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Terrestrial mosses as biomonitors of atmospheric POPs pollution: A review

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A B S T R A C T

Worldwide there is concern about the continuing release of persistent organic pollutants (POPs) into the environment. In this study we review the application of mosses as biomonitors of atmospheric deposition of POPs. Examples in the literature show that mosses are suitable organisms to monitor spatial patterns and temporal trends of atmospheric concentrations or deposition of POPs. These examples include polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs), dioxins and furans (PCDD/Fs), and polybrominated diphenyl ethers (PBDEs). The majority of studies report on PAHs concentrations in mosses and relative few studies have been conducted on other POPs. So far, many studies have focused on spatial patterns around pollution sources or the concentration in mosses in remote areas such as the polar regions, as an indication of long-range transport of POPs. Very few studies have determined temporal trends or have directly related the concentrations in mosses with measured atmospheric concentrations and/or deposition fluxes.

Keywords:
Biomonitoring
Bryophytes
Persistent organic pollutants
Polycyclic aromatic hydrocarbons
Atmospheric deposition

1. Introduction

1.1. Background

Persistent organic pollutants (POPs) are organic substances which are a toxic to the environment and human health as they: possess toxic characteristics; are persistent; bioaccumulate; are prone to long-range transboundary atmospheric transport and deposition; and are likely to cause significant adverse human health or environmental effects near to and distant from their source (LRTAP Convention, 1998). POPs are mainly of anthropogenic origin (Breivik et al., 2006), for example from waste incineration, industrial production and application (e.g. pesticides, flame retardants, coolant fluids) and fossil fuel burning. They show weak degradation and consequently are accumulating in the environment across the globe, including in remote areas such as the polar regions. The combination of resistance to metabolism and lipophilicity ('fat-loving') means that POPs accumulate in food chains (Jones and De Voogt, 1999), POPs are readily absorbed in fatty tissue, where concentrations can become magnified by up to 70,000 times the background levels. Fish, predatory birds, mammals, and humans are high up the food chain and therefore absorb the greatest concentrations. Specific effects of POPs can include inducing cancer, allergies and hypersensitivity, damage to the central and peripheral nervous systems, reproductive disorders, and disruption of the immune system. Some POPs are also considered to be endocrine disruptors, which, by altering the hormonal system, can damage the reproductive and immune systems of exposed individuals as well as their offspring and affect development (Belpomme et al., 2007; Jones and De Voogt, 1999; TFHTAP, 2010; WHO, 2003). Their ecotoxicity has been highlighted in aquatic (Leipe et al., 2005) and terrestrial ecosystems (e.g. Oguntumehin et al., 2008; Smith et al., 2007).

Spatial and some temporal trends in the concentration of selected POPs in fish were reviewed by the International Cooperative Programme on Assessment and Monitoring of Effects of Air Pollution on Rivers and Lakes (ICP Waters, 2005). Recent results indicate that atmospherically transported POPs can impact the health of fish in remote ecosystems and that they can reach concentrations in fish that exceed health threshold values for consumption by wildlife and humans (TFHTAP, 2010). However, these impacts and exceedances were not observed at Alaskan parks where the contaminant load is due solely to long-range atmospheric transport and not influenced strongly by regional sources. There is currently no strong evidence that Antarctic organisms or ecosystems are being impacted by POPs associated solely with long-range atmospheric transport. However, bioaccumulation of POPs with time might result in impacts in the...
future. There are also reasons to believe that Antarctic organisms might be more susceptible to effects of POPs than temperate organisms, though more research is needed in this area (TFHTAP, 2010).

1.2. International agreements to protect the environment from POPs pollution

The 1998 Aarhus Protocol on POPs of the Convention on Long-range Transboundary Air Pollution (LRTAP Convention, 1998) and the 2001 Stockholm Convention on POPs, a global treaty under the United Nations Environment Programme (UNEP), aim to eliminate and/or restrict the production and use of selected POPs (Table 1). Originally, the Aarhus Protocol focused on a list of 16 substances that have been singled out according to agreed risk criteria; many substances on the list are chlororganic pesticides. The ultimate objective is to eliminate any discharges, emissions and losses of POPs. The Aarhus Protocol bans the production and use of some products outright: aldrin, chlordane, chlordanes, dieldrin, endrin, hexachlorobenzene, mirex and toxaphene.

Others are scheduled for elimination at a later stage: dichlorodiphenyltrichloroethane (DDT), heptachlor, hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs). The Aarhus Protocol severely restricts the use of DDT, hexachlorocyclohexanes (HCHs) (including lindane) and PCBs and it obliges Parties to reduce their emissions of dioxins (PCDDs), furans (PCDFs), polycyclic aromatic hydrocarbons (PAHs) and HCB below their levels in 1990 (or an alternative year between 1985 and 1995). For the incineration of municipal, hazardous and medical waste, it lays down specific limit values. On 18th December 2009, seven new substances were included in the Aarhus Protocol. The Stockholm Convention generally includes the same substances as the Aarhus Protocol but not all, e.g. it does not include PAHs and hexachlorobutadiene. Whilst the Stockholm Convention is a global treaty, the LRTAP Convention Protocol is limited to the region of the United Nations Economic Commission for Europe (UNECE), currently 50 countries covering almost all of Europe plus the USA and Canada. The Stockholm Convention originally focused on 12 substances but was extended in 2009 to include nine new substances.

