Mosses as biomonitors of atmospheric POPs pollution: A review

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Executive summary

Background

Worldwide there is concern at the continuing release of persistent organic pollutants (POPs) into the environment. These chemical substances are transported across international boundaries far from their sources and they persist in the environment, bioaccumulate through the food chain, and pose a risk to human health and the environment. International action has therefore been taken in the form of two international agreements to protect human health and the environment from POPs:

- The Protocol on Persistent Organic Pollutants to the Convention on Long-Range Transboundary Air Pollution (treaty for the UNECE region[1]);
- The Stockholm Convention on Persistent Organic Pollutants (a global treaty).

Regulation (EC) No 850/2004 of the European Parliament on persistent organic pollutants and amending Directive 79/117/EEC1 implement both of these agreements for all of EU member states.

In Europe the emission and deposition of POPs are monitored and modelled by the European Monitoring and Evaluation Programme (EMEP). EMEP has established a model for calculating air concentrations, atmospheric transport and deposition fluxes of selected POPs using emission data as input. In 2009, there were 23 EMEP monitoring sites in total in 17 countries measuring selected POPs for model validation. Mosses adsorb/absorb pollutants and nutrients directly from the air as they not have a root system or cuticle. The accumulation of these substances is aided by the high surface to volume ratio of moss tissue. Mosses are successfully being used to monitor spatial patterns and temporal trends of heavy metals and nitrogen at a high spatial resolution in a cost-effective manner. In this report we review whether mosses can also be applied as biomonitors of POPs.

Aims

- To review current knowledge on the application of mosses as biomonitors of POPs;
- To identify knowledge gaps and make recommendations for future research.

Mosses as biomonitors of POPs

The majority of published studies have focussed on the determination of polycyclic aromatic hydrocarbons (PAHs) in mosses and relative few studies have been conducted on other 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. Few studies have determined temporal trends or have directly related the concentrations in mosses with measured atmospheric concentrations and/or deposition fluxes. Examples in the literature show that mosses are suitable organisms to monitor spatial patterns and temporal trends of atmospheric concentrations and deposition of POPs to vegetation. These examples include PAHs, polychlorobiphenyls (PCBs), dioxins and furans, and polybrominated diphenyl ethers (PBDEs).

In the currently ongoing European moss survey of 2010/11 coordinated by the ICP Vegetation, six countries will determine the concentration of selected POPs (PAHs in particular) in mosses in a pilot study to investigate the suitability of mosses as biomonitors of

[1] United Nations Economic Commission for Europe

POPs at a regional scale. 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 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 to assess the performance of the EMEP model for POPs in a cost-effective manner.

Research recommendations

- To establish the relationship between air concentrations and/or deposition fluxes of POPs and their concentration in mosses, mosses should be sampled near measurement sites for air concentrations and/or deposition fluxes.

- The impacts of factors that might affect such a relationship should be studied in more detail. Such factors might include: different moss species, altitude, amount of precipitation, temperature, seasonality.

- To establish spatial trends in mosses across Europe, bearing in mind the outcome of the above research recommendations, more countries should determine the concentration of various, suitable POPs in mosses as part of the European moss survey.

- To establish temporal trends in mosses across Europe, the POPs survey in mosses should be repeated at regular time intervals, e.g. every five years.

- To assure good quality and comparable data, an inter-laboratory calibration exercise is required to assess the performance of laboratories participating in a European moss survey. In addition, an agreed sampling protocol should be developed.

Contents

1 Introduction

1.1 Aims

- To review current knowledge on the application of mosses as biomonitors of POPs;
- To identify knowledge gaps and make recommendations for future research.

1.2 Background

Worldwide there is concern at the continuing release of persistent organic pollutants (POPs) into the environment. POPs are organic substances that (LRTAP Convention, 1998):

- 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.

