

ATMOSPHERIC PERSISTENT ORGANIC POLLUTANTS IN MAINLAND CHINA RECORDED BY TREE BARKS AND A TREE BARK POCKET

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Introduction

Persistent organic pollutants (POPs) including polycyclic aromatic hydrocarbons (PAHs), organic chlorinated pesticides (OCPs), polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs), have become a pressing environmental issue because of their persistence, bioaccumulation and toxicity. Due to their potential for long-range atmospheric transport, worldwide attempts have been made towards air monitoring of POPs on different scales from local to global. In China, regional monitoring of POPs has been performed in various environmental media focusing on the economically developed eastern and southern coastal areas as well as northern China. However, few extensive surveys of the concentrations of POPs in the atmosphere on a national scale have been carried out so far, and therefore data concerning the overall contamination status, and spatiotemporal trends of atmospheric POPs in China is still absent. This study therefore aims to monitor the spatial distribution and historical evolution of atmospheric POPs in Mainland China using tree barks and a tree bark pocket^{1, 2}, respectively, in order to fill some of the gaps in the data of Chinese atmospheric POPs.

Material and methods

Fifteen species of barks representing different bark characteristics and 12 Masson pine barks representing differing environmental conditions were collected from the Campus of Xiamen University from October 2006 to September 2007, and air samples of gaseous and particulate POPs were monthly collected on PUF/Tenax/PUF sorbents and quartz filters; these paired bark/air samples were analyzed for modeling bark/air partitioning of POPs. For the spatial distribution survey of POPs across Mainland China, a total of 163 bark samples were collected at 68 urban sites (latitude from N 18.27° to N 49.22°, and longitude from E 84.77° to E 126.63°) between 2004 and 2007 as shown in Figure 1. At each site, one to four species of trees were sampled with preference given to the widely geographically-distributed Masson pine, poplar, camphor, and Chinese fir. A section of Chinese fir tree trunk containing a bark pocket formed from 1952 to 2005 was sampled from a 60-year-old Chinese fir tree that fell in March 2005 in Dexing, Jiangxi Province, China. The bark pocket was segmented into 18 parts at intervals of 0.5 cm, and each was dated according to the surrounding annual rings. Details of the bark sampling, characters measurement and pretreatment are described elsewhere^{3, 4, 5}. GC-MS analyses were conducted using a GC-MS QP2010 equipped with electron impact ionization (EI) and electron capture negative ionization (ECNI) sources, an auto injector and a programmed temperature vaporizer (Shimadzu, Japan)⁵. Eighteen PAHs (Σ_{18} PAHs, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, retene, benz[a]anthracene, chrysene, benzo[b]fluoranthene,

benzo[k]fluoranthene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene and dibenz[a,h]anthracene) were analyzed using EI^{3,4}, while H-POPs referring to 5 OCPs (Σ_5 OCPs, including α , β , γ , δ -HCH isomers and HCB), 10 PCBs (Σ_{10} PCBs, PCB-28, 52, 101, 105, 118, 138, 153, 163, 180 and 209; IUPAC no.) and 17 BFRs (Σ_{17} BFRs, including 15 PBDEs of BDE-17, 28, 47, 49, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190 and 209, PBB-153 and TBBPA) were simultaneously analyzed using ECNI⁵.

Results and discussion

Modeling bark/air partitioning of POPs

POPs accumulate from air into tree bark via two pathways of gas diffusion and particle entrapment depending on their existing phases in the atmosphere^{3,6}. Assuming that the accumulation behavior of atmospheric POPs into bark is a partition process between bark and air, pseudo-bark/air equilibrium partition coefficients (K_{BA} , the quotient of the bark concentration divided by the air concentration) are defined for the atmospheric POPs, and measured for the 15 different barks and at 12 different environmental conditions. Results indicated that gas-phase hydrophobic POPs are primarily accumulated through interactions with lipid substances in bark depending on the POPs octanol/air partition coefficients (K_{OA}) and influenced by bark lipid content (LipCont, g/m³ bark) and ambient temperature (T , K)^{3,7,8}; while particle-phase POPs are accumulated in the bark through dry and wet depositions mainly via impaction, which is governed by bark specific surface area (SSA, m²/m³ bark), and influenced by precipitation ($Pptn$, mm)⁹. The effects of pollutant physicochemical properties, bark characteristics and environmental conditions on the K_{BA} were quantified by using statistical analysis, and thus a mathematical model describing the accumulation processes of POPs from air into bark was established as $K_{BA} = (mK_{OA}^n + b \cdot B \cdot TSP \cdot K_{OA}) / (1 + B \cdot TSP \cdot K_{OA})$, where m and n are empirical constants that principally correlated with bark LipCont (g lipid/m³ bark) and lipid chemical composition, respectively; b is an empirical constant that should be correlated with bark SSA (m² area /m³ bark); the values of B are 1.88, 1.50, 0.915×10^{-12} m³/μg for PAHs, OCPs and PCBs, BFRs, respectively. This model provides a theoretical basis for estimating the compound-specific K_{BA} for a given bark/air interface, and it provides possibilities for the estimation of air POP concentrations from bark POP concentration measurements.

