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Lichens as biomonitors for organic air pollutants

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A B S T R A C T

Lichens are useful biomonitors for semi-volatile organic air pollutants, particularly polyaromatic hydrocarbons (PAHs), as a result of their ability to respond to air pollutants at different levels, their slow growth rate, their longevity and their ability to indicate the presence and the concentrations of these pollutants. Consequently, there has been a recent global trend in environmental analytical research to utilize lichens in this way, with Soxhlet and ultrasound-assisted extractions being the most common analyte extraction techniques. A wide range of total PAH concentrations has been determined in lichens from different environments, although phenanthrene, fluoranthene, naphthalene and pyrene tend to dominate the PAH profiles, with higher 2-ring and 3-ring PAH concentrations than 6-ring. In order to facilitate inter-study comparison, there is a need to develop a reproducible, sensitive analytical method for organic pollutants in lichens.

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1. Introduction

Lichens are symbiotic organisms found on trees, rocks, in soils and even on weevils and giant Galapagos turtles [1]. They are perennial, resilient and are able to live for many years in extreme conditions – being found in locations from the icy Himalayas to deserts [2,3]. The use of lichens as biomonitors comes as a result of the ability of lichens to respond to air pollutants at different levels, their slow growth rate, their longevity and their ability to indicate the presence and the concentrations of these pollutants [4,5].

Lichens have the unusual capability of taking up ions and substrates at concentrations beyond their needs. Metal ions are typically absorbed in a passive, extracellular manner and are bound reversibly by an ion-exchange mechanism. It has been found that lichens are able to bind cadmium, lead, tin and zinc at higher concentrations than higher plants, even mosses [6]. It has been suggested that these trace elements are absorbed and stored by particulate entrapment as well as passive and active intracellular uptake in addition to ion exchange [7,8]. There are many factors that determine the absorption and release processes in lichens, namely the chemical nature of the compound, the presence and the influence of other

Abbreviations: Ace, Acenaphthylene; Ant, Anthracene; BaA, Benzo[*a*]anthracene; Chry, Chrysene; DbA, Dibenzo[*ah*]anthracene; DAD/V-UV, Diode-array detector/ultraviolet-visible detector; DSASE, Dynamic sonication-assisted solvent extraction; FluAn, Fluoranthene; Flu, Fluorene; FLD, Fluorescence detector; GC-MS, Gas chromatography-mass spectrometry; HpCDD, Heptachlorodibenzo-*p*-dioxin; HPLC, High-performance liquid chromatography; LOD, Limit of detection; MW, Molecular weight; Naph, Naphthalene; OCDD, Octachlorodibenzodioxin; OCDF, Octachlorodibenzofuran; PeCDD, Pentachlorodibenzo-*p*-dioxin; PeCDF, Pentachlorodibenzofuran; Phe, Phenanthrene; POP, Persistent organic pollutant; PAH, Polyaromatic hydrocarbon; PCDD/F, Polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran; Pyr, Pyrene; SPE, Solid-phase extraction; SVOC, Semi-volatile organic compounds; TeCDF, Tetrachlorodibenzofuran.

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compounds, the size of the particles to be absorbed, and the chemical composition of the particles [9].

One of the earliest successful uses of lichens as biomonitors was by Sloof and Wolterbeek [10], who studied the concentrations of pollutants in lichens and compared them qualitatively with the atmospheric concentrations of suspended and deposited particulate matter. Sloof and Wolterbeek [10] performed some elemental analyses (including cobalt, scandium and zinc) on lichens and successfully related the determined concentrations with atmospheric concentrations. In addition, a ^{137}Cs study after the Chernobyl accident on both lichens and wet and dry depositions showed good correlations with dispersion model data sets [11]. It was consequently shown by Sloof [9] that elemental concentrations within lichens appear to equilibrate with the concentration levels of the surrounding atmosphere, and proved that lichens are suitable candidates for biomonitoring air pollution.

The absorption of atmospheric pollutants by lichens has consequently been a field of interest for many years, including investigation into the uptake of sulfur dioxide by Hawksworth and Rose [12] and Rogers [13]. It is understood that lichens absorb pollutants (metals and organic air pollutants) by wet or dry deposition. The absence of a cuticular wax layer on lichens means that they are able to absorb pollutants much more easily than other higher plants.

The absorption of lead by lichens has been extensively studied due to the toxic nature of the heavy metal. An early application in this regard was a study by Garty, who used lichens as biomonitors to track the lead emissions from automobiles along highways [14]. Over the years, lichen biomonitoring research has been conducted into a range of inorganic analytes, including mercury, most transition metals, radionuclides, fluoride, sulfur, nitrogen and acid rain, which all accumulate in the lichen thallus [15–20].