POPs are mainly of anthropogenic origin, show weak degradability and consequently are accumulating in the environment across the globe, including remote areas such as the (Ant)Arctica. The combination of resistance to metabolism and lipophilicity ('fat-loving') means that POPs will 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 so absorb the greatest concentrations. Specific effects of POPs can include 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; they can also have developmental effects (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. Oguntimehin et al., 2008; Smith et al., 2007).

Spatial and some temporal trends in the concentration of selected POPs in fish were reviewed by ICP Waters (2005). Recent results indicated 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. There are reasons to believe, however, that Antarctic organisms might be more susceptible to effects of POPs than temperate organisms, though more research is needed in this area (TFHTAP, 2010). Currently there is little information on long-term trends of POPs concentrations in the environment, food and human media

1.3 International agreements to protect the environment from POPs

The 1998 Aarhus Protocol on POPs of the Convention on Long-range Transboundary Air Pollution (LTRAP) 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.

LRTAP Convention Protocol on Persistent Organic Pollutants

The Executive Body of the LRTAP Convention adopted the Protocol on POPs on 24 June 1998 in Aarhus (Denmark). It 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 (Figure 1, Table 1). The ultimate objective is to eliminate any discharges, emissions and losses of POPs. The 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 (DDT, heptachlor, hexaclorobenzene, PCBs). Finally, the Protocol severely restricts the use of DDT, HCH (including lindane) and PCBs. The Protocol includes provisions for dealing with the wastes of products that will be banned. It also obliges Parties to reduce their emissions of dioxins, furans, 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.

