POLYCHLORINATED BIPHENYLS IN CHINESE AIR

Zhang Z[1,2], Liu LY[1], Ren NQ[1], Li YF[3,1], Liu Y[4], Wan XN[5], Xu DD[6], Sverko E[3,7], Harner T[3], Pozo K[3]

[1]International Joint Research Center for Persistent Toxic Substances (IJRC-PTS), Harbin Institute of Technology, Harbin, China; [2]Heilongjiang University, Harbin, China; [3]Science and Technology Branch, Environment Canada, Toronto/Burlington, Canada; [4]IJRC-PTS, Dalian Maritime University, Dalian, China; [5]IJRC-PTS, Chengdu University of Technology, Chengdu, China; [6]IJRC-PTS, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, China; [7]IJRC-PTS, McMaster University, Hamilton, Canada

Abstract

Polychlorinated biphenyl (PCB) concentrations in air from 52 sites (4 background, 39 rural, and 9 urban) in a concurrent air/soil sampling program across China are presented. In 2005, air samples were deployed for approximately 3 months from mid July to mid November. An average of 310 pg m^{-3} for all 52 samples was found, with a range of 30 pg m^{-3} to 970 pg m^{-3} for Tibet and the City of Harbin, Heilongjiang Province, respectively. Differences of only 1 order of magnitude were found between all sites, indicating a generally uniform distribution of PCBs in Chinese air. The composition of PCB homologues in urban, rural, and background areas were similar. A comparison was made with PCB in Chinese air to that in Chinese PCB product, transformer oil, and surface soil. Results indicate that the profile of PCB congeners in Chinese air is more similar to that of Chinese transformer oil showing a higher percentage of the lighter molecular weight PCBs. Whereas PCB concentrations in Chinese soils exhibit a profile preferring the higher molecular weight PCBs, as a result of numerous years of deposition and accumulation of the chemical. This suggests that PCBs in Chinese air are mainly due to the emission of PCBs from primary sources and not from re-emission from soil.

Introduction

Polychlorinated biphenyls (PCBs), listed along with eleven other compounds as persistent organic pollutants (POPs) by the Stockholm Convention on May 22, 2001, are stable in the environment, undergo long-range atmospheric transport (LRAT), and possess the ability to bioaccumulate through the food chain which can impose a serious threat to human health and the environment. Thus, PCBs have been extensively studied during the last 30 years.

Under the "Chinese POPs Soil and Air Monitoring Program" (SAMP), which started in 2004, concurrent sampling of PCBs in soil and air across China was carried out. The results of PCBs in surface soil across China have been published[1]. In this paper, the results of PCB concentrations in air from 52 sites across China are presented, and the relationship with those in surface soil collected from the same sites are also discussed.

Material and methods

Sampling. Passive Air Samplers (PASs) with polyurethane foam (PUF) disks[2,3] were deployed at 52 sites (4 background, 39 rural, and 9 urban) across China in 2005 for 3 months. Disks were pre-cleaned by extraction at the laboratories at International Joint Research Center for Persistent Toxic Pollutants (IJRC-PTS), Harbin Institute of Technology and Dalian Maritime University, China, and then transferred to the sampling locations in sealed, solvent-cleaned brown glass jars with Teflon-lined cap. At the end of the deployment period, the PUF disks were retrieved, resealed in their original solvent-cleaned brown glass jars at the sampling locations, and returned to the laboratories of the IJRC-PTS, where they were stored frozen (-20^{o}C) until extraction. Samples were deployed for approximately 3 months from mid July, 2005, to mid November, 2005.

Analytical methods. In the laboratory, samples were treated, extracted, and analyzed according to the methods established at the Hazardous Air Pollutants (HAPs) Laboratory and the National Laboratory for Environmental Testing (NLET), Science and Technology Branch, Environment Canada. The samples were Soxhlet extracted for 24 h using acetone and hexane (1:1 v/v). Extracts were cleaned using silica chromatography column which consisted of 5g silica gel, and topped with 2.5 cm of anhydrous sodium sulfate. Following a pre-rinse of the column with 25 mL of dichloromethane (DCM), then 25 mL of hexane, the sample was added and eluted with 30 mL of DCM and hexane (1:1 v/v). Eluants were blown down to about 300 µL under a gentle stream of UHP nitrogen and solvent-exchanged into isooctane. PCB congeners 30 and 204 were added as internal standards.

Details of sample analysis are presented elsewhere[1]. Briefly, 62 PCB congeners were determined by gas

chromatography-negative ion chemical ionization mass spectrometry (GC-NICIMS) using an Agilent 6890 GC-5973N mass selective detector (MSD) equipped with a split/splitless injector. A 60-m DB-5MS column (J&W Scientific) with 0.25 mm i.d. and 0. 25 µm film thickness was operated with a helium carrier gas with a flow of 1 mL min^{-1}. The instrument was operated in selected ion mode (SIM). All samples were spiked with a labeled recovery standard (PCB 155) prior to extraction. Sample recoveries ranged from 75 to106% for PCB 155 in all samples. Blank samples were included at a rate of one for every 10 PUF extracted.

