

Levels and Vertical Distributions of PCBs, PBDEs, and OCPs in the Atmospheric Boundary Layer: Observation from the Beijing 325-m Meteorological Tower

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Polyurethane foam disk passive air sampling was carried out to investigate the levels, vertical distributions, and potential sources of polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and organochlorine pesticides (OCPs) in the atmospheric boundary layer of an urban site in Asia. Sampling was performed at nine heights (15, 47, 80, 120, 160, 200, 240, 280, 320 m) of the 325-m meteorological tower in Beijing, China over three 2-month periods between December 2006 and August 2007. This is the first study to report vertical variations of PBDEs in the ABL and one of only a few studies to investigate vertical distributions of persistent organic pollutants. The levels of Σ_{19} PCBs and Σ_8 PBDEs were relatively low, ranging from 22 to 65 and from 2.3 to 18 pg m^{-3} , respectively. Air concentrations of γ -HCH were high, with values in the range of 39–103 pg m^{-3} in winter, 100–180 pg m^{-3} in spring, and 115–242 pg m^{-3} in summer, respectively. α -HCH concentrations ranged from 20 to 86 pg m^{-3} , p,p' -DDT between 7.3 and 78 pg m^{-3} , and HCB between 15 and 160 pg m^{-3} . The seasonal variations of PCBs, PBDEs, and OCPs may reflect different sources for these chemicals, such as those related with regional use (γ -HCH), volatilization/re-emission (PBDEs, PCBs, α -HCH), and pesticide impurities (HCB). Although the performance reference compounds (PRCs) were spiked before deployment, the sampling rates showed strong dependency on wind speeds, resulting in large variations in uptake rates in the ABL, ranging from $\sim 7.0 \text{ m}^3 \text{ day}^{-1}$ at ground level to $11 \text{ m}^3 \text{ day}^{-1}$ at 320 m. Levels of PCBs, PBDEs, and OCPs decreased with increasing ABL height, indicating the potential of Beijing as the local sources.

Introduction

Persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and organochlorine pesticides (OCPs), continue to arouse great concern as they are persistent in the environment and undergo long-range transport through the atmosphere. These chemicals are also toxic, bioaccumulative, and therefore pose great health risks to biota and humans (1). Although the production and use of PCBs and many OCPs have been banned in most countries since 1970s, their residues in environmental reservoirs (e.g., soil) can still continue to be sources of current atmospheric contamination (2, 3).

Different types of passive air samplers (PAS) have been developed (4–7) to assess atmospheric POP levels and investigate their global distribution and long-range transport, including absorption onto polyurethane foam (PUF) (5), semipermeable membrane (SPMD) (6), and XAD adsorbent resins (7). Compared to conventional high-volume air samplers, the PAS is economical and does not require electricity. Therefore, PAS devices have been successfully used on various geographical scales from local (8) to continental (9) and global (3). In 2004, a large-scale PAS survey was conducted across Asia including China (10). However, field monitoring data in China are still very scarce, especially regarding atmospheric POPs.

The atmospheric boundary layer (ABL), typically regarded as being up to $\sim 1000 \text{ m}$ from ground level, is closely associated with human activities, transportation of atmospheric pollutants, and potential inhalation risks to humans. Until now, only one elevated construction has been used to study vertical distribution of POPs in the ABL, the CN Tower in Toronto (11, 12). In their work, Farrar et al. (11) showed compound distribution in the ABL is a function of emissions, advection, and vertical mixing rates. As a result, vertical concentration profiles can be classified as one of three profiles: even distributions with height, higher concentrations at ground level, or higher concentrations with height. Moreau-Guigon et al. (12) used PAS at five elevations on the CN tower and reported different vertical profiles for various pesticide classes. The vertical profile of the current-use OCP (i.e., endosulfan) is homogeneous, whereas the concentrations of recent-use OCP (i.e., γ -HCH) decrease with height. However, so far, there is no literature report on vertical PBDE distributions in the ABL.

