Mechanisms of Plant Pollutant Uptake as Related to Effective Biomonitoring

4

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Abstract

Biomonitoring is a method that uses the responses of plants or animals to their surroundings to evaluate the status of an environment. Among taxonomic groups, pine needles and mosses are widely used for biomonitoring, especially for atmospheric environments. However, several studies have indicated that each of these plants reacts differently to changes in their habitat. Here, we characterized these contrasting responses and investigated the causes of these differences by comparing atmospheric pollutants (polycyclic hydrocarbons: PAHs) that accumulated in pine needles and mosses. Our results revealed that pine needles absorbed lower molecular weight PAHs, whereas mosses preferentially accumulated higher molecular weight PAHs. Furthermore, the comparison of their PAH isomer ratios showed that the pollution sources were not identical, even though the plant samples were collected from nearly the same sites. These differences can be explained by their distinct leaf structures and uptake mechanisms, as well as the influence of soil particles. Our novel results suggest that both pine needles and mosses can be used as bioindicators to assess PAH pollution multi-directionally.

Keywords

Air pollution • Biomonitoring • Plant uptake • Accumulation • Mechanisms

4.1 Introduction

In this chapter, we discuss the mechanisms of plant pollutant uptake and how this process can be applied to environmental evaluation. More specifically, this chapter first introduces an environmental evaluation method that utilizes the responses of living organisms to their surroundings, which is called as “biomonitoring”. We then

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focus on two plant groups widely used for biomonitoring (pine trees and mosses) and explore the differences in how these species accumulate polycyclic aromatic hydrocarbons (PAHs), a hazardous atmospheric pollutant (Sect. 4.2). Furthermore, we evaluate the causes of plant-to-plant differences observed in PAH accumulation (Sect. 4.3). Finally, based on these findings, we demonstrate how to efficiently use biomonitoring to evaluate atmospheric environments (Sect. 4.4). These results highlight the importance of the understanding of plant uptake mechanisms when attempting to establish effective biomonitoring programs.

Air Pollution and Biomonitoring

Environmental problems have intensified because of an increase in human activities, and, among these, air pollution is one of the most concerning threats (Gurjar et al. 2010; Kopáček and Posch 2011; OECD 2012; WMO/IGAC 2012; Shibata et al. 2014). Atmospheric pollutants include a variety of substances (e.g., metals, sulfur oxide, nitrogen, and organic compounds) that can easily move over wide areas, resulting in transboundary pollution. Therefore, monitoring programs for atmospheric environments have been instituted in many parts of the world (e.g., Schröder et al. 2010; Harmens et al. 2015).

Air pollution has both direct and indirect effects on plants and animals, and therefore changes in these organisms can be correlated with the level of air contamination. For example, severe air pollution can cause a disappearance of epiphytes such as bryophytes and lichens, and an index based on the sensitivity of these plants to air pollution can indicate the level of contamination in the atmosphere (LeBlanc and De Sloover 1970). This type of environmental evaluation that uses the responses of living organisms to their surroundings has been termed "biomonitoring," and the subject organisms are known as "bioindicators."

Environmental conditions are generally evaluated with measuring devices (e.g., a stack gas analyzer), which would presumably produce more exact results than those of biomonitoring. Are there any advantages then to using biomonitoring for environmental evaluation? Of course, the answer is YES. One of the most important benefits of biomonitoring is that they can assess environments at a low cost and on a large scale. Imagine that we are measuring the concentration of atmospheric pollutants, which are affected by many factors such as human activities and weather and can even change drastically in a day. In order to obtain reliable data, we must therefore measure the concentration repeatedly with measuring devices. In contrast, if we were to perform this same environmental assessment using bioindicators, we can eliminate the steps of repeated measuring because by their nature, bioindicators have been exposed continuously to atmospheric pollutants, reflecting the time-integral effects of air pollution. These valuable characteristics enable the evaluation of air pollution on a large scale.

Plants as Bioindicators

Vegetation has been utilized as a bioindicator to identify point sources of pollutants and evaluate regional and global contamination patterns (Simonich and Hites 1995), particularly in atmospheric environments. Each plant group has its own morphology and life-strategy, qualities that are directly correlated with their usefulness as bioindicators. Among plant groups, pine trees (specifically their needles) (Tremolada et al. 1996; Piccardo et al. 2005; Klánová et al. 2009; Lehndorff and Schwark 2009; Wang et al. 2009; Ratola et al. 2010, 2011) and mosses (Holoubek et al. 2000; Gerdol et al. 2002; Migaszewski et al. 2002; Ötvös et al. 2004; Liu et al. 2005; Gałuszka 2007; Krommer et al. 2007; Skert et al. 2010; Oishi 2012, 2013) are valuable bioindicators for airborne contaminants because of their unique ecological characteristics (Figs. 4.1 and 4.2). Here, we describe the advantages of these plant groups for the evaluation of air pollution.

Pine needles are one of the most well-known bioindicators for atmospheric environments.

