



Open Archive TOULOUSE Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in : <http://oatao.univ-toulouse.fr/>
Eprints ID : 9601

To link to this article : DOI:10.1016/j.envpol.2012.10.005
URL : <http://dx.doi.org/10.1016/j.envpol.2012.10.005>

To cite this version : Harmens, Harry and Foan, Louise and Simon, Valérie and Mills, Gina. *Terrestrial mosses as biomonitors of atmospheric POPs pollution: a review*. (2013) Environmental Pollution, vol. 173 . pp. 245-254. ISSN 0269-7491

Any correspondence concerning this service should be sent to the repository administrator: staff-oatao@listes-diff.inp-toulouse.fr

Terrestrial mosses as biomonitors of atmospheric POPs pollution: A review

H. Harmens^{a,*}, L. Foan^{b,c}, V. Simon^{b,c}, G. Mills^a

^a Centre for Ecology and Hydrology, Environment Centre Wales, Deiniol Road, Bangor LL57 2UW, UK

^b Université de Toulouse, INPT, LCA (Laboratoire de Chimie Agro-Industrielle), ENSIACET, 4 Allée, Emile Monso, BP 44362, F-31030 Toulouse Cedex 4, France

^c INRA, LCA (Laboratoire de Chimie Agro-Industrielle), F-31030 Toulouse, France

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 concern for the environment and human health as they: possess toxic characteristics; are persistent; bioaccumulate; are prone to long-range transboundary atmospheric transport and deposition; 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 degradability 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 disrupters, 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. Oguntimohin 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 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

* Corresponding author.

E-mail addresses: hh@ceh.ac.uk (H. Harmens), louise.foan@gmail.com (L. Foan), valerie.simon@ensiacet.fr (V. Simon), gmi@ceh.ac.uk (G. Mills).

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, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene. Others are scheduled for elimination at a later stage: dichlorodiphenyltrichloroethane (DDT), heptachlor, hexachlorobenzene (HCB) and polychlorobiphenyls (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 benzo[a]pyrene 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 adsorb/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 1
POPs included in the Protocol of the LRTAP Convention and the Stockholm Convention. Note: some substances have been grouped.

POP	LRTAP Convention Protocol on POPs	Stockholm Convention	Pesticide	Industrial chemical	By-product
Aldrin	1998	2001	X		
Chlordane	1998	2001	X		
Dichlorodiphenyltrichloroethane (DDT)	1998	2001	X		
Dieldrin	1998	2001	X		
Endrin	1998	2001	X		
Heptachlor	1998	2001	X		
Hexachlorobenzene (HCB)	1998	2001	X	X	X
Mirex	1998	2001	X		
Toxaphene	1998	2001	X		
Polychlorobiphenyls (PCBs)	1998	2001		X	X
Dioxins (PCDDs)	1998	2001			X
Furans (PCDFs)	1998	2001			X
Chlordecone	1998	2009	X		
Hexachlorocyclohexane (HCH) (including lindane)	1998	2009	X		X
Hexabromobiphenyl (HBB)	1998	2009		X	
Polycyclic aromatic hydrocarbons (PAHs)	1998				X
Hexachlorobutadiene	2009				X
Pentachlorobenzene	2009	2009	X	X	X
Polybrominated diphenyl ethers (PBDEs)	2009	2009		X	
Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (PFOS)	2009	2009		X	
Polychlorinated naphthalenes	2009			X	X
Short-chain chlorinated paraffins (SCCPs)	2009			X	X

and remobilised from senescing tissue (in contrast to the non-essential 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 biomonitors of POPs pollution, identify knowledge gaps and make recommendations for future research.

2. Mosses as biomonitors 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 pyrosynthesis. 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 Namieśnik, 2012; Wegener et al., 1992). Eight have been classified by the US Environmental Protection Agency (US EPA, 1997) as potentially carcinogenic: benz[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]perylene. Some PAHs also are mutagenic, teratogenic,

immunosuppressive and/or neurotoxic (Gałuszka, 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^{-3} (measurement with PM_{10} , the atmospheric suspended particles with a diameter smaller than $10 \text{ }\mu\text{m}$).

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 atmospheric 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