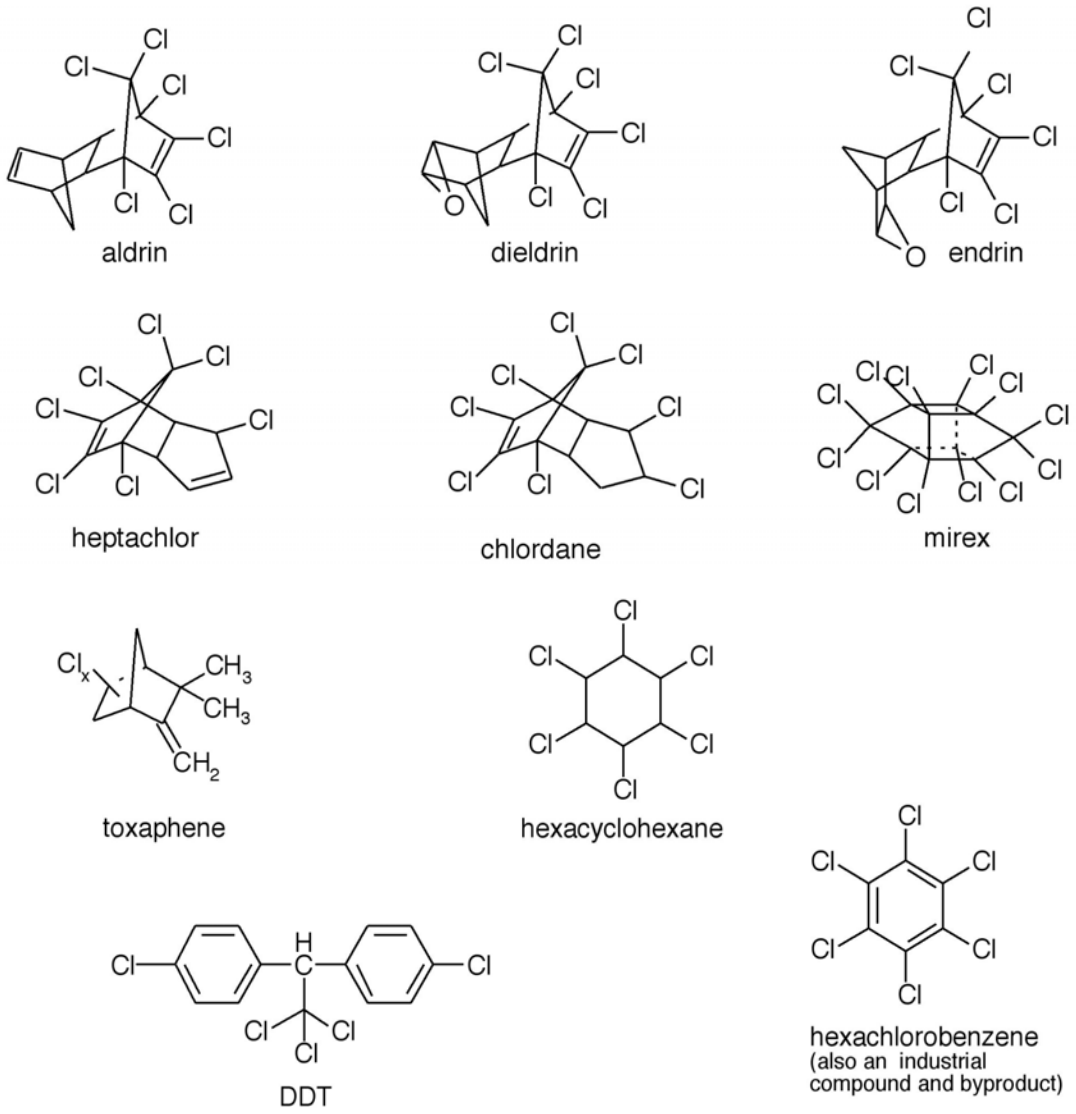

Figure 1. Structural formulas of selected chlororganic pesticides.

The Protocol entered into force on 23 October 2003 and has been signed by 30 Parties to the LRTAP Convention. On 18 December 2009, seven new substances were included in the Protocol (Table 1). Furthermore, the obligations for DDT, heptachlor, hexachlorobenzene and PCBs as well as emission limit values from waste incineration were revised. These amendments have not yet entered into force for the Parties that adopted them.

Stockholm Convention on Persistent Organic Pollutants

The text of the Stockholm Convention on POPs was adopted on 22 May 2001, focusing on 12 substances, and entered into force on 17 May 2004. The Convention text was further amended in 2009 to include nine new substances (Table 1). The Stockholm Convention generally includes the same substances as the POPs Protocol of the LRTAP Convention but not all (e.g. it does not include PAHs and hexachlorobutadiene). Another difference is that the Stockholm Convention is a global treaty whereas the LRTAP Convention Protocol is limited to the UNECE region.

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

EU regulations

Regulation (EC) No 850/2004 of the European Parliament and the Council of 29 April 2004 on persistent organic pollutants and amending Directive 79/117/EEC[2] implement both of these agreements for all of EU member states. The EU regulation was implemented in the UK in 2007. The EU Regulation REACH on production and use of chemicals in the European Union entered into force in June 2007. Its purpose is to ensure a high level of protection of human health and the environment. In particular, one of the important objectives of the Regulation is to reduce emissions of substances of very high concern (SVHC) by restriction of use and replacement by less dangerous substances or technologies (TFHTAP, 2010). POPs are a subclass of SVHC. REACH implements the precautionary principle and requires the industry to prove that the substances do not adversely affect human health or the environment before they are allowed on the market. According to the Regulation, chemical substances shall not be manufactured or placed on the market in the European Community unless they have been registered in the European Chemical Agency (ECHA). Within the registration process certain information on a substance should be submitted by the industry. In particular, this includes the information on physical-chemical properties of a substance, its environmental fate properties, its toxicological and ecotoxicological properties, possible harmful effects on human health and the environment, emission estimates, and monitoring data for SVHC.