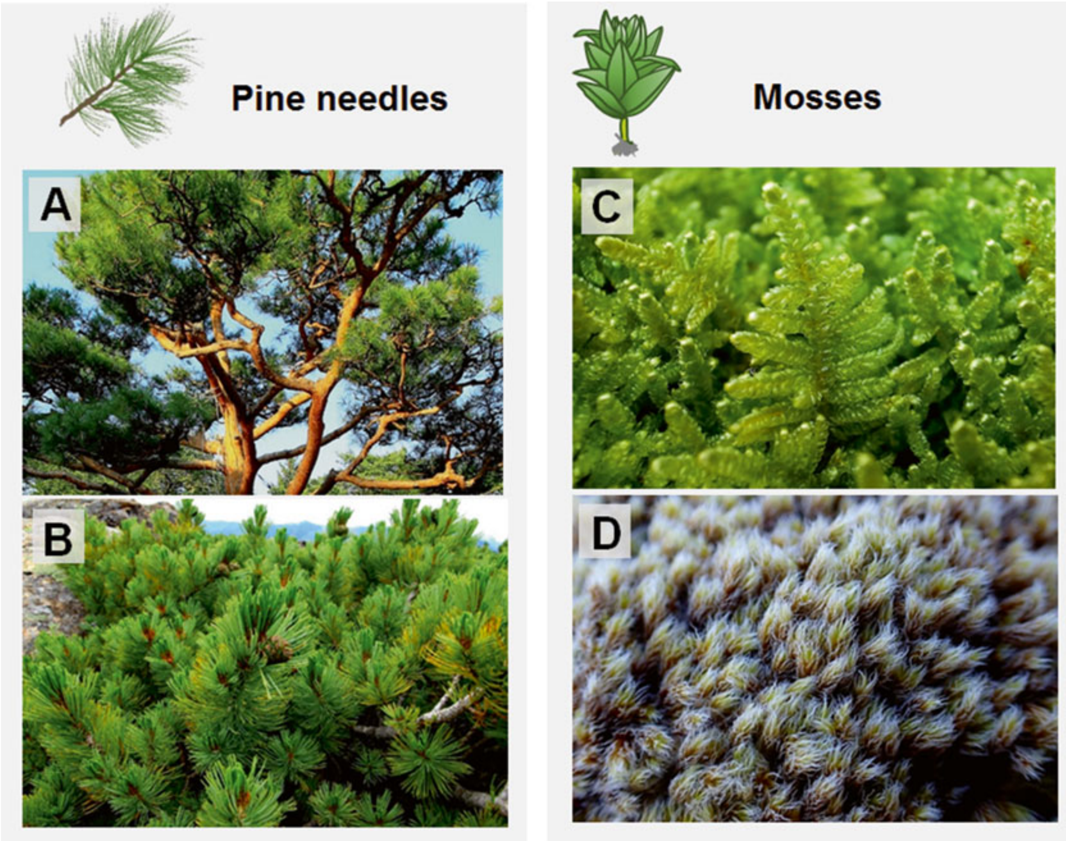

Fig. 4.1 Pine needles and mosses. (**a**) *Pinus densiflora* Sieb. et Zucc., (**b**) *Pinus pumila* (Pall.) Regel, (**c**) *Hypnum plumaeforme* Wilson, (**d**) *Racomitrium lanuginosum* (Hedw.) Brid. *P. densiflora* and *H. plumaeforme* (**a**, **c**) are distributed mainly in lowland areas, whereas *P. pumila* and *R. lanuginosum* (**b**, **d**) are found in mountainous areas. All species are used as bioindicators for air pollutants

Their leaves can persist for several years, and pine trees are widely distributed from urban to rural areas. A notable characteristic of pine needles is that their age can be determined easily, which enables us to calculate how long the leaves have been exposed to air pollution. Therefore, we can evaluate temporal trends of air pollution by analyzing different populations of same-age needles. Furthermore, the surface of the leaf is covered with a waxy cuticle that accumulates lipophilic organic contaminants from the air (Piccardo et al. 2005).

Bryophytes are characterized by a lack of vascular bundles and waxy cuticle layers. They absorb water and nutrients through their leaf cells, which allows them to grow on surfaces without soil, such as rocks and tree trunks (Fig. 4.3). As they take in pollutants efficiently from atmospheric environments, their pollutant contents are indicative of contamination by atmospheric fallout.

4.2 Comparison of PAH Accumulation in Plants

PAH Accumulation in Pine Needles and Mosses

Pine trees and mosses belong to different taxa, and their morphology and ecology is distinct. How then, and to what extent, can these contrasting characteristics affect their use as bioindicators? Here, we refer to the study by Holoubek et al. (2000) that described the accumulation of PAHs in pine needles and mosses in several parts of the Czech Republic. The results indicated that

