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Modeling Persistent Organic Pollutant (POP) Partitioning between Tree Bark and Air and Its Application to Spatial Monitoring of Atmospheric POPs in Mainland China

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A mathematical model describing the bark/air partitioning of persistent organic pollutants (POPs) was established taking into consideration the accumulation processes of POPs from air into bark and compound-, species-, and site-specific air-to-bark accumulation factors. It allows the assessment of the concentrations of atmospheric POPs based on those recorded in tree bark. The spatial distribution of atmospheric POPs including 18 polycyclic aromatic hydrocarbons (Σ_{18}PAHs), 5 organic chlorinated pesticides (Σ_5OCPs), 10 polychlorinated biphenyls (Σ_{10}PCBs), and 17 brominated flame retardants (Σ_{17}BFRs) were investigated by analyzing 163 bark samples from 68 sites across mainland China. The atmospheric POPs were estimated to be 4.1–399 ng/m^3 air, and 11.3–553, 4.5–130, and 0.9–624 pg/m^3 air with geometric means of 71 ng/m^3 air, and 99, 26, and 25 pg/m^3 air for Σ_{18}PAHs, Σ_5OCPs, Σ_{10}PCBs, and Σ_{17}BFRs, respectively, based on those recorded in the tree barks of 5.1–1770, 0.05–12.9, 0.21–21.6, and 0.02–48.3 ng/g bark on dry weight basis, with geometric means of 295, 1.47, 3.12, and 2.79 ng/g bark. These results generally indicated that contamination by atmospheric POPs is more serious in eastern and mid China than that in western China.

Introduction

Persistent organic pollutants (POPs) have, during the past decades, become a pressing environmental issue because of their persistence, bioaccumulation, and toxicity. Because of their potential for long-range atmospheric transport, worldwide attempts have been made toward air monitoring of POPs on different scales from local to global. In China, regional monitoring of POPs has been performed, focusing on the economically developed eastern and southern coastal areas (*1, 2*) and northern China (*3*); recently, a national survey

of the concentrations of PCBs in Chinese surface soils has been reported (*4*). 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 of atmospheric POPs in China are still absent. This study therefore aims to monitor the spatial distribution of atmospheric POPs across mainland China using tree barks, in order to fill some of the gaps in the data concerning Chinese atmospheric POPs.

Tree bark has been used since the late 1980s as a passive sampling medium for atmospheric POPs (*5, 6*) and has played important roles in identifying source/sink regions (*7*), exploring spatial and temporal trends (*8, 9*), and understanding global cycling (*10, 11*). This sampling medium has unique features: it accumulates both gas-phase and particle-phase POPs simultaneously from the surrounding air (*12*) and reflects time-integrated overall air pollution levels (*13*); it can conveniently reveal the history of air pollution by the so-called "tree bark pocket" (*12, 14–16*); the sample collection is easy and inexpensive and no power is required; finally, it is a typically "green" air sampler of natural environmental materials. However, previous studies of the monitoring of POPs using tree bark have focused on assessing the spatially and/or temporally resolved pollution trends by direct comparison of bark POP measurements in several forms. Initially, bark mass concentration on a dry weight basis (ng/g bark) was used (*6, 8*) for a comparison of POPs pollution at various sites or times. On the basis of the findings that the bark lipid content and surface area influence the air-to-bark accumulation of POPs, Simonich and Hites (*17, 18*) recommend using lipid mass concentration (ng/g lipid of bark) and/or area mass concentration (ng/m^2 surface area of bark). More recently, we proposed a normalization method involving the concentration ratio of target POPs to a "natural internal compound" (*12, 19*) for minimizing the uncertainty resulting from the variabilities in not only the inherent bark characteristics but also the external meteorological conditions. Unfortunately, few investigations have involved estimating the ambient air POPs concentration from their bark measurements (*20*), generally because there is lack of a mathematic model for bark/air partitioning of POPs taking into consideration the accumulation processes of POPs from air into bark and compound-, species-, and site-specific air-to-bark accumulation factors. This limits the further application of this promising green passive sampling medium to the spatial monitoring of atmospheric POPs on a large scale.