The 325-m Meteorological Tower (325MT) in Beijing is one of the few meteorological towers in the world and is currently the tallest freestanding building in China. When built in 1976, it was situated in an open field of a suburban area. Over time, this location has become part of an urban center owing to the rapid development of Beijing city (13), providing an opportunity to study vertical POP variations in the ABL of the Asian mega-city. In the present study, PUF disk PAS devices were deployed at nine elevations (up to 320 m) of the Beijing 325MT over three 2-month periods between December 2006 and August 2007, to investigate levels, long-term vertical distributions and potential sources of PCBs, PBDEs, and OCPs in the urban area. In contrast to the concrete structure of the Toronto tower, the 325MT consists of a steel framework, so that samplers were freely exposed to wind from all directions. Correlations between sampling rates and the meteorological factors were investigated in detail.

Experimental Section

Sample Collection. The Beijing 325MT ($39^\circ 58' 27'' \text{ N}$, $116^\circ 22' 19'' \text{ E}$) is located between the North third Ring Road

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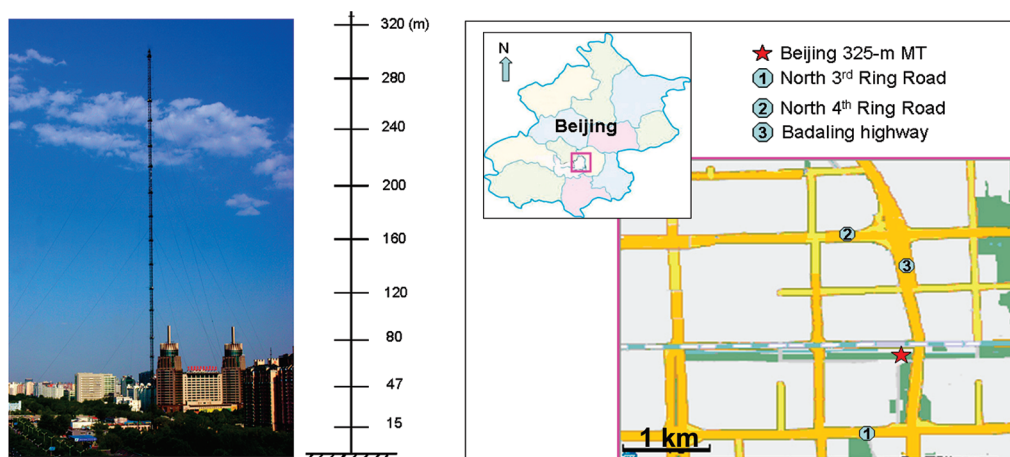


FIGURE 1. Sampling location in Beijing 325-m Meteorological Tower.

and the North fourth Ring Road, ~4 km North of the Forbidden City of Beijing, China. The Badaling Highway and Beitucheng West Road are situated 200 m east and 50 m north of the 325MT, respectively (Figure 1).

Two PUF samplers (4) were collected on the southeast and northwest leg of the 325MT at nine different elevations (15, 47, 80, 120, 160, 200, 240, 280, and 320 m) for three 2-month periods (6 December 2006–15 January 2007, 10 May–3 July 2007, and 4 July–24 August 2007). One field blank was collected during each period. Meteorological information, including wind speed and temperature at each height, was recorded automatically every 5 min.

The PUF disks (diameter, 14 cm; thickness, 1.35 cm; surface area, 365 cm²; volume, 207 cm³) were housed in stainless steel domed chambers to reduce the influence of wind speed and to protect the disks from direct particle deposition, precipitation and UV sunlight. Prior to use, PUF disks were rinsed with water and then extracted with acetone using an Accelerated Solvent Extraction (ASE) apparatus (Dionex; pressure, 1500 psi; temperature, 100 °C; heating, 5 min; static, 8 min; flushing, 60 vol. %; purge, 120 s; 3 cycles). A second ASE extraction with hexane: dichloromethane (1:1 v/v) was carried out and then the disks were dried in a desiccator under vacuum. During the spring and summer periods, PUF disks on the northwest leg of the 325MT were spiked with three performance reference compounds (PRCs; ¹³C₁₂-PCB-9, -52, and -194) that are normally not present in the atmosphere. The theory related to PRC for PAS has been reported in published literatures (4, 5, 14) and is summarized in the Supporting Information (SI).