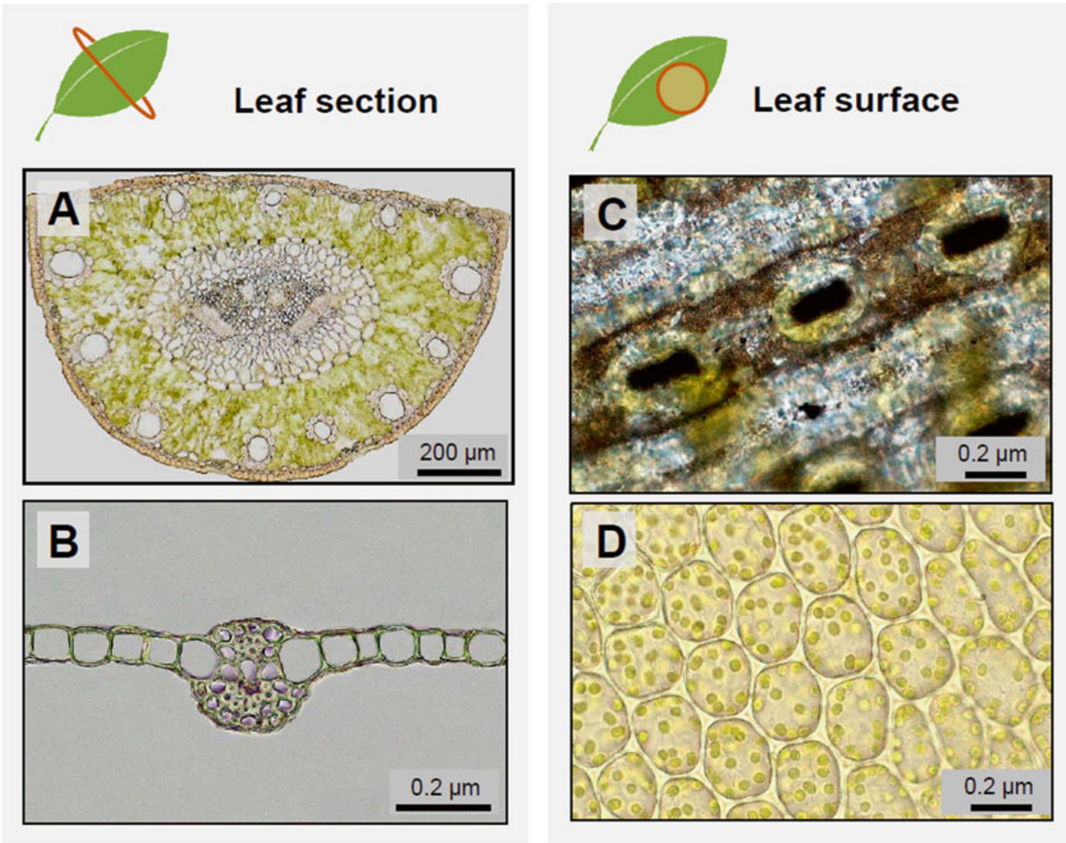

Fig. 4.2 Leaf section and leaf surface of pine needles and mosses. (**a**) Leaf section of pine needle (*Pinus densiflora*: photo by Azuma, W.), (**b**) leaf section of moss [*Plagiomnium acutum* (Lindb.) T.J. Kop.], (**c**) leaf surface of pine needle, (**d**) leaf surface of moss. The leaf section of moss (**b**) shows a simpler structure compared to that of a pine needle (**a**). Stomata are clearly identified in the leaf surface of pine needles (**c**), whereas mosses lack stomata (**d**)

the pattern of PAH accumulation in these plants was different.

Why did this contrast occur, and how did the differences between the structures of these plants affect the results? To answer these questions, one must understand how plants absorb air pollutants. Such knowledge is also essential in order to propose effective plant biomonitoring strategies. For these reasons, we investigated the characteristics and pollution uptake mechanisms of pine needles and mosses so that we could evaluate the most effective means of instituting biomonitoring. The questions we sought to answer were as follows:

1. Are the differences in PAH accumulation in Holoubek et al. (2000) also observed in our study site?
2. If so, why do these differences occur?
3. How can these results be applied to effective biomonitoring?

Characteristics of PAHs

PAHs are organic compounds with two or more fused aromatic rings (Fig. 4.4). They are emitted into the atmosphere through incomplete combustion from both anthropogenic and natural sources and are ubiquitous environmental contaminants (Maliszewska-Kordybach 1999). The predominant human-related sources of PAHs are activities that generate energy, such as vehicular movement, domestic heating, industrial processes, and electric power generation (Mastral and Callén 2000). Among them, motor vehicle exhaust is one of the major sources of PAHs in urban areas