In this study, a mathematical model was established in an attempt to estimate the bark/air partitioning coefficient of POPs from their physicochemical properties, the bark characteristics, and prevailing meteorological conditions; it was subsequently applied to 163 geographically distributed tree bark samples for assessing the spatial distribution of air POPs across mainland China. The POPs investigated included polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organic chlorinated pesticides, and brominated flame retardants.

Experimental Section

Sampling. In August 2007, tree barks of 15 species (Table S1) representing different bark characteristics along with the corresponding air samples were collected from the main campus of Xiamen University (longitude 118°05′23″, latitude 24°26′24″, altitude 2 m above sea level). From October 2006 to September 2007, Masson pine (*Pinus massoniana*) bark and the surrounding air were collected monthly, representing

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different meteorological conditions. During one-month intervals, four air samples were continually collected, and each sampling event lasted one week, while one bark sample was collected at the end of each of the four air sampling periods. These paired bark/air samples were used to investigate the influence of bark characteristics and meteorological conditions on POPs' bark/air partitioning. In May 2003, July 2003, January 2004, and February 2006, tree bark of Masson pine, poplar (*Populus devidiana*), camphor (*Cinnamomum camphora*), and Chinese fir (*Cunninghamia lanceolata*), together with air samples, were collected from Nanjing (longitude 117°12′42″, latitude 24°30′05″, altitude 437 m above sea level), Yong'an (longitude 117°0′12″, latitude 25°50′51″, altitude 580 m above sea level), Wuyishan (longitude 117°37′22″, latitude 27°27′31″, altitude 210 m above sea level), and Taishan (longitude 117°16′24″, latitude 36°10′44″, altitude 474 m above sea level) (see Table S2), and these paired bark/air samples were used for validating the proposed POPs bark/air partitioning model. Atmospheric temperature (T, K) over the period was monitored and recorded while precipitation values (Pptn, mm) were obtained from the local meteorological station. For the air sampling, a Leland Legacy sample pump (SKC Inc., Eighty Four, PA) was used; it was placed 1.5 m above the ground beside the tree and run at a flow rate of 9 L/min, resulting in a bulk air volume of about 91 m³. Gas-phase POPs were collected on PUF/Tenax/PUF (2 cm diameter, and 30 mm/750 mg/30 mm length/mass/length) "sandwich" tube sorbents; simultaneously, particle-phase POPs (total suspended particles, TSP) were collected on a quartz fiber filter (diameter 47 mm, Whatman). Prior to sampling, PUF/Tenax/PUF sorbents were precleaned by Soxhlet extraction with acetone for 24 h followed by a 16-h extraction with 5% diethyl ether in hexane and dried in a vacuum oven at 30 °C for 6 h, while the filters were baked at 400 °C for 12 h. After sample collections, the filters and sorbents were separately wrapped in hexane-rinsed aluminum foil and then sealed in airtight plastic sample bags and stored in glass sample jars at −20 °C before pretreatment. For the bark sampling, trees of around 15−20 years old and about 20 cm trunk diameter at breast height were chosen, and the outer bark (approximate 5 cm length × 3 cm width × 4 mm thickness) was removed with a clean bistoury at a height of about 1.5 m above the ground. Bark with epiphytes on the surface was avoided. The barks were sampled from three to six trees of the same species nearby, and from each tree, six pieces of bark were taken from different directions around the tree trunk. Then the barks were pooled to be one sample. The bark samples were wrapped in hexane-rinsed aluminum foil, put into airtight plastic sample bags, and stored at −20 °C before pretreatment.

Between 2004 and 2007, a total of 163 bark samples were collected at 68 urban sites (Figure S1) across mainland China in order to survey the spatial distribution of POPs across mainland China. The sampling sites were chosen at least 5 km away from the possible point emission sources of POPs in order to be representative of the general pollution status of the corresponding cities. At each site, one to four bark samples of different tree species (with preference given to the widely geographically distributed Masson pine, poplar, camphor, and Chinese fir) were taken. Detailed information of the sampling sites and time as well as the species of bark samples are presented in Table S3.