Analysis. Retrieved PUF disks were spiked with labeled surrogate standards that included 27 ¹³C₁₂-PCB congeners, ¹³C₁₂-BDE-47, -99, and -153 after the ASE extraction with hexane: dichloromethane (1:1 v/v). For PCB and PBDE analysis, isotope dilution/HRGC/HRMS method based on US EPA method 1668A and draft method 1614 was used after some modification, with details given in the Supporting Information. For OCP (HCHs, HCB, DDTs) analysis, samples were spiked with PCB-209 and 2,4,5,6-tetrachloro-*m*-xylene (TMX) as internal standards, and analyzed by GC/ECD. PASs were analyzed for 19 PCB congeners, eight PBDEs, and nine OCPs. Detailed information on the extraction and analysis of the chemicals can be found in the SI.

Results and Discussion

Sampling Rates and Influence Factors. By measuring the remaining amounts of PRCs in the PUF disks at the end of the sampling session, the relationship described in eq 2 (SI) could be used to calculate k_A and the sampling rate was estimated as $k_A \cdot A$. Table 1 summarizes the PAS sampling rates in spring and summer. Sampling rates were based on

TABLE 1. PAS Sampling Rate during the Deployment in Spring and Summer^a

	recovery ^b (%)	log K_{oa} ^c	sampling rate (m ³ day ⁻¹)
spring			
15 m	53	8.39	7.0
80 m	48	8.39	8.0
120 m	37	8.41	11
160 m	45	8.42	9.2
200 m	29	8.43	14
280 m	43	8.47	10
320 m	39	8.46	11
summer			
15 m	50	8.29	6.9
47 m	48	8.29	7.2
80 m	45	8.29	7.8
120 m	34	8.31	11
160 m	40	8.32	9.4
200 m	28	8.35	14
240 m	32	8.37	12
320 m	35	8.38	12

^a Samples at 47 m, 240 m in spring and at 280 m in summer in the NW leg were lost during deployment due to the high wind effect. ^b Recovery of ¹³C₁₂-PCB-52. ^c The log K_{oa} values at specific temperature for each height were calculated using the regression reported by Harner and Bidleman (14) and the regression described by Falconer (15).

¹³PCB₁₂52 recovery, which was within desired range of 20–80% (8), whereas ¹³PCB₁₂-194 recovery was >80% and ¹³PCB₁₂-9 was not detectable, primarily because of their high and low volatility, respectively. The variation in sampling rate between spring and summer periods was within 3% of the mean value. Although the uptake rate for winter was not available, the variability in sampling rate between seasons should be limited (8). Therefore, average sampling rates were used to calculate sampling volumes. Large variations were observed for different elevations, from 7.0 m³ day⁻¹ at ground level to 11 m³ day⁻¹ at 320 m. This large variation in PAS sampling rate in the ABL has not been reported in the literature. In the CN Tower study, Moreau-Guigon et al. (12) reported a low variation in sampling rate at different elevations, contradicting the results of our study. This is probably because the PUF disk samplers were positioned up against the CN Tower, which can act as a barrier and shelter samplers from the wind, whereas the samplers in our study were mounted on the steel framework of the 325MT and were freely exposed to winds from all directions.

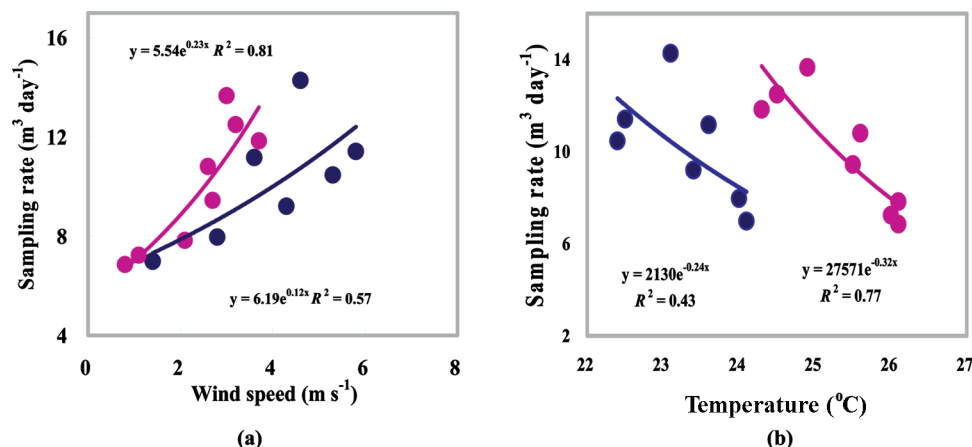


FIGURE 2. Dependence of sampling rates on wind speed and temperature.

