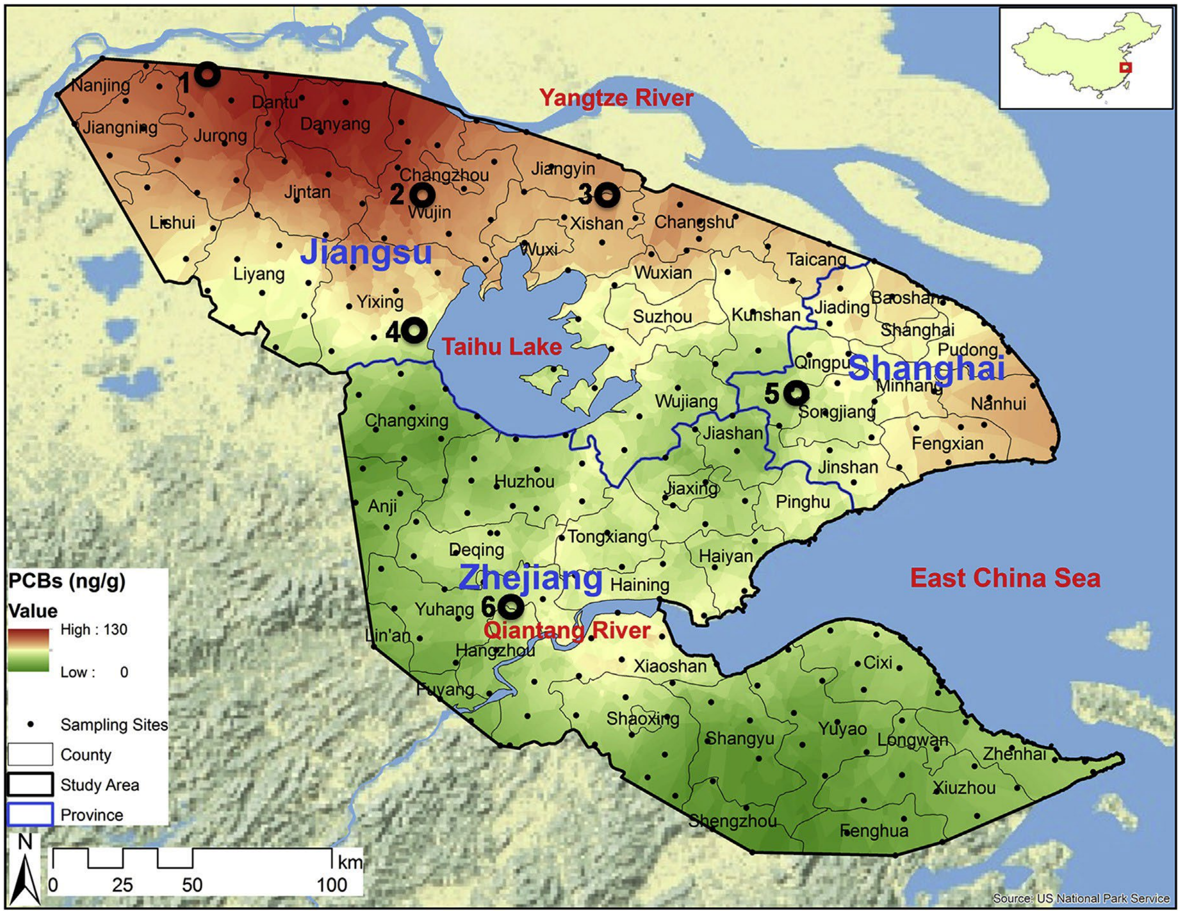

Fig. 1. Sampling sites and spatial distribution of the total concentrations of PCBs in the agricultural soils of the YRD region. The six sampling sites with soil profiles are marked with bold numbers. The legend labels, “High: 130” and “Low: 0”, represent the highest and lowest concentrations.

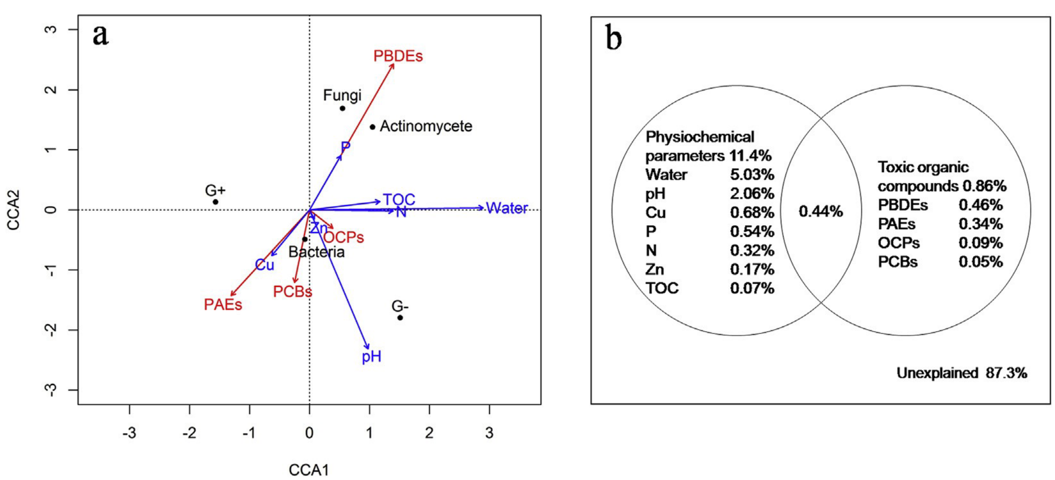

Fig. 2. (a) Canonical correspondence analysis of microbial data and the subset of 11 environmental variables (including water content, pH, TOC, total nitrogen, total phosphorus, copper, zinc, PCBs, PBDEs, OCPs, and PAEs); and (b) partial canonical correspondence analysis of the effects of

seven physicochemical parameters and four groups of organic compounds on the microbial community composition in the YRD soils.

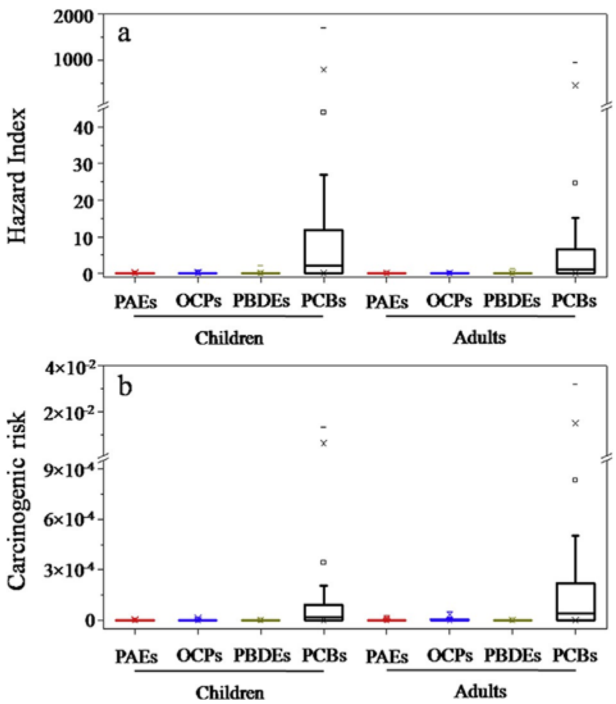

Fig. 3. Comparison of non-cancer exposure risk (a) and carcinogenic exposure risks (b) to adults and children among selected toxic organic compounds including PCBs, OCPs, PBDEs, and PAEs.

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