Environment International 66 (2014) 28–37

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Review

Biomonitoring persistent organic pollutants in the atmosphere with mosses: Performance and application

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ARTICLE INFO

Article history:
Received 31 October 2013
Accepted 31 December 2013
Available online 8 February 2014

Keywords:
Moss
Biomonitoring
Persistent organic pollutant (POP)
Atmosphere

ABSTRACT

Persistent organic pollutants (POPs) have aroused environmentalists and public concerns due to their toxicity, bioaccumulation and persistency in the environment. However, monitoring atmospheric POPs using conventional instrumental methods is difficult and expensive, and POP levels in air samples represent an instantaneous value at a sampling time. Biomonitoring methods can overcome this limitation, because biomonitors can accumulate POPs, serve as long-term integrators of POPs and provide reliable information to assess the impact of pollutants on the biota and various ecosystems. Recently, mosses are increasingly employed to monitor atmospheric POPs. Mosses have been applied to indicate POP pollution levels in the remote continent of Antarctica, trace distribution of POPs in the vicinity of pollution sources, describe the spatial patterns at the regional scale, and monitor the changes in the pollution intensity along time. In the future, many aspects need to be improved and strengthened: (i) the relationship between the concentrations of POPs in mosses and in the atmosphere (different size particulates and vapor phases); and (ii) the application of biomonitoring with mosses in human health studies.

Contents

1. Introduction

In the process of industrial production, agricultural activity and daily life, many organic compounds were released into water, soil and atmospheric environment (Muir and Howard, 2006; Zhou and Huang, 2001). Organic pollutants, especially persistent organic pollutants (POPs), have aroused wide concerns because they are harmful to plants, animals, microorganisms and even people (Ciesielczuk et al., 2012; Zhou et al., 2004, 2008). POPs become a research focus in the environmental field for recent years due to the following characteristics: toxic effects, bioaccumulation, persistence, and prone to long-range atmospheric transport (Klanova et al., 2008; Lohmann et al., 2007; Nash, 2011). POPs are now globally distributed and detected in abiotic and biotic samples (Li et al., 2013; Zhou and Huang, 2001). In 1998, 16 substances were focused by the Aarhus Protocol on POPs of the Convention on Long-range Transboundary Air Pollution (UNECE, 1998). In the 2001 Stockholm convention, 12 POPs termed “dirty dozen” or ‘legacy’ POPs were listed as priority control chemicals (UNEP, 2001). Additional 9 POPs were added to the list of the Stockholm convention in 2009 (UNEP, 2009).

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0160-4120/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envint.2013.12.021

The aims of these two conventions are to eliminate and/or restrict the production and use of selected POPs. National and international environmental monitoring programs have continued to measure POPs since the 1970s (Muir and Howard, 2006).

Once emitted into the atmosphere, POPs will be rapidly diluted by air. Thus, to monitor POP levels in the atmosphere using conventional instruments is difficult and expensive, and the concentrations of POPs in air samples represent an instantaneous value at a sampling time. Biomonitors can be used as passive collectors of POPs in the atmosphere without mechanical or electrical devices, serve as long-term integrators of POPs, and provide reliable information to assess the impact of pollutants on the biota and ecosystems (Carballeira et al., 2006; Ciesielczuk et al., 2012; Ratola et al., 2010). Biomonitoring can perform the high-density sampling at virtually any desired spatial and temporal scales at low cost and permit the measurement of a wide range of pollutants (Ares et al., 2011; Cipro et al., 2011; De Nicola et al., 2013; P. Wang et al., 2012; Wappelhorst et al., 2000). In this sense, biomonitoring methods are more popular than conventional instrumental monitoring methods. Among bioindicators, mosses have been proved to be a useful tool for monitoring atmospheric pollution because of the following aspects. Firstly, mosses attained nutrients from the air rather than substrates because of lacking roots. Secondly, the outermost epidermal cells of mosses do not have a layer of waxy cutin compounds so that foliar cells are directly exposed to pollutants in the air. Thirdly, mosses showed tolerance and sensitivity to a wide range of pollutants, such as dioxin (Carballeira et al., 2006). Fourthly, the high ratio of surface to volume of moss tissues facilitates more accumulation of pollutants. Zilli et al. (1996) estimated that the surface area of 1.0 g mosses was about 1.6 m^2. Fifthly, mosses can grow in various habitats all around the world, even in Antarctica characterized by drought and cold weather (Cannone et al., 2013; Peat et al., 2007). Sixthly, the growth rate of mosses was very slow, therefore the sampled naturally growing mosses may integrate information on accumulation of pollutants over a long time (Carballeira et al., 2006; Leblond et al., 2004; Mariussen et al., 2008a). In addition, transplants (moss bags) are better indicators for short-time monitoring about one month exposure to pollutants due to the low lipid content (<1%) and total organic matter (<5% of fresh weight) (Knulst et al., 1995). Because of abundance and wide distribution, special morphology structure and physiological features, mosses have been increasingly employed to monitor atmospheric POPs in recent years. In this review, the application of mosses to monitor POPs in the atmosphere is retrospected and commented.

