POLYCHLORINATED BIPHENYLS AND POLYBROMINATED DIPHENYL ETHERS IN TREE BARK FROM SOUTHERN JIANGSU, CHINA: LEVELS, DISTRIBUTION, AND POSSIBLE SOURCES

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Introduction

Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are persistent organic pollutants (POPs) that have been banned by the Stockholm Convention because of their environmental persistence and high toxicity to the ecosystem and human. As an useful passive air sampling media in vegetation, tree bark has been used to measure the concentrations of inorganic and organic compounds and investigate the pollution sources[1]. Several cities in southern Jiangsu province such as Suzhou, Wuxi and Nantong have been developed dramatically with a variety of industries in recent decades. But with the rapid economic development, pollution by organic pollutants such as PBDEs, PCBs and pesticides is becoming serious in this region[2]. The primary aim of this study was to use tree bark as a kind of passive sampler to comprehensively evaluate the status of PBDEs and PCBs contamination in Southern Jiangsu and the potential sources were investigated. In addition, the comparison of tree bark and polyurethane foam (PUF) disks was made in monitoring PCBs concentrations in atmosphere.

Materials and methods

Detailed information on the sampling location and procedure has been reported elsewhere[3]. The tree bark samples were freeze-dried and milled. Before extraction, all samples were spiked with known amounts of $\Sigma_7{}^{13}C_{12}$-PBDEs, $^{13}C_{12}$-BDE209, $\Sigma_{10}{}^{13}C_{12}$-PCBs. Approximately 18 g of the bark sample with 3 g diatomite was extracted in an Accelerated Solvent Extraction (ASE, Dionex 300) with a mixture of acetone and hexane (V/V = 1:1). Then, the extract was filtered and concentrated by a rotary evaporator, solvent exchange to hexane and evaporated to ~15 ml, added 3 g $MgSiO_3$, the extract was freezed in the refrigerator for one night to remove the bark lipids. After filtration, the solution was concentrated by rotary evaporation to 1 ml before clean-up. The concentrated extract was then further cleaned with one multilayer silica column filled from the bottom with 1 g of anhydrous Na_2SO_4, 1 g of activated silica, 2 g of florisil, 1 g of activated silica, 3 g of silica/NaOH 33% (w/w), 1 g of activated silica, 8 g of silica/H_2SO_4 44% (w/w), 1 g of activated silica and 1 g of anhydrous Na_2SO_4. The sample was eluted with 120 ml DCM/hexane (1:4), then reduced to 1 ml for analysis. The samples were analyzed by GCMS-QP2010 Ultra (Shimadzu, Japan). For PCBs analysis, the analytical column was a Rtx-PCB capillary column (60 m×0.25 mm i.d.; 0.25 μm film thickness; Restek). The GC oven temperature was programmed from 110 ℃ (3 min) to 210 ℃ at 15 ℃/min, increased to 310 ℃ at 3 ℃/min, then to 320 ℃ at 5 ℃/min and held for 10 min. For PBDEs analysis, a 15-m DB-1MS capillary column (0.25 mm i.d., 0.10 μm film thickness; J&W Scientific) was used. The column temperature was initiated at 60 ℃ (held for 1 min), and increased to 200 ℃ at 20 ℃/min (held for 1 min), 280 ℃ at 10 ℃/min, and 320 ℃ at 20 ℃/min (held for 3 min).

Results and discussion

PCBs

Σ_7PCB_{ind} were in the range 0.439-2.73 ng g^{-1} dry weight (dw) (mean 1.03 ng g^{-1} dw) (Fig. 1). The Σ_{32}PCBs concentrations ranged from 0.576 to 5.19 ng g^{-1} dw with a mean value of 1.79 ng g^{-1} dw. The indicator PCBs (CB28, 52, 101, 118, 138, 153 and 180) including CB49, 44, 74, 70, 66, 101 and 99 were detected in all tree bark samples. Σ_7PCB_{ind} accounted for 57.8% of Σ_{32}PCBs and significant positive correlations were found between them (r^2=0.897, P=0.01). Among all the sampling sites (Fig. 2), #15 showed the highest concentrations of Σ_7PCB_{ind} and Σ_{32}PCBs (2.73 and 5.19 ng g^{-1} dw). There was a steel plant located around this site, which could be responsible for the highest concentrations of ΣPCBs. Zhang et al. (2013b)[4] also reported that this site had the higher PCB concentration than the other sites in the atmosphere. #26 had the lowest Σ_7PCB_{ind} and Σ_{32}PCBs concentrations (0.439 and 0.576 ng g^{-1} dw). The relatively high concentrations of Σ_7PCB_{ind} and Σ_{32}PCBs were