Sample Pretreatment and Analysis. Bark and air samples were pretreated and analyzed for POPs according to previously published methods (*12, 19, 21*). Briefly, the sample was Soxhlet extracted for 24 h after being spiked with corresponding ¹³C-labeled or perdeuterated internal standards [¹³C-BDE-28, 47, 99, 100, 153, 154, 183, 209 and ¹³C-PCB-28, 52, 101, 138, 153, 180, 209 (CIL, Andover, MA); ¹³C-HCB and α-HCH-d_6 (Dr. Ehrenstorfer GmbH, Augsburg, Germany) for

determining the halogenated POPs (H-POPs); and naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, pyrene-d_{10}, chrysene-d_{12}, benzo[*a*]pyrene-d_{12}, and perylene-d_{12} (AccuStandard, New Haven, CT) for determining the PAHs]. The extract obtained was then divided into two parts: 10% of the extract was used for analysis of the 18 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], while the other 90% was used to determine the H-POPs including: 5 OCPs (Σ_5OCPs: 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) and 17 BFRs [Σ_{17}BFRs: 15 polybrominated diphenyl ethers (PBDEs) (BDE-17, 28, 47, 49, 66, 71, 85, 99, 100, 138, 153, 154, 183,190, and 209), 1 polybrominated biphenyl (PBB-153), and tetrabromobisphenol A (TBBPA)]. GC-MS analyses were conducted using a GC-MS QP2010 (Shimadzu, Japan) equipped with an autoinjector (AOC-20i, Shimadzu, Japan) and a programmed temperature vaporizer (Shimadzu, Japan). The PAHs were analyzed using electron impact (EI) ionization (*12, 19*), while the H-POPs were analyzed using electron capture negative ionization (*21*).

Blanks were measured every six samples. The blank values were undetected for all the analytes with the exception of naphthalene, phenanthrene, BDE-47, BDE-99, and BDE-209, the values of which were 2730, 210, 25, 38, and 12 pg/m³ air, and 31, 2.4, 0.3, 0.4, and 0.1 ng/g bark, respectively. For the bark, all the blank values were less than 6.6% of the bark concentrations, and thus the concentrations reported were not blank corrected. For the air samples, blank corrections were performed for BDE-47 and BDE-99 in most samples when the blank values were more than 20% of the sample values. Recoveries of the internal standards were 76−102%, 81−96%, 85−92%, and 69% for the perdeuterated PAHs (except for naphthalene-d_8 at 61%), ¹³C-PCBs, ¹³C-PBDEs (except for ¹³C-BDE-209 at 54%) and α-HCH-d_6. Further quality assurance measurements and criteria are discussed in detail in refs *12, 19*, and *21*.

Determination of Bark Characteristics. Bark water content (%) and lipid content (LipCont, %) were determined using the gravimetric method. The chemical composition of bark lipids was characterized using the GC-MS with both EI and chemical ionization methods as well as FT-IR (Avatar 360 FT-IR, Thermo Nicolet). The true density (ρ, g/m³) of bark was determined using the water displacement method. The specific surface area (SSA, m²/g) of the bark was determined by nitrogen sorption using SORPTOMATIC-1900 (Carl Erba, Italy) (*19*). Average pore diameter (D) of the bark was then estimated from the formula, $D = 6/(SSA × \rho)$, assuming all the pores of a certain bark have the same spherical shape and size (See Table S1).

Modeling Bark/Air Partitioning of POPs. POPs, on account of their semivolatility, are present in the atmosphere in both the gas- and particle-phase, and their proportion can be estimated from the corresponding octanol−air partition coefficient (K_{OA}) (*22*) as shown in eq 1

$$C_P / C_G = B(TSP)K_{OA} \tag{1}$$

where C_G and C_P are the volume-based gas-phase and particle-phase POP concentrations (pg/m³ air) in air, B is a constant (m³/μg), and TSP is the concentration of total suspended particles (μg/m³). Typical values of B are reported for PAHs as $1.88 × 10^{-12}$, and for OCPs and PCBs as $1.50 × 10^{-12}$ m³/μg (*22*). On the basis of C_P, C_G, TSP measurements, and K_{OA}, we determined B as $0.915 × 10^{-12}$ m³/μg for the BFRs. TBBPA and BDE-209 were excluded since their gas-phase concentrations were not detected.

