CHANGES OF PBDES AND PCBS POLLUTANTS IN SURFACE SOILS FROM THE YANGTZE RIVER DELTA URBAN AGGLOMERATION, CHINA BETWEEN 2003 AND 2012

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Introduction

PBDEs and PCBs are semi-volatile organic compounds and ubiquitous environmental pollutants. Soils can receive inputs of them via atmospheric deposition of dry particle, wet, and dry gaseous, and have a high capacity to store these chemicals for a long period of time[1]. Soil PBDEs and PCBs may have adverse effects on the terrestrial and aquatic ecosystem, and may lead to contamination of vegetables and food chains. In addition, soils have been shown to act as important secondary sources supplying these chemicals to the atmosphere[1]. It is therefore important to obtain information on the levels and fate of these compounds in this reservoir. To date, there has not been any comprehensive survey for PBDEs and PCBs concentration in soils from the city cluster regions in China.

Suzhou, Wuxi and Nantong are the emerging industrial cities in the YRD. Except for Shanghai, they are the most urbanized area in this region, with a residential population of 18.4 million. Since1991, they are growing into a major production center for machinery, metallurgy, chemical, electronics, textiles and telecommunication equipment in east China[2]. At present, this region is facing serious PBDEs and PCBs pollution problems, due to the rapid growth of industrial production, energy consumption, construction activities and traffic density[3]. In order to gain more information about whether there had been any spatiotemporal change of PBDEs and PCBs in soils from this region due to the rapid industrialization and urbanization process, surface soil samples were collected in 2003 and 2012 were analyzed for PBDEs and PCBs.

Materials and methods

The sampling sites are located in Suzhou, Wuxi and Nantong, covering an area from 120.2º-121.0ºE and 29.9º-32.1ºN in the YRD, China. Surface soil samples (0-5 cm, undisturbed barren land) were collected from 33 sites across the study area in August 2012. In 2003, a monitoring program about organochlorine pesticides in surface soils from this region was carried out. The investigation area and the type of surface soil were selected as same as 2012 samples (Fig. 1). The 2003 samples were kept at –20°C in the refrigerator of our laboratory for nine years. All sampling sites were divided into three area groups, urban, urban-rural transition, and rural area.
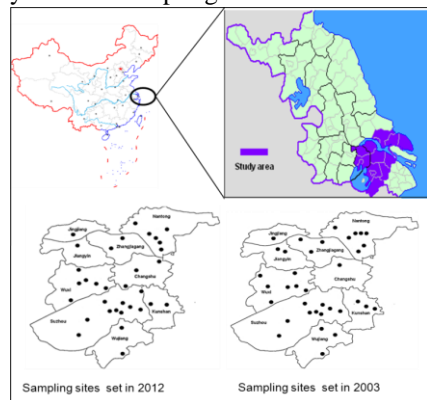

Fig.1. Map of the study area and sampling sites in the Yangtze River Delta, China.

The mixed standards of eight native PBDEs (BDE-28, 47, 99, 100, 153, 154, 183 and 209), $^{13}C_{12}$-PCB209 and the mixed standards of thirty two native PCBs were obtained from Accustandard Inc. The mixed standards of eight $^{13}C_{12}$-labeled PBDEs and ten $^{13}C_{12}$-labeled PCBs were obtained from the Cambridge Isotope Laboratories, Inc. All solvents used were of pesticide grade. Na_2SO_4, H_2SO_4 and NaOH were guaranteed reagent. Sodium sulfate was baked at 450°C and stored in a sealed container. Silica gel was twice washed with n-hexane in a glass flask and activated overnight at 160°C. ASE300 was chosen as the sample extraction method for the soil samples. Prior to extraction, all samples were spiked with surrogate standard ($^{13}C_{12}$-labeled PCBs and PBDEs) to monitor the analytical recovery efficiency. Extraction was performed with the same method we established[4]. The extracts of samples were cleaned by concentrated H_2SO_4 and a multilayer silica gel column. This pre-treatment procedure we established was described in a previous report (Shi et al. 2014). Extracts were analyzed for PBDEs using Shimadzu GCMS-2010 Ultra operated electron ionization and ZB-5HT MS column (15 m×0.25 mm×0.1μm). Extracts were analyzed for PCBs using DB-5 MS column (60 m×0.32 mm×0.25μm). The instrument analytical methods were