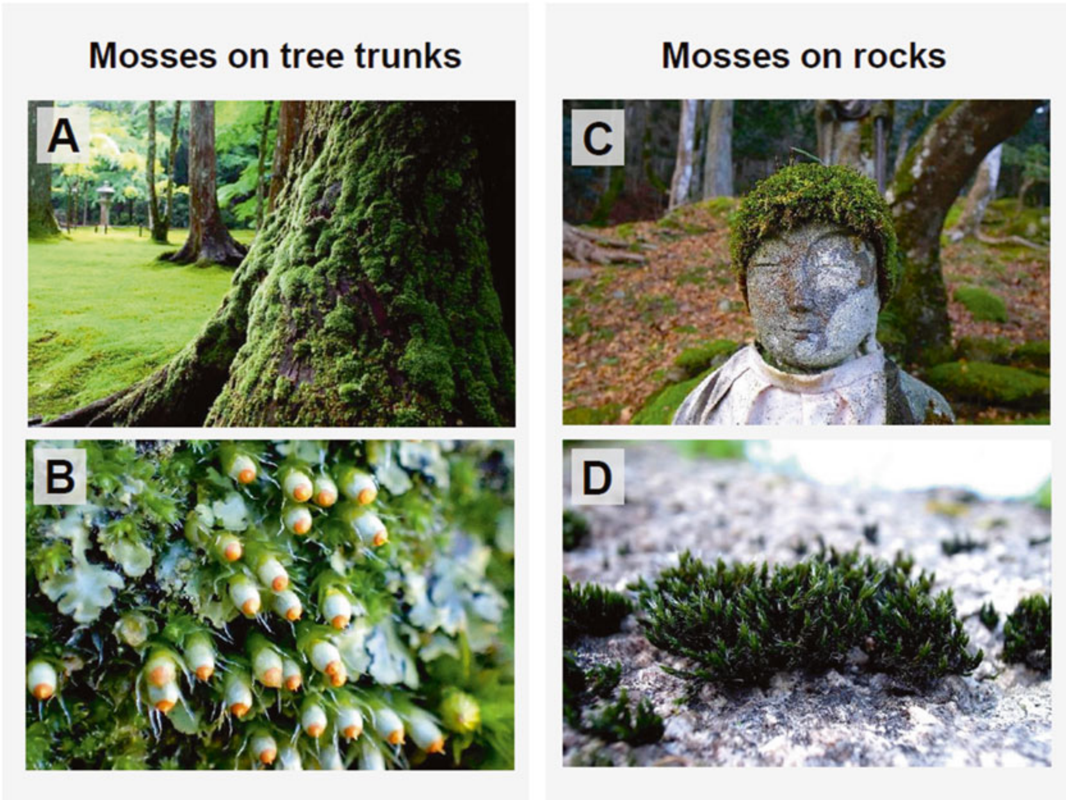

Fig. 4.3 Mosses on substrates without soil layers. (**a**) *Leucobryum juniperoideum* (Brid.) Müll. Hal., (**b**) *Venturiella sinensis* (Vent.) Müll. Hal., (**c**) A stone figure (Ojizo-sama) covered with mosses, (**d**) *Grimmia pilifera* P. Beauv. Mosses absorb water and nutriment from the surrounding environment (e.g., rain, dews, and fogs) through the surface of their leaves. Therefore, they can grow on tree trunks or rocks that have scant soil layers

(Piccardo et al. 2005). PAHs are hazardous to human health and several have mutagenic and carcinogenic properties (Maliszewska-Kordybach 1999; Aas et al. 2001). For these reasons, there is increasing concern regarding the monitoring and regulation of PAHs in ambient air.

Aerosolized PAHs can exist in either a gaseous or a particle-bound phase. These phases are determined by several factors such as air temperature, the physicochemical characteristics of the compound, and the types of the absorbing surface (Pankow 1987). In general, PAHs with two to three aromatic rings exist primarily in the gas phase of the atmosphere because of their relatively low molecular weight (LMW). In contrast, PAHs with five to six rings have a relatively high molecular weight (HMW) and are more likely to be present in the particle-bound phase (Bidleman 1988; Maliszewska-Kordybach 1999). A temperature-dependent gas/particle phase partitioning occurs at intermediate vapor pressures with four-ring PAHs (Bidleman 1988; Liu et al. 2005; Wang et al. 2009).

An interesting property of PAHs is that their isomer ratio differs according to their source and the processes that they experienced. Using these properties, we can determine the source of a PAH based on the concept that isomeric PAHs behave similarly and may also experience comparable environmental transformations during their atmospheric movement (Yunker et al. 2002; Bucheli et al. 2004).

Differences in PAH Accumulation in Pine Needles and Mosses

In order to examine the mechanism of pollution uptake in plants, we compared accumulated

