DISTRIBUTION OF PAHs IN SOILS AND PINE NEEDLES CORRELATED WITH THEIR PHYSICOCHEMICAL PROPERTIES

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Introduction

Due to lipid-rich cuticle and stomata structures of the surfaces, plant leaves play an important role in removing semi-volatile organic compounds (SOCs) from the atmosphere and have been employed as bio-indicators of atmospheric pollution. To date, pine needles, as one of typical natural passive air samplers, have been widely used to monitor atmospheric SOCs, such as polycyclic aromatic hydrocarbons (PAHs). Hydrophobic, persistent organic vapor contaminants reach leaves primarily from the atmosphere, and are absorbed by leaves. Some studies indicated that the measured plant/air partitioning of SOCs could be characterized with their physicochemical properties, such as the sub-cooled liquid vapor pressure (p°_{L})[1].

Soil is considered as one of the major reservoirs of SOCs, especially for SOCs with lower p°_{L}. Many studies have found that soil receives SOCs mainly from dry/wet deposition of particles and litterfall, with dry/wet deposition of particles being the most important, and the soil/air partition coefficients of SOCs correlate with their octanol/air partition coefficient (K_{OA}). In general, SOCs with lower p°_{L} or higher K_{OA}, are favored for accumulation in the surface soils. Excellent log/log-linear relationships between the soil/air partition coefficients and p°_{L} (or K_{OA}) of SOCs have been reported[2].

The gas/particle partition coefficient, K_P, a parameter describing the gas/particle partitioning of SOCs in the atmosphere, is a decisive process concerning their potential to undergo long range atmospheric transport, dry/wet deposition and environmental fates. Many previous studies have shown that there is a significant linear correlation between $\log K_P$ and $\log p^{\circ}_{L}$ of SOCs and the slope should equal to -1 under the condition of gas/particle partitioning equilibrium. Moreover, the physicochemical properties, such as p°_{L} and K_{OA}, were suitable for characterizing the accumulation trends of SOCs between soil and air, as well as between vegetation and air. Based on above analysis, a significant linear correlation between soil/needle quotient and the physicochemical properties is expected.

PAHs are ubiquitous pollutants in the environment and generally formed by incomplete combustion of fossil fuels or organic matter. They possess different profiles of distribution in various environmental media due to their wide range of physicochemical properties. For instance, $\log p^{\circ}_{L}$ (Pa) ranges from 0.71 for 3-ring acenaphthene to -6.98 for 6-ring dibenz(a,h)anthracene. Thus, it became the primary objects of the present study to verify the above hypothesis about the relation of p°_{L} and the distribution of SOCs in soils and pine needles by using PAHs as target compounds.

Materials and methods

Three sampling sites, Shihezi (43°20´-45°20´N, 84°45´-86°40´E), Beitun (47°20´-47°22´N, 87°47´-87°53´E) and Kanas (48°43´-48°46´N, 86°59´-87°01´E), where locate in the northern of Xinjiang Autonomous Region of China, were selected to represent the urban region, rural area and untrodden mountain, respectively. Surface soil (0-5 cm) and pine needle (one-year-old needles) samples were collected simultaneously from 25 sites in the three sites in August, 2010.

Briefly, 5 g of soil samples (dry weight) and 10 g of pine needles mixed with the surrogate standard (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}) were extracted with 50 mL hexane/dichloromethane (1:1, v:v) in an ultrasonic bath for 30 min, respectively. This procedure was repeated two times. Activated copper powder was added to the extract of soil to remove elemental sulfur. The extracts were concentrated with a rotary evaporator, cleaned with multilayer silica columns filled from the bottom with 2 g of activated silica gel and 4 g of florisil topped with 2 g of anhydrous Na2SO4, and eluted with 30 mL hexane and 50 mL hexane/dichloromethane (1:1). The second fraction was collected and concentrated to 1 mL. A known amount of internal standard was added and mixed completely prior to instrumental analysis.

PAHs were analyzed using an Agilent 6890N GC-5975B MS equipped with a DB-5 column. Helium was used as carrier gas (1.0 mL/min) and the sample (1 μL) was injected in the splitless mode. The temperature program was as follows: initial temperature of 50°C, held for 2 min, increased at a rate of 20°C/min to 200°C, then held for 2 min, raised to 260°C at 5°C/min, maintained for 2 min and raised to 300°C at 10°C/min followed by a hold of 5.5 min. PAHs contains 15 compounds: acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene.