The sampling rate at the elevation of 15 m was $\sim 7.0 \text{ m}^3 \text{ day}^{-1}$. This is higher than the conventional rate used for outdoor studies ($3\text{--}4 \text{ m}^3 \text{ day}^{-1}$) (4). It can be explained by the higher K_{oa} value for $^{13}\text{PCB}_{12-52}$ used as PRC than for PCB-30 and $d_6\gamma\text{-HCH}$ (8), which are typically used as PRCs, because compounds with higher K_{oa} values have higher sampling rates (5, 16, 17). The other reason was due to the effect of high wind speed during the sampling periods, with 5-min maximum wind speed reaching 15 m s^{-1} in spring and 9.2 m s^{-1} in summer. The rate of chemical exchange between samplers and the atmosphere is predominantly controlled by the thickness of the air-side boundary layer. An increase in wind speed can then reduce the thickness of the boundary layer, resulting in higher exchange rates (18).

Wind tunnel experiments demonstrated that sampler devices could significantly dampen the wind speed effect under ambient conditions (18, 19). However, the wind speed effect on the sampling rate in the present study should be taken into account because the wind speed at each height varied greatly and increased sharply from 0.8 m s^{-1} at 15 to 5.8 m s^{-1} at 320 m. Figure 2a shows the dependence of the PRC-calibrated sampling rate on wind speed. Uptake rates increased sharply and showed an exponential correlation with wind speed ($R^2 = 0.57$, $P = 0.05$ in spring; $R^2 = 0.81$, $P < 0.01$ in summer), which is consistent with results from laboratory and wind tunnel experiments (18, 19). For instance, Tuduri et al. (19) reported that PUF-based sampling rates showed strong wind dependence and increased sharply for indoor air velocities greater than 1.0 m s^{-1} .

Temperature also has an effect on PAS sampling rates since K_{PUF-A} is related to K_{oa} (14). Typically, K_{oa} increases log-linearly with reciprocal temperature, with an increasing factor of 50–300 over the temperature range -10 to 30°C (14). This results in an increase in effective sampling volume. Figure 2b shows the dependence of the sampling rate on temperature. The sampling rate increased with decreasing ambient temperature. There was exponential correlation between the sampling rate and temperature over the range $21.9\text{--}25.6^\circ \text{C}$ ($R^2 = 0.43$, $P = 0.10$ in spring; $R^2 = 0.77$, $P < 0.01$ in summer). Similar behavior was reported by Ockenden et al. (17), with compounds in SPMD-based PAS accumulating at a greater rate at low than at high temperatures.

Air Mass Backward Trajectory. The origins and pathways of air masses during the deployment in winter, spring, and summer were determined to assess potential source regions using backward trajectories from the hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) model (www.arl.noaa.gov/ready/hysplit4.html). Backward trajectories were calculated at 0:00 h for the night time at an interval of 6 h. The calculation heights were set at elevations of 15 and 200 m above the ground (Figure S1–S3 of the SI). Variable trajectories were observed in different seasons, reflecting the

variations of potential source regions due to the Asian monsoon effect. During most of the deployment period, the trajectories at 15 m were very similar to those found at 200 m, suggesting that the air mass effect on different height would be distinguishable.

Levels and Vertical Distributions. PCBs. Annual PCB production in China was estimated to be ten thousand tonnes between 1965 and 1974 (20). Because PCBs have been banned, current atmospheric PCB pollution is likely due to emissions from disposal or accidental release of products containing PCBs and volatilization from environmental reservoirs. Figure 3a presents the PAS data, with air concentrations of $\Sigma_{19}\text{PCBs}$ in the range $22\text{--}65 \text{ pg m}^{-3}$. The results were lower than the data from another PAS study in China, for which PCB concentrations were in the range $7\text{--}117 \text{ pg m}^{-3}$ (10). However, the levels were slightly higher than the data from other Asian countries (Singapore $1.5\text{--}14 \text{ pg m}^{-3}$; Japan $1.6\text{--}76 \text{ pg m}^{-3}$; Korea $4\text{--}29 \text{ pg m}^{-3}$) (10) and lower than those reported for Europe ($\sim 14\text{--}870 \text{ pg m}^{-3}$) (9) and North America (Great Lakes $15\text{--}960 \text{ pg m}^{-3}$) (8).