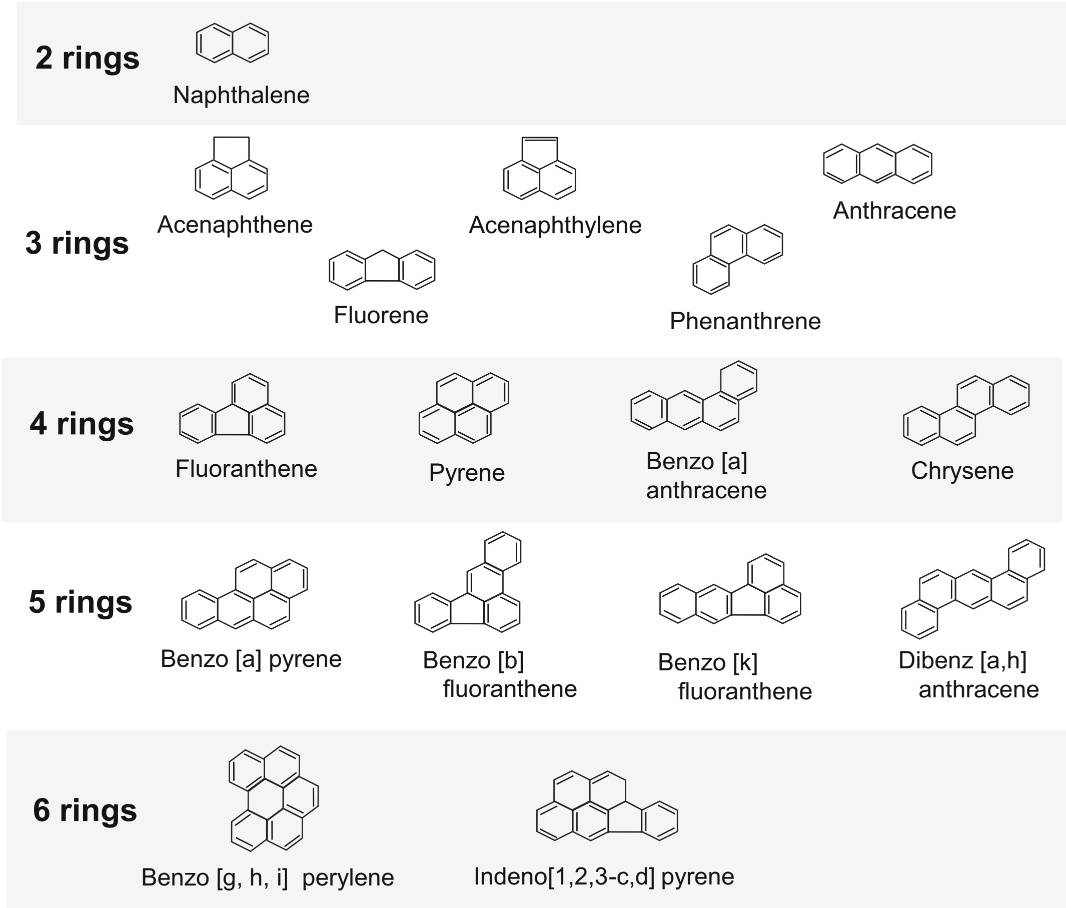

Fig. 4.4 Sixteen polycyclic aromatic hydrocarbons (PAHs) analyzed in this study. PAHs are characterized by the presence of two or more aromatic rings. PAHs with two to three rings exist mainly in the gas phase, whereas PAHs with five to six rings are in the particle-bound phase

PAHs in pine needles and mosses by collecting five sets of both pine needles (*Pinus thunbergii* Parl.) and moss (*Hypnum plumaeforme* Wilson) samples in a green area of Kyoto city. Each set of samples grew within 2 m diameter circular plots. The PAHs analyzed were as the follows: naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACL), anthracene (ANT), fluorene (FLU), phenanthrene (PHE), benz[a]anthracene (BaA), chrysene (CHR), fluoranthene (FLR), pyrene (PYR), benzo[a]pyrene (BaP), benzo[b] fluoranthene (BbF), benzo[k]fluoranthene (BkF), dibenz[a,h]anthracene (DBA), benzo[g,h,i]perylene (BPE), and indeno[1,2,3-cd]pyrene (INP).

In this section, we show two main results of this comparison: "Differences in PAH proportions in pine needles and mosses" and "Differences in PAH isomer ratios." These results are adapted from Oishi (2013).

PAH Proportions

The PAH analysis indicated that the total PAH content was 122.6 ± 50.5 ng g^{-1} dry weight (mean ± SD) in pine needles and 44.5 ± 10.7 ng g^{-1} in the moss samples, respectively. The PAH content was significantly higher in pine needles than in the mosses (d.f. = 8, *t*-value = 3.0, $p = 0.016$).

The percentage contribution to the total PAH content by each individual compound is shown in Fig. 4.5. NAP was the most predominant PAH (29.5 %) in the pine needles, followed by PHE (26.8 %), FLU (16.3 %), and FLR (10.7 %). The

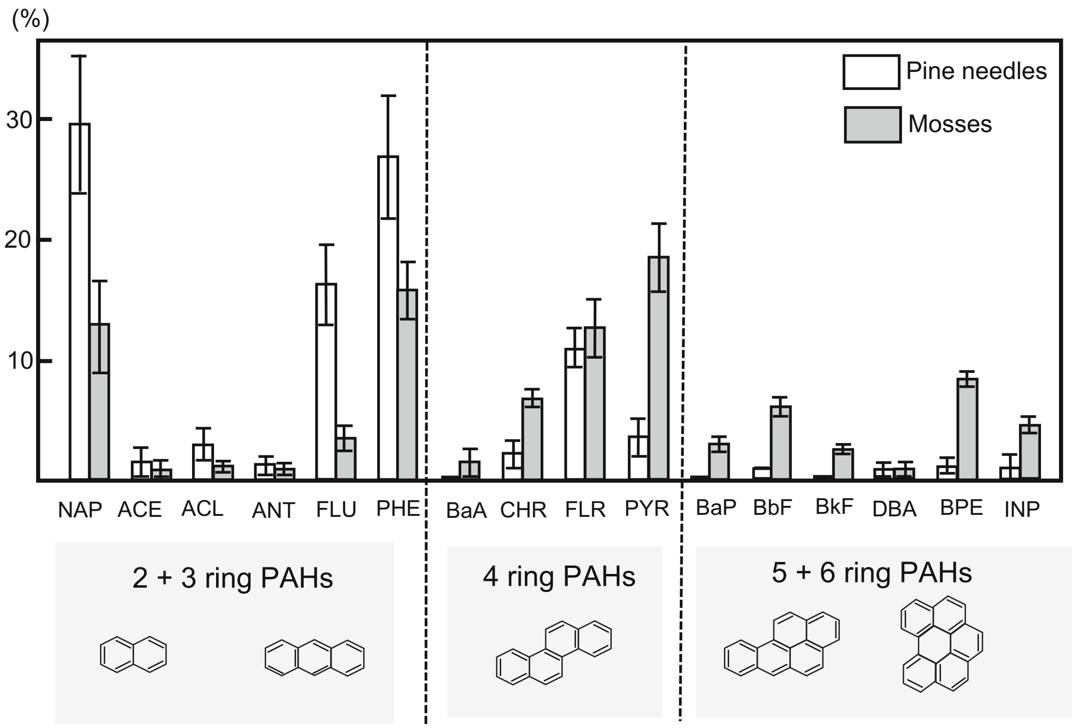

Fig. 4.5 Proportion of total polycyclic aromatic hydrocarbon (PAH) concentration attributable to each of three PAH groups (two to three rings, four rings, and five to six rings) in pine needles and mosses. *Bars* represent standard deviations (this figure was adapted from Fig. 4.2 in Oishi (2013)). Abbreviations of the 16 PAHs are as follows: *NAP* naphthalene, *ACE* acenaphthene, *ACL* acenaphthylene, *ANT* anthracene, *FLU* fluorene, *PHE* phenanthrene, *BaA* benzo[a]anthracene, *CHR* chrysene, *FLR* fluoranthene, *PYR* pyrene, *BaP* benzo[a]pyrene, *BbF* benzo[b]fluoranthene, *BkF* benzo[k]fluoranthene, *DBA* dibenz[a,h]anthracene, *BPE* benzo[g,h,i]perylene, *INP* indeno[1,2,3-cd]pyrene