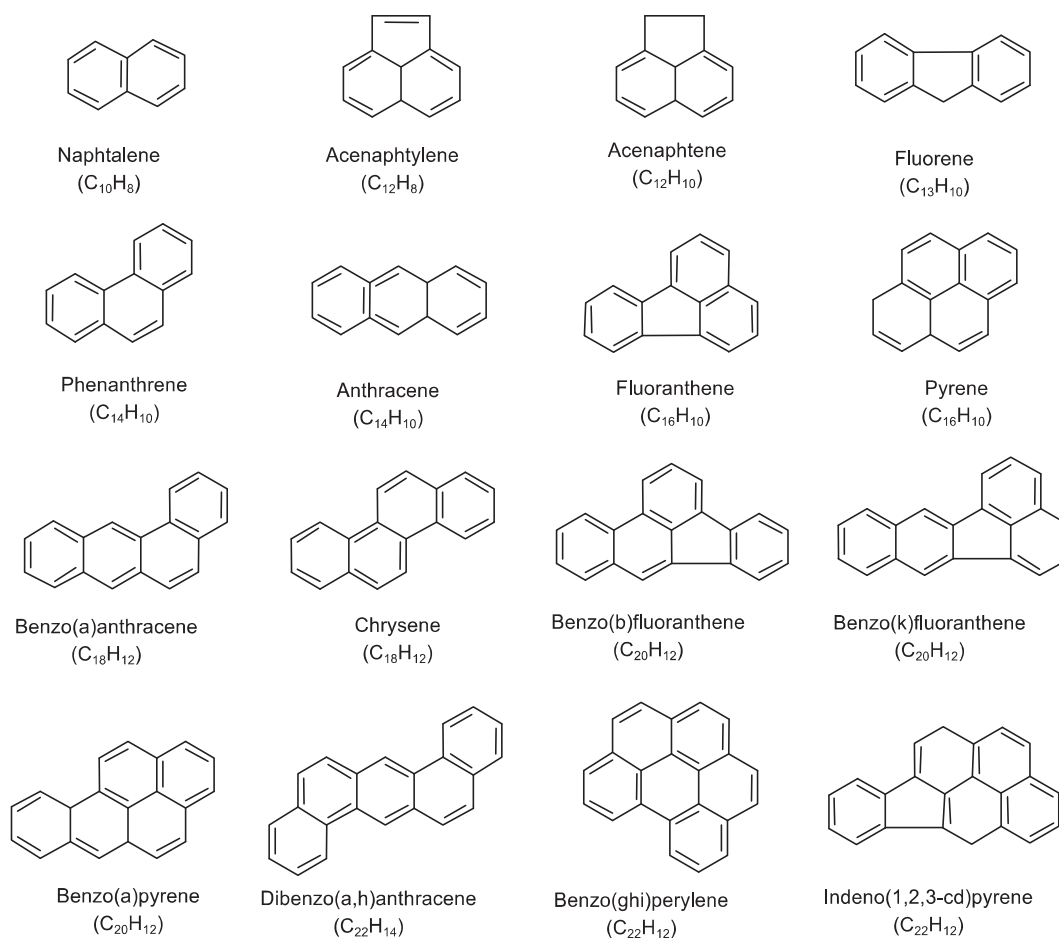


Fig. 1. Structural formula of the 16 PAHs classed as priority pollutants by the US EPA (US EPA, 1997).

pollution sources are dominated by those with smaller ring numbers of three or four (Dołęgowska and Migaszewski, 2011; Gałuszka, 2007; Migaszewski et al., 2009; Orliński, 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 Haluwyn, 2002). The majority of PAHs is associated with particles with a diameter smaller than 2 µm (Allen et al., 1996; Baek 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 (Knulst 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 (Foan et al., 2010). Phenanthrene, fluoranthene and pyrene have often been reported as the dominant PAHs in mosses sampled away from pollution sources (Foan et al., 2010; Gałuszka, 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 *Hypnum cupressiforme* Hedw. and traffic volume was observed, but there was no such correlation with population density (Ötvös 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 *Sanionia uncinata* at Antarctica (Cabrerizo et al., 2012).

Ares et al. (2009) showed an exponential decay of PAHs levels in mosses around emission sources. Using moss bags in active biomonitoring 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 pleurocarpous mosses as biomonitors because they generally form broad carpets which almost completely isolate them from the soil (Table 3). However, pleurocarpous 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
Average PAH concentrations (ng g⁻¹, dry wt) and ranges (in brackets) measured in mosses sampled in rural areas; BQL = below quantification limit.

Sampling period	Holoubek et al. (2000)	Migaszewski et al. (2002)	Zechmeister et al. (2006)	Krommer et al. (2007)	Gałuszka (2007)	Foan et al. (2010)
	Czech Republic	Poland	Austria	Austria	Poland	Spain
PAHs analysed (number of rings)	16 (US EPA)	17	16 (US EPA)	17	16	13
Naphtalene (2)	2.6 (<1–640)		6.7	7.3 (1–13)		
Acenaphthene (2)	45.3 (<1–1183)	<4	1.8	3.1 (2.1–5.7)	2 (<1–3)	4.1 (<1.5–12.7)
Acenaphthylene (2)	7.8 (<0.5–163)	5 (4–6)	BQL	0.6 (0.3–6.6)	5 (2–11)	
Fluorene (2)	68.8 (<1–933)	11.5 (10–13)	3.9	4.6 (3.8–6.6)	13 (8–23)	15.1 (<10.4–21.3)
Phenanthrene (3)	43.3 (<0.6–380)	82.5 (82–83)	55	30.1 (24–63)	85 (46–162)	81.1 (26.9–142.2)
Anthracene (3)	68.6 (<0.6–2280)	<4	1.4	1.6 (1.2–12)	5 (2–21)	3.2 (1.2–9.9)
Fluoranthene (3)	18.9 (<0.6–325)	96 (88–104)	14	16.4 (13–140)	112 (40–420)	38.1 (10.2–152.7)
Pyrene (4)	128.5 (<0.9–525)	68.5 (65–72)	12	12.7 (8.5–94)	87 (31–356)	18.5 (6.8–39.0)
Benzo[a]pyrene (5)	13.7 (<0.9–311)	22 (18–26)	1.5	4.4 (2.9–32)	21 (4–123)	3.1 (<1.2–7.0)
Chrysene (4)	74.6 (<0.6–1190)	69.5 (61–78)	4.0	8.4 (5.6–27)	44 (15–141)	
Benzo[b]fluoranthene (4)	5.3 (<0.6–84)	71.5 (64–79)	4.3	12.9 (8.3–46)	41 (19–83)	3.0 (1.8–5.5)
Benzo[k]fluoranthene (4)	6.0 (<0.6–120)	33.5 (31–36)	2.7	5.3 (3.6–18)	11 (<3–38)	0.8 (<0.5–1.8)
Benzo[a]pyrene (5)	37.9 (<0.3–540)	21.5 (12–31)	3.5	8.4 (7.3–59)	19 (5–71)	2.4 (<1.4–1.7)
Benzo[e]pyrene (5)		47.5 (43–52)			22 (5–71)	
Dibenzof[a,h]anthracene (5)	23 (<0.6–460)	<20	0.8	3 (0.5–9)	6 (<5–16)	4.2 (<1.3–7.8)
Perylene (5)		<12				
Benzo[g,h,i]perylene (6)	14.5 (<0.3–290)	39 (37–41)	3.8	10.3 (7.1–57)	18 (<5–63)	5.6 (2.0–16.1)
Dibenz[a,h]anthracene (5)	94.5 (<0.6–1087)	42.5 (39–46)	2.6	10.8 (8.2–27)	21 (<5–68)	2.0 (<2.0–2.5)
Coronene (6)			3.6	3.5 (2.2–18)		
ΣPAHs	609.1 (<0.3–4700)	604.5 (587–622)	120	137 (120–730)	512 (183–1629)	172 (86–372)

Table 3
Moss species used as passive biomonitoring of atmospheric PAH deposition.

