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Contact CEH NORA team at  
[noraceh@ceh.ac.uk](mailto:noraceh@ceh.ac.uk)

1 **Terrestrial mosses as biomonitors of atmospheric POPs pollution: A review**

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3 H. Harmens<sup>1</sup>, L. Foan<sup>2,3</sup>, V. Simon<sup>2,3</sup>, G. Mills<sup>1</sup>

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5 <sup>1</sup> Centre for Ecology and Hydrology, Environment Centre Wales, Deiniol Road, Bangor LL57

6 2UW, UK. [hh@ceh.ac.uk](mailto:hh@ceh.ac.uk); [gmi@ceh.ac.uk](mailto:gmi@ceh.ac.uk)

7 <sup>2</sup> Université de Toulouse, INPT, LCA (Laboratoire de Chimie Agro-Industrielle),

8 ENSIACET, 4 Allée, Emile Monso, BP 44362, F-31030 TOULOUSE Cedex 4, France.

9 [louise.foan@gmail.com](mailto:louise.foan@gmail.com); [valerie.simon@ensiacet.fr](mailto:valerie.simon@ensiacet.fr)

10 <sup>3</sup> INRA; LCA (Laboratoire de Chimie Agro-Industrielle), F-31030 Toulouse, France

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13 \* Corresponding Author: Harry Harmens

14 E-mail address: [hh@ceh.ac.uk](mailto:hh@ceh.ac.uk)

15 Tel.: +44-1248-374512

16 Fax: +44-1248-362133

17

18 **Abstract**

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

31

32 **Capsule:** Mosses are suitable biomonitors of persistent organic pollutants (POPs).

33

34 **Keywords:** biomonitoring; bryophytes; persistent organic pollutants; polycyclic aromatic  
35 hydrocarbons; atmospheric deposition

36

37 **1. Introduction**

38

39 *1.1. Background*

40 Persistent organic pollutants (POPs) are organic substances which are a concern for the  
41 environment and human health as they: possess toxic characteristics; are persistent;  
42 bioaccumulate; are prone to long-range transboundary atmospheric transport and deposition;

43 are likely to cause significant adverse human health or environmental effects near to and  
44 distant from their source (LRTAP Convention, 1998). POPs are mainly of anthropogenic  
45 origin (Breivik et al., 2006), for example from waste incineration, industrial production and  
46 application (e.g. pesticides, flame retardants, coolant fluids) and fossil fuel burning. They  
47 show weak degradability and consequently are accumulating in the environment across the  
48 globe, including in remote areas such as the polar regions. The combination of resistance to  
49 metabolism and lipophilicity ('fat-loving') means that POPs accumulate in food chains (Jones  
50 and de Voogt, 1999). POPs are readily absorbed in fatty tissue, where concentrations can  
51 become magnified by up to 70,000 times the background levels. Fish, predatory birds,  
52 mammals, and humans are high up the food chain and therefore absorb the greatest  
53 concentrations. Specific effects of POPs can include inducing cancer, allergies and  
54 hypersensitivity, damage to the central and peripheral nervous systems, reproductive  
55 disorders, and disruption of the immune system. Some POPs are also considered to be  
56 endocrine disrupters, which, by altering the hormonal system, can damage the reproductive  
57 and immune systems of exposed individuals as well as their offspring and affect development  
58 (Belpomme et al., 2007; Jones and de Voogt, 1999; TFHTAP, 2010; WHO, 2003). Their  
59 ecotoxicity has been highlighted in aquatic (Leipe et al., 2005) and terrestrial ecosystems (e.g.  
60 Oguntimehin et al., 2008; Smith et al., 2007).

61 Spatial and some temporal trends in the concentration of selected POPs in fish were  
62 reviewed by the International Cooperative Programme on Assessment and Monitoring Effects  
63 of Air Pollution on Rivers and Lakes (ICP Waters, 2005). Recent results indicate that  
64 atmospherically transported POPs can impact the health of fish in remote ecosystems and that  
65 they can reach concentrations in fish that exceed health threshold values for consumption by  
66 wildlife and humans (TFHTAP, 2010). However, these impacts and exceedances were not  
67 observed at Alaskan parks where the contaminant load is due solely to long-range

68 atmospheric transport and not influenced strongly by regional sources. There is currently no  
69 strong evidence that Antarctic organisms or ecosystems are being impacted by POPs  
70 associated solely with long-range atmospheric transport. However, bioaccumulation of POPs  
71 with time might result in impacts in the future. There are also reasons to believe that Antarctic  
72 organisms might be more susceptible to effects of POPs than temperate organisms, though  
73 more research is needed in this area (TFHTAP, 2010).

74

#### 75 *1.2. International agreements to protect the environment from POPs pollution*

76 The 1998 Aarhus Protocol on POPs of the Convention on Long-range Transboundary Air  
77 Pollution (LRTAP Convention, 1998) and the 2001 Stockholm Convention on POPs, a global  
78 treaty under the United Nations Environment Programme (UNEP), aim to eliminate and/or  
79 restrict the production and use of selected POPs (Table 1). Originally, the Aarhus Protocol  
80 focused on a list of 16 substances that have been singled out according to agreed risk criteria;  
81 many substances on the list are chlororganic pesticides. The ultimate objective is to eliminate  
82 any discharges, emissions and losses of POPs. The Aarhus Protocol bans the production and  
83 use of some products outright: aldrin, chlordane, chlordecone, dieldrin, endrin,  
84 hexabromobiphenyl, mirex and toxaphene. Others are scheduled for elimination at a later  
85 stage: dichlorodiphenyltrichloroethane (DDT), heptachlor, hexachlorobenzene (HCB) and  
86 polychlorobiphenyls (PCBs). The Aarhus Protocol severely restricts the use of DDT,  
87 hexachlorocyclohexanes (HCHs) (including lindane) and PCBs and it obliges Parties to  
88 reduce their emissions of dioxins (PCDDs), furans (PCDFs), polycyclic aromatic  
89 hydrocarbons (PAHs) and HCB below their levels in 1990 (or an alternative year between  
90 1985 and 1995). For the incineration of municipal, hazardous and medical waste, it lays down  
91 specific limit values. On 18<sup>th</sup> December 2009, seven new substances were included in the  
92 Aarhus Protocol. The Stockholm Convention generally includes the same substances as the

93 Aarhus Protocol but not all, e.g. it does not include PAHs and hexachlorobutadiene. Whilst  
94 the Stockholm Convention is a global treaty, the LRTAP Convention Protocol is limited to  
95 the region of the United Nations Economic Commission for Europe (UNECE), currently 50  
96 countries covering almost all of Europe plus the USA and Canada. The Stockholm  
97 Convention originally focused on 12 substances but was extended in 2009 to include nine new  
98 substances.

