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Comparison of moss and pine needles as bioindicators of transboundary polycyclic aromatic hydrocarbon pollution in central Japan☆

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Atmospheric pollution by polycyclic aromatic hydrocarbons (PAHs) has become a serious problem, especially in Asia, as PAHs can severely affect ecologically important mountainous areas. Using pine needles and mosses as bio-indicators, this study examined PAH pollution in a mountainous study area and evaluated the influence of transboundary PAHs. PAHs in urban areas were also evaluated for comparison. The study sites were alpine areas and urban areas (inland or coastal cities) across central Japan, in the easternmost part of Asia where atmospheric pollutants are transported from mainland Asia. The mean PAH concentrations of pine needles and mosses were 198.9 ± 184.2 ng g^{-1} dry weight (dw) and 131.8 ± 60.7 ng g^{-1} dw (mean ± SD), respectively. Pine needles preferentially accumulated PAHs with low molecular weights (LMW PAHs) and exhibited large differences in both PAH concentration and isomer ratios between alpine and urban sites. These differences can be explained by the strong influence of LMW PAHs emitted from domestic sources, which decreased and changed during transport from urban to alpine sites due to dry/wet deposition and photodegradation. In contrast, mosses accumulated a higher ratio of PAHs with high molecular weight (HMW PAHs). A comparison of isomer ratios showed that the PAH source for alpine moss was similar to that for northern coastal cities, which are typically influenced by long-transported PAHs from East Asia. Thus, these results indicate that alpine moss can also be strongly affected by the transboundary PAHs. It is likely that the uptake characteristics of moss, alpine climate, and alpine locations far from urban areas can strengthen the influence of transboundary pollution. Based on these results, the limitations and most effective use of bioindicators of PAH pollution for preserving alpine ecosystems are discussed.

1. Introduction

Atmospheric pollution is of serious concern globally because of the substantial increase in atmospheric pollutants after the industrial revolution (Thevenon et al., 2011). Among them, polycyclic aromatic hydrocarbons (PAHs) have received particular attention owing to their hazardous properties and wide distribution in the atmosphere (Masiol et al., 2012; Yang et al., 2007). PAHs are defined as an organic compound group with two or more fused aromatic rings, and are emitted by incomplete combustion processes during energy generation (Maliszewska-Kordybach, 1999). In general, lower molecular weight PAHs with 2–3-aromatic rings (LMW PAHs) occur primarily in the gaseous phase; while those of higher molecular weight, with 5–6 rings (HMW PAHs), exist in the particle-bound phase (Bidleman, 1988; Maliszewska-Kordybach, 1999). PAHs with intermediate molecular weight (4 rings) have a temperature-dependent gas/particle phase partitioning (Bidleman, 1988; Liu et al., 2005; Wang et al., 2009). Once PAHs are emitted into the environment, they accumulate in soils, plants, and animals and are condensed through the food chain. Some PAHs are not easily decomposed, remaining in the environment for several years (Howsam et al., 2001). These PAHs can have negative impacts on both ecosystem functions and human health because of their mutagenic and carcinogenic properties (Maliszewska-Kordybach, 1999; Masiol et al., 2012).

Since PAHs have become ubiquitous environmental contaminants, they are widespread even in alpine areas located far from large cities (Carrera et al., 2001). In the European Alps, PAHs

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showed the highest bulk emissions and loads among several types of persistent organic pollutants (Belis et al., 2009). In China, even areas with altitudes between 4700 m and 5600 m on Mt. Qomolangma have been polluted by PAHs (Wang et al., 2007). PAH pollution in high-altitude mountainous areas should be studied because these areas contain food and water sources and are important for the conservation of the ecosystem (Daly and Wania, 2005).

Most PAHs are emitted from Asia due to the rapid increase in population and industries (Zhang and Tao, 2009); hence, research into the impact of PAHs on mountainous areas in this region is important. Japan is located in the easternmost part of Asia, where pollutants are transported by the winter monsoon (Yang et al., 2007). Therefore, understanding the behavior of transboundary PAHs in this area can reveal their transport mechanisms and influence in East Asia.

To monitor PAH pollution in remote areas such as mountains, plants are often used as bioindicators because they effectively accumulate PAHs. PAH measurements using physical equipment are more accurate than those by bioindicators; however, they are expensive and time-consuming, and often difficult to install in these areas due to poor access and harsh environments. Furthermore, bioindicators reflect the cumulative effects of pollutants in the ecosystem. Plant types used for PAH assessment include trees (Howsam et al., 2000; Navarro-Ortega et al., 2012; Tremolada et al., 1996; Wang et al., 2009), grasses (Gworek et al., 2016; Wang et al., 2007), mosses (Gałuszka, 2007; Godzik et al., 2014; Krommer et al., 2007; Liu et al., 2005; Oishi, 2013; Ötvös et al., 2004), and lichens (e.g., Augusto et al., 2010; Blasco et al., 2008; Schrlau et al., 2011). Among them, pine needles and mosses are often used because of their wide distribution and the strong correlation between PAH deposition and accumulated PAH measurements. Some studies used the combination of plant groups for the evaluation of PAHs and showed different PAH uptake properties between them (De Nicola et al., 2013; Oishi, 2012, 2013). These studies were conducted in the same areas (Oishi, 2012, 2013) or in areas within the same climatic zone (De Nicola et al., 2013); therefore, it still remains to be examined how differently these bioindicators accumulate PAHs if they are applied in PAH assessments in areas with diversified environments (e.g., climate, elevation, and land-use characteristics). Furthermore, how these differences in PAH uptake by bioindicators contribute to the evaluation of PAH pollution should also be discussed. This information is essential for the proper understanding of PAH pollution in mountains because climates in mountains differ by elevation, and the land-use types are also completely different from those in lowland urban areas.