1.3. Monitoring and modelling of air concentrations and deposition of POPs in Europe

In Europe the emission and deposition of POPs are monitored and modelled by the European Monitoring and Evaluation Programme (EMEP), reporting to the LRTAP Convention. EMEP has established a model for calculating air concentrations, atmospheric transport and deposition fluxes of selected PAHs, dioxins, furans, PCBs and lindane. In 2009, there were 23 EMEP monitoring sites in total in 17 countries measuring POPs for model validation, of which 13 conducted measurements of POP concentrations in both air and precipitation (Gusev et al., 2011). POPs measured using passive air samplers included pesticides, PAHs, HCHs, HCB and PCBs. Model simulations of benzene pollution within the EMEP region showed that transboundary transport is a significant source of pollution for many of the EMEP countries contributing between 30 and 70% to the total annual deposition. For 25 countries the contribution from transboundary transport exceeded 50% in 2009.

1.4. Mosses as biomonitors of air pollution

As mosses do not have roots, they absorb nutrients and pollutants from the air, which often accumulate on or in their tissue. The accumulation is aided by the high surface to volume ratio of moss tissue. Monitoring of heavy metal and nitrogen concentrations in naturally growing mosses allows determination of spatial patterns and temporal trends of heavy metal and nitrogen pollution and deposition at a high spatial resolution in a cost-effective manner (Harmens et al., 2010, 2011b, 2012). Detailed statistical analysis of the factors affecting heavy metal concentration in mosses confirmed that EMEP modelled heavy metal deposition was the main predictor for cadmium and lead concentrations in mosses; this was not the case for mercury (Holy et al., 2010; Schröder et al., 2010b). The latter might be related to the specific chemistry of mercury (Harmens et al., 2010). Detailed statistical analysis of the factors affecting nitrogen concentration in mosses also showed that EMEP modelled air concentrations of different nitrogen forms and total nitrogen deposition are the main predictors for the total nitrogen concentrations in mosses (Schröder et al., 2010a), despite the fact that nitrogen is an essential macronutrient.

<table>
<thead>
<tr>
<th>POP</th>
<th>LRTAP Convention Protocol on POPs</th>
<th>Stockholm Convention</th>
<th>Pesticide</th>
<th>Industrial chemical</th>
<th>By-product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin</td>
<td>1998</td>
<td>2001</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlordane</td>
<td>1998</td>
<td>2001</td>
<td>X</td>
<td></td>
<td></td>
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<tr>
<td>Dichlorodiphenyltrichloroethane (DDT)</td>
<td>1998</td>
<td>2001</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dieldrin</td>
<td>1998</td>
<td>2001</td>
<td>X</td>
<td></td>
<td></td>
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<tr>
<td>Endrin</td>
<td>1998</td>
<td>2001</td>
<td>X</td>
<td></td>
<td></td>
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<tr>
<td>Hexachlorobenzene (HCB)</td>
<td>1998</td>
<td>2001</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Mirex</td>
<td>1998</td>
<td>2001</td>
<td>X</td>
<td></td>
<td></td>
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<tr>
<td>Texaphene</td>
<td>1998</td>
<td>2001</td>
<td>X</td>
<td></td>
<td></td>
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<tr>
<td>Polychlorinated biphenyls (PCBs)</td>
<td>1998</td>
<td>2001</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Dioxins (PCDDs)</td>
<td>1998</td>
<td>2001</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Furans (PCDFs)</td>
<td>1998</td>
<td>2001</td>
<td>X</td>
<td></td>
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</tr>
<tr>
<td>Chlordecone</td>
<td>1998</td>
<td>2009</td>
<td>X</td>
<td></td>
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<tr>
<td>Hexachlorocyclohexane (HCH) (including lindane)</td>
<td>1998</td>
<td>2009</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Hexachlorobenzene (HCB)</td>
<td>1998</td>
<td>2009</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbons (PAHs)</td>
<td>1998</td>
<td>2009</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexachlorobutadiene</td>
<td>2009</td>
<td>2009</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>2009</td>
<td>2009</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Polychlorinated diphenyl ethers (PBDEs)</td>
<td>2009</td>
<td>2009</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perfluoroacetic acid, its salts and perfluorooctane sulfonamide (PFOS)</td>
<td>2009</td>
<td>2009</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polychlorinated napthalenes</td>
<td>2009</td>
<td>2009</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Short-chain chlorinated paraffins (SCCPs)</td>
<td>2009</td>
<td>2009</td>
<td>X</td>
<td></td>
<td>X</td>
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</tbody>
</table>
and remobilised from senescing tissue (in contrast to the non-
esential heavy metals cadmium, lead and mercury). Although
mosses have also been used to monitor POPs pollution, the number
of studies and the range of POPs studied is limited. Here we review
current knowledge on the application of mosses as biomarkers of
POPs pollution, identify knowledge gaps and make recommenda-
tions for future research.