Atmospheric POPs are accumulated in tree bark via two pathways, gas diffusion and particle entrapment (*12, 19, 23, 24*). The radial dilution model of McDonald and Hites (*20*) suggests that POPs in the air and in the tree bark are in rough equilibrium. Accordingly, pseudobark/air equilibrium partition coefficients, K_{BA}^g and K_{BA}^p, are defined for the gas-phase and particle-phase atmospheric POPs, respectively, by the following equations:

$$K_{BA}^g = C_B^g / C_G \tag{2}$$

$$K_{BA}^P = C_B^P / C_P \tag{3}$$

where C_B^g and C_B^p are the volume-based concentrations of POPs in the bark (pg/m^3 bark) contributed by the gas- and particle-phase POPs, respectively.

Then the total pseudobark/air equilibrium partition coefficient $K_{BA} = C_B / C_A$ for a specific POP can be expressed as

$$K_{BA} = (C_B^g + C_B^P)/(C_G + C_P) = $$
$$(K_{BA}^g + B(TSP)K_{OA}K_{BA}^P)/(1 + B(TSP)K_{OA}) \tag{4}$$

Previous studies have suggested that gas-phase hydrophobic POPs are primarily accumulated through interactions with lipid substances in bark, and the K_{BA}^g is related to K_{OA} (*12, 25, 26*). Thus one obtains

$$K_{BA}^g = mK_{OA}^n \tag{5}$$

where m and n are empirical constants, which should be principally correlated with bark LipCont (g lipid/m^3 bark) and lipid chemical composition, respectively.

On the basis of the model of Bohme et al. (*27*), particle-phase POPs are accumulated in the bark through dry and wet depositions mainly via impaction but not via sedimentation, because the horizontally projected surface area of bark is negligible relative to the overall bark surface area. Thus the K_{BA}^P values of different POPs are hypothesized to be the same for different particulate POPs:

$$K_{BA}^P = b \tag{6}$$

where b is an empirical constant that should be correlated with bark SSA (m^2 area/m^3 bark). Then, eq 4 can be expressed as

$$K_{BA} = (mK_{OA}^n + bB(TSP)K_{OA})/(1 + B(TSP)K_{OA}) \tag{7}$$

which describes K_{BA} as a function of the K_{OA} of the POPs, and various properties of the bark and air, and provides a theoretical basis for estimating the compound-specific K_{BA} for a given bark/air interface.

Results and Discussion

Influence of Bark Characteristics and Meteorological Conditions on K_{BA}. K_{BA} values were calculated from the measured C_A and C_B values for all the POPs in the case of the 15 species of tree barks with different LipCont between 2.15 and 10.1 $\times 10^6$ g/m^3 and different SSA between 0.97 and 12.1 $\times 10^6$ m^2/m^3 (Table S1). They were also calculated for the 12 Masson pine barks under different meteorological conditions of T varying from 12.4 to 29.1 °C and Pptn varying from 24.6 to 212 mm. The K_{BA} data were plotted against the K_{OA} values corresponding to different POPs and nonlinear curve fitting to eq 7 was carried out on each of the 15 species of bark, and thus their respective empirical constants m, n, and b were obtained. For example, the plot of Masson pine bark under a T of 28.9 °C (302.05 K) and Pptn of 154 mm are shown in Figure 1. It should be noted that the TBBPA and BDE-209 data points were excluded from the fittings because they are
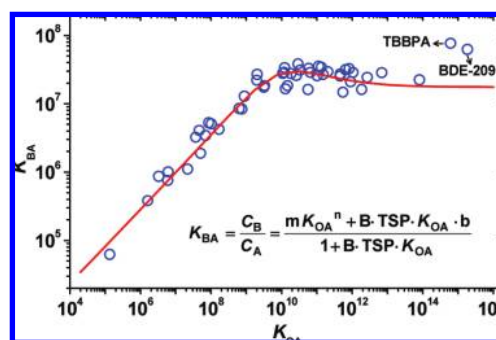

FIGURE 1. Plots of K_{BA} against K_{OA} of the POPs in Masson pine bark sampled at the main campus of Xiamen University, in August 2007.

predominantly present in the particle-phase, and their K_{BA} values are well above the average of other POPs with $K_{OA} > 10^{10}$ (Figure 1). This might imply that TBBPA and BDE-209 degrade more easily in air (primarily in suspended particles) than in the bark, resulting in a higher K_{BA}.