Results and discussion

Concentrations of distribution of PAHs

The total concentrations ranges of 15 PAHs (ΣPAHs) and their average values in soils of Shijezi, Beitun and Kanas were 50.4-676.9 ng/g (average value: 382.2 ng/g), 39.9-602.4 ng/g (177.0 ng/g) and 30.7-178.8 ng/g (86.5 ng/g), respectively, and the ranges and average values in pine needles were 17.2-279.4 ng/g (174.8 ng/g), 44.5-320.6 ng/g (171.0 ng/g) and 21.6-51.4 ng/g (34.8 ng/g) , respectively. ΣPAHs in both soils and pine needles of Kanas were lower than the concentrations of PAHs in soils and vegetation in Ny-Ålsund[2], thus can be viewed as the background level of PAHs.

To investigate the distribution characteristics of various rings PAHs in soils and pine needles, all PAHs were divided into three groups based on their ring number: 3-ring, 4-ring and 5 + 6-ring PAHs. Fig. 1 presents the ternary diagram for three groups of PAHs in soils and pine needles collected from Shihezi, Beitun and Kanas. The composition profiles of different ring PAHs varied obviously in soils and pine needles among the three sampling sites. The proportions of 3-ring PAHs in soils were between 0.25 and 0.75 and most samples in the range of 0.25 and 0.50, while the proportions in pine needles lay in the range of 0.50~0.85 and their values were higher than those in soils. For the 4-ring species, the proportions were similar (between 0.12 and 0.50) in soils and pine needles. On the contrary, the percentages of 5 + 6-ring PAHs in pine needles were lower than 0.20, and lower clearly than those in soils.

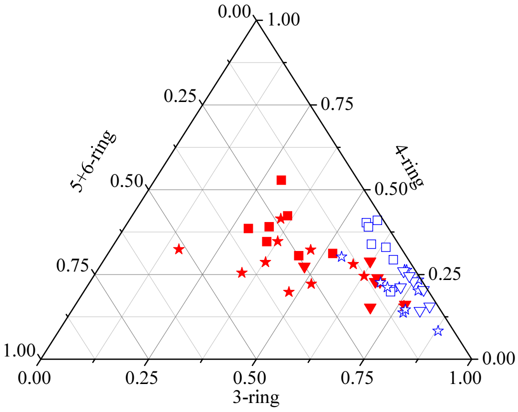

Fig. 1 Ternary diagram for various ring PAHs in soils and pine needles
(■ soil in Shihezi ★ soil in Beitun ▼ soil in Kanas □ pine needle in Shihezi ☆ pine needle in Beitun ▽ pine needle in Kanas)

The variation of PAH composition profiles in soils and pine needles was a result of the different accumulation routes into soils and pine needles and different physicochemical properties of PAHs. As stated above, gas phase PAHs are prone to be absorbed by pine needles and soil receives PAHs mainly from dry/wet deposition of particles. Furthermore, PAHs with higher logp°_{L} (3-ring PAHs) mainly exist in the gas phase and can be easily sequestered by pine needles, while compounds with lower $\log p^{\circ}_{L}$ (5 + 6-ring PAHs) mainly associate with particles and can easily deposit into soils. For 4-ring PAHs with median $\log p^{\circ}_{L}$, they can partition between gas and particle phases and contribute to soils and pine needles to a similar extent. As a result, higher proportions of 3-ring PAHs were observed in pine needles and more 5 + 6-ring species were accumulated in soils.

Moreover, the different proportions of the three groups were also observed in different sampling sites. In soils, the proportions of 3-ring PAHs were higher in Kanas than those in Shihezi, while the values were lower in Kanas for 5 + 6-ring PAHs compared to Shihezi (Fig. 1). Similar trends were also found in pine needles, and the proportions of 3-ring PAHs in pine needles were obviously higher in Kanas than those in Shihezi.

This can be explained by the different potential of atmospheric transport associated with the wide range of $\log p^{\circ}_{L}$. Due to lower $\log p^{\circ}_{L}$ values of 5 + 6-ring PAHs, they are prone to bind to particles and tend to deposit near the sources of PAHs. On the contrary, the 3-ring compounds in gas phase may undertake a longer range atmospheric transport owing to their higher $\log p^{\circ}_{L}$ compared with their heavy counterparts. Thus, higher proportions of 3-ring PAHs were expected to be observed in soils and pine needles of the remote sites (Kanas), while higher percentages of 5 + 6-ring PAHs were detected at urban sites near the sources of PAHs (Shihezi). This phenomenon can be called ''urban fractionation'' or ''local distillation'' effect, which was reported firstly by Harner et al.[3] by investigating typical polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in the atmosphere of Toronto. Wang et al.[4,5] also found similar effects with the urban-suburban-rural gradient of soil PAHs in Dalian.