concentrations of PYR, PHE, FLR, and NAP were relatively higher (18.4 %, 15.7 %, 13.0 %, and 12.6 %, respectively) in the mosses compared to other PAHs. Notably, NAP, ACL, ACE, FLU, and PHE were primarily found in the pine needle samples, whereas BaA, PYR, BaP, BbF, BkF, BPE, and INP were predominantly detected in the moss samples. We also found that in general, pine needles preferentially accumulated LMW PAHs and few HMW PAHs, as compared to mosses. These comparisons indicate that the accumulation patterns of pine needles and mosses are dissimilar.

To distinguish differences in PAH accumulations, we grouped the PAHs into three types (two to three rings, four rings, and five to six rings), according to their phase in the atmosphere (gas, intermediate, and particle bound), and compared the total amounts and proportions of each type (Fig. 4.6). The LMW PAHs were preferentially accumulated in pine needles, whereas the HMW PAHs were more often found in the moss samples (Fig. 4.6). The proportions of two + three rings, four rings, and five + six rings for pine needles were 78.5 ± 4.8 % (mean ± SD), 17.2 ± 2.6 %, and 4.3 ± 2.9 %, respectively (Fig. 4.6a), whereas those for mosses were 35.4 ± 6.8 %, 39.5 ± 4.5 %, and 25.1 ± 3.3 %, respectively (Fig. 4.6b). In this way, the proportion of each PAH group to the total decreased as the number of aromatic rings in the pine needles increased. Mosses showed a similar but less distinct decreasing trend. These differences were statically significant; the proportions of two + three rings in pine needles were significantly higher (d.f. = 8, t-value = 10.4, $p < 0.01$), whereas those of four rings and five + six rings were significantly higher in the moss

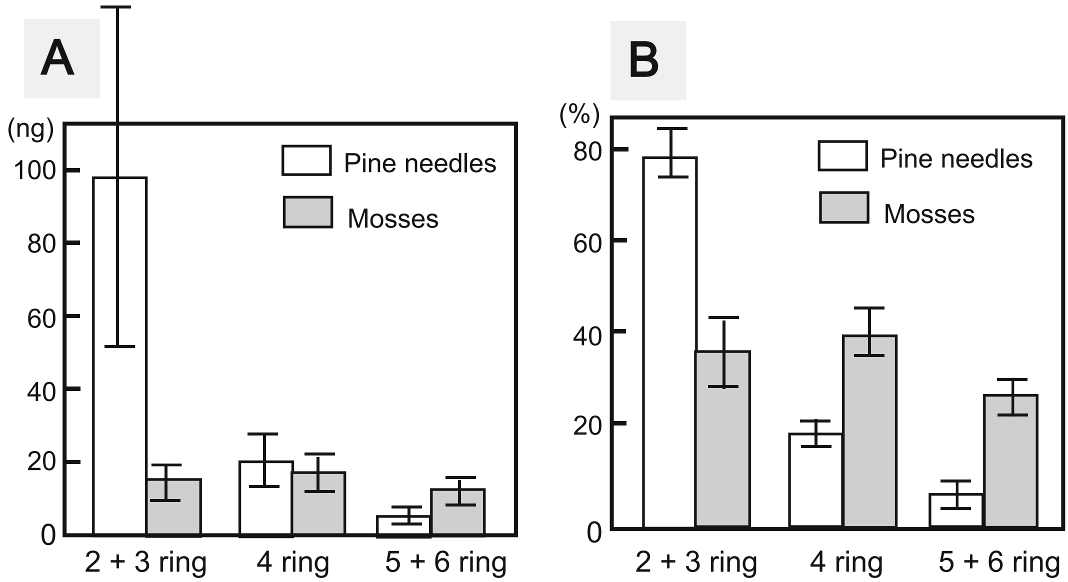

Fig. 4.6 Total amount (**a**) and proportion of total polycyclic aromatic hydrocarbon (PAH) concentration (**b**) attributable to each of three PAH groups (two to three rings, four rings, and five to six rings) in pine needles and mosses. *Bars* represent standard deviations (This figure was adapted from Fig. 4.3 in Oishi (2013))

samples (d.f. = 8, *t*-value = −8.6, $p < 0.01$; d.f. = 8, *t*-value = −9.5, $p < 0.01$).

PAH Isomer Ratios

Next, we used PAH ratios to examine the differences in PAH sources between pine needles and mosses. We compared the ratio of ANT and PHE and the ratio of FLR and PYR. The plots of the ANT/(ANT + PHE) versus the FLR/(FLR + PYR) ratios for pine needle and moss samples are shown in Fig. 4.7. The ANT/(ANT + PHE) ratio for all samples except one was <0.1 [0.05 ± 0.02 (mean ± SD) for pine needles; 0.07 ± 0.02 for mosses]. The FLR/(FLR + PYR) ratio for pine needles was approximately 0.7 [0.74 ± 0.06 (mean ± SD)] and approximately 0.40 [0.40 ± 0.07 (mean ± SD)] in the moss samples.