	Pleurocarpous mosses					Acrocarpous mosses				
	<i>Abietinella abietina</i>	<i>Hylocomium splendens</i>	<i>Hypnum cupressiforme</i>	<i>Pleurozium schreberi</i>	<i>Pseudoscleropodium purum</i>	<i>Scleropodium purum</i>	<i>Thamnobryum alopecurum</i>	<i>Thuidium tamariscinum</i>	<i>Dicranum scoparium</i>	<i>Tortula muralis</i>
Knulst et al. (1995)	▲			▲						
Milukaite (1998)	▲			▲						▲
Gerdol et al. (2002)										
Migaszewski et al. (2002)			▲							
Ötvös et al. (2004)				▲						
Gatuszka (2007)										
Holoubek et al. (2000, 2007)			▲							
Krommer et al. (2007)			▲							
Ares et al. (2009)					▲					
Migaszewski et al. (2009)										
Foan et al. (2010)										
Dotęgowska and Migaszewski (2011)										
Cabrero et al. (2012)										
Domeño et al. (2012)										
Foan and Simon (2012)										

One should take care with comparing concentrations between different moss species and different studies. Bioaccumulation of PAHs in mosses might be species-specific as Gatuszka (2007) and Dotęgowska and Migaszewski (2011) observed a higher accumulation of PAHs in *Hylocomium splendens* (Hedw.) B.S.G. than *Pleurozium schreberi* (Brid.) Mitt. However, Milukaite (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:

$$C_1 = 1.62 \cdot C_2 + 259.60 \cdot C_3 + 0.74 \cdot P \quad (R = 0.74 \text{ for } n = 15; P = 0.002)$$

Benzo[a]pyrene:

$$C_1 = 1.31 \cdot C_2 + 180.26 \cdot C_3 + 0.16 \cdot P \quad (R = 0.66 \text{ for } n = 15; P = 0.007)$$

Fluoranthene:

$$C_1 = 0.33 \cdot C_2 + 26.21 \cdot C_3 + 0.19 \cdot P \quad (R = 0.91 \text{ for } n = 15; P < 0.001)$$

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. Milukaite (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 $44 \pm 18\%$ 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

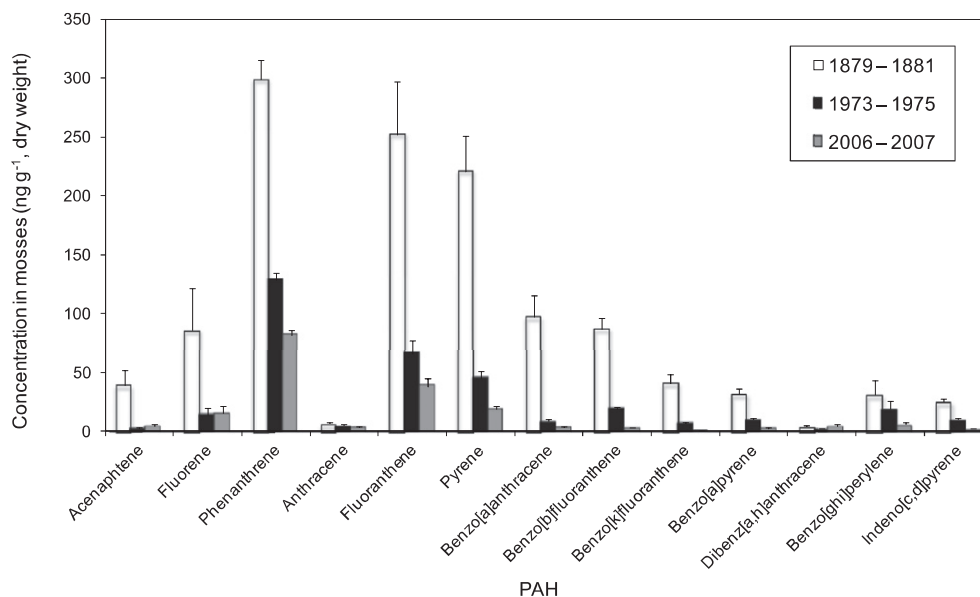


Fig. 2. PAH concentrations (mean + standard deviation) measured in herbarium mosses sampled during the periods 1879–1881, 1973–1975 and 2006–2007 at a rural site in northern Spain (Foan et al., 2010; Foan, 2012).

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; Brorström-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 lipophilic, 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 Σ PAHs content in mosses ranged from <0.3 to 4700 ng g^{-1} dry weight (mean value 609), whereas the Σ PAHs content in pine needles ranged from <0.3 to $18,590 \text{ ng g}^{-1}$ 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

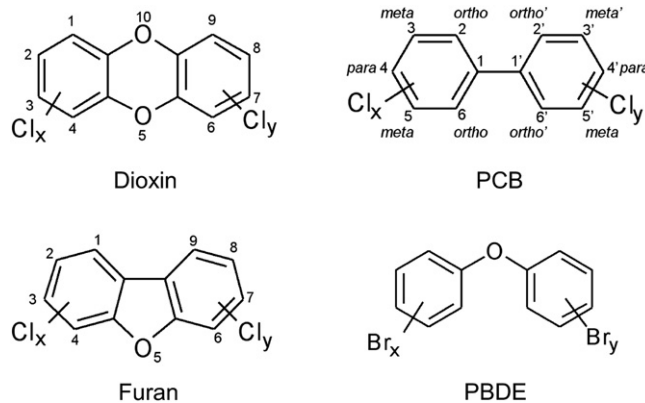


Fig. 3. General structural formula of dioxin, furan, PCB and PBDE.