1.4 Measurements and modelling of air concentrations and deposition of POPs

In Europe the emission and deposition of POPs are monitored and modelled by the European Monitoring and Evaluation Programme (EMEP; Gusev et al., 2011). 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, and 13 of them conducted measurements of POP concentrations in both air and precipitation. POPs measured using passive air samplers included pesticides, PAHs, HCHs, HCB and PCBs (Gusev et al., 2011). Most of the recent additions to EMEP were the sites measuring PAHs which is required by the EU air quality directive. The EMEP model calculated elevated levels of contamination by PAHs for Central and Eastern Europe, Portugal and the western part of Spain in 2009. Benzo[a]pyrene (B[a]P) concentrations at EMEP measurement sites for 2009 are shown in Figure 2. Model simulations of benzo[a]pyrene (B[a]P) pollution within the EMEP region showed that transboundary transport was a significant source of pollution for a lot of the EMEP countries contributing between 30% to 70% to total annual deposition. For 25 countries in 2009 its contribution exceeded 50%. Comparison of modelling results and measurements of B[a]P in air for 2009 showed that for most of the sites differences between the modelled and observed concentrations ranged within 10-30%. According to officially submitted data and expert estimates, emissions of four indicator PAHs within the EMEP domain decreased by 30-40% depending on the compound in the period of 1990-2009. Model evaluation of trends in B[a]P pollution levels showed that levels of its annual mean air concentrations declined in this period by about 30% (Gusev et al., 2011).

High uncertainties exist in the modelling of dioxins and furans (PCDD/F) with modelling values underestimating measurement values by a factor 5 on average. Different level of underestimation for different congeners indicated that there are essential uncertainties in

[2] Available at http://eur-lex.europa.eu/LexUriServ/site/en/oj/2004/l_229/l_22920040629en00050022.pdf

determination of congener composition of PCDD/F emissions. The reasons for model underestimation of air concentrations and deposition fluxes are both uncertainties of emission totals and uncertainties in evaluation of congener composition of emissions. In addition, uncertainties in measuring PCCD/F were observed with large inter-laboratory differences. In comparison with PAHs and PCDD/Fs, evaluation of HCB pollution levels is complicated by more essential uncertainties in information on current sources of HCB release into the environment and historical emissions. Analysis of modelling results on HCB using available measurements of air concentrations revealed that model predictions underestimated observed pollution levels. This underestimation can be related to the incompleteness of available officially submitted emission data and expert estimates as well as with the underestimation of the role of secondary emission sources. Re-volatilization of HCB from environmental compartments can contribute significantly to the contemporary pollution levels. To evaluate HCB re-emissions elaboration of scenarios of historical HCB emissions is required. The environmental levels of lindane (γ-HCH) have been significantly decreased within the European region during two recent decades due to the reduction of its application. Reduced influence of primary γ-HCH emission sources increase the importance of the contributions of secondary emissions and intercontinental transport to the contamination of the EMEP region (Shatalov et al., 2010).

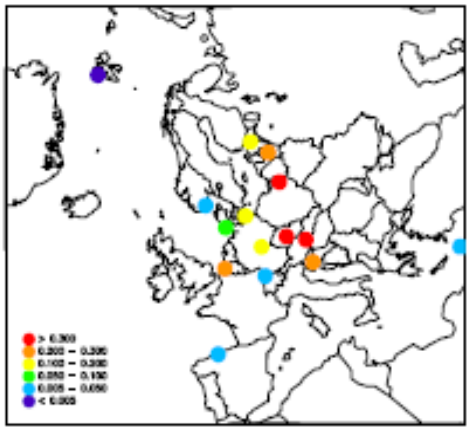

Figure 2. Spatial distribution of the annual average concentrations (ng m^{-3}) of B[a]P in 2009 at EMEP measurement sites (Gusev et al., 2011).

Analysis of sensitivity of POP pollution levels to variation of meteorological and environmental factors showed that factors such as temperature, precipitation amount, wind speed and direction, outflow of air masses through the country boundaries, and vegetation cover, can in most cases explain 90–95% of seasonal variability of chemicals air concentrations for a country. The effect of changes of meteorological and environmental conditions can be different for different POPs due to wide range of variations of their physical-chemical properties. Besides, the sensitivity of POP pollution levels to variations of meteorological and environmental parameters varies within the EMEP region which can lead to varied response to the climatic changes across Europe.