99

### 100 *1.3. Monitoring and modelling of air concentrations and deposition of POPs in Europe*

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

112

### 113 *1.4. Mosses as biomonitors of air pollution*

114 As mosses do not have roots, they adsorb/absorb nutrients and pollutants from the air, which  
115 often accumulate on or in their tissue. The accumulation is aided by the high surface to  
116 volume ratio of moss tissue. Monitoring of heavy metal and nitrogen concentrations in  
117 naturally growing mosses allows determination of spatial patterns and temporal trends of

118 heavy metal and nitrogen pollution and deposition at a high spatial resolution in a cost-  
119 effective manner (Harmens et al., 2010, 2011b, 2012). Detailed statistical analysis of the  
120 factors affecting heavy metal concentration in mosses confirmed that EMEP modelled heavy  
121 metal deposition was the main predictor for cadmium and lead concentrations in mosses; this  
122 was not the case for mercury (Holy et al., 2010; Schröder et al., 2010b). The latter might be  
123 related to the specific chemistry of mercury (Harmens et al., 2010). Detailed statistical  
124 analysis of the factors affecting nitrogen concentration in mosses also showed that EMEP  
125 modelled air concentrations of different nitrogen forms and total nitrogen deposition are the  
126 main predictors for the total nitrogen concentrations in mosses (Schröder et al., 2010a),  
127 despite the fact that nitrogen is an essential macronutrient and remobilised from senescing  
128 tissue (in contrast to the non-essential heavy metals cadmium, lead and mercury). Although  
129 mosses have also been used to monitor POPs pollution, the number of studies and the range of  
130 POPs studied is limited. Here we review current knowledge on the application of mosses as  
131 biomonitors of POPs pollution, identify knowledge gaps and make recommendations for  
132 future research.

133

## 134 **2. Mosses as biomonitors of POPs**

135

### 136 *2.1. Polycyclic aromatic hydrocarbons (PAHs)*

137 PAHs are a family of chemical compounds constituted by carbon and hydrogen atoms which  
138 form at least two condensed aromatic rings. The majority of PAHs originate from fossil or  
139 non-fossil fuels by pyrolysis or pyrosynthesis. PAHs are emitted in the atmosphere mainly  
140 from anthropogenic sources but they also originate from natural sources such as volcanic  
141 eruptions and forest fires (Simonich and Hites, 1995). The main sources of PAHs in the  
142 environment are aluminium production, coke production from coal, wood preservation and

143 fossil fuel combustion (traffic, domestic heating, electricity production) (Ravindra et al.,  
144 2008; Tobieszewski and Namiesnik, 2012; Wegener et al., 1992). Eight have been classified  
145 by the US Environmental Protection Agency (US EPA, 1997) as potentially carcinogenic:  
146 benz[a]anthracene, chrysene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene,  
147 dibenzo[a,h]anthracene, indeno[1,2,3-c,d]pyrene and benzo[ghi]perylene. Some PAHs also  
148 are mutagenic, teratogenic, immunosuppressive and/or neurotoxic (Gałuszka, 2000). The US  
149 EPA has listed 16 priority PAHs (out of 32) for monitoring (Figure 1). Although many are  
150 also listed in the European list of priority pollutants, only benzo[a]pyrene is regulated by the  
151 Directive 2004/107/EC (EU, 2004) which sets the maximum atmospheric concentration  
152 acceptable at  $1 \text{ ng m}^{-3}$  (measurement with  $\text{PM}_{10}$ , the atmospheric suspended particles with a  
153 diameter smaller than  $10 \text{ }\mu\text{m}$ ).

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



168 sampled away from local pollution sources are dominated by those with smaller ring numbers  
169 of three or four (Dołęgowska and Migaszewski, 2011; Gałuszka, 2007; Migaszewski et al.,  
170 2009; Orliński, 2002).

171         The high surface to volume ratio of mosses and the lack of a cuticle favour the  
172 deposition of POPs associated with particles to the surface of mosses. The absorption  
173 efficiency of organic molecules associated with the particles depends on the octanol/water  
174 partitioning coefficient of the POP (Garrec and Van Haluwyn, 2002). The majority of PAHs  
175 is associated with particles with a diameter smaller than 2  $\mu\text{m}$  (Allen et al., 1996; Baek et al.,  
176 1991; Kiss et al., 1998). However, the partitioning of PAHs differs in urban and rural samples  
177 (Allen et al., 1996). In urban samples, PAHs were distributed among aerosol size fractions  
178 based on molecular weight. PAHs with molecular weights between 178 and 202 were evenly  
179 distributed between the fine (diameter < 2  $\mu\text{m}$ ) and coarse (diameter > 2  $\mu\text{m}$ ) aerosols. PAHs  
180 with molecular weights greater than 228 were associated primarily with the fine aerosol  
181 fraction. In rural samples, low and high molecular weight PAHs were associated with both the  
182 fine and coarse aerosols. We are not aware of any study showing which particle size  
183 associated with PAHs is preferentially adsorbed by mosses. Little is known about the  
184 persistence and potential for washout of POPs from the surface of mosses. For plants it's  
185 known that organic pollutants can be transferred from the leaf surface to the atmosphere when  
186 the air temperature increases or when atmospheric concentrations are low (Knulst et al.,  
187 1995). Volatilization of PAHs from pine needles was negatively correlated with their  
188 molecular mass (Wang et al., 2005). Furthermore, studies have shown degradation of PAHs  
189 by microflora and sunlight on leaves and needles (Paterson et al., 1990). The latter is both a  
190 function of the molecular mass of PAHs and the chemical properties of the plant tissue (Wang  
191 et al., 2005; Chen et al., 2010).

192 Table 2 provides an overview of published concentrations measured in various mosses  
193 sampled in rural environments away from pollution sources. The average concentration  
194 measured for up to 17 PAHs ranged from ca. 100 to 600 ng g<sup>-1</sup> dry wt. Gerdol et al. (2002)  
195 observed that the fraction of low molecular weight volatile PAHs was greater in rural  
196 compared to urban sites. On the other hand, the dominance of three ring compounds appears  
197 to be related to the type of pollution source (Foan et al., 2010). Phenanthrene, fluoranthene  
198 and pyrene have often been reported as the dominant PAHs in mosses sampled away from  
199 pollution sources (Foan et al, 2010; Gałuszka, 2007; Krommer et al., 2007; Zechmeister et al.,  
200 2006). In Hungary, where 99% of the total PAHs concentration in the moss consists of low  
201 molecular weight, a good correlation between total PAHs concentrations in *Hypnum*  
202 *cupressiforme* Hedw. and traffic volume was observed, but there was no such correlation with  
203 population density (Ötvös et al., 2004). Local and regional emission sources therefore appear  
204 to have a strong influence on PAH levels in mosses. However, long-range transboundary air  
205 pollution also contributes to the contamination of mosses by PAHs, as concentrations of 4.4 to  
206 34 ng g<sup>-1</sup> were measured for 14 compounds in *Sanionia uncinata* at Antarctica (Cabrerizo et  
207 al., 2012).

