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Review

Moss and lichen biomonitoring of atmospheric mercury: A review

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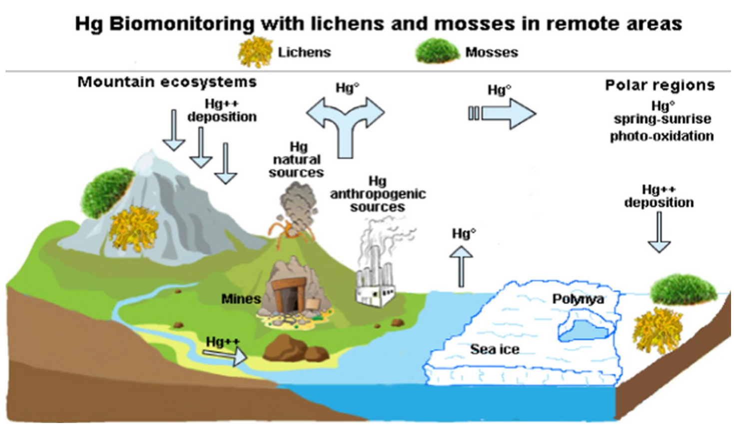
HIGHLIGHTS

- Studies on Hg cycling in land ecosystems and accumulation in cryptogams are reviewed.
- Cryptogams are good biomonitors of Hg natural/anthropogenic point sources.
- Mosses and lichens release Hg in a dynamic equilibrium with air concentrations.
- Estimates of air Hg concentrations and fluxes based on cryptogams are not reliable.
- Monitoring with cryptogams is effective in assessing deposition trends in remote areas.

GRAPHICAL ABSTRACT



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ABSTRACT

Long-range transport and residence time of elemental Hg (Hg°) in air promote global dispersion and deposition in remote ecosystems. Many biotic and abiotic factors contribute to the photoreduction and phytovolatilization of Hg from terrestrial ecosystems, and the assessment of deposition and volatilization fluxes is very challenging. Mosses and lichens are widespread in nature and constitute the dominant vegetation in alpine and polar ecosystems. This review surveys the results of Hg biomonitoring with cryptogams in areas with different Hg sources and deposition processes. Lichen and moss ecophysiology, and factors affecting Hg uptake and bioaccumulation are discussed. Although some laboratory experiments indicate a linear accumulation of Hg in cryptogams exposed to Hg°, without any significant release, in nature the Hg accumulated in cryptogams is in a dynamic equilibrium with Hg in air and decreases when organisms are transplanted to clean environments. Mercury concentrations in mosses and lichens have often been used to estimate concentrations and deposition fluxes of atmospheric Hg; however, Hg° exchanges between cryptogams and air, and the time necessary for mosses and lichens to equilibrate elemental composition with changing atmospheric chemistry, preclude reliable estimates. Biological processes of Hg uptake and exchange with air cannot be reproduced by mechanical collectors, and comparisons between Hg concentrations in biomonitors and those in atmospheric deposition are scarcely reliable. However, the Hg biomonitoring with mosses and lichens is easy and cheap and allows to locate "hot spots" of natural or anthropogenic emissions and to assess spatio-temporal changes in Hg deposition patterns. Climate change is affecting the global Hg cycle through the melting of sea-ice in coastal Polar Regions, and modifying Hg sequestration in mountain ecosystems. Despite limitations, large-scale monitoring of Hg with mosses and lichens may be used as a tool to evaluate the impact of global processes in remote ecosystems.

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Contents

1. Lichens and mosses as accumulators of airborne trace elements

1.1. Metal uptake by lichens

Lichens are stable mutualistic associations between a fungal partner (mycobiont; usually an ascomycete) and algal or cyanobacterial species (phycobionts). The mycobionts are mostly unable to live without the algal partner and through the symbiosis they can colonize extreme subaerial environments. On the contrary, the phycobionts can also occur in a free living state. In this association, the alga provides organic carbon and receives from the fungus water, minerals, and protection from light and other external stress factors. This is one of the most successful examples of mutualism in nature, and lichens are among the first colonizers of exposed rocks in all climatic regions. They are perennial, and grow slowly on soil (epigeic), rocks (epilithic), mosses, and trees (epiphytic). Lichens have no roots, waxy cuticles or specialized structures for water and gas exchange, and do not shed parts during growth. They absorb water, minerals, and contaminants from wet, dry, and occult (mist and dew) atmospheric deposition over the entire surface of the thallus. Thus, the well-known species-specific sensitivity of lichens to air pollutants (e.g., Hawksworth and Rose, 1970; Gilbert, 1973; Bennett et al., 1996; Bennett, 2008) depends above all on their morphology and surface exchange with air, and decreases from fruticose species (with a thallus extended up into a tufted or pendant branched structure), to foliose (leaf-like thallus), and crustose (crust-forming) ones. The rich branching of thallus in many species and the large intercellular spaces within thalli also facilitate the trapping of airborne particulates.