A seasonal variation in PCB concentrations was evident from the results, with higher PCB concentrations during the spring period than those in summer and winter. This is consistent with the so-called spring pulse effect that has been shown to be prominent in urban areas (21). As temperature increases during the springtime, chemicals that were accumulated in the soil during the winter are consequently released to the atmosphere.

From Figure 3a, a decrease of PCBs levels could be distinguished, which may be associated with ground-level volatilization from historical residues. Farrar et al. (11) reported vertical distributions of PCBs for the Toronto CN Tower and also found decreasing trends for PCBs in the ABL. This result may reflect urban areas as sources of PCBs, as reported in the literature (5, 8).

Among the PCB congeners, dioxin-like PCBs (CB-77, -81, -105, -114, -118, -123, -126, -156, -157, -167, -169, -189), indicator PCBs (CB-28, -52, -101, -138, -153, -180) and PCB-209 were detected in all air samples. PCB-28 dominated the profile patterns, accounting for 61–78% of the total mass of PCBs. The other indicator congeners accounted for 19–28% and dioxin-like PCBs accounted for another 3.0–8.1% (Figure 3b).

PBDEs. PBDEs can enter the environment via volatilization of products containing PBDEs. In Asia, deca-BDE is produced and used in large quantities, whereas penta-BDE production largely ceased in the mid-1990s (22). Figure 4a presents the air concentrations of $\Sigma_6\text{BDEs}$, with values ranging from 2.3 to 16 pg m^{-3} in winter, 7.3 to 13 pg m^{-3} in spring, and 10 to 18 pg m^{-3} in summer, respectively. This is in agreement with data reported for other Asian countries ($5.0\text{--}71$, $10\text{--}29$, and $2.0\text{--}27 \text{ pg m}^{-3}$ for Japan, Singapore, and Korea, respectively)

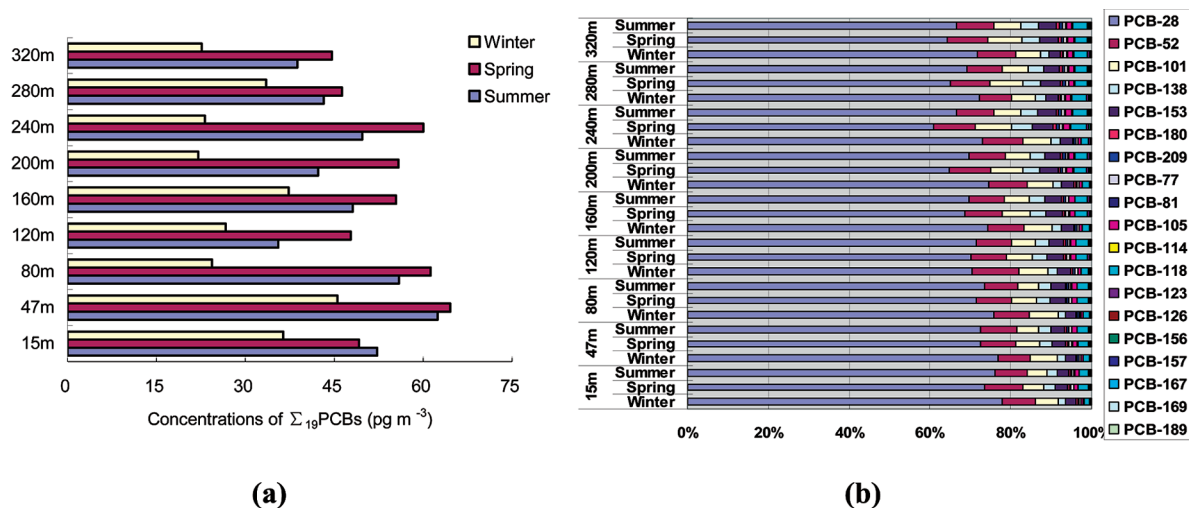


FIGURE 3. Air concentrations and profiles of PCBs at each height.