208 Ares et al. (2009) showed an exponential decay of PAHs levels in mosses around  
209 emission sources. Using moss bags in active biomonitoring of PAHs near a road in Finland,  
210 Viskari et al. (1997) found that downwind of the road the concentrations of most PAHs in  
211 mosses declined to background levels between 60 – 100 m from the road. Therefore, studies  
212 carried out in remote areas, located at a significant distance from emission sources, provide an  
213 indication of background levels of atmospheric PAH contamination due to long-range  
214 transboundary air pollution. Zechmeister et al. (2006) concluded that moss bags are suitable  
215 to monitor PAHs from traffic emissions in tunnels, even better than in the open field because  
216 confounding effects of other sources of pollution and noise in the accumulation process (e.g.

217 washout through wet deposition) are minimised. Many moss analysis studies on atmospheric  
218 pollution (including PAHs) use pleurocarpous mosses as biomonitors because they generally  
219 form broad carpets which almost completely isolate them from the soil (Table 3). However,  
220 pleurocarpous mosses are sensitive to pollution and to dryness, and therefore are rare,  
221 sometimes absent, in urban areas. Thus, acrocarpous mosses, which grow on stone or brick  
222 walls, are used for studying urban environments (Burton, 1990).

223 One should take care with comparing concentrations between different moss species  
224 and different studies. Bioaccumulation of PAHs in mosses might be species-specific as  
225 Gałuszka (2007) and Dołęgowska and Migaszewski (2011) observed a higher accumulation  
226 of PAHs in *Hylocomium splendens* (Hedw.) B.S.G. than *Pleurozium schreberi* (Brid.) Mitt.  
227 However, Milukaite (1998) reported a similar retention of benzo[a]pyrene in both species.  
228 Migaszewski et al. (2009) found that differences in the accumulation of PAHs between the  
229 moss species varied with sampling site and region. Moreover, Ares et al. (2009) noted a  
230 seasonal variability due to changes in emissions and climate throughout the year. They also  
231 observed spatial variability due to the geomorphology of the study area and the presence of  
232 prevailing winds.

233 Most studies so far have determined the concentration of POPs in mosses as an  
234 indication of pollution levels, especially in remote areas. Few studies have related the  
235 concentration in mosses with total atmospheric concentrations or deposition rates. Thomas  
236 (1984, 1986) found linear relationships between the accumulation of selected PAHs in *H.*  
237 *cupressiforme* sampled from tree trunks and their concentration in rain water and atmospheric  
238 particulate matter, taking into account the amount of precipitation. The following linear  
239 relationships were reported for 1980 (Thomas, 1986):

240 Benzo[ghi]perylene:

241 
$$C_1 = 1.62 * C_2 + 259.60 * C_3 + 0.74 * P \text{ (R} = 0.74 \text{ for } n = 15; \text{ P} = 0.002)$$

242 Benzo[a]pyrene:

243 
$$C_1 = 1.31 \cdot C_2 + 180.26 \cdot C_3 + 0.16 \cdot P \text{ (R} = 0.66 \text{ for } n = 15; P = 0.007)$$

244 Fluoranthene:

245 
$$C_1 = 0.33 \cdot C_2 + 26.21 \cdot C_3 + 0.19 \cdot P \text{ (R} = 0.91 \text{ for } n = 15; P < 0.001)$$

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

258 Vegetation intercepts 26-62% of the atmospheric PAH deposition (Simonich and  
259 Hites, 1994). Based on measurements of PAHs in vegetation (sugar maple (*Acer saccharum*)  
260 leaves, seeds and bark; white pine (*Pinus strobus*) needles and bark) from Bloomington,  
261 Indiana, U.S.A., the mass balance model developed by Simonich and Hites (1994) estimated  
262 that  $44 \pm 18\%$  of the PAHs emitted into the atmosphere from sources in the region are  
263 removed by vegetation. Although the equilibrium between the atmosphere and vegetation  
264 depends on ambient temperature, Simonich and Hites (1994) suggested that most of the PAHs  
265 absorbed by vegetation at the end of the growing season are incorporated into the soil and  
266 permanently removed from the atmosphere. In addition to mosses, other main

267 bioaccumulators used to date for monitoring atmospheric PAH deposition are lichens  
268 (Augusto et al., 2010; Blasco et al., 2011; Guidotti et al., 2003; Migaszewski et al., 2002;  
269 Shukla and Upreti, 2009), leaves from deciduous broad-leave trees (Howsam et al., 2000;  
270 Jouraeva et al., 2002; Tian et al., 2008; Wang et al., 2008) or evergreen broad-leave trees (De  
271 Nicola et al., 2011; Müller et al., 2001; Prajapati and Tripathi, 2008) and conifer needles  
272 (Amigo, 2011; Augusto, 2010; Brorström-Lundén and Löfgren, 1998; Holoubek et al., 2007;  
273 Klánová et al., 2009; Lehndorff and Schwark, 2009a,b; Migaszewski et al., 2002; Piccardo et  
274 al., 2005; Tian et al., 2008). In higher plants, uptake of POPs from the air will either be in  
275 gaseous form via the stomata or via deposition to the cuticle and subsequent absorption of the  
276 lipophylic, organic compound (Paterson et al., 1990). Holoubek et al. (2000, 2007) measured  
277 a large range of POPs (PAHs, PCBs and OCPs) at a remote site during several years in both  
278 mosses and pine needles. The  $\Sigma$ PAHs content in mosses ranged from  $< 0.3$  to  $4700 \text{ ng g}^{-1}$  dry  
279 weight (mean value 609), whereas the  $\Sigma$ PAHs content in pine needles ranged from  $< 0.3$  to  
280  $18,590 \text{ ng g}^{-1}$  dry weight (mean value 1345) at the background site (Houlebek et al., 2000).  
281 Although the concentration of PAHs tended to be lower in mosses than in pine needles, this  
282 was not always the case (Houlebek et al., 2000, 2007). We are not aware other studies  
283 reporting on potential correlations between concentrations of PAHs in mosses and other  
284 bioindicator species.

285         Only a few studies have reported on temporal trends, generally indicating that the  
286 change in concentration and/or composition of PAHs with time reflects the changes in  
287 emission sources and levels. Herbarium moss samples appear to be an effective tool for  
288 reconstructing historical tendencies of atmospheric PAH deposition (Foan et al., 2010). The  
289 disappearance of the charcoal pits and foundries at the end of the 19<sup>th</sup> Century, combined with  
290 the evolution of domestic heating towards less polluting systems during the 20<sup>th</sup> Century,  
291 explains the significant decline of PAHs in mosses over that period at a remote site in

292 northern Spain (Figure 2). Between 1973-1975 and 2006-2007, PAH distribution in mosses  
293 changed noticeably with a tendency towards 3-benzene ring PAH enrichment, due to the  
294 implementation of policies limiting 4- and 5-benzene ring PAH emissions, and a steadily  
295 increasing traffic in the area, especially heavy vehicles. However, it should be noted that  
296 natural degradation or volatilization might have occurred in the herbarium moss samples  
297 during storage in the dark at room temperature. Holoubek et al. (2000, 2007) observed a  
298 significant decrease in total PAH concentrations in mosses between 1988-1994 and 1996-  
299 2005 in the Czech Republic. The small decline in the period 1996-2005 reflected the small  
300 decline in PAH concentrations in air (Holoubek et al., 2007).