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; Cabrerizo 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 Antarctica 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 concentration 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 differences 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 (Himberg 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 biomonitors 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; BQL: below quantification limit, x = number of compounds determined.

	Sampling period	Country	Σ _x PCBs	HCB	α-HCH	β-HCH	γ-HCH	δ-HCH	Σ _x HCH	p,p'-DDE	p,p'-DDT	p,p'-DDD	Σ _x DDT	PCBz
Carlberg et al. (1983)	1979	Norway	10–35	0.4–22	9–49		3–43			0.1–1.4	0.4–6.6			
Bacci et al. (1986)		Antarctica	<5–12	0.30–0.68						0.17–0.53				
Focardi et al. (1991)		Antarctica	<5–16 (x = 21)	0.3–0.8	0.2–1.1		0.4–1.7			0.2–0.5	0.2–0.5			
Knulst et al. (1995)	1990–1991	Sweden	13.27 2–28 (x = 7)	0.4–1.7										
Lead et al. (1996)	1977–1990	Norway	6.1–52.1 (x = 37)											
Holoubek et al. (2000)	1988–1994	Czech Republic	0.44 <0.3–1.1 (x = 3)	<0.1–18	<0.1–3.8	<0.1	1.28	<0.3		0.15	1.14			
Borghini et al. (2005)	1999	Antarctica	23–34 (x = 21)	0.85–1.9	0.43–4.0		0.18–1.6			1.1–7.9	0.54–0.91			1.0–2.4
Lim et al. (2006)	2004	Singapore	31–69 (x = 40)		0.65 BQL-1.78	21.19 BQL-22.57	BQL BQL	0.574 BQL-1.53		1.86 BQL-1.56	2.08 BQL-1.56	2.08 BQL-1.96		
Holoubek et al. (2007)	1996–2005	Czech Republic	7.1 0.87–20 (x = 7)	2.7 BQL-47					4.6				2.2	
Cipro et al. (2011)	2004–2005	Antarctica	7.76–18.6 (x = 51)	0.141–1.06										BQL-7.2 (x = 3) BQL-1.73 (x = 6)
Cabrerizo et al. (2012)	2005–2009	Antarctica	0.04–0.76 (x = 38)	0.021–0.12						0.005–0.04				

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 a 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. uncinata* and Cipro et al. (2011) reported levels from 146 to 811 pg g^{-1} (for 36 compounds) in three moss species including *S. uncinata*. 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 $\mu\text{g g}^{-1}$ 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 biomonitors of POPs at a regional scale (Harmens et al., 2011a). To further establish the suitability of mosses as biomonitors 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 European 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.

Acknowledgements

We thank the United Kingdom Department for Environment, Food and Rural Affairs (Defra; contract AQ0816), the UNECE (Trust

Fund) and the Natural Environment Research Council (NERC) for funding the ICP Vegetation Programme Coordination Centre at CEH Bangor, UK.