Power relationships were observed between m and LipCont values as well as between b and SSA values with excellent correlation coefficients (r) of 0.951 and 0.935 ($p < 0.01$, $n = 15$), respectively (Figure 2, parts a and c):

$$m = (LipCont)^{1.67} \times 10^{-9} \tag{8}$$

$$b = 210 \times (SSA)^{0.706} \tag{9}$$

These results in turn provide evidence for the previous assumptions that gas-phase POPs accumulate in the bark mainly through the interaction with lipids, and particle-phase POPs through entrapment by the porous bark surface, which has an average pore diameter range of 0.50 to 6.06 μm (Table S1). The n values for the 15 species of barks are all below 1, ranging from 0.493 to 0.579, with an insignificant variation coefficient of 4.92% (Figure 2b), indicating that all the barks behaved as a less soluble solvent than octanol (*25*) and the polarity differences among the 15 species of barks are much less than those between the barks and octanol. Thus, a mean value of 0.542 was chosen and used as the empirical constant n.

Using eqs 5 and 6, K_{BA}^g and K_{BA}^p of the POPs for the Masson pine bark were calculated from their corresponding m, n, and b values. We previously found that T influenced the interaction of gas-phase POPs with bark lipids while Pptn influenced the entrapment of particle-phase POPs in the bark (*12*); as a result, T and Pptn could influence K_{BA}^g and K_{BA}^p, respectively. Based on the van't Hoff equation of $\ln K = -\Delta H/RT + C$, describing the T dependence of the equilibrium constant, the $\ln K_{BA}^g$ were plotted against the reciprocal of the absolute temperature ($1/T$, K^{-1}) for each of the POPs. As typical examples, the plots for naphthalene, benzo[*a*]pyrene, HCB, γ-HCH, PCB-138, PCB-180, BDE-47, BDE-99, and BDE-154 are shown in Figure 2d. As theoretically expected, significant linear relationships were obtained between the $\ln K_{BA}^g$ and the $1/T$ for all the POPs ($r = 0.601-0.766$, $p < 0.05$, $n = 12$):

$$\ln K_{BA}^g = -\Delta H_{BA}/RT + C \tag{10}$$

where ΔH_{BA} is the enthalpy of phase transfer between the bark and air (J/mol), R is the gas constant of 8.314 Pa m^3/mol K, T is the ambient temperature (K), and C is a constant. The ΔH_{BA} values were calculated using the slopes of the regression lines ($-\Delta H_{BA}/R$). The $-\Delta H_{BA}$ values for all the POPs were found to be linearly related to the negative enthalpies of vaporization of the subcooled liquid ($-\Delta H_{vap}$) ($r = 0.899$, $p < 0.01$, $n = 50$) (Figure 2e):

$$-\Delta H_{BA} = -0.964\Delta H_{vap} + 3.130 \qquad (11)$$

When plotting the log K_{BA}^P against the Pptn (mm), a significant logarithmic relationship ($r = 0.937$, $p < 0.01$, $n = 12$) was obtained (Figure 2f):

$$\log K_{BA}^P = -0.766 \log P_{ptn} + 8.856 \qquad (12)$$

On the basis of the above findings, the K_{BA} can be expressed in detail as in the following equation:

$$K_{BA} = \{(LipCont)^{1.67} K_{OA}^{0.542} \cdot \exp[(-0.964\,\Delta H_{vap} + 3.130)$$
$$(1/T - 1/302.05) \cdot 10^3/R] \cdot 10^{-9} +$$
$$210\, B\, (SSA)^{0.706} (P_{ptn}/154)^{-0.766} (TSP)\, K_{OA}\} /(1 + $$
$$B(TSP)\, K_{OA}) \qquad (13)$$

The values of 302.05 and 154 refer to the absolute temperature (K) and precipitation (mm), respectively, under which the interspecies variations of K_{BA} were investigated.