2 Mosses as biomonitors of POPs

2.1 Introduction

As mosses do not have a root system or cuticle, they adsorb/absorb nutrients and pollutants from the air, which often accumulate on or in moss tissue. The accumulation is aided by the high surface to volume ratio of moss tissue. The 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, 2011). 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 and remobilised from senescing tissue (in contrast to the non-essential heavy metals cadmium, lead and mercury). In Switzerland, a high correlation (r^2 = 0.91) was found between site-specific measurements of bulk nitrogen deposition and the total nitrogen concentration in mosses, confirming the potential to use mosses as biomonitors of nitrogen deposition at a high spatial resolution (Harmens et al., 2011).

Although mosses have also been used to monitor POPs pollution, the number of studies is limited and most studies have focussed on PAHs. In this chapter we review the application of mosses as monitors of POPs pollution.

2.2 PAHs pollution and biomonitoring with mosses

PAHs are a family of chemical compounds constituted by carbon and hydrogen atoms which form at least two condensed aromatic rings (Figure 3). The majority of PAHs originate from fossil or non-fossil fuels by pyrolysis or pyrosynthesis. PAHs are emitted in the atmosphere mainly from anthropogenic source 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; Wegener et al., 1992). Eight PAHs have been classified by 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(g,h,i)perylene). Some PAHs also are mutagenic, teratogenic, immunosuppressive and/or neurotoxic (Gałuszka, 2000). They are all listed in the European lists of priority pollutants. However, 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 PM10, the atmospheric suspended particles of diameter under 10 µm).

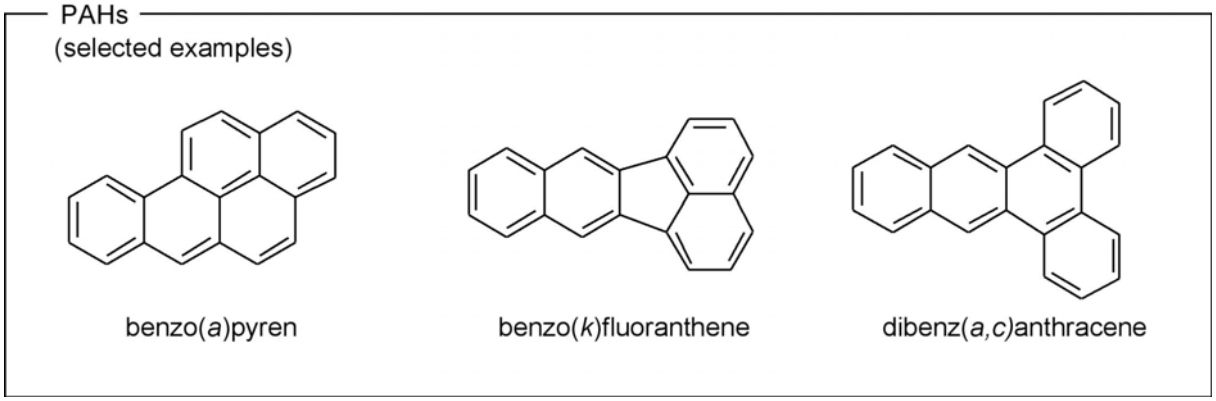

Figure 3. Structural formulas of selected PAHs.

The mechanism of uptake of organic pollutants by vegetation is governed by the chemical and physical properties of the pollutant (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, the most volatile PAHs remain in gaseous phase whereas the least volatile (5 or 6 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 for example higher ambient temperatures. PAHs of intermediate volatility (3 or 4 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 pollution sources are dominated by smaller ring numbers of 3 or 4 (Dołęgowska and Migaszewski, in press; Gałuszka, 2007; Migaszewski et al., 2009; Orliński, 2002). Table 2 provides an overview of the concentrations measured in various mosses sampled in rural environments away from pollution sources. 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 3 ring compounds appears to be related to the type of pollution source as are the dominance of individual PAHs (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; see Table 2). In Hungary, a good correlation between total PAHs concentrations in *Hypnum cupressiforme* and traffic volume was observed, but not with population density, with 99% of the total PAHs concentration in the moss consisting of low molecular weight (Ötvös et al., 2004).