performed with the same methods we established[3, 4]. Surrogate recoveries in samples were as follows: $^{13}C_{12}$ BDE-209, 51.3% to 148%, $^{13}C_{12}$ PBDEs, 79.4% to 112%, $^{13}C_{12}$ PCBs, 72.5% to 117%. Concentrations of BDE congeners were corrected by recoveries of $^{13}C_{12}$- labeled BDEs. MDLs for seven BDE congeners and thirty two PCB congeners ranged from 0.1 to 0.2 and 0.08 to 0.12µg/kg respectively. MDL for BDE-209 was 4.0µg/kg. Concentrations of BDE-209 in all samples were corrected by subtracting value of blank.

Results and discussion

Table 1. Descriptive data for Σ_7PBDEs, BDE-209 and Σ_{32} PCB in the soil samples (µg/kg dw).

	Data for 2012(n = 33)			Data for 2003(n = 36)		
	Σ_7PBDEs	BDE-209	Σ_{32}PCBs	Σ_7PBDEs	BDE-209	Σ_{32}PCBs
Mean ± STD	0.543±0.57	9.47±10.2	0.991±0.764	0.178±0.181	3.13±3.16	1.01±0.727
Median	0.280	5.41	0.873	0.114	2.09	0.727
Geomean	0.319	5.69	0.801	0.115	2.04	0.735
Range	0.041-2.23	1.02-41.7	0.205-3.96	0.01-0.557	0.532-12.8	0.301-3.29

BDE-209 was detected at all sites both in 2003 and 2012, which indicated that this compound have ever been a ubiquitous environmental pollutant in soils of the YRD from 2003-2012. The detection frequency for7 BDE congeners was between 51.5% and 93.9% in the 2012 samples, 25.0% and 88.9% in the 2003 samples, which showed that the 7 BDE congeners have become more widespread in the 2012 samples compared to the 2003 samples. The statistical information also showed that similar detection frequency for each PCB congeners were observed in the 2003 and 2012 samples, which indicated that there were no significant changes of PCB congener pollution in soils these years. To establish if there were changes for the PBDEs and PCBs concentrations in soils between 2003 and 2012, independent samples group t test were applied. The results showed that there existed significant difference Σ_7PBDE(P=0.001＜0.05) and BDE-209(P=0.001＜0.05) between the sampling years with 2012 > 2003 concentrations. However, no significant difference were observed for PCBs data sets (Sig=0.75, P=0.924＞0.05). PBDEs concentrations in the study region increased significantly between the sampling years from 2003-2012, which could infer there might be much higher usage and emissions of PBDEs in 2012 than in 2003. In China, the unbanned deca-BDE (BDE-209) congener is still being produced and continues to be deployed as a flame retardant, with no early prospect of termination and replacement. Other study reported that the domestic demand of PBDEs (including BDE-209) has increased at a rate of ~8% per year since 1999. Therefore, some PBDEs, past production, current consumption, continuing disposal mean and various combustion processes are all important emission sources, and could contribute continuous PBDEs to the soil environment. Differently, there were no significant differences in the PCBs concentrations between 2003 and 2012. In China, the production of PCBs was prohibited in 1981. The concentration of PCBs should have been declined in surface soils during these years. The results suggested that PCBs might approach a removal–input equilibrium in soils during these years.

BDE-209 was the major BDE congener in all samples, accounting for 92.2% (73.3–99.7%) and 92.9% (69.3–99.6%) to Σ_8PBDEs in the 2003 and 2012 data, respectively. The proportions of BDE-209 in the soil samples did not significant change between the sampling years from 2003 to 2012, even though PBDEs concentrations increased significantly. Studies demonstrated BDE-209 is the main congener in two Deca-formulations. The results showed that the dominant PBDE mixture production and usage in the YRD had ever been the commercial deca-BDE mixture these years.
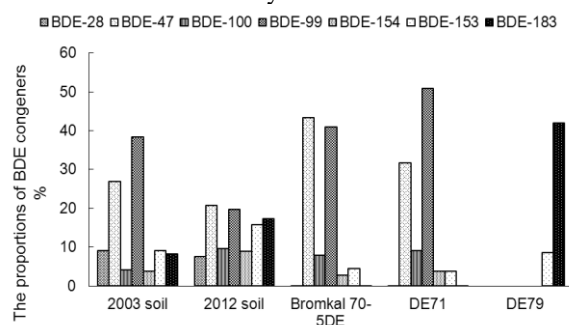

Fig. 2. Comparison of BDE congener profile between the PBDE technical mixture and samples.