found in downtown and suburban regions, such as #6, #19, #10, #2 and #5. There was no significant difference between industrial park and the other areas ($p > 0.05$). A comparison of PCB concentrations in tree bark was made. The ΣPCBs levels in our study were relatively lower. The higher PCB concentrations were found in other study regions, especially in an E-waste recycling area in Luqiao District[5], the industrial zones in Rhine Valley and the PCB contamination area around Bloomington[6].

The PCB homologue profiles detected in tree bark samples were predominated by tri- to penta-PCBs, contributing 16.9-60.6%, 24.4-61.0% and 24.4-61.0% to the total PCBs respectively (Fig. 3). The PCB congener profiles in our study were similar to those found in an E-waste recycling area in east China[5]. Tri-PCBs were also the major PCB homologs in Chinese air[7], background /rural surface soil[8] and sediments of the Liaohe River[9]. The PCA results showed that the PCB homologue profiles in almost all of sampling sites were similar to Ar1242 and KC300 except for site #3 and #26, which had the similar PCB profile with Chinese technical PCBs, #1 PCB (Fig. 4). #1 PCB had the similar PCB homologues with those in PCB formulation Ar1242 and KC300，but in comparison with Ar1242, number 1 PCB contained much more tri-PCBs and less tetra-PCBs[8], #1 PCB was mainly used in power capacitors and transformers in China. Therefore, the most important PCB source in Southern Jiangsu was likely from the leakage of abandoned electrical equipment containing PCB formulation Ar1242 or #1 PCB.

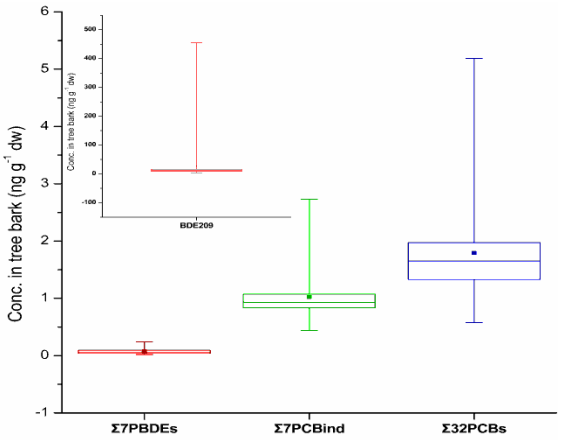

Fig.1 Σ_7PCB_{ind}, $\Sigma_{32}PCBs$, Σ_7PBDEs and BDE209 concentration in tree bark

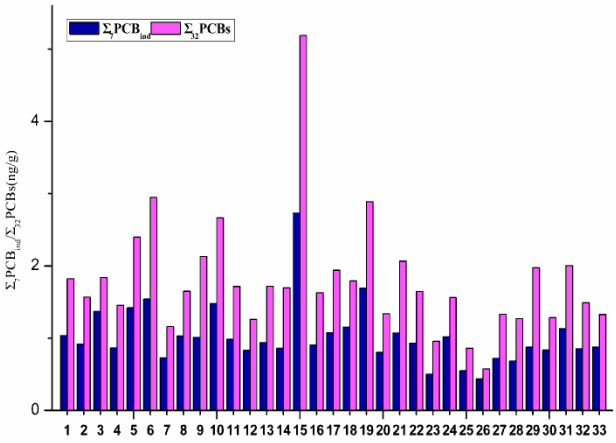

Fig.2 Distribution of Σ_7PCB_{ind} and $\Sigma_{32}PCBs$ (ng g^{-1} dw) in tree bark from Southern Jiangsu