301

## 302 2.2. *Organochlorines (OCs)*

303 Mosses have also been sampled to determine the levels of atmospheric pollution from POPs  
304 other than PAHs, although the number of studies for each POP is limited, and no attempts  
305 have been made so far to relate the concentration in mosses with atmospheric concentrations  
306 and/or deposition fluxes. Below we review the application of mosses as biomonitors of OCs  
307 such as pentachlorobenzene (PCBz), DDT, HCB, HCHs and PCBs. In the 1960s and 70s,  
308 many OCs were used as pesticides, for example DDT (insecticide), HCB (fungicide in seed  
309 treatment), or produced as a byproduct in the production of pesticides (HCHs). PCBs (Figure  
310 3) were widely used as dielectric and coolant fluids, for example in transformers and electric  
311 motors. PCBz was once used for a variety of applications (e.g. as an intermediate in the  
312 manufacture of pesticides and as flame retardant), but today the majority is emitted as a result  
313 of waste burning and incineration. Table 4 provides an overview of the published  
314 concentrations of OCs measured in various mosses sampled at rural and remote sites over the  
315 last 30 years. OC levels in mosses are lower than PAHs, with individual compounds often  
316 showing concentrations lower than 1 ng g<sup>-1</sup>. PCBs tend to be the major compounds, with

317 maximal published concentrations measured for 40 congeners in Singapore of 69 ng g<sup>-1</sup> (Lim  
318 et al., 2006).

319 Chlorinated hydrocarbons were present in measurable concentrations in mosses in  
320 Antarctica (Bacci et al., 1986; Cabrerizo et al., 2012; Focardi et al., 1991). HCB levels from  
321 the Antarctic Peninsula were rather similar to those reported for mosses from Sweden and  
322 Finland. Although levels of DDT and its derivative were lower in Antarctica when compared  
323 to plant data from Italy and Germany, levels observed in lichens were similar to those  
324 observed in Sweden (Bacci et al., 1986). The levels of DDT derivatives appears to originate  
325 mainly from DDT deposited in the past. Although levels of PCBs were near or below the  
326 quantification limit in the Antarctica in the past (Bacci et al., 1986), recently Borghini et al.  
327 (2005) reported PCBs and PCBz being the dominant OCs in mosses from Victoria Land  
328 (Antarctica). The PCBs concentrations from Victoria Land were similar to those reported for  
329 mosses in Norway (Lead et al., 1996). In Singapore the concentration of OCs in mosses was  
330 also rather uniform, indicating that air masses distributed the pollutants rather evenly over the  
331 island; high concentrations of DDT derivatives and PCBs were observed compared to those  
332 found in mosses in for example the Czech Republic (Lim et al., 2006).

333 In Norway, the sum of the concentration of the 37 PCB congeners in *H. splendens*  
334 declined at all locations between 1977 and 1990 (Lead et al., 1996). This decline most likely  
335 reflects the reduction in the global use and manufacture of PCBs. While the sum of PCB  
336 concentrations have declined, temporal changes in the congener pattern in the samples  
337 collected from the same locations were noted. For example, in the south of Norway the  
338 relative concentrations of hexa- and heptachlorinated homologue groups decreased to a  
339 greater extent than they did in the north. This observation can be interpreted as evidence for  
340 differences in congener recycling through the environment according to their volatility, and it  
341 was tentatively suggested that this may provide evidence in support of the global fractionation

342 hypothesis (Wania and Mackay, 1993), i.e. compounds will volatilize in warm and temperate  
343 areas, will move northward in the Northern Hemisphere (even though atmospheric air flow  
344 may not always be in this direction), and will then re-condense when they reach colder  
345 circumpolar regions. It has also been hypothesized that differences in the volatility and  
346 lability of the individual compounds and in the ambient temperature will lead to a latitudinal  
347 fractionation of OCs. In Finland, PCB concentrations in *Sphagnum* have shown a consistent  
348 decline from the 1970s to 1980s and higher total PCB concentrations were observed in the  
349 south compared to the north (Himberg and Pakarinen, 1994).

350

### 351 2.3. Dioxins and furans (PCDD/Fs)

352 Dioxins occur as by-products in the manufacture of some OCs, in the incineration of chlorine-  
353 containing substances, in chlorine bleaching of paper, and from natural sources such as  
354 volcanoes and forest fires (Beychok, 1987). Furans tend to co-occur with dioxins (Figure 3).  
355 Carballeira et al. (2006) concluded that mosses are good biomonitors for PCDD/Fs.

356 Concentrations of PCDD/F in *Pseudoscleropodium purum* (Hedw.) Fleisch. in Broth collected  
357 in Spain ranged from 10 to 442 pg g<sup>-1</sup> (for 17 compounds), with the lowest concentrations  
358 measured in a woodland and the highest around a landfill. The mosses allowed the detection  
359 of strong and weak pollution sources. Furthermore, the measurements were sensitive enough  
360 (quantification limits: 0.025 – 0.211 pg g<sup>-1</sup>) to monitor changes in pollution intensity with  
361 time, to determine spatial gradients near pollution sources as well as differences in the relative  
362 abundance of isomers from different sources.

363

### 364 2.4. Polybrominated diphenyl ethers (PBDEs)

365 PBDEs (Figure 3) are used as flame retardants in a variety of material. For 15 PBDEs,  
366 Mariussen et al. (2008) measured concentrations ranging between 112 and 1937 pg g<sup>-1</sup> in *H.*



367 *splendens* sampled in Norway, with a general decline towards the north of the country. In  
368 addition, there was a significant decrease in the concentration of the lower brominated PBDE-  
369 congeners in mosses from the south towards the north. This is consistent with the expected  
370 atmospheric transport behaviour of these compounds and the known source regions on a  
371 European scale (Prevedouros et al., 2004). The PBDE levels in Norway were low and are  
372 probably of limited toxicological significance. PBDEs were also detected at low levels in  
373 mosses sampled in Antarctica. Yogui and Sericano (2008) measured concentrations ranging  
374 from 319 to 1187 pg g<sup>-1</sup> (for three compounds) in *S. uncinata* and Cipro et al. (2011) reported  
375 levels from 146 to 811 pg g<sup>-1</sup> (for 36 compounds) in three moss species including *S. uncinata*.  
376 The minimal values were generally not significantly different from procedure blanks.  
377 Concentrations were not statistically different at sites close to and distant from human  
378 facilities, hence long-range atmospheric transport is believed to be the primary source of  
379 PBDEs.

380

### 381 **3. Conclusions and research recommendations**

382 As for many other air pollutants such as heavy metals and nitrogen (Harmens et al., 2010,  
383 2011b, 2012), mosses appear to be suitable organisms to monitor spatial patterns and  
384 temporal trends of the atmospheric concentrations and deposition of POPs. So far, many  
385 studies have focused on spatial trends around pollution sources or the concentration in mosses  
386 in remote areas as an indication of long-range transport of POPs. Very few studies have  
387 determined temporal trends or have directly related the concentrations in mosses with  
388 measured atmospheric concentrations in deposition or deposition fluxes. The majority of  
389 studies have focussed on PAHs and relatively few studies have been conducted on other  
390 POPs. Levels determined in mosses collected at rural or remote sites are highly variable

391 between POPs, with values ranging from approximately 1 pg g<sup>-1</sup> to 0.1 µg g<sup>-1</sup> for PCDD/F and  
392 PAHs respectively.