Compared with the commercial penta-BDE product, it was found relatively higher proportions of BDE-153 in the 2012 samples than in Bromkal 70-5DE, DE-71(Fig. 2). Previous research reported that BDE-153 could be from octa-BDE products, and the percentages of BDE-183 and BDE-153 were 42% and 8.7% in it. In

present study, relatively good correlation ($r^2 = 0.7749$, >0.05) was found between BDE-153and BDE-183 in the 2012 samples, indicating the likely additional input from octa-BDE sources in this region recent years, while the quantity was much lower than that of deca-BDE. Due to the low detection frequency (27.8%) for BDE-153 in the 2003 samples, so it is impossible to reach appropriate conclusions.

It was noted that BDE-47and 99 are major congeners of penta -BDE products, and the BDE-47:-99 ratios is 1.05 in Bromkal 70-5DE and 0.76 in DE-71. Due to BDE-99 has higher K_{OA} (octanol-air partition coefficients) relative to BDE-47, the ratio of BDE-47 to BDE-99 usually bellows 0.8 in soils[5]. The ratio was 0.73±0.34 in the 2003 samples, indicating there might be input from penta -BDE sources in 2003. However, the ratio was1.12 ±0.33 in the 2012 samples, which differed from those in penta-BDE product and background soil reported in other literature[5]. In addition, the proportions of BDE-28 and BDE-154 in the 2012 samples were higher than that in penta -BDE products. Such difference might result from BDE congener fractionation changing by transport, mixing, microbial degradation or photodegradation and depositional mechanisms in the environment, due to their different physicochemical properties.

There was little change in the pattern of soil PCB profiles over the nine years. The major homologue in all samples was penta-PCBs, followed by tetra -PCBs and hexa-PCBs. It was found that the percentage of lighter weighted molecular PCBs in the 2003 samples were slightly higher than those in the 2012 samples, whereas high chlorinated PCBs were just the opposite. This was due to the fact that lower chlorinated congeners are more mobile, and thus have been transported deeper into the soil. Another factor could be that the lower congeners are more volatile, and hence may be preferentially lost to the atmosphere. Principal component analysis (PCA) was used to evaluate the distribution pattern of PCBs and determine possible origins in the samples. Homolog from di-PCBs to hepta-PCBs were selected as variables for principal component analysis. The first principal component (PC1) had higher loading for the lower chlorinated PCB, and PC2 had higher loading for the higher chlorinated congeners. The principal component scores for each site and PCBs mixtures were displayed in Fig 3. It may be found from the loading plot that several samples in 2003 and 2012 as well as Aroclor1254 constituted similar scores of PC1 and PC2. The possible source of PCBs in these samples might be the emission from Aroclor1254. In China, Aroclor1242 and Aroclor 1254 were the two major PCBs mixture, with production of 9000 tons and 1000 tons prior to 1974, respectively. These samples might have polluted by primary or secondary sources containing Aroclor1254, such as outdated equipment, contaminated water, air and sediment. However, the PC1 and PC2 scores of Aroclor1242 were significantly distinct from all sample sites, both in the 2003 and 2012 data. It was difficult to make a conclusion that there was no input from Aroclor1242 in soils. This mostly due to the transportation of the low chlorinated PCBs from the surface soil to the deeper soil, or the volatilization of them to the atmosphere. Another consequence was relatively higher proportion of the high chlorinated PCBs was residual in soils. In addition, the majority of sample sites had different PC values of Aroclor1260 or Aroclor1248, which consistent with the fact that there had not been any large scale use of them in China.
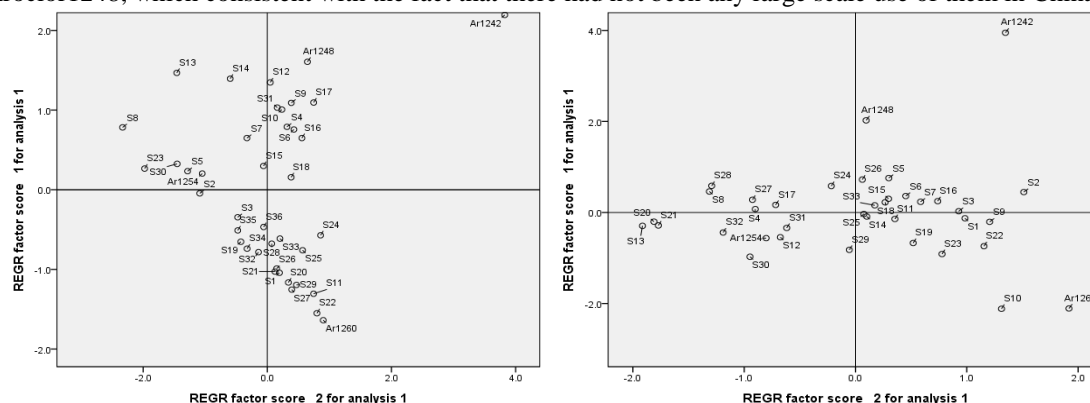