Relations of the distribution with $\log p^{\circ}_{L}$ of PAHs

Previous studies have indicated that the gas/particle partition coefficient (K_P) of PAHs is one of key parameters describing their environmental behaviors and fates, and there is a significant correlation between $\log K_P$ and $\log p^{\circ}_{L}$:

$$\log K_P = m_r \log p^{\circ}_{L} + b_r \quad (1)$$

where m_r and b_r are constants. As discussed above, soil accumulates PAHs mainly through dry/wet deposition of particles and pine needle sequesters PAHs mainly from the vapor phase. Then, the distribution of PAHs in soils and pine needles is expected to be responsible for their gas/particle partitioning and relates to the physicochemical porperties of PAHs, such as p°_{L}. To verify the hypothesis, a dimensionless soil/needle quotient (Q_{SP}) was defined:

$$Q_{SP} = C_S/C_P \quad (2)$$

where C_S and C_P are concentrations of PAHs in soils and pine needles (ng/g), respectively.

For 14 PAHs (except acenaphthene) in soils and pine needles collected from the three sites, an excellent log/log-linear relationship between Q_{SP} and p°_{L} was observed:

$$\log Q_{SP} = (-0.16 \pm 0.08) \log p^{\circ}_{L} + (-0.14 \pm 0.47) \quad (3)$$

$$(n = 24, r = 0.69, p < 0.01)$$

Here $\log p^{\circ}_{L}$ of PAHs were calculated at the average ambient temperature (10ºC) based on the method of Huang et al.[6]. $\log Q_{SP}$ increases with the decrease of $\log p^{\circ}_{L}$, proving more hydrophobic PAHs are prone to accumulation in soil compared with pine needles. Although some factors, such as meteorological conditions, different uptake and accumulation processes, source types and transport potential, would result in the variation of the relation, the results showed that the distribution of PAHs in soil and pine needles can be well characterized with their physicochemical properties (p°_{L}).

Weiss[7] investigated the relation of the physicochemical properties and the distribution of typical SOCs (OCPs, PCBs, PAHs and PCDD/Fs) in soils and spruce needles in Austria and reported the following significant correlation:

$$\log(C_S/C_P) = -0.161 \log p^{\circ}_{L} - 0.498 \quad (4)$$

(Austria, average temperature: 6.4 ºC)

Wang et al.[1,2] also reported the similar significant relationships between $\log p^{\circ}_{L}$ and soil/vegetation (pine needle and moss) quotients of PAHs in Liaoning Province of China and Ny-Ålesund of the Arctic:

$$\log Q_{SP} = (-0.22 \pm 0.02) \log p^{\circ}_{L} + (-0.44 \pm 0.09) \quad (5)$$

(soil/needle, Liaoning, average temperature: 10ºC)[1]

$$\log(C_{S}/C_{M}) = -0.14 \log p^{\circ}_{L} - 0.51 \quad (6)$$

(soil/moss, Ny-Ålesund, average temperature: 5ºC)[2]

It was worth noting that the slopes of Eqs. (3)-(6) were -0.16, -0.161, -0.22 and -0.14, respectively, and they did not vary greatly. Similar trends were also observed for their intercepts, which were -0.14, -0.498, -0.44 and -0.51, respectively. The similar slopes and intercepts of the regressions implied that the trends of the accumulation in soil and vegetation (moss and pine needle) were similar in relation to physicochemical properties (such as p°_{L}) of PAHs. In briefly, considering similar correlations of $\log Q_{SP} \sim \log p^{\circ}_{L}$ and $\log K_{P} \sim \log p^{\circ}_{L}$, the distribution of PAHs in soils and pine needles can be viewed as a "mirror image" of the gas/particle partitioning of PAHs.

With regarding to gas/particle partitioning of PAHs, the value m_{r} of should equal to -1 under the equilibrium condition and in theory there is a significant correlation between m_{r} and b_{r} in Eq. (1). However, previous studies indicated that the variations of ambient temperature and surface characters of particles could result in the changes of m_{r} and b_{r}. The partitioning of PAHs between air and soils (pine needles) can be considered in equilibrium, thus the slope of linear relation of $\log Q_{SP} \sim \log p^{\circ}_{L}$ is expected to be approaching a fixed value. The similar slopes and intercepts of Eqs. (3)–(6) gave the field evidence in support of the hypothesis. However, to date, the quantitative methods for describing the processes and mechanism of the enrichment in soil and vegetation have been poorly discussed, further research is necessary before the theoretical value can be identified.

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