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

407

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413

#### 414 **References**

415 Allen, J.O., Dookeran, N.M., Smith, K.A., Sarofim, A.F., Taghizadeh, K., Lafleur, A.L.,  
416 (1996). Measurement of polycyclic aromatic hydrocarbons associated with size-  
417 segregated atmospheric aerosols in Massachusetts. *Environmental Science and*  
418 *Technology* 30: 1023-1031.

419 Amigo, J.M., Ratola, N., Alves, A. (2011). Study of geographical trends of polycyclic  
420 aromatic hydrocarbons using pine needles. *Atmospheric Environment* 45: 5988-5996.

421 Ares, A., Aboal, J.R., Fernández, J.A., Real, C., Carballeira, A. (2009). Use of the terrestrial  
422 moss *Pseudoscleropodium purum* to detect sources of small scale contamination by  
423 PAHs. *Atmospheric Environment* 43: 5501-5509.

424 Augusto, S., Máguas, C., Matos, J., Pereira, M.J., Branquinho, C. (2010). Lichens as an  
425 integrating tool for monitoring PAH atmospheric deposition: A comparison with soil,  
426 air and pine needles. *Environmental Pollution* 158: 483-489.

427 Bacci, E., Calamari, D., Gaggi, C., Fanelli, R., Focardi, S., Morosini, M. (1986). Chlorinated  
428 hydrocarbons in lichen and moss samples from the Antarctic Peninsula. *Chemosphere*  
429 15: 747-754.

430 Baek, S.O., Goldstone, M.E., Kirk, P.W.W., Lester, J.N., Perry, R. (1991). Phase distribution  
431 and particle size dependency of polycyclic aromatic hydrocarbons in the urban  
432 atmosphere. *Chemosphere* 22: 503-520.

433 Belpomme D., Irigaray P., Hardell L., Clapp R., Montagnier L., Epstein S., Sascó A.J. (2007).  
434 The multitude and diversity of environmental carcinogens – Review. *Environmental*  
435 *Research* 105: 414-429.

436 Beychok, M. R. (1987). A data base for dioxin and furan emissions from refuse incinerators.  
437 *Atmospheric Environment* 21: 29–36.

438 Blasco, M., Domeno, C., Lopez, P., Nerin, C. (2011). Behaviour of different lichen species as  
439 biomonitors of air pollution by PAHs in natural ecosystems. *Journal of Environmental*  
440 *Monitoring* 13: 2588-2596.

441 Borghini, F., Grimalt, J.O., Sanchez-Hernandez, J.C., Bargagli, R. (2005). Organochlorine  
442 pollutants in soils and mosses from Victoria Land (Antarctica). *Chemosphere* 58: 271–  
443 278.

444 Breivik K., Vestreng V., Rozovskaya O., Pacyna J.M. (2006). Atmospheric emissions of  
445 some POPs in Europe: a discussion of existing inventories and data needs.  
446 *Environmental Science and Policy* 9: 663 – 674.

447 Brorström-Lundén, E., Löfgren, C. (1998). Atmospheric fluxes of persistent semivolatile  
448 organic pollutants to a forest ecological system at the Swedish west coast and  
449 accumulation in spruce needles. *Environmental Pollution* 102: 139-149.

450 Burton M.A.S. (1990). Terrestrial and aquatic bryophytes as monitors of environmental  
451 contaminants in urban and industrial habitats. *Botanical Journal of the Linnean*  
452 *Society* 104: 267-280.

453 Cabrerizo, A., Dachs, J., Barceló, D., Jones, K.C. (2012). Influence of organic matter content  
454 and human activities on the occurrence of organic pollutants in Antarctic soils,  
455 lichens, grass, and mosses. *Environmental Science and Technology* 46: 1396–1405.

456 Carballeira, A., Fernandez, J.A., Aboal, J.R., Real, C., Couto, J.A. (2006). Moss: A powerful  
457 tool for dioxin monitoring. *Atmospheric Environment* 40: 5776–5786.

458 Carlberg, G.E., Ofstad, E.B., Drangsholt, H., Steinnes, E. (1983). Atmospheric deposition of  
459 organic micropollutants in Norway studied by means of moss and lichen analysis.  
460 *Chemosphere* 12: 341-356.

461 Chen, L., Zhang, Y., Liu, B. (2010). In situ simultaneous determination the photolysis of  
462 multi-component PAHs adsorbed on the leaf surfaces of living *Kandelia candel*  
463 seedlings. *Talanta* 83: 324-331.

464 Cipro, C.V.Z., Yogui, G.T., Bustamante, P., Taniguchi, S., Sericano, J.L., Montone, R.C.  
465 (2011). Organic pollutants and their correlation with stable isotopes in vegetation  
466 from King George Island, Antarctica. *Chemosphere* 85: 393-398.

467 De Nicola, F., Claudia, L., MariaVittoria, P., Giulia, M., Anna, A. (2011). Biomonitoring of  
468 PAHs by using *Quercus ilex* leaves: Source diagnostic and toxicity assessment.  
469 *Atmospheric Environment* 45: 1428-1433.

470 Dołęgowska S., Migaszewski Z.M. (2011). PAH concentrations in the moss species  
471 *Hylocomium splendens* (Hedw.) B.S.G. and *Pleurozium schreberi* (Brid.) Mitt. from  
472 the Kielce area (south-central Poland). *Ecotoxicology and Environmental Safety* 74:  
473 1636-1644.

474 Domeño, C., Canellas, E., Alfaro, P., Rodriguez-Lafuente, A., Nerin, C. (2012). Atmospheric  
475 pressure gas chromatography with quadrupole time of flight mass spectrometry for  
476 simultaneous detection and quantification of polycyclic aromatic hydrocarbons and  
477 nitro-polycyclic aromatic hydrocarbons in mosses. *Journal of Chromatography A*  
478 1252: 146-154.

479 EU (2004). Directive 2004/107/EC of the European parliament and of the council of 15  
480 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic  
481 hydrocarbons in ambient air. Official journal L 023, 26/01/2005, pp. 3 - 16.

482 Foan, L. (2012). *Biomonitoring atmospheric deposition of polycyclic aromatic hydrocarbons*  
483 *(PAHs) with bryophytes at various spatial and temporal scales* (in French), PhD  
484 Thesis, Institut National Polytechnique de Toulouse, Université de Toulouse, France.

485 Foan, L., Sablayrolles, C., Elustondo, D., Laceras, E., González, L., Hederá, A., Simon, V.,  
486 Santamaría, J.M. (2010). Reconstructing historical trends of polycyclic aromatic  
487 hydrocarbon deposition in a remote area of Spain using herbarium moss material.  
488 Atmospheric Environment 44: 3207-3214.