According to Yunker et al. (2002), the ANT/(ANT + PHE) ratios of most samples fell predominantly in the range of petrogenic area (<0.1), although the values of mosses tended to be higher than those of pine needles. The high FLR/(FLR + PYR) ratios in pine needles (>0.5) indicate that pine needles accumulated PAHs released by the combustion of coal and biomass. In contrast, the FLR/(FLR + PYR) ratios in mosses showed that they accumulated PAHs produced by petroleum or petroleum combustion.

In summary, these results indicate that pine needles and mosses do not accumulate PAHs from the same sources, even though they grow in similar regions.

4.3 Influence of Plant Uptake Mechanisms on Their PAH Accumulation

What Causes the Differences in the Accumulation of PAHs?

Our results are in agreement with previous research that reported high concentrations of LMW PAHs in pine needles (Simonich and Hites 1995; Wang et al. 2009) and high concentrations of HMW PAHs in mosses (Holoubek et al. 2000; Migaszewski et al. 2002; Liu et al. 2005). We will now discuss why these differences were observed from the following three viewpoints: (a) Leaf structure, (b) Uptake mechanism, and (c) Influence of soil particles. A graphic summary of these differences is shown in Fig. 4.8.

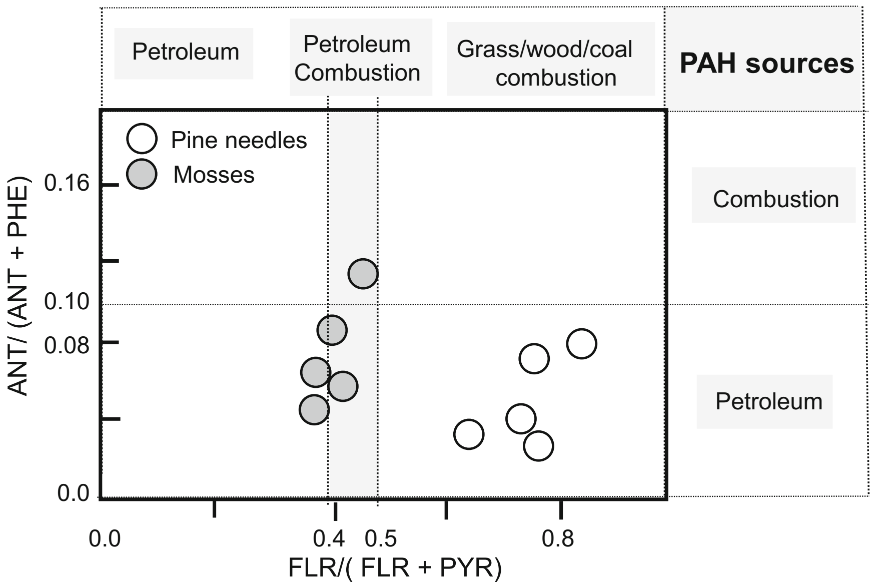

Fig. 4.7 Cross-plot for ANT/(ANT + PHE) and FLR/(FLR + PYR) ratios for pine needle and moss samples (This figure was adapted from Fig. 4.4 in Oishi (2013)). Abbreviations: *ANT* anthracene, *FLR* fluoranthene, *PHE* phenanthrene, *PYR* pyrene

Leaf Structure

External leaf properties of plant bioindicators greatly influence the characteristics of their PAH profiles (Howsam et al. 2000; Jouraeva et al. 2002; Niu et al. 2003; Piccardo et al. 2005; Wang et al. 2005). For example, the surface area of leaves directly affects the efficiency of PAH uptake; the larger the surface area is, the more PAHs it can absorb (Simonich and Hites 1995). In addition, according to Howsam et al. (2000), hairs, or trichomes, on the leaf surface can effectively trap PAHs. The presence of a waxy cuticle can also affect the uptake of organic pollutants (Simonich and Hites 1995; Piccardo et al. 2005).

Based on these previous studies, we conclude that the lack of a waxy cuticle layer on moss leaves may be a major factor in the differences in PAH accumulation between pine needles and mosses. As Piccardo et al. (2005) showed, LMW PAHs diffuse and accumulate in the tissues of pine needles either through the stomata or by diffusion through the cuticle. However, HMW PAHs tend to remain on the surface of the cuticle because of their strong interactions with the constituents of this waxy layer, making them more susceptible to external environmental factors (e.g., rain, temperature, ozone, and solar radiation). These dynamics may cause the loss of HMW PAHs from the leaves of pine needles (Jouraeva et al. 2002; Piccardo et al. 2005). In contrast, mosses lack the cuticle layers that facilitate the selective uptake of LMW PAHs, a distinction that can increase HMW PAH ratios in mosses compared to pine needles.

The presence of a waxy cuticle layer can also affect the total amount of PAHs accumulated in pine needles. We again focus on the comparison of the total amount of PAHs absorbed by pine needles and mosses in Fig. 4.6a. The pine needles examined in this study accumulated a significantly greater total PAH concentration than mosses. As Fig. 4.6b shows, this high PAH content can be attributed to the high content of LMW PAHs preferentially absorbed by pine needles.