Spatial distribution of atmospheric POPs across mainland China

The bark concentrations of Σ_{18} PAHs, Σ_5 OCPs, Σ_{10} PCBs and Σ_{17} BFRs at the 68 sites were 5.1-1770, 0.05-12.9, 0.21-21.6 and 0.02-48.3 ng/g bark, with geometric mean (GM) values of 295, 1.47, 3.12 and 2.79 ng/g bark, respectively, across mainland China. The Σ_{18} PAHs were mostly contributed by the 2- to 4-ring naphthalene, acenaphthylene, phenanthrene, pyrene and fluoranthene accounting for 9.9-30.5%, 3.1-10.5%, 8.3-26.2%, 7.1-21.4% and 5.7-18.7%, respectively. Of the PCB congeners determined, tri-, tetra-, penta-, hexa-, and hepta-PCB accounted for $\leq 0.9\%$, $\leq 1.1\%$, 5.7-22.9%, 29.8-71.5%, and 6.5-27.3%, respectively. The Σ_{17} BFRs in most barks were dominated by BDE-209 (37.7-88.4%). Considering the degradation of BDE-209 in the atmosphere, this is consistent with the fact that BDE-209 accounts for 97-98% of the technical Deca-BDE mixture, which is a major BFR produced and used in China.

Applying the bark/air partition model of POPs to all the barks, air POP concentrations were estimated for each site. The air Σ_{18} PAHs concentrations in the 68 sites were in the range of 4-400 ng/m³, while the air concentrations of Σ_5 OCPs, Σ_{10} PCBs and Σ_{17} BFRs were at relatively lower levels of 10-550, 4-130 and 1-620 pg/m³, respectively. The GM values of all the 68 sites were 71 ng/m³ for Σ_{18} PAHs, 99 pg/m³ for Σ_5 OCPs, 26 pg/m³ for Σ_{10} PCBs and 25 pg/m³ for Σ_{17} BFRs. The model-estimated air POP concentrations mostly agreed with the reported values available, which were directly measured using active air sampling methods, with discrepancies ranging from -61% to 98%. The POP concentrations in eastern and middle China are generally higher than those in western China. When plotting the air concentrations of Σ_{18} PAHs, Σ_5 OCPs, Σ_{10} PCBs and Σ_{17} BFRs respectively versus the city gross domestic product of the 68 sites, positive linear relationships were obtained between their log transformed values with correlation coefficients of 0.618, 0.524, 0.616 and 0.812 as shown in Figure 2.

Historical evolution of atmospheric POPs in southeastern China

From 1952 to 2005, the concentrations of Σ_5 OCPs and Σ_{10} PCBs in the bark samples and the air increased progressively from the background levels of 0.10 and 0.75 ng/g bark and 8 and 2 pg/m³ air in the early 1950s to the maxima of 1.05 and 6.23 ng/g bark and 100 and 40 pg/m³ air during the late 1980s, respectively; they then decreased to 0.68 and 3.39 ng/g bark and 10 and 10 pg/m³ air in 2005. The Σ_{17} BFRs concentrations, however, fluctuate around the background levels of 0.14 ng/g bark and 0.6 pg/m³ air before 1980, and then exponentially increased by a factor of about two orders of magnitude to 4.38 ng/g bark and 50 pg/m³ air. These increasing trends are similar to the sedimentary records in the Pearl River Estuary, south China¹⁰. The production and use of HCHs, HCB, and PCBs began in the early and late 1950s in China, and they were controlled or banned completely in the mid 1980s, the early 2000s and 1980s, respectively. The time trends of the various classes of POPs estimated from the bark pocket generally agree with their history of production, usage and import in China¹¹.

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Figure 1: Location map of the sampling sites

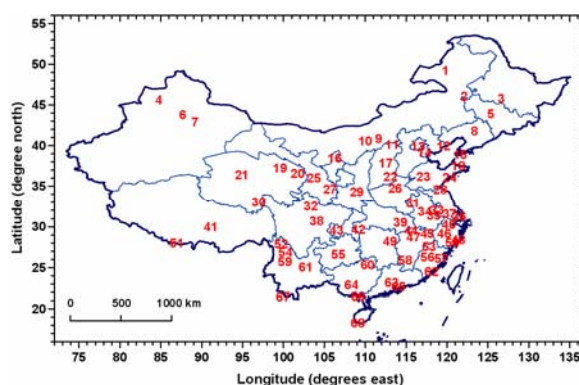


Figure 2: Relationships between the estimated atmospheric air concentration of the total (a) PAHs ($\Sigma_{18}\text{PAH}$, ng/m^3), (b) OCPs ($\Sigma_5\text{OCP}$, pg/m^3), (c) PCBs ($\Sigma_{10}\text{PCB}$, pg/m^3) and (d) BFRs ($\Sigma_{17}\text{BFR}$, pg/m^3) and the gross domestic product (GDP, in hundred million Yuan) of the 68 cities. Arabic numbers from 1 to 68 are shown in Figure 1.