2. Mosses as biomarkers of POPs

2.1. Polycyclic aromatic hydrocarbons (PAHs)

PAHs are a family of chemical compounds constituted by
carbon and hydrogen atoms which form at least two condensed
aromatic rings. The majority of PAHs originate from fossil or non-
fossil fuels by pyrolysis or pyrolysis. PAHs are emitted in the
atmosphere mainly from anthropogenic sources but they also
originate from natural sources such as volcanic eruptions and
forest fires (Simonich and Hites, 1995). The main sources of PAHs
in the environment are aluminium production, coke production
from coal, wood preservation and fossil fuel combustion (traffic,
domestic heating, electricity production) (Ravindra et al., 2008;
Tobiszewski and Namiesnik, 2012; Wegener et al., 1992). Eight
have been classified by the US Environmental Protection Agency
(US EPA, 1997) as potentially carcinogenic: benzo[a]anthracene,
chrysene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene,
dibenzo[a,h]anthracene, indeno[1,2,3-c,d]pyrene and
benzo[ghi]perylen. Some PAHs also are mutagenic, teratogenic,
immunosuppressive and/or neurotoxic (Gatuszka, 2000). The US
EPA has listed 16 priority PAHs (out of 32) for monitoring (Fig. 1).
Although many are also listed in the European list of priority
pollutants, only benzo[a]pyrene is regulated by the Directive
2004/107/EC (EU, 2004) which sets the maximum atmospheric
concentration acceptable at 1 ng m$^{-1}$ (measurement with PM$_{10}$,
the atmospheric suspended particles with a diameter smaller
than 10 μm).

The mechanism of uptake of organic pollutants by vegetation is
governed by the chemical and physical properties of the
compounds (such as their molecular weight, aqueous solubility and
vapour pressure), environmental conditions (e.g. atmospheric
temperature), and the plant species and structure (Simonich and
Hites, 1995). After emission in the atmosphere, generally the
most volatile PAHs remain in gaseous phase whereas the least
volatile (those with five or six rings) are adsorbed on solid atmos-
pheric particles. Deposition to vegetation occurs through uptake of
the lipophilic compounds in both vapour and particle phases, but
there may also be a removal at higher ambient temperatures. PAHs
of intermediate volatility (those with three or four rings) are
distributed between gaseous and particulate phases (Viskari et al.,
1997). In the winter, however, PAHs are predominantly in the
particulate phase due to increased emissions and their low degree
of volatilization at low temperatures. PAHs in the gaseous phase are
generally transported to areas remote from main pollution sources,
whereas particulate absorbed PAHs are generally deposited in
higher proportions near emission sources (Thomas, 1986). This
might explain why often PAHs in mosses sampled away from local

![Fig. 1. Structural formula of the 16 PAHs classed as priority pollutants by the US EPA (US EPA, 1997).](image-url)
pollution sources are dominated by those with smaller ring numbers of three or four (Dolegowska and Migaszewski, 2011; Gatuszka et al., 2007; Migaszewski et al., 2009; Orłński, 2002).

The high surface to volume ratio of mosses and the lack of a cuticle favour the deposition of POPs associated with particles to the surface of mosses. The absorption efficiency of organic molecules associated with the particles depends on the octanol/water partitioning coefficient of the POP (Garrec and Van Haluwyyn, 2002). The majority of PAHs is associated with particles with a diameter smaller than 2 µm (Allen et al., 1996; Raek et al., 1991; Kiss et al., 1998). However, the partitioning of PAHs differs in urban and rural samples (Allen et al., 1996). In urban samples, PAHs were distributed among aerosol size fractions based on molecular weight. PAHs with molecular weights between 178 and 202 were evenly distributed between the fine (diameter < 2 µm) and coarse (diameter > 2 µm) aerosols. PAHs with molecular weights greater than 228 were associated primarily with the fine aerosol fraction. In rural samples, low and high molecular weight PAHs were associated with both the fine and coarse aerosols. We are not aware of any study showing which particle size associated with PAHs is preferentially adsorbed by mosses. Little is known about the persistence and potential for washout of POPs from the surface of mosses. For plants it's known that organic pollutants can be transferred from the leaf surface to the atmosphere when the air temperature increases or when atmospheric concentrations are low (Knust et al., 1995). Volatilization of PAHs from pine needles was negatively correlated with their molecular mass (Wang et al., 2005). Furthermore, studies have shown degradation of PAHs by microflora and sunlight on leaves and needles (Paterson et al., 1990). The latter is both a function of the molecular mass of PAHs and the chemical properties of the plant tissue (Wang et al., 2005; Chen et al., 2010).