2. Atmospheric sources and fate of POPs in mosses

A primary basis for the validity of the use of mosses for atmospheric pollution monitoring is an assumption of insignificant contribution of organic pollutant levels in soil to the levels in the mosses. Theoretical input and output of POPs in mosses were presented in Fig. 1. The concentrations of PAHs, trace metals and chlorinated hydrocarbons in mosses were caused by different sources according to the statistical models computed (Thomas, 1984). The concentrations of PAHs in mosses came from atmospheric particulates, trace metals in mosses were caused by bulk precipitation, and chlorinated hydrocarbons in mosses may be related with gaseous and particulate matters other than bulk precipitation. The content of PAHs in epiphytic mosses was mainly characterized by atmospheric particulate concentrations (Thomas, 1984). PAHs in mosses showed a similar distribution pattern as in atmospheric particulates (Liu et al., 2005). Skert et al. (2010) also demonstrated that the concentrations of PAHs in mosses had a significant correlation with those in particulate matters with the diameter lower than 10 μm. What's more, the assumption was also confirmed by the fact that the concentration of POPs in mosses was hardly correlated with that in soil (Borghini et al., 2005). According to the above-mentioned results, POPs in mosses largely came from the atmosphere rather than the soil, and POPs in mosses showed a close correlation with those in the atmosphere.

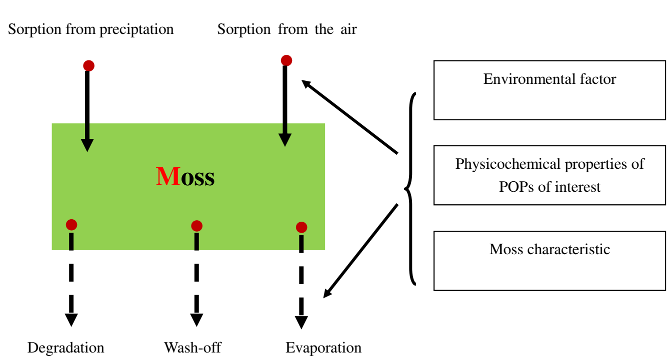

Fig. 1. Theoretical input and output of POPs in mosses and their influencing factors.

Compared with the mechanism of uptake, accumulation, elimination of heavy metals in mosses, there is limited knowledge about POPs. Keyte et al. (2009) investigated the foliar uptake and within-leaf migration of phenanthrene (PHE) by *Hypnum cupressiforme* using the two-photon excitation microscopy with autofluorescence. PHE entered rapidly into the cell walls of moss leaves because of lacking a cuticular layer considered as a barrier in the foliar uptake of organic chemicals. PHE entered into the cell walls was retained and accumulated within the cuticular matrix for a long time. After 288 h, PHE started to migrate from the cell walls across the cell membrane into the cytoplasm of adjacent cells. There were distinct differences in atmospheric uptake and within-leaf movement, storage and processing of semivolatile organic compounds (SVOCs) between vascular and nonvascular living plants. Schrenk and Steinberg (1998) reported mosses metabolized only small amounts of PHE, but POPs in mosses may be subjected to continuing photodegradation processes (Liu et al., 2005; Wild et al., 2005).

Many factors can affect the air-vegetation transfer of POPs, including physicochemical properties of the compounds of interest, environmental factors and plant characteristics (Barber et al., 2004). Mosses are prone to accumulate high-molecular-weight PAHs, especially 4-ring and 5-ring PAHs (De Nicola et al., 2013; Dołęgowska and Migaszewski, 2011; Liu et al., 2005). However, mosses had no obvious selectivity in capturing these organic compounds with the same molecular weights from the atmosphere (Liu et al., 2005). Temperature is an important factor affecting the accumulation of POPs in mosses. HCB and 4,4′-DDE showed a significant correlation between the log-transformed moss concentrations and the reciprocal of temperature (Borghini et al., 2005). Grimalt et al. (2004) also reported that the log-transformed OC concentrations showed a significant linear dependence from the reciprocal of temperature, independently of the origin of the compounds. The hydration state can affect POP concentrations in the tissue of mosses (Kylin and Bouwman, 2012). Kylin and his colleague reported the concentrations of α- and γ-HCH were 3–5 times higher in the hydrated *Hylocomium splendens* than in the desiccated material. Because of the influence of the prevailing wind, the concentrations of PAHs in mosses at the downwind side of the road were higher than those at the other side (De Nicola et al., 2013; Viskari et al., 1997). A forest cover (canopy) may reduce atmospheric deposition of POPs on the mosses (Ciesielczuk et al., 2012). The mosses growing in the dry pine forest *Cladonio-Pinetum* revealed higher mean concentrations of $\sum 16$ PAHs than those growing the continental coniferous forest *Querco-roboris-Pinetum* (Agnieszka, 2007). This is perhaps attributed to less dense canopy enabled higher deposition of air pollutants on the forest floor.

3. Moss species used as bioindicators of POPs

The number of mosses as indicators of POPs was less than that as indicators of heavy metals (Ares et al., 2012). To the best of our knowledge, up to now about 24 kinds of mosses were used to monitor POPs