489 Foan, L., Simon, V. (2012). Optimization of pressurized liquid extraction using a multivariate  
490 chemometric approach and comparison of solid-phase extraction cleanup steps for the  
491 determination of polycyclic aromatic hydrocarbons in mosses. Journal of  
492 Chromatography A 1256: 22-31.

493 Focardi, S., Gaggi, C., Chemello, G., Bacci, E. (1991). Organochlorine residues in moss and  
494 lichen samples from two Antarctic areas. Polar Record 27: 241–244.

495 Gałuszka A. (2000). Toxic organic compounds in the environment. Przegląd Geologiczny 48:  
496 3681-3688.

497 Gałuszka A. (2007). Distribution patterns of PAHs and trace elements in mosses *Hylocomium*  
498 *splendens* (Hedw.) B.S.G. and *Pleurozium schreberi* (Brid.) Mitt. from different forest  
499 communities: A case study, south-central Poland. Chemosphere 67: 1415-1422.

500 Garrec, J.P., Van Haluwyn, C. (2002). *Air quality biomonitoring with plants - Concepts,*  
501 *methods and applications* (in French). Lavoisier, Paris.

502 Gerdol, R., Bragazza, L., Marchesini, R., Medici, A., Pedrini, P., Benedetti, S., Bovolenta, A.,  
503 Coppi, S. (2002). Use of moss (*Tortula muralis* Hedw.) for monitoring organic and  
504 inorganic air pollution in urban and rural sites in Northern Italy. Atmospheric  
505 Environment 36: 4069-4075.

506 Guidotti M., Stella D., Owczarek M., De Marco A., De Simone C. (2003). Lichens as  
507 polycyclic aromatic hydrocarbon bioaccumulators used in atmospheric pollution  
508 studies. Journal of Chromatography A 985: 185-190.

509 Gusev, A., Dutchak, S., Rozovskaya, O., Shatalov, V., Sokovykh, V., Vulykh, N., Aas, W.,  
510 Breivik, K. (2011). Persistent organic pollutants in the environment. EMEP Status  
511 Report 3/2011.

512 Harmens, H., Ilyin, I., Mills, G., Aboal, J.R., Alber, R., Blum, O., Coşkun, M., De  
513 Temmerman, L., Fernández, J.A., Figueira, R., Frontasyeva, M., Godzik, B., Goltsova,  
514 N., Jeran, Z., Korzekwa, S., Kubin, E., Kvietkus, K., Leblond, S., Liiv, S., Magnússon,  
515 S.H., Maňkovská, B., Nikodemus, O., Pesch, R., Poikolainen, J., Radnović, D.,  
516 Rühling, Å., Santamaria, J.M., Schröder, W., Spiric, Z., Stafilov, T., Steinnes, E.,  
517 Suchara, I., Tabor, G., Thöni, L., Turcsányi, G., Yurukova, L., Zechmeister, H.G.  
518 (2012). Country-specific correlations across Europe between modelled atmospheric  
519 cadmium and lead deposition and concentrations in mosses. *Environmental Pollution*  
520 166: 1-9.

521 Harmens, H., Mills, G., Hayes, F., Norris, D. and the participants of the ICP Vegetation.  
522 (2011a). Air pollution and vegetation. ICP Vegetation annual report 2010/2011. ISBN:  
523 978-1-906698-26-3.

524 Harmens, H., Norris, D. A., Cooper, D.M., Mills, G., Steinnes E., Kubin, E., Thöni, L., Aboal,  
525 J.R., Alber, R., Carballeira, A., Coşkun, M., De Temmerman, L., Frolova, M.,  
526 Frontasyeva, M., González-Miqueo, L., Jeran, Z., Leblond S., Liiv, S., Maňkovská, B.,  
527 Pesch, R., Poikolainen, J., Rühling, Å., Santamaria, J. M., Simonèiè, P., Schröder, W.,  
528 Suchara, I., Yurukova, L., Zechmeister, H. G. (2011b). Nitrogen concentrations in  
529 mosses indicate the spatial distribution of atmospheric nitrogen deposition in Europe.  
530 *Environmental Pollution* 159: 2852-2860.

531 Harmens, H., Norris, D.A., Steinnes, E., Kubin, E., Piispanen, J., Alber, R., Aleksiyenak, Y.,  
532 Blum, O., Coşkun, M., Dam, M., De Temmerman, L., Fernández, J.A., Frolova, M.,  
533 Frontasyeva, M., González-Miqueo, L., Grodzińska, K., Jeran, Z., Korzekwa, S.,

534 Krmar, M., Kvietkus, K., Leblond, S., Liiv, S., Magnússon, S.H., Maňková, B.,  
535 Pesch, R., Rühling, Å., Santamaria, J.M., Schröder, W., Spiric, Z., Suchara, I., Thöni,  
536 L., Urumov, V., Yurukova, L., Zechmeister, H.G. (2010). Mosses as biomonitors of  
537 atmospheric heavy metal deposition: spatial and temporal trends in Europe.  
538 Environmental Pollution 158: 3144-3156.

539 Himberg, K.K., Pakarinen, P. (1994). Atmospheric PCB deposition in Finland during 1970s  
540 and 1980s on the basis of concentrations in ombrotrophic peat mosses (*Sphagnum*).  
541 Chemosphere 29: 431-440.

542 Holoubek, I., Klánová, J., Jarkovský, J., Kohoutek, J. (2007). Trends in background levels of  
543 persistent organic pollutants at Kosetice observatory, Czech Republic - Part II.  
544 Aquatic air and terrestrial environments 1996–2005. Journal of Environmental  
545 Monitoring 9: 564-571.

546 Holoubek, I., Korinek, P., Seda, Z., Schneiderova, E., Holoubkova, I., Pacl, A., Triska, J.,  
547 Cudlin, P., Caslavsky, J. (2000). The use of mosses and pine needles to detect  
548 persistent organic pollutants at local and regional scales. Environmental Pollution 109:  
549 283–292.

550 Holy, M., Pesch, R., Schröder, W., Harmens, H., Ilyin, I., Alber, R., Aleksiyenak, Y., Blum,  
551 O., Coşkun, M., Dam, M., De Temmerman, L., Fedorets, N., Figueira, R., Frolova,  
552 M., Frontasyeva, M., Goltsova, N., González Miqueo, L., Grodzińska, K., Jeran, Z.,  
553 Korzekwa, S., Krmar, M., Kubin, E., Kvietkus, K., Larsen, M., Leblond, S., Liiv, S.,  
554 Magnússon, S., Maňková, B., Mocanu, R., Piispanen, J., Rühling, Å., Santamaria, J.,  
555 Steinnes, E., Suchara, I., Thöni, L., Turcsányi, G., Urumov, V., Wolterbeek, H.T.,  
556 Yurukova, L., Zechmeister, H.G. (2010). First thorough identification of factors  
557 associated with Cd, Hg and Pb concentrations in mosses sampled in the European  
558 Surveys 1990, 1995, 2000 and 2005. Journal of Atmospheric Chemistry 63: 109-124.