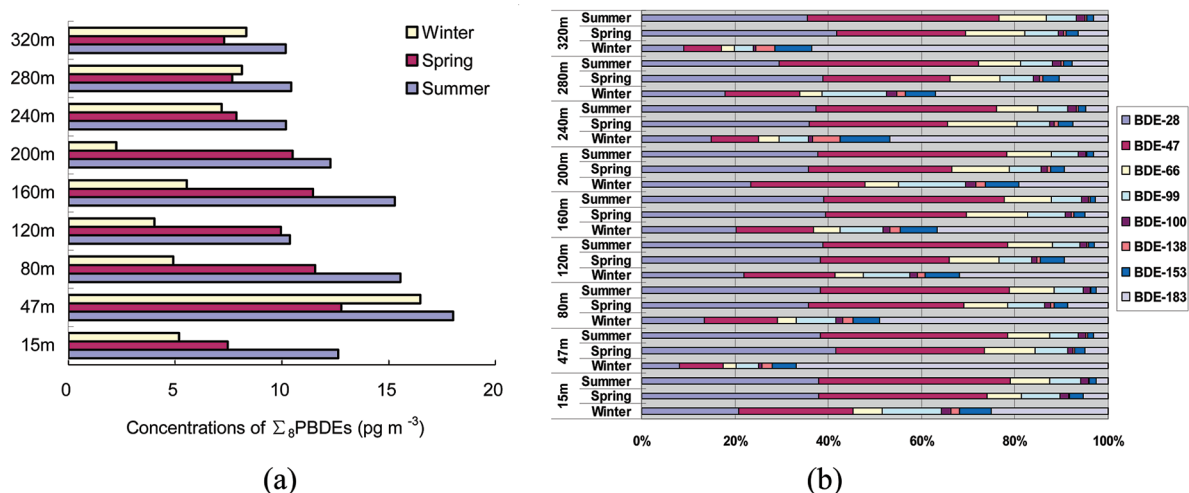


FIGURE 4. Air concentrations and profiles of PBDEs at each height.

(10). Also it is consistent with the viewpoint that atmospheric PBDE levels in China were generally low owing to the limited use of PBDE products (10).

Seasonal trends were also apparent for PBDEs, with higher concentrations during the spring–summer period than those in winter. This may reflect the enhanced volatilization due to the increase of temperature. Generally, the air concentrations of PBDEs decreased with ABL height, especially for the spring and summer period. Analysis of variance (ANOVA) showed that the PBDE and PCB concentrations near ground level (15–80 m) were significantly different from those measured at higher levels (120–320 m). This result provides a further confirmation of urban areas as potential local source of PBDEs, which was reported in previous literature (8, 23).

Of the PBDE congeners, BDE-28, -47, -66, -99, -100, -138, -153, and -183 were detected in all air samples. BDE-28 and BDE-47 were the dominant contributors to the pattern, contributing 21–38% and 24–41% of the total mass of PBDEs, respectively. BDE-183 accounted for another 3–25% of the Σ_8 BDEs burden (Figure 4b). This composition is similar to that of penta-BDE commercial products. Table S3 of the SI shows the Pearson correlation for specific PBDE congeners. Significant correlations were present among BDE-47, -66, -99, and BDE-100 ($R \geq 0.83$, $P < 0.01$), the major components of penta-BDE. Correlations with Σ_8 PBDEs were significant for BDE-28, -47, -66, -99, and -100 ($R \geq 0.92$, $P < 0.01$), but weak for BDE-138, -153 and -183. The ratio of BDE-99 to -100 ranged from 36:10 to 69:10, which is close to the value of 84:16 reported for technical penta-BDE (Bromkal 70–5DE)

(24). These results suggest that commercial penta-BDE formulations are largely responsible for PBDE sources in the ABL of Beijing.

