Ecotoxicology and Environmental Safety 152 (2018) 151–158

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Polycyclic aromatic hydrocarbons in soils and lichen from the western Tibetan Plateau: Concentration profiles, distribution and its influencing factors

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ARTICLE INFO

Keywords:
PAHs
Tibetan Plateau
Long-range atmospheric transport (LRAT)
Alpine region
Mountain

ABSTRACT

The Tibetan Plateau (TP) is a huge area and rarely affected by human activity, and is regarded as one of the most remote regions on the earth. Many studies about the long-range atmospheric transport (LRAT) of semi-volatile organic compounds (SVOCs) were conducted in southern and central TP. However, there are very limited studies focused on PAHs in the western TP and the concentrations profiles, distribution and its controlling factors in this area remains unclear. Thus, to explore this knowledge gap, 37 surface soil samples and 23 lichen samples were collected and analyzed for PAHs. The total concentration of 16 US EPA's priority PAHs (Σ_{16}PAHs) in western TP ranges 14.4–59.5 ng/g and 38.0–133 ng/g dry weight (dw) with a mean value of 30.8 and 84.6 ng/g dw in soil and lichen, respectively, which is lower than the concentrations in most remote areas worldwide. In the western TP, low molecular weight PAHs (2–3 rings) are dominant (occupied 77.4% and 87.9% on average in soil and lichen, respectively), implying a significant contribution of LRAT in this area. The significant linear correlations (R^2 = 0.372–0.627, $p < 0.05$) between longitude and soil concentration suggest a strong impact of the westerly wind on the distribution of PAHs in soil. In addition, the concentration ratio of lichen/soil (L/S) was found to linearly increase with the increasing log K_{OA} of individual PAH, suggesting lichen has a strong ability in filtering more lipophilic airborne pollutants in western TP.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of semi-volatile organic compounds (SVOCs), which are produced by the incomplete combustion of organic substance, such as fossil fuel and biomass (Mastral and Callen, 2000). Some PAH are regarded as toxic compounds that have carcinogenicity potency (Okona-Mensah et al., 2005), and are widespread in the world (Laflamme and Hites, 1978). It was estimated that over 504 Gg of 16 US Environmental Protection Agency (EPA) priority PAHs were emitted in 2007 around the world (Shen et al., 2013). PAHs which have ability of long-range atmospheric transport (LRAT) can be transported and deposited in remote and high-altitude environments, thus pose risks to people who rely on alpine ecosystems (Friedman et al., 2013).

In terrestrial environments, soil is a major PAH reservoir which can store more than 90% of the terrestrial PAHs (Wild and Jones, 1995). Thus, monitoring the concentration of PAHs in soil is important for understanding its environmental fate. PAHs in surface soil is directly affected by dry/wet deposition which is a key component of studies focusing on global PAH cycling (Cabrerizo et al., 2011; Komprda et al., 2013).

Lichen is a useful passive air sampling media which is effective in monitoring the relative concentration of SVOCs in air and regional distribution (Blasco et al., 2011; Schrlau et al., 2011). With large surface area to volume ratio and short roots, lichen absorbs pollutants directly from ambient air (Muir et al., 1993). And pollutants in both vapor phase and particle phase could accumulate in lichen tissue (Yang et al., 2013; Zhu et al., 2015).

The Tibetan Plateau (TP), the largest and highest plateau on Earth, is also known as “the third pole” of the planet. Given the sparsely populated and less industrial activities, it has long been thought to be one of the most isolated geographical unit on the earth. However, the TP is surrounded by fast industrializing countries such as China and India (Masih et al., 2010). It is therefore exposed to the emission of various kinds of SVOCs, which have been widely detected, including organochlorine pesticides (OCPs) (Wang et al., 2010; Yang et al., 2013),

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https://doi.org/10.1016/j.ecoenv.2018.01.009
Received 21 November 2017; Received in revised form 2 January 2018; Accepted 7 January 2018
Available online 10 January 2018
0147-6513/

polychlorinated biphenyls (PCBs) (Yang et al., 2010a; Zheng et al., 2012), polybrominated diphenyl ethers (PBDEs) (Zheng et al., 2012; Zhu et al., 2014), PAHs (Yuan et al., 2015; Bi et al., 2016; Yang et al., 2016, 2017; Li et al., 2017), and so forth. LRAT is regarded as the most important pathway for SVOCs to migrate to TP (Wang et al., 2016). The orographic cold trapping of SVOCs and its spatial distribution in the TP could be complicated by many factors such as meteorological conditions, land cover, photodegradation and local emissions in some parts of TP (Yang et al., 2013).