In this study, PAH pollution and the effect of transboundary PAHs on mountainous areas across Japan were determined using pine needles and moss as bioindicators. For a better understanding of PAH pollution in mountains and the influence of mountainous environments on bioindicators, urban areas were also examined for comparison. Based on these results, the effective uses and limitations of bioindicators for future application are discussed.

2. Materials and methods

2.1. Study sites and sampling design

Study sites were selected across central Japan (Fig. 1 and Supplementary material 1), within the high mountainous area extending from north to south called the Chubusangaku Mountains. These mountains mainly consist of the Northern, Central, and Southern Japanese Alps, the Yatsugatake mountains, and several unimodal mountains (e.g., Mt. Norikuradake). According to meteorological measurements from Mt. Shogigashira (Central Alps; 2672 alt.), the mean annual temperature in 2014 was 0.1 °C, and the maximum and minimum temperatures were 23.9 °C and −23.5 °C, respectively (Kobayashi et al., 2016). Within the alpine areas of these mountains, six study sites were established (Mt. Shiroumadake, Mt. Karamatsudake, Mt. Nishikomagatake, Mt. Yokodake, Mt. Ainodake, and Mt. Okuhijiridake). Details of the study site locations are listed in Supplementary material 1. All alpine sites are located above the tree line.

To examine the characteristics of PAH pollution in alpine sites, PAH pollution was also evaluated in urban areas for comparison. Eight urban sites were selected from cities around the Chubusagak Mountains with a population of more than 0.1 million (Kanazawa, Toyama, Nagano, Matsumoto, Saku, Iida, Kofu, and Hamamatsu). Two cities (Kanazawa and Toyama) are on the northern coast (northern coastal cities). Five cities (Nagano, Saku, Matsumoto, Iida, and Kofu) are surrounded by mountains (inland cities). Nagano is located in the north (northern inland city), Saku and Matsumoto are situated in central areas (central inland cities), and Iida and Kofu are in the south (southern inland cities). Hamamatsu is located in the southernmost part of the region and faces the Pacific Ocean (southern coastal city). The average temperature and precipitation values for urban cities between 1981 and 2010 were 13.4 °C and 1522.4 mm/year, respectively (Japan Meteorological Agency, 2017).

2.2. Plant sampling and pre-treatment

To analyze PAH pollution in the study sites, both pine needle and moss samples were collected from each site. In the alpine sites, the leaves of *Pinus pumila* (Pall.) Regel. and the shoots of *Racomitrium lanuginosum* (Hedw.) Brid. were sampled as pine needle and moss samples, respectively. *P. pumila* and *R. lanuginosum* are widely distributed and are often dominant species in alpine regions of Japan. However, another *Racomitrium* species (*R. fasciculare* (Hedw.) Brid.) was sampled in one alpine site (Mt. Karamatsudake) because *R. lanuginosum* was not found. In urban sites, these alpine species could not be found owing to the higher temperature; therefore, *P. densiflora* Siebold & Zucc. and *R. japonicum* (Dozy & Molk.) Dozy & Molk. were sampled instead. These species are major lowland species throughout the urban study sites.

The environment and conditions of each sample were kept as uniform as possible. All samples were collected outside of the crown projection area of any trees. Two-year-old leaves of pine needles and green/brown-green tips of mosses, representing two-year old shoots, were used for analysis. The age of moss shoots was determined by the difference in their width caused by annual growth. To obtain homogeneous samples, both pine needles and moss samples were collected from several points in each site and then grouped together for analysis. The collected samples were briefly washed in distilled water, and residual soil and other litter were carefully removed. Plant samples were wrapped in aluminum foil, air-dried at the ambient temperature, and stored in paper and sealed polyethylene bags in the dark at room temperature until PAH determinations.

2.3. PAH determinations

First, homogenized samples were Soxhlet-extracted in acetone for more than two hours and then further extracted in toluene for sixteen hours. The extracts were then analyzed using gas chromatography with high-resolution mass spectrometric detection (GC/HRMS). The GC/HRMS analyses were performed by a HP 6890 N Agilent Technologies GC coupled with a high-resolution mass spectrometer (AutoSpec Ultima). The GC was equipped with a J&W DB5-MS capillary column (60 m × 0.32 mm × 0.25 μm film thickness; Agilent Technologies), and helium was used as the