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 – 100 m from the road. Therefore, studies carried out in remote areas, located at a fair distance from emission sources, provide an indication of background levels of atmospheric PAH contamination due to long-range transboundary air pollution.

Table 2. Average and range (within brackets) of PAH concentrations (ng g^{-1} DW) in mosses sampled in rural areas. LOD = limit of detection.

	Holoubek et al., 2000 Czech Republic		**Migazewski et al., 2002 Poland**		**Zechmeister et al., 2006 Austria**	**Krommer et al., 2007 Austria**		**Galuszka, 2007 Poland**		**Foan et al., 2010 Spain**	
Sampling period	1988-1994		2000		2003	2005		2005		2006-2007	
PAHs analyzed (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)				
Acenaphtene (2)	45.3	(<1 - 1183)	<4		1.8	3.1	(2.1 - 5.7)	2	(<1 - 3)	4.1	(<1.5 - 12.7)
Acenaphtylene (2)	7.8	(<0.5 - 163)	5	(4 - 6)	< LOD	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)		
Dibenzo*(a,h)*antracene (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 biomonitors of atmospheric PAH deposition.

	Pleurocarpous mosses								**Acrocarpous mosses**	
	Abietinella abietina	*Hylocomium splendens*	*Hypnum cupressiforme*	*Pleurozium schreberi*	*Pseudoscleropodium purum*	*Scleropodium purum*	*Thamnobryum alopecurum*	*Thuidium tamariscinum*	*Dicranum scoparium*	*Tortula muralis*
Knulst et al. (1995)		▲		▲						
Milukaite (1998)		▲		▲						
Gerdol et al. (2002)										▲
Migaszewski et al. (2002)		▲								
Ötvös et al. (2004)			▲							
Gałuszka (2007)		▲		▲						
Holoubek et al. (2000, 2007)			▲							
Krommer et al. (2007)	▲		▲			▲				
Ares et al. (2009)					▲					
Migaszewski et al. (2009)		▲		▲						
Foan et al. (2010)			▲				▲	▲	▲	
Dołęgowska and Migaszewski (in press)		▲		▲						

Many studies on atmospheric pollution (including PAHs) based on moss analysis use pleurocarpous mosses as biomonitors because they generally form broad carpets which almost completely isolate them from the soil. 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 3).

One should take care with comparing concentrations between different moss species and different studies. Bioaccumulation of PAHs in mosses might be species-specific as Gałuszka (2007) and Dołęgowska and Migaszewski (in press) observed a higher accumulation of PAHs in *Hylocomium splendens* than *Pleurozium schreberi*. However, Milukaite (1998) reported a similar retention of benzo(a)pyrene in *Hylocomium splendens* and *Pleurozium schreberi*. 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, in particular 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 *Hypnum cupressiforme* sampled from tree trunks and their concentration in rain water and atmospheric particulate matter, taking into account also the amount of precipitation. The concentration in mosses in the autumn represented mean atmospheric pollution levels in the previous year. He 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 parameters which describe physiological parameters as well as pollutant characteristics (Thomas, 1984). In addition, the presence of water from precipitation might be necessary for PAH accumulation in mosses. Thomas (1986) reported on a marked gradient of the concentration of selected PAHs in mosses in western-northern Europe in agreement with the presence of pollution sources.

Vegetation intercepts 26-62% of the atmospheric PAH deposition (Simonich and Hites, 1994). In addition to mosses, other main bioaccumulators used to date for monitoring atmospheric PAH deposition are lichens (Guidotti et al., 2003; Migaszewski et al., 2002; Blasco et al., 2008), leaves from deciduous trees (Howsam et al., 2000; Jouraeva et al., 2002; Wang et al., 2008; Tian et al., 2008) and conifer needles (Holoubek et al., 2000, 2007b; Migaszewski et al., 2002; Piccardo et al., 2005; Lehndorff and Schwark, 2009a,b; Tian et al., 2008).