However, in most of the western TP, due to extremely harsh and primitive environment, there are hardly any human activities, which minimize the possible local emissions. Its climate is meteorologically controlled by the westerly winds and the Indian monsoon (Zhang et al., 2009; Yao et al., 2012), which play an important role on the distribution and transport of SVOCs. Gong et al. (2015) found the seasonal patterns of OCPs in atmosphere in Ngari in the western TP which were influenced both by the westerly wind and the Indian monsoon. Tao et al. (2011) reported low concentrations of PAHs in soil in the western and northwest TP and suggest it is a background level of East Asia by comparing to other regions. Wang et al. (2014) and He et al. (2015) observed relatively low concentrations in the western TP by analyzing PAHs in soils across the TP but paid little attention to PAH distributions in western TP. The research about concentration profiles and spatial patterns of SVOCs in western TP is still very limited, and the controlling factors on the distribution of SVOCs in this region remains unclear.

In this study, soil and lichen samples were collected in western and central TP. The specific objectives are to investigate the concentration profiles and comparing the different factors in influencing spatial distribution of PAHs in western TP. The combined data in soil and lichen could not only reveal the distribution of PAHs but also help better understanding of complex influencing factors. Furthermore, the role of lichen in enrichment of PAHs in dry and desert environment of the western TP was discussed. To our knowledge, this is the first set of data on PAHs using lichen as a passive air-samplers in the western TP.

2. Experimental section

2.1. Study area

The western TP is surrounded by Nepal, North India, Pakistan, and Northwest China. The atmospheric circulation in this region is seasonally shifted by the westerly winds and Indian monsoon (Gong et al., 2015). The major part of the western TP is desert and sandy soils are the most common soil type (Wang et al., 2014). The annual average precipitation and temperature in the western TP are 69 mm and 0.5 °C, respectively (Chen et al., 2017). This region has a low population density (< 0.5 people/km^2) (Gong et al., 2015). As a contrast to the western TP, some samples were also collected from the central TP where significant PAH emission is expected due to a denser population and more tourists.

A total of 37 soil samples and 23 lichen samples were collected at the altitude between 3590 m and 5235 m above sea level. All sampling sites are divided into three areas (Fig. 1). Areas II and III belong to the western TP. Area II is located in the northwest TP, which is the least developed area and low population density. Area III is located in the southwestern TP. In contrast, Area I is part of the central TP for comparison with the western TP. Two large cities, Lhasa and Shigatse (more than 0.5 and 0.7 million people, respectively), are located in this area. The detailed sampling information and related parameters are listed in Table S1 of the supporting information (SI).

2.2. Sample collection

The samples were collected in September 2014. Each sampling location was selected about 500 m to 1 km away from the road to minimize the traffic influence. The surface soil (0–5 cm) was collected at 5 different spots at each site. Lichen sample was collected from at least 5 different spots near the soil site at the same time when it was available. A steel shovel and clean nitrile gloves were used for sampling. The shovel was thoroughly cleaned before sampling. All samples were sealed in plastic bags and placed in an ice chest during the transport and then keep frozen at − 20 °C in a freezer in the lab.

2.3. Chemical analysis

In total, 24 types of PAH standard solutions were purchased from Accustandard Inc. USA. The detailed full name of individual PAH and its abbreviation is listed in Table S2. In addition, 2-fluorobiphenyl was used as internal standard and five deuterated PAHs, naphthalene-d8 (NAP-d8), Acenaphthylene-d10 (ACY-d10), (phenanthrene-d10 (PHE-d10), chrysene-d12 (CHR-d12), and perylene-d12 (PER-d12), were used as surrogate standards.

Soil or lichen samples were freeze-dried and ground. Five gram of homogenized samples were spiked with the five deuterated surrogate standard And then extracted by the Dionex 350 Accelerated Solvent Extractor (ASE) using 60 ml mixed solvent (hexane: dichloromethane, 1:1, v/v). The extract was concentrated to 2 ml and then cleaned up using 6 g of 3% water-deactivated silica gel 4 g of 2% water-deactivated alumina, and 4 g of anhydrous sodium sulfate packed in a glass column from the bottom to the top. The elution was conducted using 50 ml mixed solvent (hexane: dichloromethane, 3:2, v/v) and concentrated to a final volume approximately 0.5 ml. The internal standard of 2-fluorobiphenyl (200 ng) was added before instrumental analysis.

A gas chromatograph (Agilent 7890 GC) coupled with a mass spectrometer (Agilent 5975 MS) was used for the analysis. PAH separation was conducted using a DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm). The oven temperature was as follows: initial 60 °C for 1 min, then increased to 310 °C at 8 °C/min, finally, maintained at 310 °C for 15 min. The mass spectrometer was operated in selective ion monitoring (SIM) mode with electron ionization (EI) ion source. The detailed SIM ions of the PAHs are listed in Table S2.

Soil organic carbon (SOC) content was measured using a TOC Analyzer (TOC-V, Shimadzu) according to the method described by Wang et al. (2012). The lipid contents of the lichen extracts were analyzed by gravimetric method.