The purpose for establishing this mathematic model was to estimate the ambient air concentrations of the POPs from the bark measurements without any direct air sampling events. Setting Chinese air quality standard values (28) as an example, the estimated C_A values when substituting TSP as $80\,\mu g/m^3$ (Grade I) are 0.8−1.1 times those when substituting TSP as 200 $\mu g/m^3$ (Grade II), while the C_A values when substituting TSP as 200 $\mu g/m^3$ (Grade II) are 0.9−1.1 times those when substituting TSP as 300 $\mu g/m^3$ (Grade III), suggesting that the TSP term in the model can be substituted by their roughly estimated values based on the threshold values of the National Ambient Air Quality Standards, which would introduce insignificant error to K_{BA}.

Comparison of Model-Estimated and Measured K_{BA}. In Table S2, the K_{BA} values measured at the four sampling sites, where T ranged from −3.4 to 28.0 °C and Pptn from 23.8 to 137 mm, were compared with the model-estimated values as a test of the model accuracy. The results showed that the bark/air partitioning model enables estimation of the atmospheric POP concentrations from the bark measurements within factors of 0.5−2.8 for all the POPs except BDE-209 and TBBPA, which are overestimated by a factor of 7.5.

The large uncertainties of the model estimations for BDE-209 and TBBPA were related to their environmental degradation being neglected in the model. Nevertheless, it could be effective for estimating the overall air concentrations of the POPs from their corresponding concentrations recorded in the barks and could be used for the evaluation of air POPs status. In the case of BDE-209 and TBBPA, the estimated air concentrations should be further corrected by their overestimation factors.

Spatial Distribution of Atmospheric POPs across Mainland China. The bark concentrations at the 68 sites were 5.1−1770, 0.05−12.9, 0.21−21.6, and 0.02−48.3 ng/g bark for Σ_{18}PAHs, Σ_5OCPs, Σ_{10}PCBs, and Σ_{17}BFRs, with geometric mean (GM) values of 295, 1.47, 3.12, and 2.79 ng/g bark, respectively (Table S3 and Figure 3). The Σ_{18}PAHs were mostly contributed by the two- to four-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 ≤0.9%, ≤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 its degradation 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.