Table 2 provides an overview of published concentrations measured in various mosses sampled in rural environments away from pollution sources. The average concentration measured for up to 17 PAHs ranged from ca. 100 to 600 ng g⁻¹ dry wt. Gerdol et al. (2002) observed that the fraction of low molecular weight volatile PAHs was greater in rural compared to urban sites. On the other hand, the dominance of three ring compounds appears to be related to the type of pollution source (Fano et al., 2010). Phenanthrene, fluoranthene and pyrene have often been reported as the dominant PAHs in mosses sampled away from pollution sources (Fano et al., 2010; Gatuszka et al., 2007; Krommer et al., 2007; Zechmeister et al., 2006). In Hungary, where 99% of the total PAHs concentration in the moss consists of low molecular weight, a good correlation between total PAHs concentrations in *Hyppnum cupressiforme* Hedw. and traffic volume was observed, but there was no such correlation with population density (Otvös et al., 2004). Local and regional emission sources therefore appear to have a strong influence on PAH levels in mosses. However, long-range transboundary air pollution also contributes to the contamination of mosses by PAHs, as concentrations of 4.4–34 ng g⁻¹ were measured for 14 compounds in *Santinia uncinata* at Antarctica (Cabrero et al., 2012).

Ares et al. (2009) showed an exponential decay of PAHs levels in mosses around emission sources. Using moss bags in active biomonitimating of PAHs near a road in Finland, Viskari et al. (1997) found that downwind of the road the concentrations of most PAHs in mosses declined to background levels between 60 and 100 m from the road. Therefore, studies carried out in remote areas, located at a significant distance from emission sources, provide an indication of background levels of atmospheric PAH contamination due to long-range transboundary air pollution. Zechmeister et al. (2006) concluded that moss bags are suitable to monitor PAHs from traffic emissions in tunnels, even better than in the open field because confounding effects of other sources of pollution and noise in the accumulation process (e.g. washout through wet deposition) are minimised. Many moss analysis studies on atmospheric pollution (including PAHs) use pleurocortous mosses as biomonitors because they generally form broad carpets which almost completely isolate them from the soil (Table 3). However, pleurocortous mosses are sensitive to pollution and to dryness, and therefore are rare, sometimes absent, in urban areas. Thus, acrocarpous mosses, which grow on stone or brick walls, are used for studying urban environments (Burton, 1990).

### Table 2

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>PAHs analysed</td>
<td>(number of rings)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>16 (US EPA)</td>
<td>17</td>
<td>16 (US EPA)</td>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>Naphthalene (2)</td>
<td>2.6 (1-640)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acenaphthene (2)</td>
<td>45.3 (11-183)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acenaphthylene (2)</td>
<td>7.8 (0.5-163)</td>
<td>5 (4-6)</td>
<td>BQL</td>
<td>0.6 (0.3-6.6)</td>
<td>5 (2-11)</td>
</tr>
<tr>
<td>Fluorene (2)</td>
<td>68.8 (1-333)</td>
<td>11.5 (10-13)</td>
<td>3.9</td>
<td>4.6 (3.8-6.6)</td>
<td>13 (8-23)</td>
</tr>
<tr>
<td>Phenanthrene (3)</td>
<td>43.3 (0.6-380)</td>
<td>82.5 (82-83)</td>
<td>55</td>
<td>30.1 (24-63)</td>
<td>85 (46-162)</td>
</tr>
<tr>
<td>Anthracene (3)</td>
<td>86.8 (0.6-2280)</td>
<td></td>
<td>1.4</td>
<td>1.6 (1.2-12)</td>
<td>5 (2-21)</td>
</tr>
<tr>
<td>Fluoranthene (3)</td>
<td>18.9 (0.6-325)</td>
<td>96 (88-104)</td>
<td>14</td>
<td>16.4 (13-140)</td>
<td>112 (40-420)</td>
</tr>
<tr>
<td>Pyrene (4)</td>
<td>128.5 (0.9-525)</td>
<td>68.5 (65-72)</td>
<td>12</td>
<td>12.7 (8.5-94)</td>
<td>87 (31-356)</td>
</tr>
<tr>
<td>Benzo[a]pyrene (5)</td>
<td>13.7 (9-311)</td>
<td>22 (18-26)</td>
<td>1.5</td>
<td>4.4 (2.9-32)</td>
<td>21 (4-123)</td>
</tr>
<tr>
<td>Chrysene (4)</td>
<td>74.6 (0.6-1190)</td>
<td>69.5 (61-78)</td>
<td>4.0</td>
<td>8.4 (5.5-27)</td>
<td>44 (15-141)</td>
</tr>
<tr>
<td>Benz[ghi]fluoranthene (4)</td>
<td>5.5 (0.6-84)</td>
<td>71.5 (64-79)</td>
<td>4.1</td>
<td>12.9 (8.3-46)</td>
<td>41 (19-41)</td>
</tr>
<tr>
<td>Benz[b,k]fluoranthene (4)</td>
<td>6.0 (0.6-120)</td>
<td>33.5 (31-36)</td>
<td>2.7</td>
<td>5.3 (3-18)</td>
<td>11 (3-38)</td>
</tr>
<tr>
<td>Benz[a]anthracene (5)</td>
<td>37.9 (0.1-540)</td>
<td>21.5 (12-31)</td>
<td>3.5</td>
<td>8.4 (7.3-59)</td>
<td>19 (5-71)</td>
</tr>
<tr>
<td>Benzo[e]pyrene (5)</td>
<td>47.5 (43-52)</td>
<td></td>
<td>2.3</td>
<td>47.5 (43-52)</td>
<td>22 (5-71)</td>
</tr>
<tr>
<td>Dibenz[a,h]anthracene (5)</td>
<td>22 (0.6-460)</td>
<td>3 (0.5-9)</td>
<td>0.8</td>
<td>0.6 (&lt;5-16)</td>
<td>4.2 (1-78)</td>
</tr>
<tr>
<td>Perylene (5)</td>
<td>14.5 (0.6-290)</td>
<td>39 (37-41)</td>
<td>3.8</td>
<td>10.3 (7-57)</td>
<td>18 (&lt;5-63)</td>
</tr>
<tr>
<td>Benzo[g,h,i]perylene (6)</td>
<td>94.5 (0.6-1087)</td>
<td>42.5 (39-46)</td>
<td>3.6</td>
<td>10.8 (8.2-27)</td>
<td>21 (&lt;5-68)</td>
</tr>
<tr>
<td>2PAMS</td>
<td>609 (0.1-4700)</td>
<td>604.5 (587-622)</td>
<td>120</td>
<td>137 (120-730)</td>
<td>512 (183-1629)</td>
</tr>
</tbody>
</table>