2.4. Quality control

A procedural blank was run every batch of 10 samples to monitor potential pollution in the lab. The method detection limits (MDLs) defined as three times the signal-to-noise ratio were 0.02–1.03 ng/g for all 24 PAHs. Any concentrations below the MDL were defined as non-detected (N.D.). The recoveries of the five deuterated surrogates, NAP-d8, ACP-d10, PHE-d10, CHR-d12, and PER-d12, in all samples were 68.2% ± 11.6%, 72.8% ± 10.3%, 81.7% ± 8.80%, 102% ± 9.30%, and 114% ± 17.5%, respectively. The final concentrations were corrected using recoveries of the surrogates. Five soil and 3 lichen samples were analyzed in duplicate. The relative percentage differences (RPDs) were in the range of 0.77–22.3%.

2.5. Statistical analysis

The SPSS 20.0 was used for statistical analysis. Pearson correlation was applied to find the correlation between PAH concentrations with longitude, altitude and soil organic carbon (SOC) with a significance of 0.05. Principal component analysis (PCA) was used for classification of the sampling sites. Air mass backward trajectories were performed using the HYSPLIT model developed by the US NOAA. The 6-day (144 h) backward trajectories ended in single site with a height of 500, 1000, 1500 m above ground level were calculated.

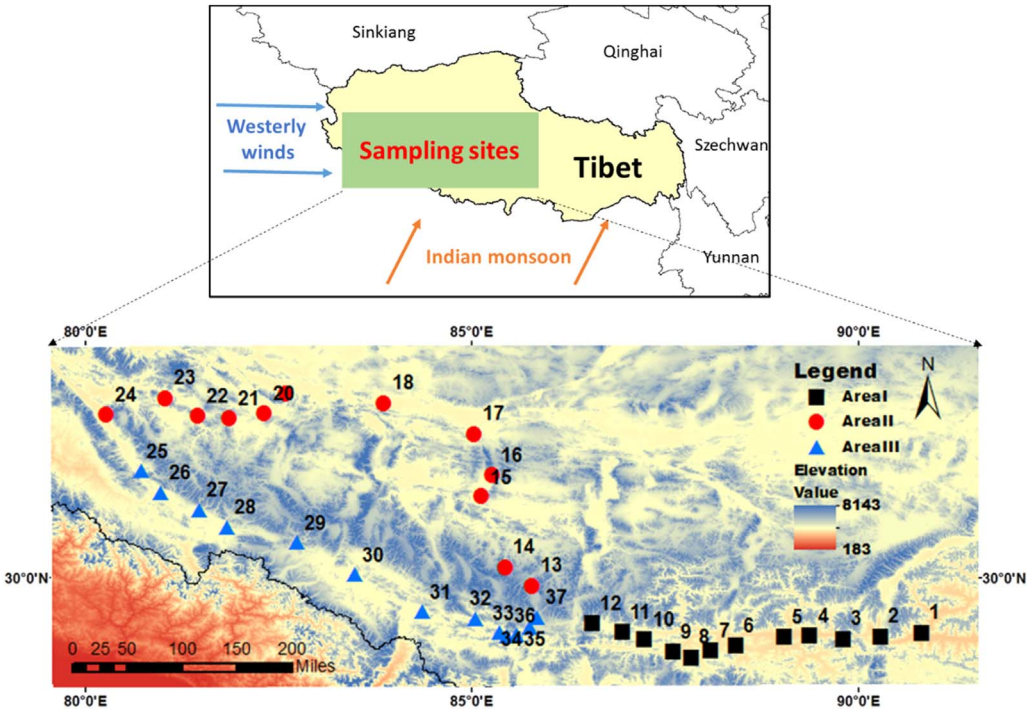

Fig. 1. Map showing the sample locations of this study.

3. Results and discussion

3.1. Sample area categories

Principal component analysis (PCA) is a method which can be used to investigate relationships of PAH constitution between different samples (Tao et al., 2011). In this study, PCA was performed to categorize the sampling sites. Due to a lack of lichen samples in some sites, only soil samples were used for statistical analysis. The concentration of 24 types of individual PAHs at each site was used as a PCA variable; geographical factors and soil organic carbon (SOC) were also taken into consideration. The results of the analysis are shown in Table S3. Fig. 2 displays the correlation between the principal component 1 (PC1) and principal component 2 (PC2) for each site. The sampling sites are classified into three groups corresponding to the three sub-areas; the PAHs of each area have similar compositions or characteristics. The results of the PCA further support the division of the sampling sites into three sub-areas.

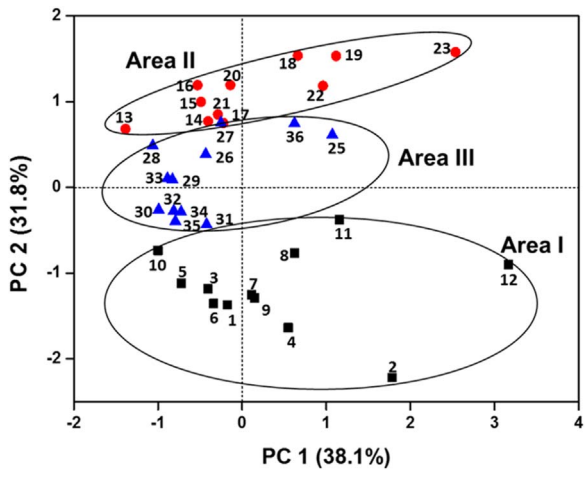

Fig. 2. Principal factor 1 (PC1) plotted against principal factor 2 (PC2) using the PCA of 37 soil samples.