The spatial distributions of the Σ_{18}PAHs, Σ_5OCPs, Σ_{10}PCBs, and Σ_{17}BFRs in the barks and air across mainland China are mapped in Figure 3, visually showing the national scale source areas of each POPs class. Figure 3 was created by using Surfer 8.0 software, and the Kriging spatial interpolation method was used for the distribution maps of air POP concentrations. The highest Σ_{18}PAHs of 180−400 ng/m³ were estimated in Shanxi province, which is famous in China for coal mines and coke plants. Higher Σ_{18}PAHs estimations occurred in northeastern areas (150−210 ng/m³) and the midlands (110−150 ng/m³), where the more concentrated heavy industries and significant burning of coal during winter are probably responsible for the results. The Σ_5OCPs were estimated to be highest in Jiangsu province (260−550 pg/m³), which was probably due to the extensively historical
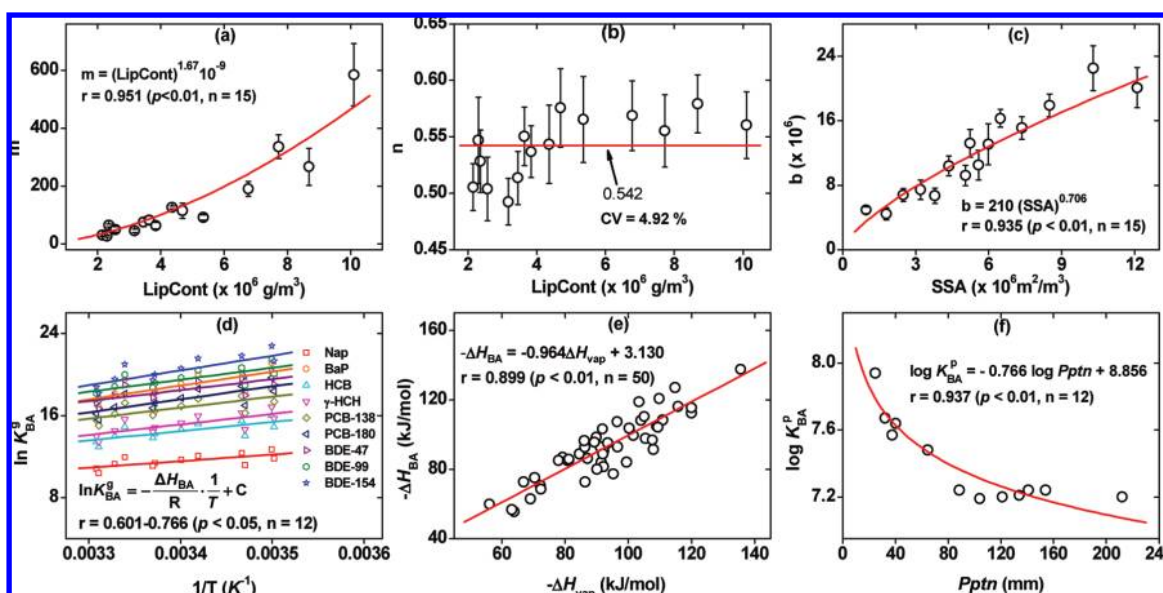

FIGURE 2. Plots of (a) the *m* values as a function of bark lipid content (LipCont); (b) the variation of *n* values among the 15 species of barks; (c) the *b* values as a function of bark specific surface area (SSA); (d) the bark/gas-phase partition coefficients (K_{BA}^g) for typical POPs as a function of the reciprocal temperature (*T*); (e) the enthalpies of phase transfer between the bark and air (ΔH_{BA}) for the POPs as a function of the enthalpy of vaporization of the subcooled liquid (ΔH_{vap}); and (f) the bark/particle-phase partition coefficient (K_{BA}^P) for the POPs as a function of precipitation (Pptn).
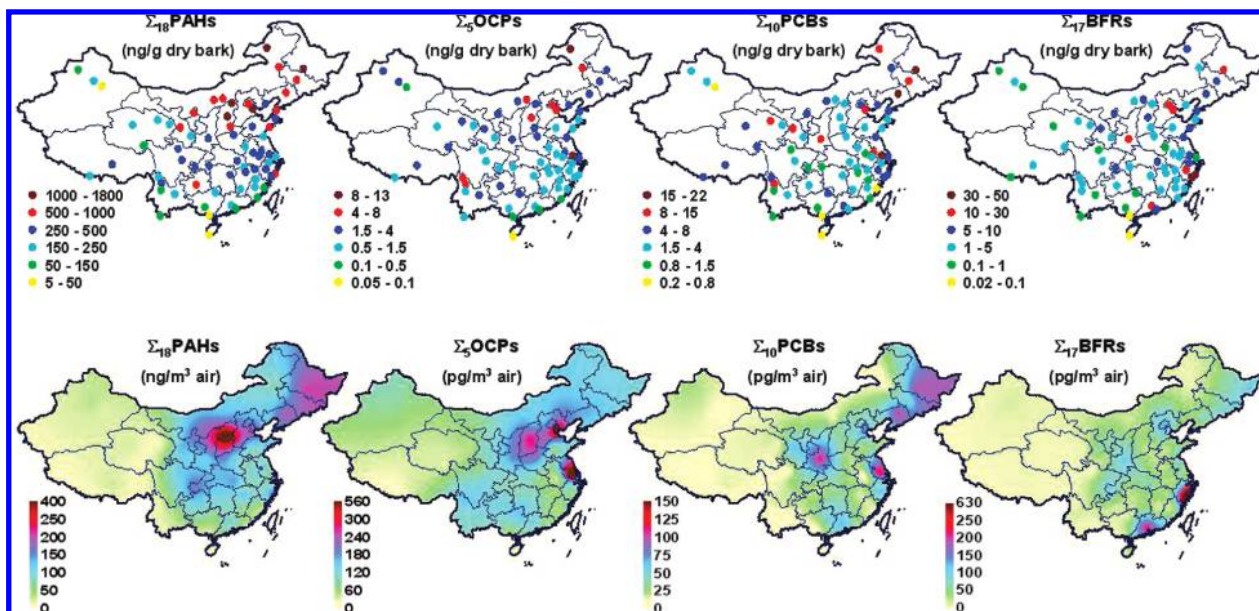
FIGURE 3. Spatial distribution of the measured bark concentrations and the estimated air concentrations of Σ_{18}PAHs, Σ_5OCPs, Σ_{10}PCBs, and Σ_{17}BFRs across mainland China. Each value of bark concentration represents the geometric mean of the concentrations determined for the various species of tree barks (Table S3) at each of the sampling sites (see Figure S1).