The use of lichens as indicators of healthy air dates back to Nylander's (1866) observations in the Jardin du Luxembourg in Paris; since then, the assessment of changes in lichen community composition has become one of the most used tools to evaluate "air quality" (e.g., Ferry et al., 1973; Nimis, 1990). Lichens behave as long-living collectors of airborne pollutants and several species can accumulate in their thalli, at levels well above ambient air concentrations, metals, radionuclides and persistent organic pollutants (POPs), without evident signs of damage. The introduction of atomic absorption spectrophotometry and gas chromatography allowed the development of methods for the determination of persistent pollutant concentrations in lichen thalli and during the last four decades these organisms have been one of the most used biomonitors of atmospheric deposition. Many studies (e.g., Nieboer et al., 1972; Pilegaard et al., 1979; Nash, 1989; Garty, 1993; Bargagli et al., 1997a; Conti and Cecchetti, 2001; Grangeon et al., 2012) have stressed the reliability of epiphytic lichens as quantitative biomonitors of persistent atmospheric pollutants, especially those not measurable by automatic monitoring devices. In polar and alpine ecosystems lichens constitute with mosses a large proportion of the terrestrial biomass, play a major role in the biogeochemical cycling of elements and allow for generation of trace deposition maps of long-range transported pollutants. In contaminated areas, devoid of native lichen species, an "active" biomonitoring can be performed by transplanting thalli of suitable lichen species from an uncontaminated area.

Essentially, inorganic contaminants may occur in lichens as: (1) particles (adsorbed onto the thallus surface or within intercellular spaces, (2) ions bound to extra-or intracellular exchange sites, and (3) soluble intracellular ions (Bargagli and Mikhailova, 2002). Airborne particles from natural (soil, volcanic eruptions, sea salt aerosols, wild forest fires, volatile non-methane hydrocarbons, pollen and spores) and anthropogenic sources (e.g., mining and smelting, metallurgical activities, combustion of fossil fuels, incineration of refuse, cement production) are effectively intercepted by lichens. The interception depends on the particle size and species-specific features of the thallus such as the presence/absence of a cortex, the roughness of epicortex and the size of pores. The ad/absorption of airborne particles in lichens occurs through different mechanisms than those in automatic monitoring devices of particulate matter (PM) and metals concentrations in lichens are usually scarcely related to those in exposed filters. Direct observations with an environmental scanning electron microscope (ESEM) of particles intercepted by lichens and mosses exposed in bags in a urban environment (Adamo et al., 2008) showed that, compared to mosses, the chemical composition of exposed lichens was less affected by the interception of airborne soil particles and showed a higher efficiency for those released by anthropogenic sources. In dry environments such as cold and hot deserts, only epilithic lichens can be used as biomonitors and their thalli often show high and intercorrelated concentrations of Al, Ti, Si and other lithophilic elements. Bargagli (1995) showed that irrespective of the lichen species used as biomonitor, average regional background concentrations of trace elements quoted in the literature increase proportionally to lichen Al, Ti or Fe content (as a rule, from forests to more open and dry environments such as farmlands, upland prairies and tundra). The remote and pristine SW Chilean Patagonia has a very steep climatic gradient, and baseline element concentrations in epiphytic lichens growing in rainforest were significantly different from those growing in drier environments (Monaci et al., 2012). On using lichens as biomonitors of trace element deposition from anthropogenic sources, it is necessary to minimize the element contribution by soil particles: for instance, by normalizing raw concentrations of elements to those of soil tracers such as Al, Ti or Si (Bargagli et al., 1995). Some ad/absorbed particles may be solubilized by acid precipitation