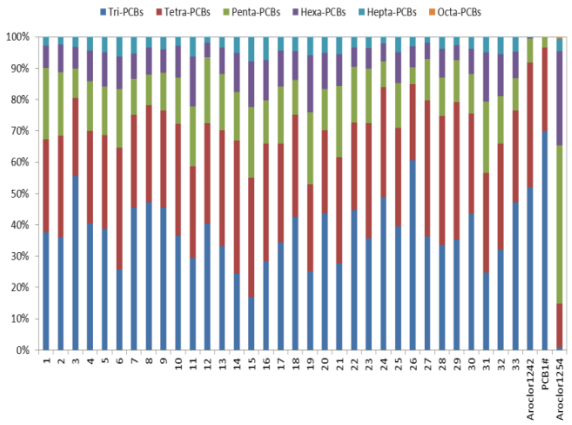

Fig.3 Congener profiles of PCBs in tree bark from Southern Jiangsu

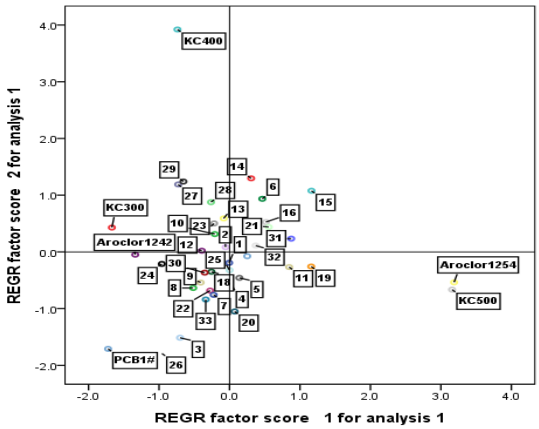

Fig.4 PCA analysis of PCBs congeners in camphor tree bark from Southern Jiangsu

PBDEs

The Σ_7PBDEs concentrations varied from 17.9 to 243 pg g^{-1} dw with a mean value of 74.7 pg g^{-1} dw and the concentrations of BDE209 ranged from 4.29 to 456 ng g^{-1} dw (mean 27.3 ng g^{-1} dw) (Fig. 1). The spatial distributions of PBDEs were shown in Fig. 5.The highest Σ_7PBDEs concentrations were found in sample #6 (243 pg g^{-1} dw) and #5 (226 pg g^{-1} dw). Relatively high concentrations of Σ_7PBDEs (116 to 152 pg g^{-1} dw) were observed in sample #8 (close to several chemical factories), #15 (near Shagang steel plant), #19 (downtown area)

and #21 (close to some textile factories). The lowest Σ_7PBDEs concentrations (17.9 pg g^{-1} dw) were found in a rural area (sample #12). Extremely high concentrations of BDE209 were observed at site #8 (456 ng g^{-1} dw), which were 10 and 100 times higher than the second highest site #28 (44.5ng g^{-1} dw) and the lowest site # 26 (4.29 ng g^{-1} dw) respectively. For Σ_7PBDEs, there was no significant difference ($p > 0.05$) between industrial park and the other areas. But for BDE209, significant difference ($p < 0.05$) was observed between them. Compared to other levels reported for tree bark, Σ_7PBDEs levels in the present study area were lower. The level of BDE209 in our study region was similar to those found at an E-waste recycling area[5], which showed that BDE209 pollution in Southern Jiangsu was very serious. According to Ma et al. (2012)[10], there were several BFRs manufactories that mainly produced deca-BDE technical mixture in Jiangsu province. The greater BDE209 concentrations in air samples were also found in this area[2].

BDE209 was the predominant congener, contributing ~99% of the total PBDEs in all tree bark samples. Generally, BDE209 was the most abundant compound reported in various environmental media in China. This was probably due to the fact that the commercial deca-BDE mixture accounted for most of the total PBDE mixture production and usage in China. Except for BDE209, BDE47, 99 and 183 were also the dominant components (Fig. 6), which accounted for 51-73% of Σ_7PBDEs and their concentrations were in the order: BDE209 > 47 > 99 > 183. The PBDE compositions in this study were comparable to those found in Great Lakes in United States[11], an e-waste recycling area in China[5] and in North America. The PBDE patterns in the samples collected from #5, #6 and #15 were similar to that in the technical penta-BDE mixture (Bromkal 70-5DE and DE-71). Three main components, BDE47, 99 and 100, had a combined relative abundance in the range from 64.3% to 72.4% of Σ_7PBDEs, similar to the compositions of the penta-BDE mixtures. Larger contributions of BDE183 were found in sample #8 (59%) and #27 (35%), BDE-183 was considered to be the major component of the technical octa-BDE mixture. This suggested that octa-BDE formula was also an important source of PBDEs in this study.