3.2. PAH concentrations and composition

3.2.1. Soil concentration

The statistical PAH concentrations in soil and lichen are summarized in Table S4. The concentrations of the 37 soil samples in this study were in the range of 14.6–142 ng/g for the sum of all 24 PAHs (Σ_{24}PAHs) and 14.4–119 ng/g for the sum of 16 US EPA's priority PAHs (Σ_{16}PAHs); the average concentrations were 40.3 ng/g and 35.1 ng/g, respectively (Table S4). The compound of the highest concentration was NAP, with a mean concentration of 10.1 ng/g. In each area, soil PAH concentrations in the western TP (including Area II and III) in Σ_{24}PAHs and Σ_{16}PAHs were in the range of 14.6–66.9 and 14.4–59.5 ng/g, and the average concentrations were 33.6 ng/g and 30.8 ng/g, respectively (Table S4). The site with the highest PAH concentration in western TP was site 23, which is the westernmost site (near the Shiquanhe town), with Σ_{24}PAHs of 66.9 ng/g. Area I (located in central TP) has a higher PAH concentration than Areas II and III and the mean Σ_{24}PAHs was 53.1 ng/g. The highest concentration of all 37 soil samples was site 12, which is located nearby Shigatse with a Σ_{24}PAHs of 142 ng/g (Fig. 3A).

The soil PAH concentrations in this study were compared with that of other remote areas (Table S5). The PAH concentrations in the western TP were 5–6 times lower than that in southeastern TP where the climate is dominated by the summer Indian monsoon with humid airstream transported from the Indian Subcontinent (Yang et al., 2013). The western TP has a considerable lower precipitation than the southeastern TP, which is an important factor for SVOC transport and deposition (Chen et al., 2017). In this study, the concentration of Σ_{16}PAHs in soils in the western TP is similar with that of the northern TP (Tao et al., 2011) and slightly lower than the average concentration of the whole TP (Wang et al., 2014). This indicates that the PAH concentrations in the western TP were comparatively lower than other parts of the TP; While in the southern Himalayan region (Devi et al., 2016) and Nepal (Bi et al., 2016), the PAH concentration was ten times higher than that in western TP, suggesting a potential source of PAHs for TP. The PAH concentration in soils in the Italy Alps was at the same level as in the western TP (Tremolada et al., 2009). While Quiroz et al. (2011) found a much higher PAH concentrations in European high

