LEVELS AND SOURCES OF TYPICAL PERSISTENT ORGANIC POLLUTANTS IN PINE NEEDLES AND SOILS FROM DALIAN, CHINA

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Abstract

The levels and primary sources of polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in pine (*Cedrus deodara*) needles and soils from Dalian, China, were investigated. It was re-proved that pine needles could be used as passive air samplers to indicate spatial variations of persistent organic pollutants (POPs). However, it was suggested that the local meteorological conditions and source variations should be taken into account when pine needles were used to implicate temporal variations of atmospheric POPs. An improvement method, factor analysis with nonnegative constraints (FA-NNC), was employed to apportion the primary sources of POPs. Four primary sources of PCDD/Fs were identified: various combustion process (74%), pentachlorophenol (PCP) contamination (15%), secondary aluminum smelters (9%) and traffic emissions (2%). PCBs in pine needles were from the two typical Chinese technical PCB products PCB3 and PCB5, accounting for 80% and 20% of the total amounts, respectively. PAHs were mainly originated from traffic emission and domestic coal combustion. The contributions of the two sources showed spatial variations.

Introduction

Polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are compounds, which, because of their physical-chemical properties, are persistent and mobile in the environment. These persistent organic pollutants (POPs) also tend to be bio-accumulating and toxic, and therefore they pose risks to biota and humans.

These pollutants, depending on their phase existing in the atmosphere, can reach vegetation as vapor and/or particulate phase, and diffuse into cuticular waxes or by stomatal uptake. Many leaves, such as pine needles, have a relatively large surface area covered with waxes that facilitates the accumulation of POPs. The use of pine needles as “passive samplers” of POPs in the atmosphere has been suggested by many studies. Thus pine needles were widely used as passive air samplers to identify point sources of POPs and to determine regional contamination within cities, countries and continents.[1]

When POPs are released into the atmosphere, they redistribute between vapor and particulate phases and then reach soil by dry/wet deposition. POPs tend to be strongly adsorbed to soil and are difficult to dissipate owing to their high octanol-air partition coefficients or low subcooled liquid vapor pressures. Thus soil is considered as a major environmental reservoir for POPs. Furthermore, soil can provide the best pollution “snapshot” of the environment, and POP concentrations measured in soil have been regarded as a good indicator of the

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surrounding air pollution.

In this study, the levels of PCDD/Fs, PCBs and PAHs in pine needles and soils were investigated, and the sources of these POPs were apportioned employing an improvement method, factor analysis with nonnegative constraints (FA-NNC).

Materials and Methods

For the analysis of PCDD/Fs and PCBs, pine (*Cedrus deodara*) needles were collected from Dalian, a coastal city in Northeastern China in 2002. The samples were analyzed by the isotope dilution method using HRGC-MS.[2] For the analysis of PAHs, pine needles and soils were collected from Dalian in 2005. After pre-treatment, the samples were analyzed using Agilent 1100 HPLC coupled with a fluorescence detector.[3]

Factor analysis (FA) with nonnegative constraints (FA-NNC) is an improvement method for source apportionment. In the traditional FA models, factor loadings and factor scores could be negative, which makes the interpretation of the sources very difficult. While FA-NNC provides a new method for matrix factorization, which ensures factor axes to become less orthogonal and makes factor loadings and scores more interpretable due to fewer negative values.

The details of FA-NNC were described by Rachdawong and Christensen.[4] The fundamental equation underlying the FA-NNC model is

$$\underset{(m \times r)}{\boldsymbol{D}} = \underset{(m \times n)}{\boldsymbol{C}} \times \underset{(n \times r)}{\boldsymbol{R}} \qquad (1)$$

where the concentration matrix $\boldsymbol{D}$ is fractioned into factor loading matrix $\boldsymbol{C}$ and factor score matrix $\boldsymbol{R}$. The $\boldsymbol{C}$ matrix represents source profiles and $\boldsymbol{R}$ represents source contributions. m, n, and r stand for the number of compounds, sources, and samples, respectively.

In short, the data matrix $\boldsymbol{D}$ was averagely scaled to reduce the effects of bias from compounds with high concentrations. Then a covariance matrix was calculated with dimensions of $m \times m$ using the scaled data matrix, and factor loading matrix $\boldsymbol{C}$ and factor score matrix $\boldsymbol{R}$ were determined based on the computation method described by Imamoglu et al.[5] Coefficient of determination, cumulative percent variance and Exner function were considered for the determination of the significant factors.[6] The reduced $\boldsymbol{C}$ and $\boldsymbol{R}$ matrices were rotated with nonnegative constraints until the sum of square of the negative entries in the $\boldsymbol{C}$ matrix was below a very small value (0.0001).

Results and Discussion

The summation of tetra- to octachlorinated PCDD/Fs and 209 PCB congeners in Dalian pine needles averaged 127 ± 40 pg/g and 4389 ± 1575 pg/g, respectively. Average toxic equivalent (TEQ) for PCDD/Fs and PCBs were

2.1 and 0.4 pg/g, respectively. The levels of PCDD/Fs and PCBs in Dalian pine needles were low and/or comparable with other regions that were not impacted by evident point sources.[2] However, PAH levels in pine needles (490-3241 ng/g) were higher than other international cities. The total concentrations of 14 PAHs decreased significantly with the distance from traffic areas, which implied that pine needle PAHs were strongly influenced by traffic.