More recently, the use of lichens as biomonitors for organic air pollutants has been investigated. Although lichens do not have a waxy cuticle or stomata, they produce and release onto their surfaces lipid metabolites, which are suspected of behaving in a manner similar to the cuticle in plants [21]. The lipophilic nature of the surface of lichens then readily attracts lipophilic compounds, such as atmospheric semi-volatile organic compounds (SVOCs), and facilitates their uptake, where their incorporation into cells would be metabolically controlled [22,23].

Organic air pollutants are typically hydrophobic and this means that uptake tends toward dry deposition [24,25]. Metal ions and other water-soluble compounds are deposited on the lichen surface by other mechanisms. Both hydrophobic and hydrophilic compounds can be assimilated by lichens as a result of the volatilization of compounds from soils – or by direct methods, such as wind impaction or splashing from the ground during rainfall episodes [26,27].

Here, we review the current trend of using lichens as biomonitors of SVOC air pollutants, focusing on polyaromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs). POPs are typically chemicals that partition favorably to organic matter of a non-polar nature. They are deliberately produced (e.g., agrochemicals) or form accidentally through processes, such as combustion [e.g., polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs)]. They are known to have long half-lives and therefore accumulate in organic matter [28]. The associated health risks often relate to chronic exposure to POPs, and the effects of exposure include endocrine disruption as well as carcinogenic and mutagenic effects [29].

In this article, we discuss the use to date of lichens as biomonitors for SVOC air pollutants (primarily PAHs), and we review the sample preparation and analytical techniques employed for such biomonitoring. We also present a comparison of the levels of organic pollutants found in lichens from different studies and geographical areas. Reviews on the progress made in biomonitoring of metal pollution using lichens are available [30,31].

2. Lichens as bioindicators and biomonitors of air pollution

The lichen thallus is a complex symbiotic vegetative lower plant composed of two organisms: a fungus and an algae or cyanobacteria. The cell wall consists of a multilaminate and a granular layer. Adhering to the outside of the cells is a fibrous polysaccharide layer. The lichen hyphae can orientate randomly or regularly in a parallel manner – these two types form the basic structure of the layers. The cortex (outer layer) of the lichen serves as a regulator for gas exchange and protective support of the lichen and it is in this layer that small gaps are found, allowing the soredia (the reproductive structures of lichens) to pass into the atmosphere. This layer is covered by an epicortex, which is a porous, non-cellular polysaccharide. It is believed that the porous nature of the epicortex is what enables efficient gas exchange [32]. Fig. 1 shows the cross section of a foliose lichen.

There are three types of lichens: fruticose, foliose and crustose. The foliose lichens are known to have the largest ratio of surface area to dry weight, and are said to accumulate airborne particles more readily than fruticose lichens [33]. The foliose lichens are completely exposed to ambient air as a result of having few points of attachment to the substrate. Fruticose lichens are flatter, with a leaf-like structure with defined upper and lower layers, so only the upper layer is in contact with the ambient air. The crustose lichens are tightly attached to their substrates and are thus difficult to remove for analysis and are less exposed to their surrounds [21].

Lichens have been utilized to monitor air pollution in three different ways [30]:

- to determine the concentration of specific pollutants accumulated in the thallus;
- to use the effect of pollution sources on the lifespan and the presence or the absence of lichen species to map out the distribution and the effect of pollution in a specific area; and,
- to take healthy lichens with little background pollutant accumulation and to transplant them into polluted areas to measure the accumulation of pollutants or the consequential degradation of the thallus.

When conducting an experiment that exploits the absorptive nature of compounds by lichens, the choice of lichen species is paramount to the success of the study. The choice must be made with the method of investigation in mind: if a lichen transplant is to be done, a species that is very sensitive to changes in pollution should be chosen, whereas a hardy local species should be used if the concentration of target analytes in the thallus is to be determined at a sampling site. It is important to identify the species of lichen to be studied {e.g., the selectivity of lichen species for absorption of

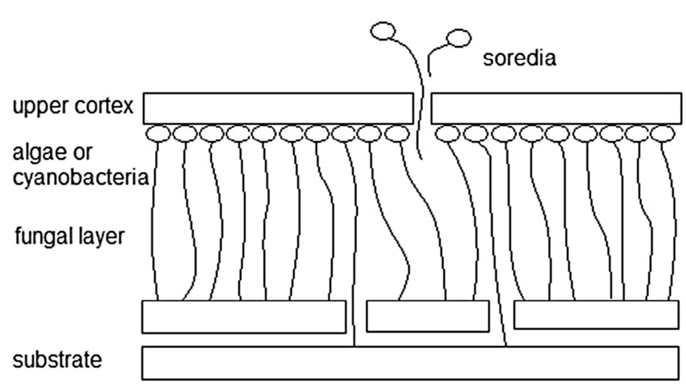

Fig. 1. Simplified cross section through a foliose lichen.