References

- Allen, J.O., Dookeran, N.M., Smith, K.A., Sarofim, A.F., Taghizadeh, K., Lafleur, A.L., 1996. Measurement of polycyclic aromatic hydrocarbons associated with size-segregated atmospheric aerosols in Massachusetts. *Environmental Science and Technology* 30, 1023–1031.
- Amigo, J.M., Ratola, N., Alves, A., 2011. Study of geographical trends of polycyclic aromatic hydrocarbons using pine needles. *Atmospheric Environment* 45, 5988–5996.
- Ares, A., Aboal, J.R., Fernández, J.A., Real, C., Carballeira, A., 2009. Use of the terrestrial moss *Pseudoscleropodium purum* to detect sources of small scale contamination by PAHs. *Atmospheric Environment* 43, 5501–5509.
- Augusto, S., Máguas, C., Matos, J., Pereira, M.J., Branquinho, C., 2010. Lichens as an integrating tool for monitoring PAH atmospheric deposition: a comparison with soil, air and pine needles. *Environmental Pollution* 158, 483–489.
- Bacci, E., Calamari, D., Gaggi, C., Fanelli, R., Focardi, S., Morosini, M., 1986. Chlorinated hydrocarbons in lichen and moss samples from the Antarctic Peninsula. *Chemosphere* 15, 747–754.
- Baek, S.O., Goldstone, M.E., Kirk, P.W.W., Lester, J.N., Perry, R., 1991. Phase distribution and particle size dependency of polycyclic aromatic hydrocarbons in the urban atmosphere. *Chemosphere* 22, 503–520.
- Belpomme, D., Irigaray, P., Hardell, L., Clapp, R., Montagnier, L., Epstein, S., Sasco, A.J., 2007. The multitude and diversity of environmental carcinogens – review. *Environmental Research* 105, 414–429.
- Beychok, M.R., 1987. A data base for dioxin and furan emissions from refuse incinerators. *Atmospheric Environment* 21, 29–36.
- Blasco, M., Domeno, C., Lopez, P., Nerin, C., 2011. Behaviour of different lichen species as biomonitors of air pollution by PAHs in natural ecosystems. *Journal of Environmental Monitoring* 13, 2588–2596.
- Borghini, F., Grimalt, J.O., Sanchez-Hernandez, J.C., Bargagli, R., 2005. Organochlorine pollutants in soils and mosses from Victoria Land (Antarctica). *Chemosphere* 58, 271–278.
- Breivik, K., Vestreng, V., Rozovskaya, O., Pacyna, J.M., 2006. Atmospheric emissions of some POPs in Europe: a discussion of existing inventories and data needs. *Environmental Science and Policy* 9, 663–674.
- Brorström-Lundén, E., Löfgren, C., 1998. Atmospheric fluxes of persistent semi-volatile organic pollutants to a forest ecological system at the Swedish west coast and accumulation in spruce needles. *Environmental Pollution* 102, 139–149.
- Burton, M.A.S., 1990. Terrestrial and aquatic bryophytes as monitors of environmental contaminants in urban and industrial habitats. *Botanical Journal of the Linnean Society* 104, 267–280.
- Cabrero, A., Dachs, J., Barceló, D., Jones, K.C., 2012. Influence of organic matter content and human activities on the occurrence of organic pollutants in Antarctic soils, lichens, grass, and mosses. *Environmental Science and Technology* 46, 1396–1405.
- Carballeira, A., Fernandez, J.A., Aboal, J.R., Real, C., Couto, J.A., 2006. Moss: a powerful tool for dioxin monitoring. *Atmospheric Environment* 40, 5776–5786.
- Carlberg, G.E., Ofstad, E.B., Drangsholt, H., Steinnes, E., 1983. Atmospheric deposition of organic micropollutants in Norway studied by means of moss and lichen analysis. *Chemosphere* 12, 341–356.
- Chen, L., Zhang, Y., Liu, B., 2010. In situ simultaneous determination of the photolysis of multi-component PAHs adsorbed on the leaf surfaces of living *Kandelia candel* seedlings. *Talanta* 83, 324–331.
- Cipro, C.V.Z., Yogui, G.T., Bustamante, P., Taniguchi, S., Sericano, J.L., Montone, R.C., 2011. Organic pollutants and their correlation with stable isotopes in vegetation from King George Island, Antarctica. *Chemosphere* 85, 393–398.
- De Nicola, F., Claudia, L., MariaVittoria, P., Giulia, M., Anna, A., 2011. Biomonitoring of PAHs by using *Quercus ilex* leaves: source diagnostic and toxicity assessment. *Atmospheric Environment* 45, 1428–1433.
- Domeño, C., Canellas, E., Alfaro, P., Rodríguez-Lafuente, A., Nerin, C., 2012. Atmospheric pressure gas chromatography with quadrupole time of flight mass spectrometry for simultaneous detection and quantification of polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons in mosses. *Journal of Chromatography A* 1252, 146–154.
- Dolęgowska, S., Migaszewski, Z.M., 2011. PAH concentrations in the moss species *Hylocomium splendens* (Hedw.) B.S.G. and *Pleurozium schreberi* (Brid.) Mitt. from the Kielce area (south-central Poland). *Ecotoxicology and Environmental Safety* 74, 1636–1644.
- EU, 2004. Directive 2004/107/EC of the European parliament and of the council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. *Official Journal L* 023, 3–16. 26/01/2005.
- Foan, L., 2012. Biomonitoring Atmospheric Deposition of Polycyclic Aromatic Hydrocarbons (PAHs) with Bryophytes at Various Spatial and Temporal Scales (in French). PhD thesis, Institut National Polytechnique de Toulouse, Université de Toulouse, France.
- Foan, L., Simon, V., 2012. Optimization of pressurized liquid extraction using a multivariate chemometric approach and comparison of solid-phase extraction