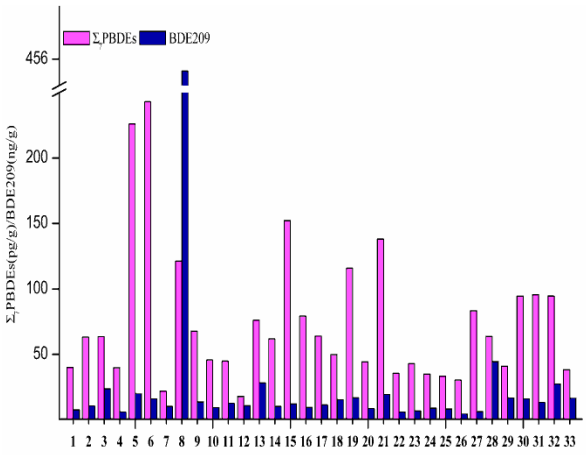

Fig.5 Distribution of Σ_7PBDEs (pg g^{-1} dw) and BDE209 (ng g^{-1} dw) in tree bark

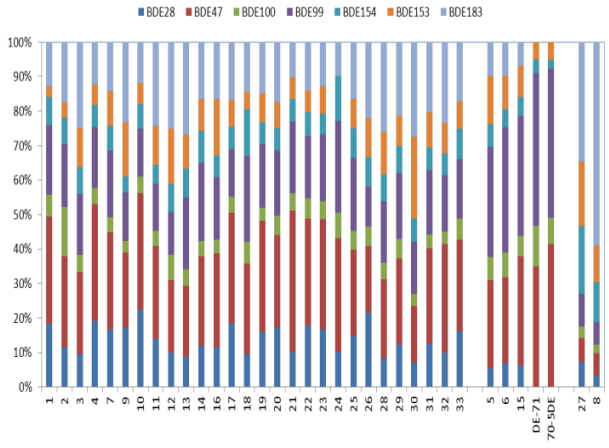

Fig.6 Congener profiles of PBDEs in tree bark from Southern Jiangsu

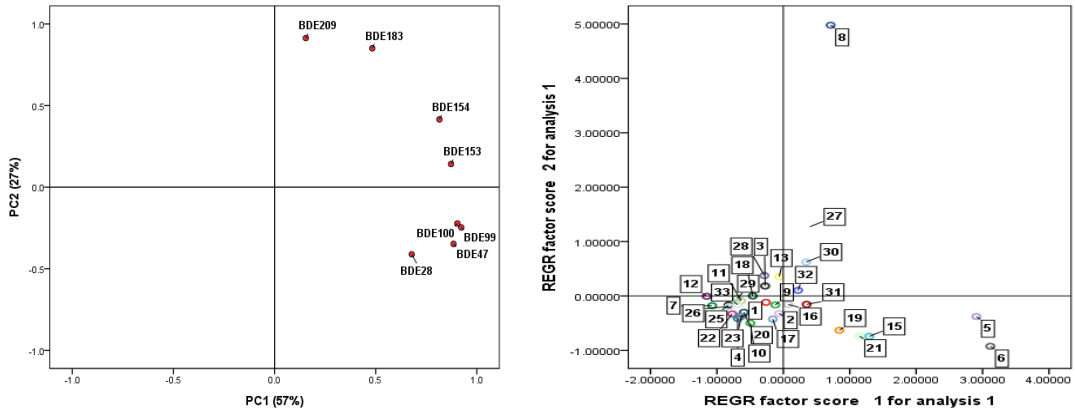

Fig.7 PCA analysis of PBDE congeners in camphor tree bark from Southern Jiangsu

To further identify the sources of PBDEs, principal component analysis (PCA) was carried out using SPSS 18.0

(Fig. 7). The first factor was responsible for 57% of the total variance. This factor had high loading values of BDE47, 99 and 100, BDE153 and 154 are also the main components. The high loading values of these compounds indicated that this factor represented the penta-BDE commercial mixtures. The second factor, which accounted for 27% of the total variance, reflected octa- and deca-BDE sources because of the high loading values of BDE183 and 209 which were considered as markers of technical octa- and deca-BDE mixtures. To sum up, it could be inferred from the above analysis that the major source of PBDEs in Southern Jiangsu originated from the deca-BDE commercial mixture with minor contributions from penta- and octa-BDE mixtures.