**Note:** Sampling period is the year range over which data were collected. PAHs analysed is the number of PAHs measured in each study. Concentrations are given in ng g⁻¹ dry wt.
One should take care with comparing concentrations between different moss species and different studies. Bioaccumulation of PAHs in mosses might be species-specific as Galiuzka (2007) and Dołęgowska and Migaszewski (2011) observed a higher accumulation of PAHs in Hylocomium splendens (Hedw.) B.S.G. than Pleurozium schreberi (Brid.) Mitt. However, Mitukaite (1998) reported a similar retention of benzo[a]pyrene in both species. Migaszewski et al. (2009) found that differences in the accumulation of PAHs between the moss species varied with sampling site and region. Moreover, Ares et al. (2009) noted a seasonal variability due to changes in emissions and climate throughout the year. They also observed spatial variability due to the geomorphology of the study area and the presence of prevailing winds.

Most studies so far have determined the concentration of POPs in mosses as an indication of pollution levels, especially in remote areas. Few studies have related the concentration in mosses with total atmospheric concentrations or deposition rates. Thomas (1984, 1986) found linear relationships between the accumulation of selected PAHs in H. cupressiforme sampled from tree trunks and their concentration in rainwater and atmospheric particulate matter, taking into account the amount of precipitation. The following linear relationships were reported for 1980 (Thomas, 1986):

Benzo[ghi]perylene:

\[ C_1 = 1.62\times C_2 + 259.60\times C_3 + 0.74\times P \ (R = 0.74 \text{ for } n = 15; \ P = 0.002) \]

Benzo[a]pyrene:

\[ C_1 = 1.31\times C_2 + 180.25\times C_3 + 0.16\times P \ (R = 0.66 \text{ for } n = 15; \ P = 0.007) \]

Fluoranthene:

\[ C_1 = 0.33\times C_2 + 26.21\times C_3 + 0.19\times P \ (R = 0.91 \text{ for } n = 15; \ P < 0.001) \]

where: \( C_1 \) = concentration in mosses (ng g\(^{-1}\)); \( C_2 \) = concentration in rainwater (ng l\(^{-1}\)); \( C_3 \) = concentration in atmospheric particulate matter (ng m\(^{-3}\)); \( P \) = amount of precipitation (mm); \( C_2 \) and \( C_3 \) are given as average values for 1980. Thomas (1984, 1986) concluded that mosses are most appropriate for measuring environmental chemicals which are deposited in particulate form on the mosses and can be physically retained by them. Mitukaite (1998) found that the flux of benzo[a]pyrene from the atmosphere to the ground surface correlated well with its concentration in mosses. However, it should be noted that the accumulation of trace substances in mosses is not only dependent on atmospheric pollution levels but also on enrichment factors which describe physiological parameters as well as pollutant characteristics (Thomas, 1984). Thomas (1986) reported on a marked gradient of the concentration of selected PAHs in mosses in north-west Europe in agreement with the presence of pollution sources.