- cleanup steps for the determination of polycyclic aromatic hydrocarbons in mosses. *Journal of Chromatography A* 1256, 22–31.
- Foan, L., Sablayrolles, C., Elustondo, D., Laceras, E., González, L., Hederá, A., Simon, V., Santamaría, J.M., 2010. Deconstructing historical trends of polycyclic aromatic hydrocarbon deposition in a remote area of Spain using herbarium moss material. *Atmospheric Environment* 44, 3207–3214.
- Focardi, S., Gaggi, C., Chemello, G., Bacci, E., 1991. Organochlorine residues in moss and lichen samples from two Antarctic areas. *Polar Record* 27, 241–244.
- Garrec, J.P., Van Haluwyn, C., 2002. Air Quality Biomonitoring with Plants – Concepts, Methods and Applications (in French). Lavoisier, Paris.
- Gatuszka, A., 2000. Toxic organic compounds in the environment. *Przegląd Geologiczny* 48, 3681–3688.
- Gatuszka, A., 2007. Distribution patterns of PAHs and trace elements in mosses *Hylocomium splendens* (Hedw.) B.S.G. and *Pleurozium schreberi* (Brid.) Mitt. from different forest communities: a case study, south-central Poland. *Chemosphere* 67, 1415–1422.
- Gerdol, R., Bragazza, L., Marchesini, R., Medici, A., Pedrini, P., Benedetti, S., Bovolenta, A., Coppi, S., 2002. Use of moss (*Tortula muralis* Hedw.) for monitoring organic and inorganic air pollution in urban and rural sites in northern Italy. *Atmospheric Environment* 36, 4069–4075.
- Guidotti, M., Stella, D., Owczarek, M., De Marco, A., De Simone, C., 2003. Lichens as polycyclic aromatic hydrocarbon bioaccumulators used in atmospheric pollution studies. *Journal of Chromatography A* 985, 185–190.
- Gusev, A., Dutchak, S., Rozovskaya, O., Shatalov, V., Sokovykh, V., Vulykh, N., Aas, W., Breivik, K., 2011. Persistent Organic Pollutants in the Environment. EMEP Status Report 3/2011.
- Harmens, H., Norris, D.A., Steinnes, E., Kubin, E., Piispanen, J., Alber, R., Aleksiyenak, Y., Blum, O., Coşkun, M., Dam, M., De Temmerman, L., Fernández, J.A., Frolova, M., Frontasyeva, M., González-Miqueo, L., Grodzińska, K., Jeran, Z., Korzekwa, S., Krmar, M., Kvietskus, K., Leblond, S., Liiv, S., Magnússon, S.H., Maňkóvská, B., Pesch, R., Rühling, A., Santamaría, J.M., Schröder, W., Spiric, Z., Suchara, I., Thöni, L., Urumov, V., Yurukova, L., Zechmeister, H.G., 2010. Mosses as biomonitors of atmospheric heavy metal deposition: spatial and temporal trends in Europe. *Environmental Pollution* 158, 3144–3156.
- Harmens, H., Mills, G., Hayes, F., Norris, D., the participants of the ICP Vegetation, 2011a. Air Pollution and Vegetation. ICP Vegetation Annual Report 2010/2011, ISBN 978-1-906698-26-3.
- Harmens, H., Norris, D.A., Cooper, D.M., Mills, G., Steinnes, E., Kubin, E., Thöni, L., Aboal, J.R., Alber, R., Carballreira, A., Coskun, M., De Temmerman, L., Frolova, M., Frontasyeva, M., González-Miqueo, L., Jeran, Z., Leblond, S., Liiv, S., Maňkóvská, B., Pesch, R., Poikolainen, J., Rühling, A., Santamaría, J.M., Simonè, P., Schröder, W., Suchara, I., Yurukova, L., Zechmeister, H.G., 2011b. Nitrogen concentrations in mosses indicate the spatial distribution of atmospheric nitrogen deposition in Europe. *Environmental Pollution* 159, 2852–2860.
- Harmens, H., Ilyin, I., Mills, G., Aboal, J.R., Alber, R., Blum, O., Coşkun, M., De Temmerman, L., Fernández, J.A., Figueira, R., Frontasyeva, M., Godzik, B., Goltsova, N., Jeran, Z., Korzekwa, S., Kubin, E., Kvietskus, K., Leblond, S., Liiv, S., Magnússon, S.H., Maňkóvská, B., Nikodemus, O., Pesch, R., Poikolainen, J., Radnović, D., Rühling, A., Santamaría, J.M., Schröder, W., Spiric, Z., Staflov, T., Steinnes, E., Suchara, I., Tabor, G., Thöni, L., Turcsányi, G., Yurukova, L., Zechmeister, H.G., 2012. Country-specific correlations across Europe between modelled atmospheric cadmium and lead deposition and concentrations in mosses. *Environmental Pollution* 166, 1–9.
- Himberg, K.K., Pakarinen, P., 1994. Atmospheric PCB deposition in Finland during 1970s and 1980s on the basis of concentrations in ombrotrophic peat mosses (*Sphagnum*). *Chemosphere* 29, 431–440.
- Holoubek, I., Korinek, P., Seda, Z., Schneiderova, E., Holoubkova, I., Pacl, A., Triska, J., Cudlin, P., Caslavsky, J., 2000. The use of mosses and pine needles to detect persistent organic pollutants at local and regional scales. *Environmental Pollution* 109, 283–292.
- Holoubek, I., Klánová, J., Jarkovský, J., Kohoutek, J., 2007. Trends in background levels of persistent organic pollutants at Kosetice observatory, Czech Republic – part II. Aquatic air and terrestrial environments 1996–2005. *Journal of Environmental Monitoring* 9, 564–571.
- Holy, M., Pesch, R., Schröder, W., Harmens, H., Ilyin, I., Alber, R., Aleksiyenak, Y., Blum, O., Coşkun, M., Dam, M., De Temmerman, L., Fedorets, N., Figueira, R., Frolova, M., Frontasyeva, M., Goltsova, N., González Miqueo, L., Grodzińska, K., Jeran, Z., Korzekwa, S., Krmar, M., Kubin, E., Kvietskus, K., Larsen, M., Leblond, S., Liiv, S., Magnússon, S., Maňkóvská, B., Mocanu, R., Piispanen, J., Rühling, A., Santamaría, J., Steinnes, E., Suchara, I., Thöni, L., Turcsányi, G., Urumov, V., Wolterbeek, H.T., Yurukova, L., Zechmeister, H.G., 2010. First thorough identification of factors associated with Cd, Hg and Pb concentrations in mosses sampled in the European Surveys 1990, 1995, 2000 and 2005. *Journal of Atmospheric Chemistry* 63, 109–124.
- Howsam, M., Jones, K.C., Ineson, P., 2000. PAHs associated with the leaves of three deciduous tree species. I – concentrations and profiles. *Environmental Pollution* 108, 413–424.
- ICP Waters, 2005. Concentrations and Levels of POPs from Long-range Transboundary Air Pollution in Freshwater Fish and Sediment. International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters) Report 79/2005.