Temporal trends of PAHs in mosses

Only a few studies have reported on the 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 PAHs 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, explain the significant decline of PAHs in mosses over that period at a remote site in northern Spain. 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. Holoubek et al. (2000, 2007) observed a significant decrease in total PAH concentrations in mosses between 1988-1994 and 1996-2005. The small decline in the period 1996-2005 reflected the small decline in PAHs in air (Houlebek et al., 2007).

2.3 **Biomonitoring of POPs other than PAHs**

Mosses have also been sampled to indicate the levels of atmospheric pollution from POPs other than PAHs, although the number of studies for each POP is limited. For these POPs, no attempts have been made so far to relate the concentration in mosses with atmospheric concentrations or deposition fluxes.

Organochlorines (OCs): pentachlorobenzene (PCBz), dichlorodiphenyltrichloroethane (DDT) hexachlorobenzene (HCB), hexachlorocyclo-hexanes (HCHs) and polychlorobiphenyls (PCBs)

Chlorinated hydrocarbons were present in measurable concentrations in mosses in the Antarctica (Bacci et al., 1986). 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 the Antarctica when compared to plant data in 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 (Figure 4) were near or below the detection 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), with all OCs being distributed rather uniformly. 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 derivates 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 *Hylocomium splendens* had 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 heptachlorinated 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, PCBs concentrations in *Sphagnum* have shown a consistent decline from the 1970s to 1980s. Higher total PCB concentrations were observed in the south compared to the north of Finland (Himberg and Pakarinen, 1994).

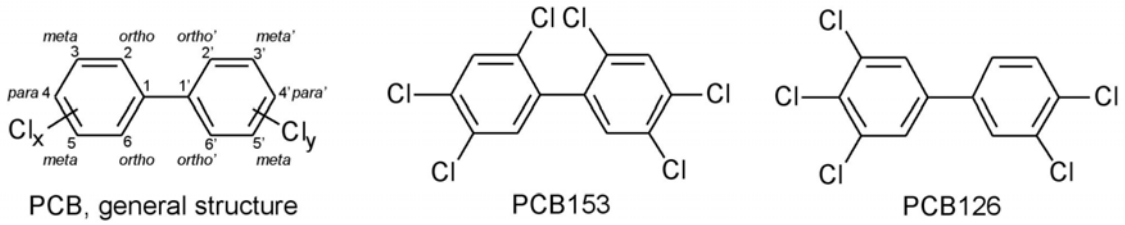

Figure 4. Structural formulas of PCBs.

Dioxins and furans (PCDD/Fs)

Carballeira et al. (2006) concluded that mosses are also good biomonitors for PCDD/Fs (Figure 5). Concentrations of PCDD/F in *Pseudoscleropodium purum* allowed the detection of strong and weak pollution sources. The measurements were sensitive enough 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.