Vegetation intercepts 26–62% of the atmospheric PAH deposition (Simonich and Hites, 1994). Based on measurements of PAHs in vegetation (sugar maple (Acer saccharum) leaves, seeds and bark; white pine (Pinus strobus) needles and bark) from Bloomington, Indiana, U.S.A., the mass balance model developed by Simonich and Hites (1994) estimated that 44 ± 18% of the PAHs emitted into the atmosphere from sources in the region are removed by vegetation. Although the equilibrium between the atmosphere and vegetation depends on ambient temperature, Simonich and Hites (1994) suggested that most of the PAHs absorbed by vegetation at the end of the growing season are incorporated into the soil and permanently removed from the atmosphere. In addition to mosses, other main bioaccumulators used to date for monitoring atmospheric PAH deposition are lichens (Augusto et al., 2010; Blasco
et al., 2011; Guidotti et al., 2003; Migaszewski et al., 2002; Shukla and Upreti, 2009), leaves from deciduous broadleaf trees (Howsam et al., 2000; Jouraeva et al., 2002; Tian et al., 2008; Wang et al., 2008) or evergreen broadleaf trees (De Nicola et al., 2011; Müller et al., 2001; Prajapati and Tripathi, 2008) and conifer needles (Amigo et al., 2011; Augusto et al., 2010; Bronström-Lundén and Löfgren, 1998; Holoubek et al., 2007; Klánová et al., 2009; Lehndorff and Schwark, 2009a,b; Migaszewski et al., 2002; Piccardo et al., 2005; Tian et al., 2008). In higher plants, uptake of POPs from the air will either be in gaseous form via the stomata or via deposition to the cuticle and subsequent absorption of the lipophytic organic compound (Paterson et al., 1990). Holoubek et al. (2000, 2007) measured a large range of POPs (PAHs, PCBs and OCPs) at a remote site during several years in both mosses and pine needles. The ΣPAHs content in mosses ranged from <0.3 to 4700 ng g⁻¹ dry weight (mean value 609), whereas the ΣPAHs content in pine needles ranged from <0.5 to 18,590 ng g⁻¹ dry weight (mean value 1345) at the background site (Holoubek et al., 2000). Although the concentration of PAHs tended to be lower in mosses than in pine needles, this was not always the case (Holoubek et al., 2000, 2007). We are not aware of other studies reporting on potential correlations between concentrations of PAHs in mosses and other bioindicator species.

Only a few studies have reported on temporal trends, generally indicating that the change in concentration and/or composition of PAHs with time reflects the changes in emission sources and levels. Herbarium moss samples appear to be an effective tool for reconstructing historical tendencies of atmospheric PAH deposition (Foan et al., 2010). The disappearance of the charcoal pits and foundries at the end of the 19th Century, combined with the evolution of domestic heating towards less polluting systems during the 20th Century, explains the significant decline of PAHs in mosses over that period at a remote site in northern Spain (Fig. 2). Between 1973–1975 and 2006–2007, PAH distribution in mosses changed noticeably with a tendency towards 3-benzene ring PAH enrichment, due to the implementation of policies limiting 4- and 5-benzene ring PAH emissions, and a steadily increasing traffic in the area, especially heavy vehicles. However, it should be noted that natural degradation or volatilization might have occurred in the herbarium moss samples during storage in the dark at room temperature. Holoubek et al. (2000, 2007) observed a significant decrease in total PAH concentrations in mosses between 1988–1994 and 1996–2005 in the Czech Republic. The small decline in the period 1996–2005 reflected the small decline in PAH concentrations in air (Holoubek et al., 2007).

2.2. Organochlorines (OCs)

Mosses have also been sampled to determine the levels of atmospheric pollution from POPs other than PAHs, although the number of studies for each POP is limited, and no attempts have been made so far to relate the concentration in mosses with atmospheric concentrations and/or deposition fluxes. Below we review the application of mosses as biomonitors of OCs such as pentachlorobenzene (PCBz), DDT, HCB, HCHs and PCBs. In the 1960s and 70s, many OCs were used as pesticides, for example DDT (insecticide), HCB (fungicide in seed treatment), or produced as a by-product in the production of pesticides (HCHs). PCBs (Fig. 3) were widely used as dielectric and coolant fluids, for example in transformers and electric motors. PCBz was once used for a variety

![General structural formula of dioxin, furan, PCB and PBDE](image-url)
of applications (e.g. as an intermediate in the manufacture of pesticides and as flame retardant), but today the majority is emitted as a result of waste burning and incineration. Table 4 provides an overview of the published concentrations of OCs measured in various mosses sampled at rural and remote sites over the last 30 years. OC levels in mosses are lower than PAHs, with individual compounds often showing concentrations lower than 1 ng g\(^{-1}\)

PCBs tend to be the major compounds, with maximal published concentrations measured for 40 congeners in Singapore of 69 ng g\(^{-1}\) (Lim et al., 2006).

Chlorinated hydrocarbons were present in measurable concentrations in mosses in Antarctica (Bacci et al., 1986; Cabreroz et al., 2012; Focardi et al., 1991). HCB levels from the Antarctic Peninsula were rather similar to those reported for mosses from Sweden and Finland. Although levels of DDT and its derivative were lower in Antarctica when compared to plant data from Italy and Germany, levels observed in lichens were similar to those observed in Sweden (Bacci et al., 1986). The levels of DDT derivatives appears to originate mainly from DDT deposited in the past. Although levels of PCBs were near or below the quantification limit in the Antarctic in the past (Bacci et al., 1986), recently Borghini et al. (2005) reported PCBs and PCBz being the dominant OCs in mosses from Victoria Land (Antarctica). The PCBs concentrations from Victoria Land were similar to those reported for mosses in Norway (Lead et al., 1996). In Singapore the concentration of OCs in mosses was also rather uniform, indicating that air masses distributed the pollutants rather evenly over the island; high concentrations of DDT derivatives and PCBs were observed compared to those found in mosses in for example the Czech Republic (Lim et al., 2006).