- Jones, K.C., De Voogt, P., 1999. Persistent organic pollutants (POPs): state of the science. *Environmental Pollution* 100, 209–221.
- Jouraeva, V.A., Johnson, D.L., Hassetta, J.P., Nowak, D.J., 2002. Differences in accumulation of PAHs and metals on the leaves of *Tilia euchlora* and *Pyrus calleryana*. *Environmental Pollution* 120, 331–338.
- Kiss, G., Varga-Puchony, Z., Rohrbacher, G.B., Hlavay, J.Z., 1998. Distribution of polycyclic aromatic hydrocarbons on atmospheric aerosol particles of different sizes. *Atmospheric Research* 46, 253–261.
- Klánová, J., Cupr, P., Baráková, D., Seda, Z., Andel, P., Holoubek, I., 2009. Can pine needles indicate trends in the air pollution levels at remote sites? *Environmental Pollution* 157, 3248–3254.
- Knulst, J.C., Olle Westling, H., Brorström-Lundén, E., 1995. Airborne organic micropollutant concentrations in mosses and humus as indicators for local versus long-range sources. *Environmental Monitoring and Assessment* 36, 75–91.
- Krommer, V., Zechmeister, H.G., Roder, I., Scharf, S., Hanus-Ilmar, A., 2007. Monitoring atmospheric pollutants in the biosphere reserve Wienerwald by a combined approach of biomonitoring methods and technical measurements. *Chemosphere* 67, 1956–1966.
- Lead, W., Steinnes, E., Jones, K., 1996. Atmospheric deposition of PCBs to moss (*Hylocomium splendens*) in Norway between 1977 and 1990. *Environmental Science and Technology* 30, 524–530.
- Lehndorff, E., Schwark, L., 2009a. Biomonitoring airborne parent and alkylated three-ring PAHs in the Greater Cologne Conurbation. I: temporal accumulation patterns. *Environmental Pollution* 157, 1323–1331.
- Lehndorff, E., Schwark, L., 2009b. Biomonitoring airborne parent and alkylated three-ring PAHs in the Greater Cologne Conurbation. II: regional distribution patterns. *Environmental Pollution* 157, 1706–1713.
- Leipe, T., Kersten, M., Heise, S., Pohl, C., Witt, G., Liehr, G., Zettler, M., Tauber, F., 2005. Ecotoxicity assessment of natural attenuation effects at a historical dumping site in the western Baltic Sea. *Marine Pollution Bulletin* 50, 446–459.
- Lim, T.B., Xu, R., Tan, B., Obbard, J.P., 2006. Persistent organic pollutants in moss as bioindicators of atmospheric pollution in Singapore. *Chemosphere* 64, 596–602.
- LRTAP Convention, 1998. Protocol to the 1979 Convention on Long-range Transboundary Air Pollution on Persistent Organic Pollutants. <http://www.unece.org/env/lrtap/>.
- Mariussen, E., Steinnes, E., Breivik, K., Nygård, T., Schlabach, M., Kálás, J.A., 2008. Spatial patterns of polybrominated diphenyl ethers (PBDEs) in mosses, herbivores and a carnivore from the Norwegian terrestrial biota. *Science of the Total Environment* 404, 162–170.
- Migaszewski, Z.M., Gatuszka, A., Pastawski, P., 2002. Polynuclear aromatic hydrocarbons, phenols and trace metals in selected soil profiles and plant bio-indicators in the Holy Cross Mountains, south-central Poland. *Environment International* 28, 303–313.
- Migaszewski, Z.M., Gatuszka, A., Crock, J.G., Lamothe, P.J., Dołęgowska, S., 2009. Interspecies and interregional comparisons of the chemistry of PAHs and trace elements in mosses *Hylocomium splendens* (Hedw.) B.S.G. and *Pleurozium schreberi* (Brid.) Mitt. from Poland and Alaska. *Atmospheric Environment* 43, 1464–1473.
- Milukaite, A., 1998. Flux of benzo(a)pyrene to the ground surface and its distribution in the ecosystem. *Water, Air and Soil Pollution* 105, 471–480.
- Müller, J.F., Hawker, D.W., McLachlan, M.S., Connell, D.W., 2001. PAHs, PCDD/Fs, PCBs and HCB in leaves from Brisbane, Australia. *Chemosphere* 43, 507–515.
- Oguntimohin, I., Nakatani, N., Sakugawa, H., 2008. Phytotoxicities of fluoranthene and phenanthrene deposited on needle surfaces of the evergreen conifer, Japanese red pine (*Pinus densiflora* Sieb. et Zucc. *Environmental Pollution* 154, 264–271.
- Orliński, R., 2002. Multipoint moss passive samplers assessment of urban airborne polycyclic aromatic hydrocarbons: concentrations profile and distribution along Warsaw main streets. *Chemosphere* 48, 181–186.
- Ötvös, E., Kozák, I.O., Fekete, J., Sharma, V.K., Tuba, Z., 2004. Atmospheric deposition of polycyclic aromatic hydrocarbons (PAHs) in mosses (*Hypnum cupressiforme*) in Hungary. *Science of the Total Environment* 330, 89–99.
- Paterson, S., MacKay, D., Tam, D., Shiu, W.Y., 1990. Uptake of organic chemicals by plants: a review of processes, correlations and models. *Chemosphere* 21, 297–331.
- Piccardo, M.T., Pala, M., Bonaccorso, B., Stella, A., Redaelli, A., Paola, G., Valerio, F., 2005. *Pinus nigra* and *Pinus pinaster* needles as passive samplers of polycyclic aromatic hydrocarbons. *Environmental Pollution* 133, 293–301.
- Prajapati, S.K., Tripathi, B.D., 2008. Biomonitoring seasonal variation of urban air polycyclic aromatic hydrocarbons (PAHs) using *Ficus benghalensis* leaves. *Environmental Pollution* 151, 543–548.
- Prevedouros, K., Jones, K.C., Sweetman, A.J., 2004. Estimation of the production, consumption, and atmospheric emissions of pentabrominated diphenyl ether in Europe between 1970 and 2000. *Environmental Science and Technology* 38, 3224–3231.
- Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmospheric Environment* 42, 2895–2921.
- Schröder, W., Holy, M., Pesch, R., Harmens, H., Fagerli, H., Alber, R., Coşkun, M., De Temmerman, L., Frolova, M., González-Miqueo, L., Jeran, Z., Kubin, E., Leblond, S., Liiv, S., Maňkóvská, B., Piispanen, J., Santamaría, J.M., Simonè, P., Suchara, I., Yurukova, L., Thöni, L., Zechmeister, H.G., 2010a. First Europe-wide correlation analysis identifying factors best explaining the total nitrogen concentration in mosses. *Atmospheric Environment* 44, 3485–3491.