Fig. 3 Score plot of PCA for the 2003 and 2012 soil samples from the Yangtze River Delta, China.

As a whole, spatial distributions of PBDEs or PCBs in surface soil samples reflect a gradient (high to low) from the central city out to rural areas both in the 2003 and 2012 data (Fig. 4). Normally, PBDEs emission sources concentrated in urban area, including the residential/commercial area or industrial area. It was reported that PBDEs could be emitted to the ambient air during production, use and disposal of PBDEs-containing products in the urban area. In addition, PBDEs could also form or not be completely destroyed in various

combustion processes. Incinerators, power plants, metallurgical processes and vehicles were recently identified as PBDEs emission sources, especially for BDE-209. In addition, in the residential/commercial area, automobiles emission (cushion, electronics, etc.), fraction of tire wear and construction materials contain amounts of PBDEs, may favor higher levels of PBDEs to the urban environment. Therefore, the concentrations of soil PBDEs from urban area were higher than urban-rural transition and rural area. It was worthwhile to note that many 2012 samples with high PBDEs concentrations were found not only in big cities but also in some small cities, such as Changshu, Kunshan, Zhangjiagang, Jiangyin and etc. In fact, the urban system in this region is made up of many secondary cities mentioned above. Since 1991, the development of rural industries and the construction of small cities are combined together, leading to emergence of rural economic development zones and many small cities group[2]. With the development of industrialization and urbanization process in this region, these small cities and rural economic development zones are facing serious PBDEs pollution problems, which should be of grave concern. The spatial distributions of the soil PCBs in the urban, suburban and rural area were similar to PBDEs. The variability in the concentrations of PCBs suggested that the major source of PCBs in soil samples from urban areas might be resulted from the impact of point source inputs. The samples with higher PCBs concentration were all observed in the industrial areas of the cities. This indicates that PCBs pollution in urban soils might come from significant PCBs stationary sources or historical contaminated soils caused by products containing PCBs, improper disposal or leakage of oil from transformers and capacitors.
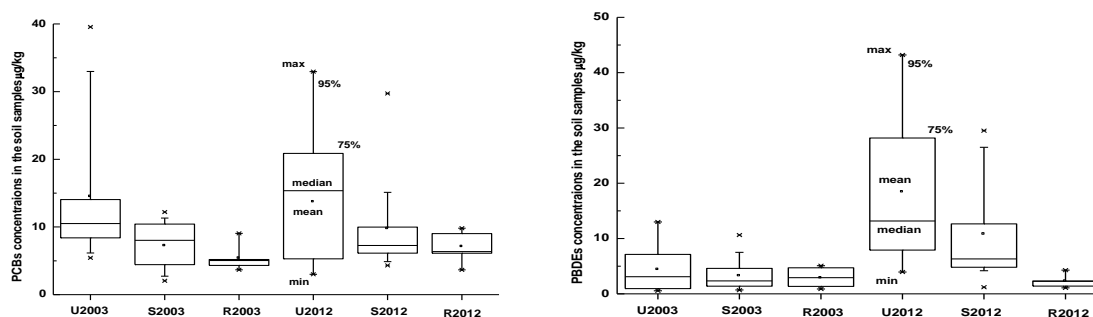

Fig. 4. Spatial distributions of PBDEs in surface soil from the Yangtze River Delta.

Error bars correspond to 95th centiles of confidence level, boxes correspond 25th to 75th centiles of confidence level. U: urban area; R: rural area; S: suburban area

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