In Norway, the sum of the 37 PCB congeners in H. splendens declined at all locations between 1977 and 1990 (Lead et al., 1996). This decline most likely reflects the reduction in the global use and manufacture of PCBs. While the sum of PCB concentrations have declined, temporal changes in the congener pattern in the samples collected from the same locations were noted. For example, in the south of Norway the relative concentrations of hexa- and hepta-chlorinated homologue groups decreased to a greater extent than they did in the north. This observation can be interpreted as evidence for changes in congener recycling through the environment according to their volatility, and it was tentatively suggested that this may provide evidence in support of the global fractionation hypothesis (Wania and Mackay, 1993), i.e. compounds will volatilize in warm and temperate areas, will move northward in the Northern Hemisphere (even though atmospheric air flow may not always be in this direction), and will then re-condense when they reach colder circumpolar regions. It has also been hypothesized that differences in the volatility and lability of the individual compounds and in the ambient temperature will lead to a latitudinal fractionation of OCs. In Finland, PCB concentrations in Sphagnum have shown a consistent decline from the 1970s to 1980s and higher total PCB concentrations were observed in the south compared to the north (Hinberg and Pakarinen, 1994).

2.3. Dioxins and furans (PCDD/Fs)

Dioxins occur as by-products in the manufacture of some OCs, in the incineration of chlorine-containing substances, in chlorine bleaching of paper, and from natural sources such as volcanoes and forest fires (Beychok, 1987). Furans tend to co-occur with dioxins (Fig. 3). Carballeira et al. (2006) concluded that mosses are good biomarkers for PCDD/Fs. Concentrations of PCDD/F in Pseudoscleropodium purum (Hedw.) Fleisch. in Broth collected in Spain ranged from 10 to 442 pg g\(^{-1}\) (for 17 compounds), with the lowest concentrations measured in a woodland and the highest around a landfill. The mosses allowed the detection of strong and weak pollution sources. Furthermore, the measurements were sensitive enough (quantification limits: 0.025–0.211 pg g\(^{-1}\)) to monitor changes in pollution intensity with time, to determine spatial gradients near pollution sources as well as differences in the relative abundance of isomers from different sources.

Table 4

Mean or ranges of OCs concentrations (ng g\(^{-1}\), dry wt) in mosses. Except for Singapore (a mixture of rural and urban sites), samples were collected in rural or remote areas; BQI: below quantitation limit, n = number of compounds determined.

<table>
<thead>
<tr>
<th>Sampling period</th>
<th>Country</th>
<th>OCs</th>
<th>HCB</th>
<th>β-HCH</th>
<th>γ-HCH</th>
<th>δ-HCH</th>
<th>ΣOCs</th>
<th>p,p'-DDE</th>
<th>p,p'-DDT</th>
<th>p,p'-DDD</th>
<th>ΣDDT</th>
<th>PCBz</th>
</tr>
</thead>
<tbody>
<tr>
<td>1979</td>
<td>Norway</td>
<td>10–35</td>
<td>0.4–22</td>
<td>9–49</td>
<td>3–43</td>
<td>0.1–1.6</td>
<td>0.4–6.6</td>
<td>0.17–0.53</td>
<td>0.2–0.5</td>
<td>0.2–0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1986</td>
<td>Antarctica</td>
<td>&lt;5–12</td>
<td>0.3–0.68</td>
<td>0.2–1.1</td>
<td>0.4–1.7</td>
<td>0.04–0.76</td>
<td>0.021–0.12</td>
<td>0.005–0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1991</td>
<td>Antarctica</td>
<td>&lt;5–16</td>
<td>0.3–0.8</td>
<td>0.2–1.1</td>
<td>0.4–1.7</td>
<td>0.04–0.76</td>
<td>0.021–0.12</td>
<td>0.005–0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N. America</td>
<td>12–28</td>
<td>0.4–1.7</td>
<td>0.4–1.7</td>
<td>0.4–1.7</td>
<td>0.04–0.76</td>
<td>0.021–0.12</td>
<td>0.005–0.04</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Asia</td>
<td>12–28</td>
<td>0.4–1.7</td>
<td>0.4–1.7</td>
<td>0.4–1.7</td>
<td>0.04–0.76</td>
<td>0.021–0.12</td>
<td>0.005–0.04</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Australia</td>
<td>12–28</td>
<td>0.4–1.7</td>
<td>0.4–1.7</td>
<td>0.4–1.7</td>
<td>0.04–0.76</td>
<td>0.021–0.12</td>
<td>0.005–0.04</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1995–1996</td>
<td>Czech Republic</td>
<td>0.44</td>
<td>1.6</td>
<td>1.07</td>
<td>&lt;0.1</td>
<td>1.28</td>
<td>&lt;0.3</td>
<td>0.15</td>
<td>1.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1999</td>
<td>Russia</td>
<td>0.3–1</td>
<td>0.18</td>
<td>0.1–3</td>
<td>0.18</td>
<td>0.1–3</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2000</td>
<td>Germany</td>
<td>23–34</td>
<td>0.85–1.9</td>
<td>0.3–6</td>
<td>0.18–1.6</td>
<td>1.1–7.9</td>
<td>0.54–0.91</td>
<td>1.0–2.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2004</td>
<td>Singapore</td>
<td>31–69</td>
<td>21.19</td>
<td>BQL-1.78</td>
<td>BQL-22.57</td>
<td>BQL-1.53</td>
<td>BQL-1.56</td>
<td>BQL-1.56</td>
<td>BQL-1.96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2006</td>
<td>Czech Republic</td>
<td>7.1</td>
<td>2.7</td>
<td>4.6</td>
<td>2.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2007</td>
<td>Switzerland</td>
<td>0.87–20</td>
<td>BQL-47</td>
<td>BQL-150</td>
<td>BQ-4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td>Switzerland</td>
<td>7.76–18.6</td>
<td>0.141–1.06</td>
<td>BQL-1.20</td>
<td>(x = 6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>Switzerland</td>
<td>7.76–18.6</td>
<td>0.141–1.06</td>
<td>BQL-1.20</td>
<td>(x = 6)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
2.4. Polybrominated diphenyl ethers (PBDEs)