- Schröder, W., Holy, M., Pesch, R., Harmens, H., Ilyin, I., Steinnes, E., Alber, R., Aleksiyayev, Y., Blum, O., Coşkun, M., Dam, M., De Temmerman, L., Frolova, M., Frontasyeva, M., González-Miqueo, L., Grodzińska, K., Jeran, Z., Korzekwa, S., Krmar, M., Kubin, E., Kvietskus, K., Leblond, S., Liiv, S., Magnússon, S., Maňkiovská, B., Piispanen, J., Rühling, Å., Santamaria, J., Spiric, Z., Suchara, I., Thöni, L., Urumov, V., Yurukova, L., Zechmeister, H.G., 2010b. Are cadmium, lead and mercury concentrations in mosses across Europe primarily determined by atmospheric deposition of these metals? *Journal of Soils and Sediments* 10, 1572–1584.
- Shukla, V., Upreti, D., 2009. Polycyclic aromatic hydrocarbon (PAH) accumulation in lichen *Phaeophyscia hispidula* of DehraDun City, Garhwal Himalayas. *Environmental Monitoring and Assessment* 149, 1–7.
- Simonich, S.L., Hites, R.A., 1994. Importance of vegetation in removing polycyclic aromatic hydrocarbons from the atmosphere. *Nature* 370, 49–51.
- Simonich, S.L., Hites, R.A., 1995. Organic pollutant accumulation in vegetation. *Environmental Science and Technology* 29, 2905–2914.
- Smith, P.N., Cobb, G.P., Godard-Codding, C., Hoff, D., McMurry, S.T., Rainwater, T.R., Reynolds, K.D., 2007. Contaminant exposure in terrestrial vertebrates. *Environmental Pollution* 150, 41–64.
- TFHTAP, 2010. Hemispheric Transport of Air Pollution 2010. Part C: Persistent Organic Pollutants. In: Dutchak, S., Zuber, A. (Eds.), *Air Pollution Studies* No. 19, LRTAP Convention. United Nations.
- Thomas, W., 1984. Statistical models for the accumulation of PAH, chlorinated hydrocarbons and trace metals in epiphytic *Hypnum cupressiforme*. *Water, Air and Soil Pollution* 22, 351–371.
- Thomas, W., 1986. Representativity of mosses as biomonitors for the accumulation of environmental chemicals in plants and soils. *Ecotoxicology and Environmental Safety* 11, 339–346.
- Tian, X., Liu, J., Zhou, G., Peng, P., Wang, X., Wang, C., 2008. Estimation of the annual scavenged amount of polycyclic aromatic hydrocarbons by forests in the Pearl River Delta of Southern China. *Environmental Pollution* 156, 306–315.
- Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. *Environmental Pollution* 162, 110–119.
- US EPA, 1997. Office of Pesticide Programs, List of Chemicals Evaluated for Carcinogenic Potential (Washington, DC, USA).
- Viskari, E.-L., Rekilä, R., Roy, S., Lehto, O., Ruuskanen, J., Karenlampi, L., 1997. Airborne pollutants along a roadside: assessment using snow, analyses and moss bags. *Environmental Pollution* 97, 153–160.
- Wang, D., Chen, J., Xu, Z., Qiao, X., Huang, L., 2005. Disappearance of polycyclic aromatic hydrocarbons sorbed on surfaces of pine [*Pinus thunbergii*] needles under irradiation of sunlight: volatilization and photolysis. *Atmospheric Environment* 39, 4583–4591.
- Wang, Y.Q., Tao, S., Jiao, X.C., Coveney, R.M., Wu, S.P., Xing, B.S., 2008. Polycyclic aromatic hydrocarbons in leaf cuticles and inner tissues of six species of trees in urban Beijing. *Environmental Pollution* 151, 158–164.
- Wania, F., Mackay, D., 1993. Global fractionation and cold condensation of volatility organochlorine compounds in polar regions. *Ambio* 22, 10–18.
- Wegener, J.W.M., Van Schaik, M.J.M., Aiking, H., 1992. Active biomonitoring of polycyclic aromatic hydrocarbons by means of mosses. *Environmental Pollution* 76, 1–15.
- WHO, 2003. Health Risks of Persistent Organic Pollutants from Long-range Transboundary Air Pollution. World Health Organization, Geneva.
- Yogui, G.T., Sericano, J.L., 2008. Polybrominated diphenyl ether flame retardants in lichens and mosses from King George Island, maritime Antarctica. *Chemosphere* 73, 1589–1593.
- Zechmeister, H.G., Dullinger, S., Hohenwallner, D., Riss, A., Hanus-Ilmar, A., Scharf, S., 2006. Pilot study on road traffic emissions (PAHs, heavy metals) measured by using mosses in a tunnel experiment in Vienna, Austria. *Environmental Science and Pollution Research* 13, 398–405.

Glossary

- DDD*: dichlorodiphenyldichloroethane
DDE: dichlorodiphenyldichloroethylene
DDT: dichlorodiphenyltrichloroethane
HCB: hexachlorobenzene
HCH: hexachlorocyclohexane
OC: organochlorine
PAH: polycyclic aromatic hydrocarbon
PBDE: polybrominated diphenyl ether
PCB: polychlorobiphenyl
PCBz: pentachlorobenzene
PCDD: dioxins
PCDF: furans
POP: persistent organic pollutant