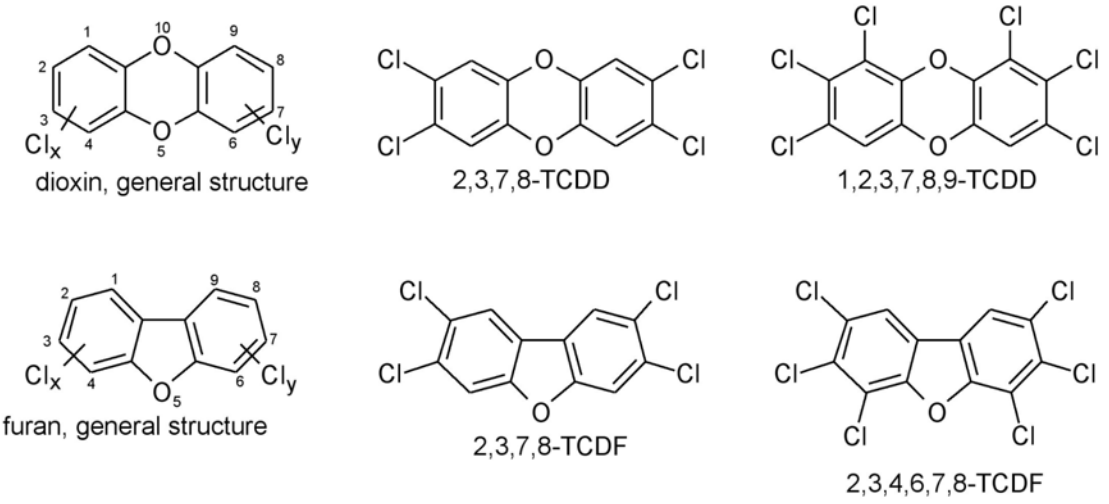

Figure 5. Structural formulas of dioxins and furans (PCDD/Fs).

Polybrominated diphenyl ethers (PBDEs)

In Norway, levels of PBDEs (Figure 6) in mosses showed a general decline towards the northern parts. 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, expected source regions on a European scale (Prevedouros et al., 2004) and results from other investigations. The PBDE levels in Norway were low and are probably of limited toxicological significance (Mariussen et al., 2008). PBDEs were also detected at low levels in mosses sampled on King George Island, Antartica. 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 (Yogui and Sericano, 2008).

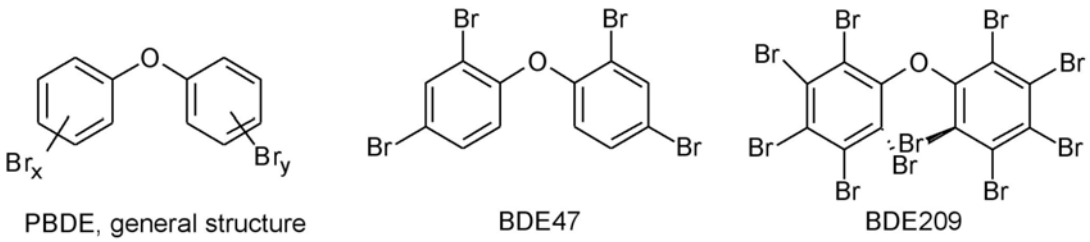

Figure 6. Structural formulas of polybrominated diphenyl ethers (PBDEs).

3 Conclusions and research recommendations

3.1 Conclusions

As for many other air pollutants such as heavy metals and nitrogen (Harmens et al., 2010, 2011), mosses appear to be suitable organisms to monitor spatial patterns and temporal trends of the atmospheric concentrations and deposition of POPs to vegetation. 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. Few studies have determined temporal trends or have directly related the concentrations in mosses with measured atmospheric concentrations in rain water or snow (wet deposition) or in particulate matter (dry deposition). The majority of studies have focussed on PAHs and relative few studies have been conducted on other POPs.

In the currently ongoing European moss survey of 2010/11 coordinated by the ICP Vegetation, six countries will determine 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. 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 to assess the performance of the EMEP model for POPs in a cost-effective manner.

3.2 Research recommendations

- To establish the relationship between air concentrations and/or deposition fluxes of POPs and their concentration in mosses, mosses should be sampled near measurement sites for air concentrations and/or deposition fluxes.

- The impacts of factors that might affect such a relationship should be studied in more detail. Such factors might include: different moss species, altitude, amount of precipitation, temperature, seasonality.

- To establish spatial trends in mosses across Europe, bearing in mind the outcome of the above research recommendations, more countries should determine the concentration of various, suitable POPs in mosses as part of the European moss survey.

- To establish temporal trends in mosses across Europe, the POPs survey in mosses should be repeated at regular time intervals, e.g. every five years.

- To assure good quality and comparable data, an inter-laboratory calibration exercise is required to assess the performance of laboratories participating in a European moss survey. In addition, an agreed sampling protocol should be developed.

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