PCBs in tree bark and PUF sampler

PUF sampling was carried out at the same locations as the tree bark collecting[4]. PUF disk samplers were exposed and collected every three months from June 2010 to April 2011. Good correlation was found between tree bark and PUF disks in Σ_6PCBs (CB28, 52, 101, 138, 153 and 180) (r=0.404，P=0.05) monitoring, suggesting that both of them respond well to the gas-phase PCB monitoring. Contour maps of PCBs in tree bark and PUF were made using the Kriging gridding method in Surfer 8.0 software. As shown in Fig. 8, the spatial distributions of PCBs in tree bark and PUF were similar which further illustrated the good correlation between them. There were also significant correlations between them in vapor-phase PAHs monitoring[3]. Because of the lack of data in PBDE concentration in air, we didn't make comparison between them. But good relationships were reported between them by Salamova and Hites (2013)[12]. Therefore, tree bark can substitute for PUF in the monitoring of organic pollutants in some situations. However, since tree bark has long life cycle and it can accumulate pollutants during the whole life, tree bark can't be used as the indicator of temporal variation of organic pollutants such as seasonal variation. Therefore, the researchers should choose different passive air samplers according to different research purposes.

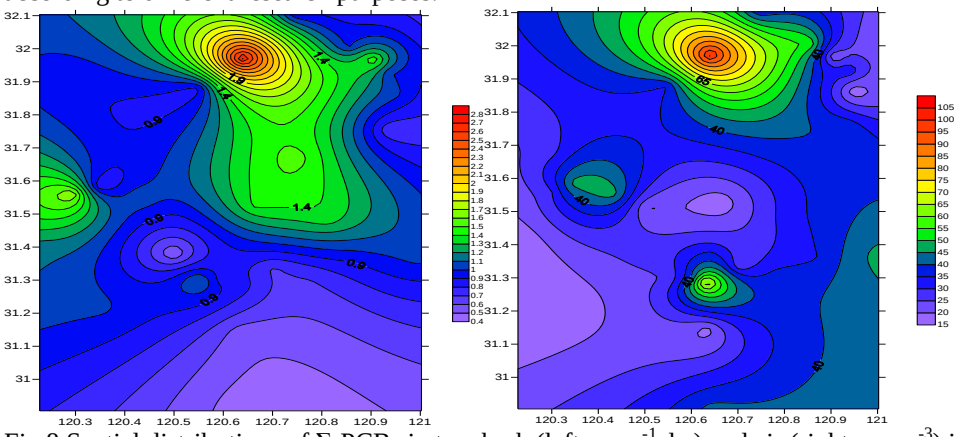

Fig.8 Spatial distributions of Σ_6PCBs in tree bark (left, ng·g^{-1} dw) and air (right, pg·m^{-3}) in Southern Jiangsu

Acknowledgements

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References:

1. Guéguen F, Stille P, Millet M. (2011); *Chemosphere*. 85:195-202
2. Zhang L, Zhang T, Dong L, Shi S, Zhou L, Huang Y. (2013a); *Sci Total Environ*. 454-455:619-26
3. Zhou L, Dong L, Huang Y R, Shi S, Zhang L, Zhang X. (2014); *Chemosphere.* (in press)
4. Zhang L, Dong L, Yang W, Zhou L, Shi S, Zhang X. (2013b); *Environ Pollut*. 181:159-66
5. Wen S, Yang F, Li JG, Gong Y, Zhang XL, Hui Y. (2009); *Chemosphere*. 74:981-7
6. Hermanson MH, Hites RA. (1990); *Environ Sci Technol*.24: 666–671
7. Zhang Z, Liu L, Li YF, Wang D, Jia H, Harner T. (2008); *Environ Sci Technol*. 42:6514-8
8. Ren N, Que M, Li YF, Liu Y, Wan X, Xu D. (2007); *Environ Sci Technol*. 41:3871-6
9. Zhang H, Zhao X, Ni Y, Lu X, Chen J, Su F. (2010); *Chemosphere*. 79:754-762
10. Ma J, Qiu X, Zhang J, Duan X, Zhu T. (2012); *Chemosphere.* 88:769-78
11. Salamova A, Hites RA. (2010); *Environ Sci Technol*. 44:6196-201
12. Salamova A, Hites RA. (2013); *Environ Sci Technol*. 47:349-54