Uptake Mechanisms

The cross-plots of the PAH isomer ratios (Fig. 4.7) show a clear distinction between the PAH sources in pine needles and mosses. Why did these differences occur? One potential explanation is that there is a stronger influence of wet deposition in mosses. Whereas mosses take up

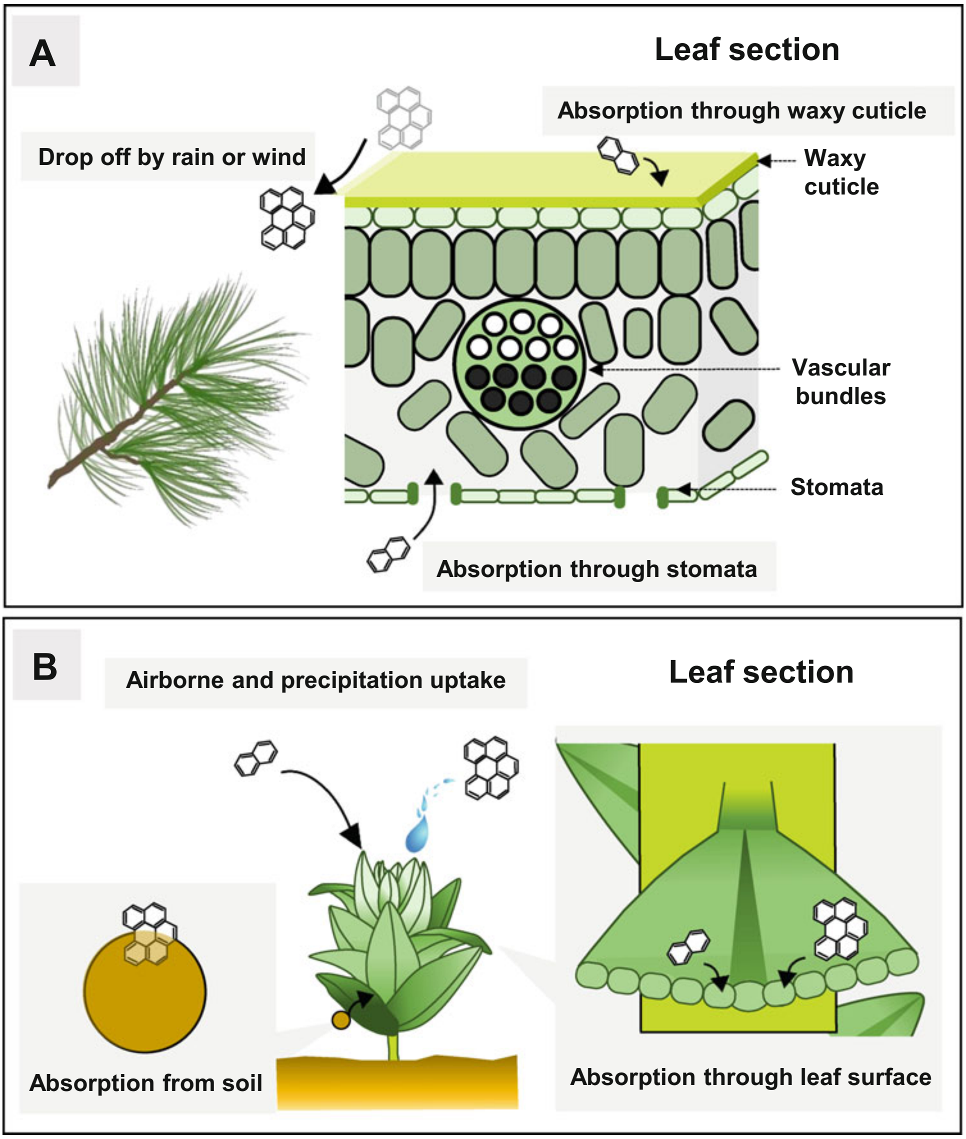

Fig. 4.8 Graphic summary of polycyclic aromatic hydrocarbon (PAH) uptake by pine needles and mosses. Pine needles (**a**) uptake low molecular weight (LMW) PAHs via stomata or diffusion across waxy cuticles. However, high molecular weight (HMW) PAHs are not as effectively absorbed because of the strong interaction between HMW PAHs and the waxy cuticle. In contrast, mosses (**b**) efficiently absorb HMW PAHs because they lack cuticle layers. Mosses on the ground can also uptake PAHs partially through soil particles

dissolved pollutants from precipitation (Thomas 1986), pine needles predominantly absorb gaseous PAHs via their stomata or diffusion (Lehndorff and Schwark 2004). This distinction in the uptake of pollutants can explain the differences in PAH sources and isomer ratios between these two plant types.

Influence of Soil Particles

In addition to the differences in leaf structures and uptake mechanisms, the relatively high concentration of HMW PAHs in mosses may partly be influenced by their ability to take up PAHs through soil particles (Migaszewski et al. 2009). Although this absorption route has not been proven experimentally, the possibility is supported by a previous study by Kłos et al. (2012), who used radioactive markers to determine that mosses absorb soil particles along with the heavy metals adhering to them. HMW PAHs exist mainly as particles and therefore can easily be absorbed into the soil (Bozlaker et al. 2008; Wang et al. 2009). Therefore, mosses can uptake HMW PAHs through soil particles in the same manner as they absorb heavy metals from soil particles.

4.4 Conclusion

Our results showed that pine needles and mosses absorb different types of PAHs, a contrast that can be explained by their unique pollutant uptake mechanisms. From the perspective of biomonitoring, these findings indicate that we can multidirectionally assess PAH pollution by using both pine needles and mosses as bioindicators. More specifically, pine needles are reliable indicators of airborne LMW PAH pollution, whereas mosses can be used to evaluate complex HMW PAH pollution in atmospheric and soil environments. Utilizing a combination of bioindicators for a more comprehensive environmental evaluation is a novel concept that can contribute to the effective biomonitoring.

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