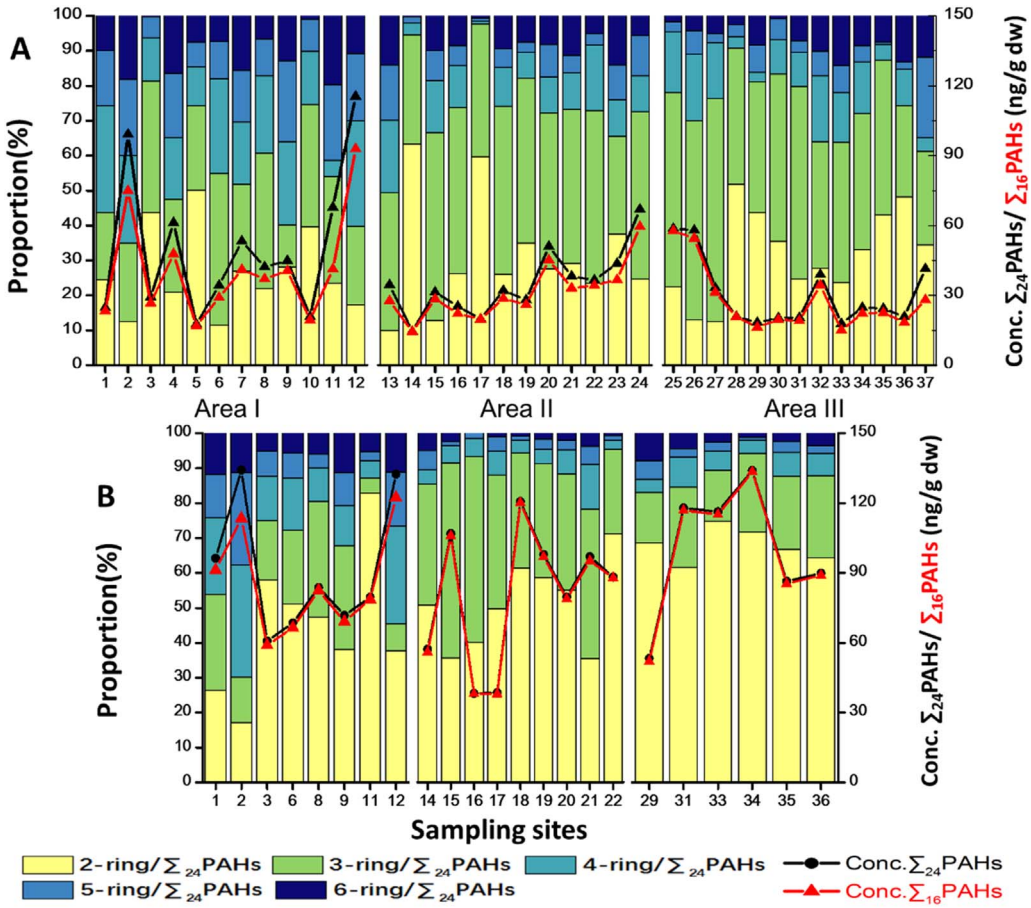

Fig. 3. Proportion of grouped compounds and the total PAH concentrations in soil (A) and lichen (B). All 24 PAH types are grouped based on the compound ring number: 2-ring (NAP), 3-ring (ACY, ACP, FLR, PHE, and ANT), 4-ring (FLA, PYR, BcP, BaA, and CHR), 5-ring (BbF, 7,12-D[*a*]A, BkF, BeP, BaP, PER, DahA and 3-MCA), and 6-ring (IcdP, BghiP, DalP, DaiP, and DahP).

mountains areas. Therefore, the PAHs concentration in the western TP was lower or similar to other background regions in the world.

3.2.2. Lichen concentration

The concentration of Σ_{24}PAHs and Σ_{16}PAHs in 23 lichen samples were in the range of 38.3–134 ng/g and 38.0–133 ng/g, with an average of 88.0 and 84.6 ng/g, respectively (Table S4). NAP was the highest concentration compound with an average of 45.9 ng/g, which accounted for 52.2% of Σ_{24}PAHs. In the western TP (Area II and III), Σ_{24}PAHs in lichen were in the range of 38.3–134 ng/g with an average of 85.2 ng/g. In Area I of the central TP, the mean Σ_{24}PAHs in lichen was 90.9 ng/g which was slightly higher than in the western TP (Fig. 3B). The mean Σ_{16}PAHs (85.2 ng/g) in the lichen samples from the western TP of this study is approximately one third of the PAH concentration in the southeast TP (Yang et al., 2013). PAH concentrations in lichen in this study is significantly lower than those reported in the Pyrenees Mountains (Blasco et al., 2011) (Table S5).

3.2.3. Composition

The PAH composition profile is often used to infer PAH sources (Tobiszewski and Namieśnik, 2012; Yang et al., 2017). In general, the light congeners are more prone to exist in gaseous phase in the atmosphere and be transported to farther places by airstream, the heavy congeners mainly attached to particulate matter are readily deposited near the source area (Daly and Wania, 2005). The combustion of biomass and coal will also contribute to the low (2- and 3-ring PAHs) and intermediate (4-ring PAHs) molecular weight PAHs (Liu et al., 2012), while high molecular weight compounds (5- and 6-ring PAHs) are always associated with high temperature combustion process such as traffic emission (Liu et al., 2013). The proportion of grouped compounds and the total concentrations of all 24 PAHs in soil and lichen samples is presented in Fig. 3.

In the soil samples, the proportion of 2- and 3-ring PAHs in western TP (both Areas II and III) ranges from 63.9% to 97.7%, with an average of 77.4% (Fig. 3A). The dominance of the low molecular weight PAHs indicates LRAT input and possible biomass combustion in the western TP (Wang et al., 2014; He et al., 2015). However, the population density in the western TP is very low (Gao et al., 2013) and vehicles are rare. Thus, the local emission should be limited. While the situation is different in Area I where the proportion of 4–6 rings PAHs ranges from 18.7% to 64.9% with an average of 44.3% in soil samples which is significantly higher than that in western TP ($p < 0.001$; Fig. 3A), suggesting more contribution from local sources. Area I is located in the central TP where both the first and the second largest cities, Lhasa and Shigatse, are located. Thus, a higher population density and more fuel consumption in Area I was expected.

For the lichen samples, the proportion of 2- and 3-ring PAHs were even higher (average of 88.8% in western TP, Fig. 3B). Due to the role of lichen in assessment of the atmospheric pollution, the higher proportion of 2- and 3-ring PAHs in the western TP indicates that PAHs in the western TP are mainly originated from LRAT. The proportion of 4-, 5-, and 6-ring PAHs in Area I (average of 43.4%) was similar with those in soil. The PAH composition in lichen samples was generally consistent with that in soils, which suggests important contribution through LRAT to the current pollution by PAH in western TP.