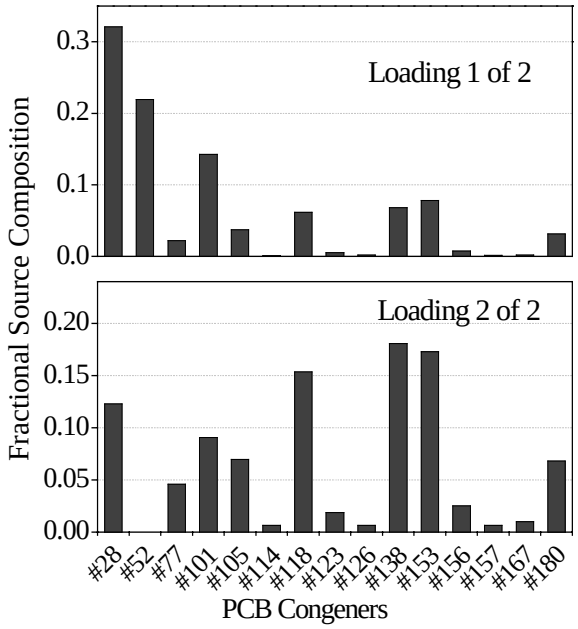

Figure 1. Factor loadings for PCBs in pine needles in Dalian

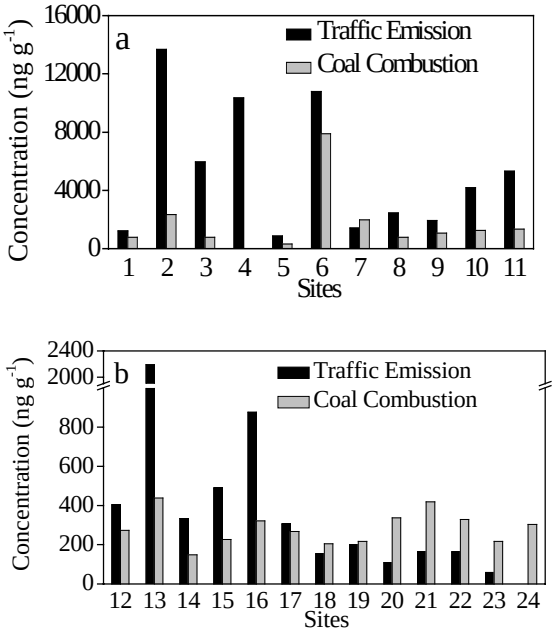

Figure 2. PAH contributions from the two sources: (a) traffic sites (1#~11#), and (b) park/residential sites (12#~17#), suburban sites (18#~22#) and rural sites (23#~24#)

It was found that the high wind speed and frequently alternating wind directions in spring of Dalian could quicken the depuration processes of pine needle PAHs and moderate the contributions of deposited particle-bound PAHs, which suggested that when using pine needles to implicate temporal variations of atmospheric POPs, the local meteorological conditions and source variations should not be neglected. A positive correlation between the contributions of particle-bound PAHs and the corresponding logarithm of octanol/air partition coefficients (logK_{OA}) was observed.

FA-NNC was shown to be successful in source identification of POPs in pine needles and soils. The four primary sources of PCDD/Fs were identified: various combustion process, pentachlorophenol (PCP) contamination, secondary aluminum smelters and traffic emissions, which accounted for 74%,15%, 9% and 2% of the total emission, respectively. There have been no municipal and medical waste incinerators in Dalian by now, thus various small-scale combustion processes could be the primary sources of PCDD/Fs. Some sampling sites

adjacent to a former wood preserving site and in the vicinity of a forest possess higher factor scores (source contributions) than at other sites. Dalian region is rich in apple and peach orchards and grapery, where PCP was extensively used as pesticides. Besides, PCP products were also widely used for wood preserving and aquaculture in Dalian.[7] Thus PCP could be one of the main sources of PCDD/Fs in the region.

As for PCBs, only two main sources were identified, PCB3 and PCB5, two typical Chinese technical PCB products. In China, only the two technical PCBs were produced from the year 1965 to 1974.[8] The chlorine content of PCB3 and PCB5 are 42% and 56%, and the congener profile are similar with Aroclor 1242 and Aroclor 1254, respectively. The factor loading 1 of 2 was highly weighted on congener #28, #52, #101, #118, #138, and #153, which resemble Aroclor 1242 (PCB3), and the factor loading 2 of 2 is heavily weighted on #28, #101, #105, #118, #138, and #153 (Figure 1). The pattern of this factor is similar to that of Aroclor 1254 (PCB5). The average contributions from PCB3 and PCB5, estimated from the factor scores, are 80% and 20%, respectively, which are qualitatively consistent with the proportions of technical PCB products, PCB3 and PCB5 synthesized and used in China.

The primary sources of PAHs in soils were also apportioned applying FA-NNC. Two main source types were identified: traffic source and domestic coal combustion. The contribution of the primary sources at each sampling sites were estimated based on the factor scores. Figure 2 shows the source contributions from traffic emission and domestic coal combustion for 24 sampling sites. As expected, the contributions from the two sources show spatial variations. Traffic emission is the significant contribution (76% on average) for the samples from the traffic sites, while the domestic coal combustion becomes the dominant source at the suburban and rural sites (66% and 90% on average, respectively). As can be seen in Figure 2, the site 13# has the relatively high contribution of traffic emission. Although the site was classified into parks, it is adjacent to one of the busiest roads in Dalian, which lead to a higher contribution of traffic emission than those at other sites.

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