559 Howsam M., Jones K.C., Ineson P. (2000). PAHs associated with the leaves of three  
560 deciduous tree species. I - Concentrations and profiles. *Environmental Pollution* 108:  
561 413-424.

562 ICP Waters (2005). Concentrations and levels of POPs from long-range transboundary air  
563 pollution in freshwater fish and sediment. International Cooperative Programme on  
564 Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP  
565 Waters) report 79/2005.

566 Jones K.C., De Voogt P. (1999). Persistent organic pollutants (POPs): State of the science.  
567 *Environmental Pollution* 100: 209-221.

568 Jouraeva V.A., Johnson D.L., Hassetta J.P., Nowak D.J. (2002). Differences in accumulation  
569 of PAHs and metals on the leaves of *Tilia euchlora* and *Pyrus calleryana*.  
570 *Environmental Pollution* 120: 331-338.

571 Kiss, G., Varga-Puchony, Z., Rohrbacher, GB., Hlavay, J.Z. (1998). Distribution of  
572 polycyclic aromatic hydrocarbons on atmospheric aerosol particles of different sizes.  
573 *Atmospheric Research* 46: 253-261.

574 Klánová, J., Cupr, P., Baráková, D., Seda, Z., Andel, P., Holoubek, I. (2009). Can pine  
575 needles indicate trends in the air pollution levels at remote sites? *Environmental*  
576 *Pollution* 157: 3248-3254.

577 Knulst J.C., Olle Westling H., Brorström-Lundén E. (1995). Airborne organic micropollutant  
578 concentrations in mosses and humus as indicators for local versus long-range sources.  
579 *Environmental Monitoring and Assessment* 36: 75-91.

580 Krommer, V., Zechmeister, H.G., Roder, I., Scharf, S., Hanus-Iltnar, A. (2007). Monitoring  
581 atmospheric pollutants in the biosphere reserve Wienerwald by a combined approach  
582 of biomonitoring methods and technical measurements. *Chemosphere* 67: 1956-1966.

583 Lead, W., Steinnes, E., Jones, K. (1996). Atmospheric deposition of PCBs to moss  
584 (*Hylocomium splendens*) in Norway between 1977 and 1990. Environmental Science  
585 and Technology 30: 524-530.

586 Lehndorff E., Schwark L. (2009a). Biomonitoring airborne parent and alkylated three-ring  
587 PAHs in the Greater Cologne Conurbation. I: Temporal accumulation patterns.  
588 Environmental Pollution 157: 1323-1331.

589 Lehndorff E., Schwark L. (2009b). Biomonitoring airborne parent and alkylated three-ring  
590 PAHs in the Greater Cologne Conurbation. II: Regional distribution patterns.  
591 Environmental Pollution 157: 1706-1713.

592 Leipe T., Kersten M., Heise S., Pohl C., Witt G., Liehr G., Zettler M., Tauber F. (2005).  
593 Ecotoxicity assessment of natural attenuation effects at a historical dumping site in the  
594 western Baltic Sea. Marine Pollution Bulletin 50: 446-459.

595 Lim, T.B., Xu, R., Tan, B., Obbard, J.P. (2006). Persistent organic pollutants in moss as  
596 bioindicators of atmospheric pollution in Singapore. Chemosphere 64: 596–602.

597 LRTAP Convention (1998). Protocol to the 1979 Convention on Long-range Transboundary  
598 Air Pollution on Persistent Organic Pollutants. <http://www.unece.org/env/lrtap/>

599 Mariussen, E., Steinnes, E., Breivik, K., Nygård, T., Schlabach, M., Kålås, J.A. (2008).  
600 Spatial patterns of polybrominated diphenyl ethers (PBDEs) in mosses, herbivores and  
601 a carnivore from the Norwegian terrestrial biota. Science of the Total Environment  
602 404: 162-170.

603 Migaszewski, Z.M., Gałuszka, A., Crock, J.G., Lamothe, P.J., Dołęgowska, S. (2009).  
604 Interspecies and interregional comparisons of the chemistry of PAHs and trace  
605 elements in mosses *Hylocomium splendens* (Hedw.) B.S.G. and *Pleurozium schreberi*  
606 (Brid.) Mitt. from Poland and Alaska. Atmospheric Environment 43: 1464-1473.

607 Migaszewski, Z.M., Gałuszka, A., Paślawski, P. (2002). Polynuclear aromatic hydrocarbons,  
608 phenols and trace metals in selected soil profiles and plant bioindicators in the Holy  
609 Cross Mountains, south-central Poland. *Environment International* 28: 303-313.

610 Milukaite A. (1998). Flux of benzo(a)pyrene to the ground surface and its distribution in the  
611 ecosystem. *Water, Air and Soil Pollution* 105: 471-480.

612 Müller, J.F., Hawker, D.W., McLachlan, M.S., Connell, D.W. (2001). PAHs, PCDD/Fs,  
613 PCBs and HCB in leaves from Brisbane, Australia. *Chemosphere* 43: 507-515.

614 Oguntimehin, I., Nakatani, N., Sakugawa, H. (2008). Phytotoxicities of fluoranthene and  
615 phenanthrene deposited on needle surfaces of the evergreen conifer, Japanese red pine  
616 (*Pinus densiflora* Sieb. et Zucc.). *Environmental Pollution* 154: 264-271.

617 Orliński, R. (2002). Multipoint moss passive samplers assessment of urban airborne  
618 polycyclic aromatic hydrocarbons: concentrations profile and distribution along  
619 Warsaw main streets. *Chemosphere* 48: 181-186.

620 Ötvös, E., Kozák, I.O., Fekete, J., Sharma, V.K., Tuba, Z. (2004). Atmospheric deposition of  
621 polycyclic aromatic hydrocarbons (PAHs) in mosses (*Hypnum cupressiforme*) in  
622 Hungary. *Science of the Total Environment* 330: 89-99.

623 Paterson, S., MacKay, D., Tam, D., Shiu, W.Y. (1990). Uptake of organic chemicals by plants:  
624 A review of processes, correlations and models. *Chemosphere* 21: 297-331.

625 Piccardo M.T., Pala M., Bonaccorso B., Stella A., Redaelli A., Paola G., Valerio F. (2005).  
626 *Pinus nigra* and *Pinus pinaster* needles as passive samplers of polycyclic aromatic  
627 hydrocarbons. *Environmental Pollution* 133: 293-301.

628 Prajapati, S.K., Tripathi, B.D. (2008). Biomonitoring seasonal variation of urban air  
629 polycyclic aromatic hydrocarbons (PAHs) using *Ficus benghalensis* leaves.  
630 *Environmental Pollution* 151: 543-548.

631 Prevedouros, K, Jones, K.C, Sweetman, A.J. (2004). Estimation of the production,  
632 consumption, and atmospheric emissions of pentabrominated diphenyl ether in Europe  
633 between 1970 and 2000. *Environmental Science and Technology* 38: 3224–31.