Results and discussion

PCB concentration and distribution. The derivation of an air concentration requires the amount of chemical accumulated on the PUF disk and the effective air sample volume for the particular chemical. The approach for calculating air concentrations from passive sampling data[4, 5] was used to calculate the effective air sample volume and then the air concentrations for each PCB congener at all 52 sites. Concentrations of ∑PCBs (total 62 PCB congeners) in air for each site, shown in Figure 1, had an average of 310 pg m^{-3} for all 52 samples and ranged from 30 pg m^{-3} at Site B2 (Tibet) to 970 pg m^{-3} at U8A (Harbin), with a difference of 1 order of magnitude, indicating a generally uniform distribution of PCBs in Chinese air. The top 10 PCB congeners/pair were PCB-33, 15, 31/28, 49, 18, 17, 52, 26, 22, and 44. The dominant PCB homologue group was tri-PCB, followed by tetra-PCB and di-PCB.

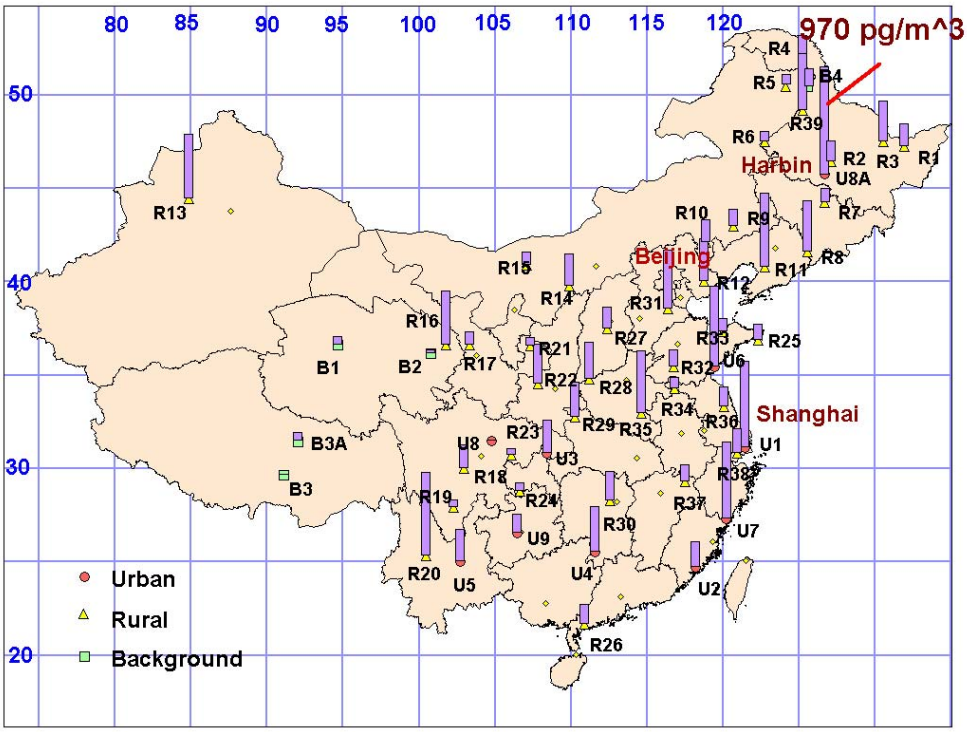

Figure 1. PUF disk sampler derived air concentrations for sum of 62 congeners from 52 sampling sites across China. The numbers from 80 to 125 on the top are longitude in °E and the numbers from 20 to 50 on the left are latitude in °N.

Concentrations of PCB homologues in the average Chinese urban, rural, and background air are depicted in Figure 2. The air concentration of ∑PCBs in urban area was higher than rural and background areas, the mean concentration of the 9 urban samples was 510 pg m^{-3}, followed by 290 pg m^{-3} for the 39 rural samples and 80 pg m^{-3} for the 4 background samples, respectively. These concentrations are consistent with air concentrations for PCBs at urban, rural and background air reported under the global atmospheric passive sampling (GAPS) study.[6]

Comparison with published data. Jaward and coworkers[7] measured PCBs in Chinese air samples in 2004 and a total of 32 samplers were successfully deployed at 13 rural and 19 urban sites. A total of 29 PCB congeners/pairs were regularly detected. Of the top 10 PCB congeners/pairs found in all air samples in this study, PCB-18, 31/28, 49, 52, and 22 are among the top 7 congeners found in the 2004 study. Figure 3 compares mean concentrations of PCB homologue groups in Chinese air among the 52 sampling sites in 2005 (this study) with the results from the 32 sites in 2004[7]. The concentrations of total PCBs in 2005 are higher than in 2004, which is expected since 62 PCBs were detected in 2005 in comparison to 29 PCB congeners/pairs in 2004. When the 2005 data is reported for the same 29 PCBs (Figure 3), the 2005 levels are still higher – especially for the tri- and tetra-PCBs which are about two times higher compared to the 2004 data. This is surprising given that the 2004 study had a greater proportion of urban sites. However, the 2004 study was conducted during a colder time of the year when PCB levels may be lower.