OCPs. HCHs and DDTs have been widely used as pesticides in China, beginning in the 1950s and continuing until their use was banned in 1983 (25). The air concentrations of OCPs are listed in Table S2 of the SI. Data for OCPs at 15 and 120 m in winter, 47 and 240 m in spring could not be attained due to error during the sample pretreatment procedure. Levels of Σ HCH ($\alpha + \beta + \gamma + \delta$ -HCH, 91–397 pg m^{-3}) were higher than those of Σ DDT (p,p' -DDT + o,p' -DDT + o,p' -DDE + p,p' -DDE, 33–269 pg m^{-3}). This indicates that HCH was the dominant OCP in the atmosphere of Beijing, consistent with the fact that HCH production and use was the highest among OCPs in China (26). Air concentrations of HCH, DDT, and HCB decreased with ABL height, indicating the potential of Beijing as a local source of OCPs. In comparison, the Toronto CN Tower study revealed similar distributions for OCPs of α -HCH and γ -HCH, with higher concentrations close to the ground (12).

HCHs. α -HCH is the main component of technical HCH, a pesticide that was once widely used. Approximately 4.46 million tons of technical HCH were used in China before its prohibition (27). Figure 5a shows the air concentrations of α -HCH in the range 20–86 pg m^{-3} , which was consistent with monitoring results for other urban sites in Europe (14–100 pg m^{-3}) (9), the Great Lakes (15–73 pg m^{-3}) (8), and Toronto (40–60 pg m^{-3}) (12), suggesting a homogeneous distribution in the global atmosphere. A seasonal trend was

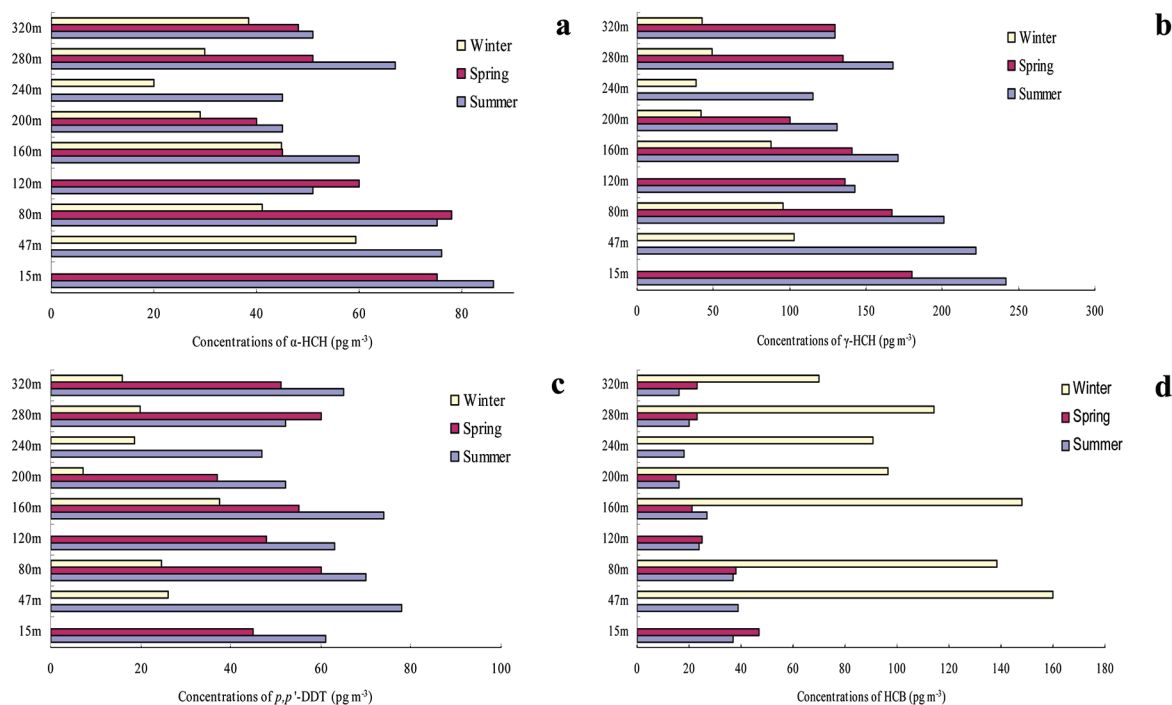


FIGURE 5. Levels and vertical distributions of OCPs at each height.

observed for α -HCH, with higher concentrations during the spring–summer period. Li et al. reported that there was no worldwide use of technical HCH in 2000 (28), and based on this, the seasonal variation should therefore be due to increased re-emissions from historical residues. Table S4 of the SI shows the Pearson correlation for specific OCP congeners. The congener of α -HCH strongly correlated with δ -HCH. This suggests that they may have common sources. Considering technical HCH has been banned in China and lindane was found as a main source in this study, the common sources may be associated with the historical use of technical HCH in China.