The statistical evaluation for grouped PAH concentrations in soil and lichen is presented in Fig. 4. It is obviously shown that PAH concentrations in both matrices in the western TP are significantly lower than the central TP. In addition, PAH concentrations in lichen is higher than in soil, especially for low molecular weight PAHs (2–3 ring PAHs) (Fig. 4A). When the concentration is normalized by soil organic carbon (SOC)/lipid content in lichen, this difference becomes even clearer

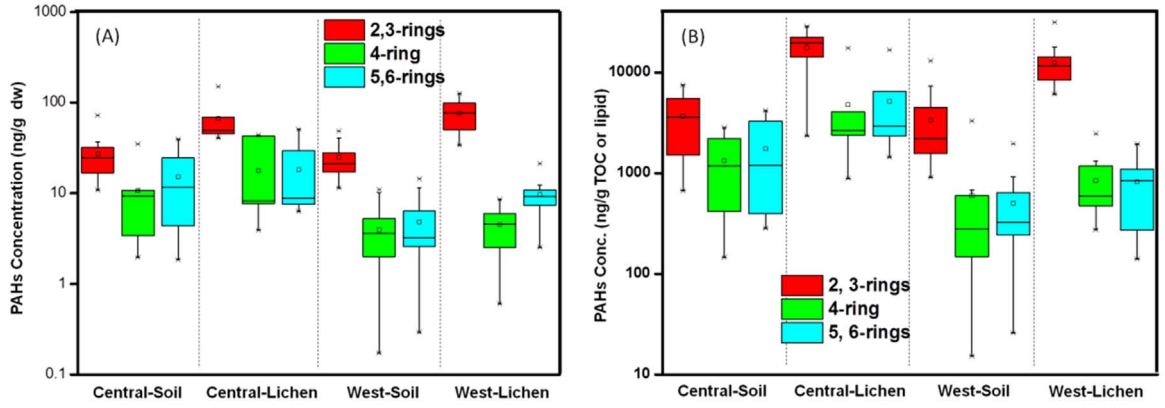

Fig. 4. Comparison of PAH concentrations in soil and lichen on dry weight (A) and TOC/lipid normalized basis (B). The box shows the data between the 25th and 75th percentiles. The inner small box and horizontal line represent the mean value and median value, respectively. The whiskers below the bottom and above the top indicate the 5th and 95th percentiles, and the symbol "×" beyond box represent the outliers.

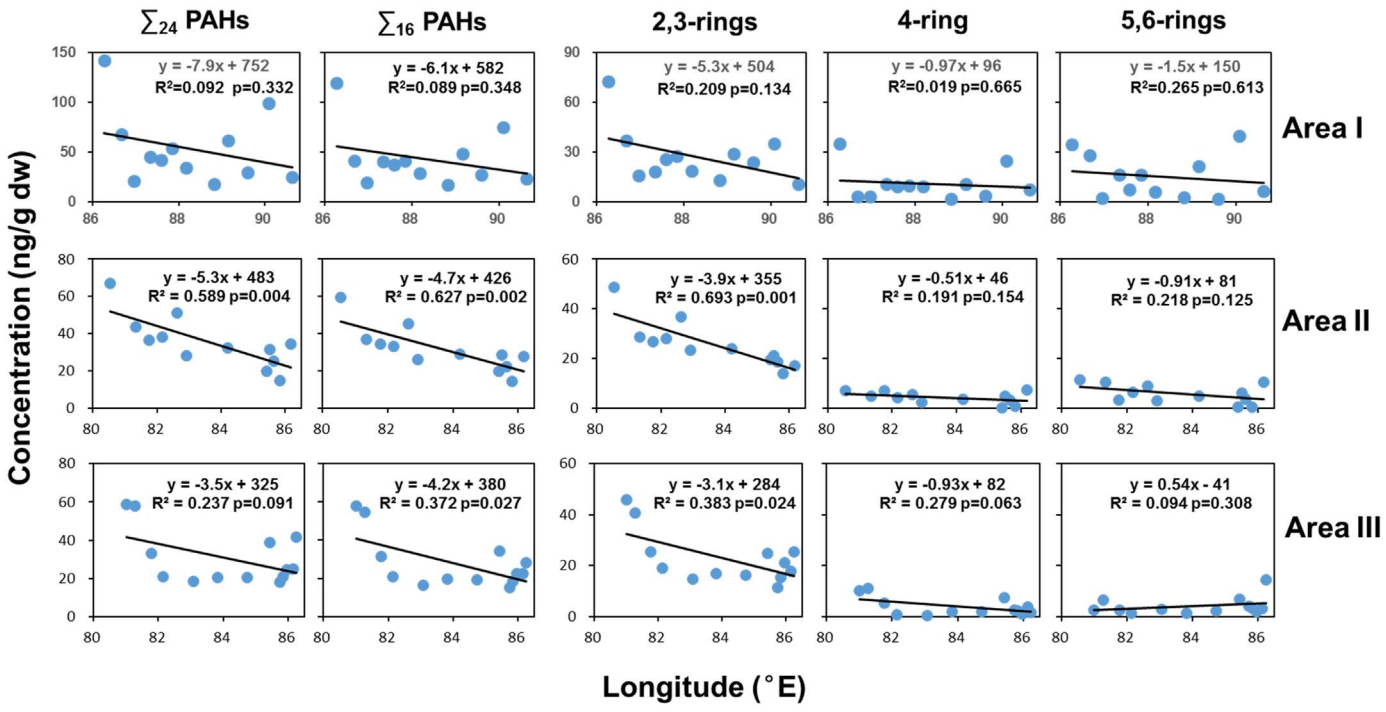

Fig. 5. Longitudinal trend of the PAH concentrations in soils. The concentrations are categorized into the total of 24 PAHs (Σ_{24}PAHs); 16 EPA priority control PAHs (Σ_{16}PAHs); 2- and 3-ring PAHs; 4-ring PAHs; and 5- and 6-ring PAHs.