PBDEs (Fig. 3) are used as flame retardants in a variety of material. For 15 PBDEs, Mariussen et al. (2008) measured concentrations ranging between 112 and 1937 pg g⁻¹ in H. splendens sampled in Norway, with a general decline towards the north of the country. In addition, there was a significant decrease in the concentration of the lower brominated PBDE-congeners in mosses from the south towards the north. This is consistent with the expected atmospheric transport behaviour of these compounds and the known source regions on an European scale (Prevedouros et al., 2004). The PBDE levels in Norway were low and are probably of limited toxicological significance. PBDEs were also detected at low levels in mosses sampled in Antarctica. Yogui and Sericano (2008) measured concentrations ranging from 319 to 1187 pg g⁻¹ (for three compounds) in S. uncinita and Cipor et al. (2011) reported levels from 146 to 811 pg g⁻¹ (for 36 compounds) in three moss species including S. uncinita. The minimal values were generally not significantly different from procedure blanks. Concentrations were not statistically different at sites close to and distant from human facilities, hence long-range atmospheric transport is believed to be the primary source of PBDEs.

3. Conclusions and research recommendations

As for many other air pollutants such as heavy metals and nitrogen (Harmens et al., 2010, 2011b, 2012), mosses appear to be suitable organisms to monitor spatial patterns and temporal trends of the atmospheric concentrations and deposition of POPs. So far, many studies have focused on spatial trends around pollution sources or the concentration in mosses in remote areas as an indication of long-range transport of POPs. Very few studies have determined temporal trends or have directly related the concentrations in mosses with measured atmospheric concentrations in deposition or deposition fluxes. The majority of studies have focussed on PAHs and relatively few studies have been conducted on other POPs. Levels determined in mosses collected at rural or remote sites are highly variable between POPs, with values ranging from approximately 1 pg g⁻¹ to 0.1 µg g⁻¹ for PCDD/F and PAHs respectively.

In the European moss survey of 2010/11 coordinated by the ICP Vegetation, six countries will report for the first time on the concentration of selected POPs (PAHs in particular) in mosses in a pilot study to investigate the suitability of mosses as biomonitor of POPs at a regional scale (Harmens et al., 2011a). To further establish the suitability of mosses as biomonitor of POPs across Europe it will be paramount to sample mosses at sites where atmospheric POPs concentrations and/or deposition fluxes are determined, for example at EMEP monitoring sites (Gusev et al., 2011) or national POPs monitoring sites. Once a good relationship has been established between POPs concentrations in mosses and measured air concentrations and/or deposition fluxes, data from the atmospheric moss monitoring network can be used to complement data from the limited number of EMEP measurement sites and to assess the performance of the EMEP model for POPs in a cost-effective manner. If the pilot study is successful, it should be extended to other countries to enhance the spatial coverage across Europe and it should be repeated regularly (e.g. every five years) to establish temporal trends in POPs concentrations in mosses in Europe.

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Glossary

DDD: dichlorodiphenyldichloroethane
DDDE: dichlorodiphenyltrichloroethane
HCB: hexachlorobenzene
HCCH: hexachlorocyclohexane
OC: organochlorine
PAH: polycyclic aromatic hydrocarbon
PBDE: polybrominated diphenyl ether
PCB: polychlorinated biphenyl
PCDD: dioxins
PCDF: furans
POP: persistent organic pollutant