γ -HCH comprises 99% of the lindane formulation that replaced technical HCH in China in 1991. Approximately 3200 tons of lindane were used between 1991 and 2000, primarily concentrated in northern China (26). Air concentrations of γ -HCH were in the range 39–103 pg m^{-3} in winter, 100–180 pg m^{-3} in spring and 115–242 pg m^{-3} in summer, respectively (Figure 5b). These appear to be on the higher end as compared to PAS-derived data from Europe (9–390 pg m^{-3}) (9), the Great Lakes (13–100 pg m^{-3}) (8), and Toronto (20–50 pg m^{-3}) (12). The higher concentrations during spring–summer period can be explained by local and/or regional use of lindane. Technical HCH has an α -/ γ -HCH ratio of approximately 3:7. The low ratios found in air samples in the present study (0.43–0.90 for winter, 0.32–0.47 for spring and 0.34–0.40 for summer) support the conclusion of no current use of technical HCH rather than fresh inputs from lindane.

DDT Isomers. Technical grade DDT consists of p,p' -DDT (80–85%) and o,p' -DDT (15–20%). In China, more than 0.4 million tons of technical DDT were used before it was banned in 1983 (26). However, DDT continued to be emitted due to the production and application of dicofol, which was extensively used for the control of mites and contains DDT as a byproduct (29). In the present study, other minor components of DDT (o,p' -DDT) and its metabolites (o,p' -DDE, p,p' -DDE) were detected in all air samples. High p,p' -DDT residues were observed, with concentrations varying from 7.3 to 38 pg m^{-3} in winter, 36 to 60 pg m^{-3} in spring, and 47 to 78 pg m^{-3} in summer, respectively (Figure 5c). The

higher concentrations during spring–summer period may reflect the increased volatilization from environmental reservoirs.

The relative abundance of DDT and its metabolite isomers can be used to distinguish fresh (p,p' -DDT/ p,p' -DDE > 1) and aged (p,p' -DDT/ p,p' -DDE < 1) sources. The p,p' -DDT/ p,p' -DDE ratios ranged from 0.54 to 1.0 during spring–summer period, suggesting no fresh DDT inputs. However, the p,p' -DDT/ p,p' -DDE ratios in winter were 0.80–2.2, indicating the potential use or advective inputs of DDT for this region.

The o,p' -DDT/ p,p' -DDT ratio was 0.28–1.1, 0.53–0.71, and 0.49–0.75 in the winter, spring and summer, respectively. The reported ratio in technical DDT and in dicofol was 0.2–0.26 and ~0.75, respectively (25). Thus, the historical use of technical DDT and dicofol may both contribute to the atmospheric DDTs. This result is in contrast to a previous study that reported the atmospheric DDT in Taihu Lake as “dicofol type” pollution (25).

HCB. Global HCB production exceeded 100 thousand tonnes and primary emissions to the atmosphere probably peaked in the 1970s (30). Bailey (31) provided a global picture of HCB emissions in the mid-1990s and identified no single overwhelming source. Figure 5d shows the air concentrations of HCB, with values ranging from 15 to 47 pg m^{-3} in spring and from 16 to 39 pg m^{-3} in summer. These levels are in agreement with average ambient HCB concentrations in the atmosphere of northern hemisphere (~50 pg m^{-3}) (30). However, very high HCB levels were observed during the winter time with air concentrations ranging from 70 to 160 pg m^{-3} . As suggested by Gouin et al. (32, 33), chlorinated fungicides, such as chlorothalonil and quintozene, contain HCB as impurities. The use of these fungicides containing HCBs to control pesticides in crops was assumed as one of the current HCB sources. Thus, the increase of HCB levels in winter time might reflect the regional use of these chlorinated fungicides in this region.

Acknowledgments

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Supporting Information Available

Detailed air concentrations, quality assurance and quality control, theories related to PRCs, Pearson correlation coefficients, and air mass backward trajectories. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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