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

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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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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.