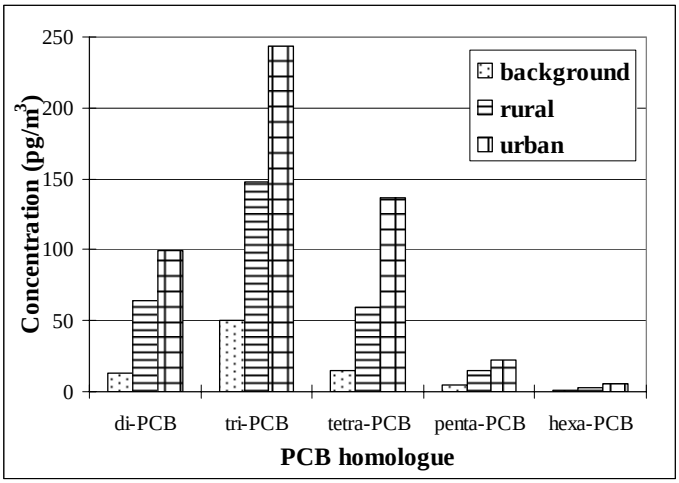

Figure 2. Concentration of PCB - homologue groups - in the average Chinese urban, rural, and background air.

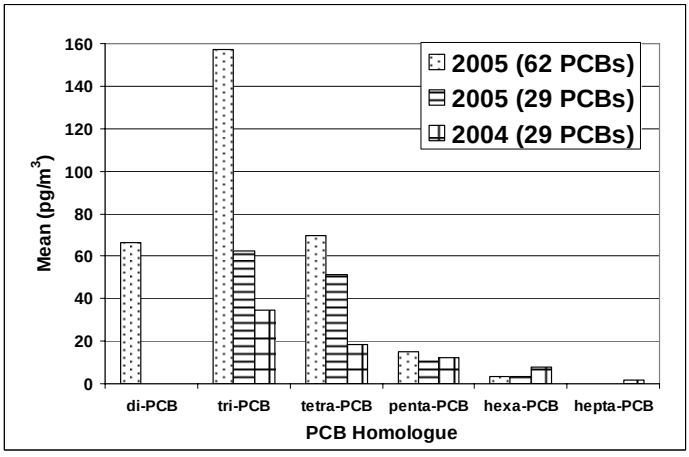

Figure 3. Mean concentrations of PCB homologue groups in Chinese air in 2005 (this study) and in 2004[7].

PCB source profiles. Figure 4 depicts PCB homologue composition in Chinese air (this study), Chinese transformer oil[1,8], Chinese PCB product[1], and Chinese surface soil[1]. As indicated in Figure 4, the profile of PCB

congeners in Chinese air is more similar to that of Chinese transformer oil and Chinese PCB product than the profile in Chinese soil. This suggests that primary sources are the main contributor to the air and not re-emission from soil. The PCB burden in Chinese soils is the result of deposition from air over many years, resulting in a high percentage of higher molecular weight PCBs in soil. Further work will investigate paired air and soil samples to assess the source/sink relationship.

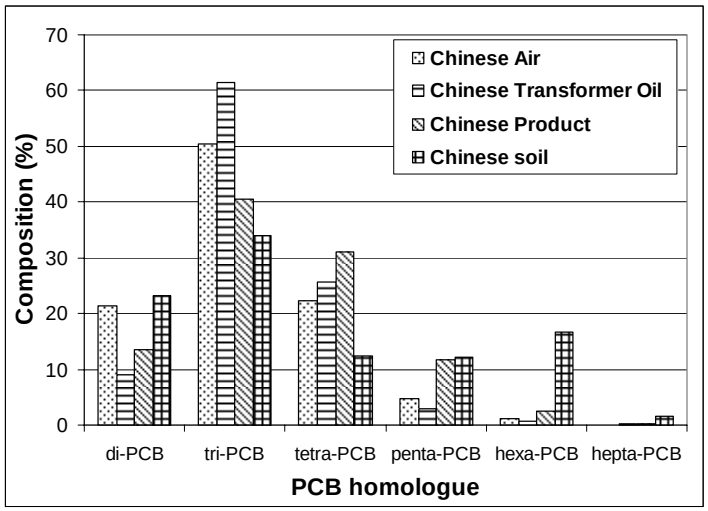

Figure 4. PCB homologue composition in the Chinese air from all 52 sites, Chinese transformer oil[1,8], and PCB produced in China[1], and Chinese soil[1].

References

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