use of OCPs and the emissions from several big chemical plants. High values (460 pg/m^3) also occurred in Tianjin where several big pesticide plants were located. In Shanxi and Hebei provinces, the high Σ_5OCP concentrations of 120−290 pg/m^3 are attributed to the extensive use of HCHs in agriculture during the 1950−1980s (*29*). The highest Σ_{10}PCBs of 110−130 pg/m^3 occurred in Jiangsu and Shaanxi, where PCBs were manufactured and used during the 1960−1970s (*29*), but they were also high (90−110 pg/m^3) in Heilongjiang and Liaoning provinces and the Tianjin area. Revolatilization of previously emitted and deposited PCBs from these industrialized regions was suggested as the primary PCB source in China at present. Highest Σ_{17}BFRs of 150−620 pg/m^3 were observed in Zhejiang province and were typically highest (624 pg/m^3) in Taizhou, a city known for electronic waste recycling, and quite higher (474 pg/m^3) in the neighboring Wenzhou. This indicated that the heavy BFR pollution of Zhejiang province resulted from electronic waste recycling. High Σ_{17}BFRs also occurred in Guangdong province (150−240 pg/m^3), followed by several industrialized mega cities such as Beijing, Tianjin, Chongqing, and Xi'an (111−140 pg/m^3). In general the model-estimated air concentrations of each class of POPs differed among the cities (see Table S4) with the Σ_{18}PAHs at levels of 4.1−399 ng/m^3 while the Σ_5OCP, Σ_{10}PCB, and Σ_{17}BFR values were relatively lower at levels of 11.3−553, 4.5−130, and 0.9−624 pg/m^3, respectively. This spatial distribution pattern agreed generally (with discrepancies ranging from −61% to 98%; see Table S4) not only with the reported values available, which were directly measured using active air sampling methods, but also with the view that contamination by atmospheric POPs in eastern and middle China are more serious than those in western China. Overall, GM values of all 68 cities were 71 ng/m^3 for Σ_{18}PAHs, 99 pg/m^3 for Σ_5OCPs, 26 pg/m^3 for Σ_{10}PCBs, and 25 pg/m^3 for Σ_{17}BFRs.

Acknowledgments

Supporting Information Available

Table S1 showing name and physical characteristics of the barks from 15 tree species on the main campus of XMU; Table S2 for comparison of model-estimated pseudobark/air partition coefficients with measured values; Table S3 showing concentrations of Σ_{18}PAHs, Σ_5OCPs, Σ_{10}PCBs, and Σ_{17}BFRs in the barks at 68 sites across mainland China along with the sampling site locations, environmental conditions, and bark characteristics; Table S4 showing estimated air concentrations of Σ_{18}PAHs, Σ_5OCPs, Σ_{10}PCBs, and Σ_{17}BFRs at 68 sites in comparison with directly measured values using active air sampling methods available in the literature; Figure S1 showing a location map of the sampling sites. This material is available free of charge via the Internet at http://pubs.acs.org.

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