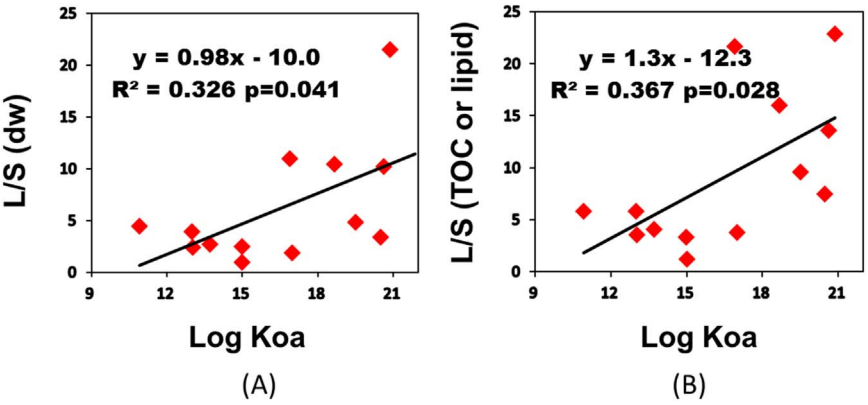

Fig. 6. The ratio of L/S in the western TP as a function of log K_{OA} for dry weight (A) and TOC/lipid weight basis (B) of PAHs at 0.5 °C (average annual temperature of the western TP (Chen et al., 2017)). The log K_{OA} is provide in Table S2.

(Fig. 4B).

3.3. Geographical distribution and influencing factors

3.3.1. SOC/Lipid

The soil organic carbon (SOC) and lipid content were measured for all soil and lichen samples respectively (Table S1). The SOC content in 37 soil samples ranged from 0.21% to 4.7% with an average of 1.2%, which were comparably lower than most other research (Yang et al., 2010b, 2013), because most part of western TP are barren or sandy soil. The SOC did not appear to correlate with altitude, longitude or latitude ($p > 0.05$). The lipid content of all lichens were ranged from 0.21% to 1.73% with a mean of 0.63%. For both SOC and lipid content, there are no significant difference between each sub-area.

SOC was often taken into consideration in studies on the SVOC distribution (Tao et al., 2011). Some studies showed that the concentration of PAHs in soil was strongly correlated with SOC, suggesting SOC plays an important role in the PAH distribution (Nam et al., 2008; Yang et al., 2010b). However, no significant correlation ($p > 0.05$) was found between total PAH concentration and SOC in this study. However, 4 individual PAH components (NAP, ACY, ACP, and FLR) were significantly correlated with SOC (R^2 = 0.139–0.411, $p < 0.05$, Table S6). These four compounds have the lowest molecular weight of all 24 types of PAHs with the lowest K_{OA}, and are more likely to exist in vapor phase. They could reach to a dynamic equilibrium state by repeatedly exchanged with SOCs in surface soils thus, strongly influenced by SOC content. While the rest of the PAHs didn't significantly correlate with SOC (except for perylene) (Table S6). Because the high molecular weight PAH compounds tend to adsorb on particles and therefore preferentially deposit near the source ground (Lei and Wania, 2004). Noted that the five compounds mentioned above were correlated with the SOC in the western TP (including Areas II and III) but uncorrelated in Area I. The fact suggests that PAH distribution in the Area I was mainly controlled by local emissions.

Correlation between concentrations of Σ_{24}PAHs and lipid contents in all 23 lichen samples was significant (R^2 = 0.402, $p = 0.001$, Table S7). Lichen has a strong ability in absorbing PAHs (Yang et al., 2013) and lipid could play an important role in this process. Even stronger correlation was observed in the western TP (R^2 = 0.561, $p = 0.001$, Table S7). In addition, the lower molecular weight PAHs have stronger correlations with lipid than the higher molecular weight ones (Table S7). As mentioned above, 2- and 3-ring PAHs which dominate in the western TP are more likely to exist in vapor phase, making it easily absorbed and influenced by lipid content in lichen. While the weaker correlation ($p > 0.1$, Table S7) observed in the Area I indicated significant influence by local source on the distribution of PAHs.

3.3.2. Altitude

Altitude is considered to be an important factor on the distribution of SVOCs in remote mountains due to the cold trapping effect (Daly and Wania, 2005). In the present study, the regressions of altitude against PAH concentration in both soil and lichen were presented in Table S8. Almost all regressions (except for 5, 6 ring PAHs in lichen) in the western TP were negative, indicating an overall decreasing trend in PAH concentration with the increasing altitude. For the total PAH concentration and 3-ring PAHs in soil, a significant negative regression was observed in Area II (R^2 = 0.529–0.549, $p < 0.05$, Table S8). Similar negative correlations were also found in southeast TP (Yang et al., 2013) and the Taurus Mountains in soil (Turgut et al., 2017). However, positive correlations between PAH concentration and altitude can also be found in the Himalayas (Luo et al., 2016) and European high mountains area (Quiroz et al., 2011). Furthermore, generally negative but insignificant correlation was also observed in lichen except for 4, 5 ring PAHs across the whole area (Table S8). PAHs could be released from various sources; and possible photolysis during the atmospheric transportation could complicate the cold-trapping-related altitudinal trend.

3.3.3. Longitude

Six-day air mass backward trajectories were calculated using the HYSPLIT model for one year before the sampling time in Area II and Area III (Fig. S1). The trajectories show that in most months of the year (from Nov. to May), the western TP was controlled by the westerly winds. The direction of the westerly wind is from west to east which is the same orientation of the increasing longitude.

In soil samples, a significant longitudinal distribution pattern was observed (Fig. 5). In all three sub-areas, the regressions were negative which suggest that the soil concentrations decreased with the increasing longitude. Moreover, the correlations were statistically significant in western TP (Area II and Area III), suggesting the westerly wind has a great influence on the PAH distribution in western TP.

The strongest correlation between PAH concentration and longitude was found in Area II, with a R^2 value of 0.589 and 0.627 for Σ_{24}PAHs and Σ_{16}PAHs, respectively ($p < 0.01$, Fig. 5). The strongly negative correlation suggests that PAHs in Area II is particularly affected by the westerly wind. Area II is located in the northwestern part of the TP and belongs to the depopulated land with very limited human activities (Gao et al., 2013). Thus local PAH emissions in Area II is very limited. For different components, concentration of 2- and 3-ring PAHs decreases significantly with the longitude, whereas the 4- and 5, 6-rings PAHs were insignificantly correlated with longitude. This comparison confirmed that PAH distribution was significantly influenced by the westerly wind in this area.

Area III shares some similarities with Areas II. The negative regression was also obtained in this area except for 5-, and 6-ring PAHs, indicating possible influence by the westerly wind. It is noted that there is a better fit between PAH concentration and longitude in a second order polynomial regression (Fig. S2). This regression indicates the PAH concentration in soil decreasing first and ascending next from west to east in Area III. In the eastern part of Area III, sites 35, 36 and 37 are near the Shigatse city and Saga County. These towns have relatively higher population density which enhance the local emissions and elevate the PAH concentration. Compared with Area I, a decreasing trend but insignificant correlation between the concentration and longitude was observed (Fig. 5). Due to more human activities and local PAH emissions, the influence of the westerly wind on PAH distribution was weakened in Area I.

Comparatively, the correlations between longitude and PAH concentration in lichen were insignificant in the three sub-areas (Fig. S3). A decreasing PAH concentrations with an increase in longitude was observed in Area II (Fig. S3), which was similar with that in soil, indicating possible influence by the westerly wind. There are not any distinct trend being observed in Area I (Fig. S3), possibly due to more local emissions and the influence by the Indian monsoon with different airflow. In addition, the age of the lichen cannot be easily identified; thus, PAH accumulation in lichen may be different due to inconsistent exposure time for atmospheric PAHs, which could account for the different spatial distribution pattern in lichen.

3.4. Lichen enrichment

The lichen/soil (L/S) ratio can be used to evaluate the ability of SVOCs enrichment from the atmosphere by lichen. In this study, lichen concentrations were significantly higher than soil at the same site (Fig. 4). The L/S ratio was calculated by dividing the PAH concentrations in lichen by concentration in soil at each site. In this study, the L/S ratio of Σ_{16}PAHs ranged from 1.31 to 7.23 with an average of 3.15, suggesting lichen has a higher ability of enrichment in PAHs than soil. For individual compounds, a significant positive correlation ($p < 0.05$) between L/S ratio and log K_{OA} was obtained (Fig. 6), suggesting that the ability of SVOCs enrichment in lichen was stronger for more lipophilic PAHs when compared with soil. The result underscores the importance

of lichen in transferring SVOCs that from atmosphere to ground in barren western TP.

4. Conclusions

Soil and lichen samples were collected from the TP and they were analyzed for 24 types of PAHs. In western TP, the Σ_{24}PAHs of soil and lichen are in the range of 14.6–66.9 and 38.3–134 ng/g with mean concentrations of 33.6 ng/g and 85.2 ng/g, respectively. The high proportion of 2- and 3-ring PAHs in the western TP indicates that LRAT has great contribution in this region. In PAH distribution, cold-trapping-related altitudinal trend was not significant in western TP. The westerly wind have a great impact on PAH distribution in soil in western TP; while PAH distribution pattern in lichen was complicated by more factors such as lipid content, exposure time and the westerly wind. Nevertheless, lichen has a strong ability in enriching PAHs, serving as a passive air-sampler for SVOCs in such remote region.

Acknowledgements

This work was funded by the National Natural Science Foundation of China (21577164 and 21777184).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2018.01.009.

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