634 Ravindra, K., Sokhi, R., Van Grieken, R. (2008). Atmospheric polycyclic aromatic  
635 hydrocarbons: Source attribution, emission factors and regulation. *Atmospheric*  
636 *Environment* 42: 2895-2921.

637 Schröder, W., Holy, M., Pesch, R., Harmens, H., Fagerli, H., Alber, R., Coşkun, M., De  
638 Temmerman, L., Frolova, M., González-Miqueo, L., Jeran, Z., Kubin, E., Leblond, S.,  
639 Liiv, S., Maňková, B., Piispanen, J., Santamaría, J.M., Simonè, P., Suchara, I.,  
640 Yurukova, L., Thöni, L., Zechmeister, H.G. (2010a). First Europe-wide correlation  
641 analysis identifying factors best explaining the total nitrogen concentration in mosses.  
642 *Atmospheric Environment* 44: 3485-3491.

643 Schröder, W., Holy, M., Pesch, R., Harmens, H., Ilyin, I., Steinnes, E., Alber, R.,  
644 Aleksiyaynak, Y., Blum, O., Coşkun, M., Dam, M., De Temmerman, L., Frolova, M.,  
645 Frontasyeva, M., González-Miqueo, L., Grodzińska, K., Jeran, Z., Korzekwa, S.,  
646 Krmar, M., Kubin, E., Kviatkus, K., Leblond, S., Liiv, S., Magnússon, S., Maňková,  
647 B., Piispanen, J., Rühling, Å., Santamaria, J., Spiric, Z., Suchara, I., Thöni, L.,  
648 Urumov, V., Yurukova, L., Zechmeister, H.G. (2010b). Are cadmium, lead and  
649 mercury concentrations in mosses across Europe primarily determined by atmospheric  
650 deposition of these metals? *Journal of Soils and Sediments* 10: 1572-1584.

651 Shukla, V., Upreti, D. (2009). Polycyclic aromatic hydrocarbon (PAH) accumulation in lichen  
652 *Phaeophyscia hispidula* of DehraDun City, Garhwal Himalayas. *Environmental*  
653 *Monitoring and Assessment* 149: 1-7.

654 Simonich S.L., Hites R.A. (1994). Importance of vegetation in removing polycyclic aromatic  
655 hydrocarbons from the atmosphere. *Nature* 370: 49-51.

656 Simonich, S.L., Hites, R.A. (1995). Organic pollutant accumulation in vegetation.  
657 Environmental Science and Technology 29: 2905-2914.

658 Smith P.N., Cobb G.P., Godard-Codding C., Hoff D., McMurry S.T., Rainwater T.R.,  
659 Reynolds K.D. (2007). Contaminant exposure in terrestrial vertebrates. Environmental  
660 Pollution 150: 41-64.

661 TFHTAP (2010). Hemispheric transport of air pollution 2010. Part C: Persistent organic  
662 pollutants. Dutchak, S., Zuber, A. (Eds.). Air pollution studies no. 19, LRTAP  
663 Convention, United Nations.

664 Thomas, W. (1984). Statistical models for the accumulation of PAH, chlorinated  
665 hydrocarbons and trace metals in epiphytic *Hypnum cupressiforme*. Water, Air and  
666 Soil Pollution 22: 351-371.

667 Thomas, W. (1986). Representativity of mosses as biomonitor organisms for the accumulation  
668 of environmental chemicals in plants and soils. Ecotoxicology and Environmental  
669 Safety 11: 339-346.

670 Tian X., Liu J., Zhou G., Peng P., Wang X., Wang C. (2008). Estimation of the annual  
671 scavenged amount of polycyclic aromatic hydrocarbons by forests in the Pearl River  
672 Delta of Southern China. Environmental Pollution 156: 306-315.

673 Tobiszewski, M., Namieśnik, J. (2012). PAH diagnostic ratios for the identification of  
674 pollution emission sources. Environmental Pollution 162: 110-119.

675 US EPA (1997). Office of Pesticide Programs, List of chemicals evaluated for carcinogenic  
676 potential, Washington, DC, USA.

677 Viskari, E-L., Rekila, R., Roy, S., Lehto, O., Ruuskanen, J., Karenlampi L. (1997). Airborne  
678 pollutants along a roadside: assessment using snow, analyses and moss bags.  
679 Environmental Pollution 97: 153-160.

680 Wang, D., Chen, J., Xu, Z., Qiao, X., Huang, L. (2005). Disappearance of polycyclic aromatic  
681 hydrocarbons sorbed on surfaces of pine [*Pinua thunbergii*] needles under irradiation  
682 of sunlight: Volatilization and photolysis. *Atmospheric Environment* 39: 4583-4591.

683 Wang Y.Q., Tao S., Jiao X.C., Coveney R.M., Wu S.P., Xing B.S. (2008). Polycyclic  
684 aromatic hydrocarbons in leaf cuticles and inner tissues of six species of trees in urban  
685 Beijing. *Environmental Pollution* 151: 158-164.

686 Wania, F., Mackay, D. (1993). Global fractionation and cold condensation of volatility  
687 organochlorine compounds in polar regions. *Ambio* 22: 10-18.

688 Wegener, J.W.M., Van Schaik, M.J.M., Aiking, H. (1992). Active biomonitoring of  
689 polycyclic aromatic hydrocarbons by means of mosses. *Environmental Pollution* 76:  
690 1-15.

691 WHO (2003). Health risks of persistent organic pollutants from long-range transboundary air  
692 pollution. World Health Organization, Geneva.

693 Yogui, G.T., Sericano, J.L. (2008). Polybrominated diphenyl ether flame retardants in lichens  
694 and mosses from King George Island, maritime Antarctica. *Chemosphere* 73: 1589-  
695 1593.

696 Zechmeister, H.G., Dullinger, S., Hohenwallner, D., Riss, A., Hanus-Illnar, A., Scharf, S.  
697 (2006). Pilot study on road traffic emissions (PAHs, heavy metals) measured by using  
698 mosses in a tunnel experiment in Vienna, Austria. *Environmental Science and*  
699 *Pollution Research* 13: 398-405.

700

701 **Abbreviations persistent organic pollutants**

702 DDD: dichlorodiphenyldichloroethane

703 DDE: dichlorodiphenyldichloroethylene

704 DDT: dichlorodiphenyltrichloroethane

705 HCB: hexachlorobenzene

706 HCH: hexachlorocyclohexane

707 OC: organochlorine

708 PAH: polycyclic aromatic hydrocarbon

709 PBDE: polybrominated diphenyl ether

710 PCB: polychlorobiphenyl

711 PCBz: pentachlorobenzene

712 PCDD: dioxins

713 PCDF: furans

714 POP: persistent organic pollutant

715

716 **Figure legends**

717

718 **Figure 1.** Structural formula of the 16 PAHs classed as priority pollutants by the US EPA

719 (US EPA, 1997).

720

721 **Figure 2.** PAH concentrations (mean  $\pm$  standard deviation) measured in herbarium mosses

722 sampled during the periods 1879-1881, 1973-1975 and 2006-2007 at a rural site in Northern

723 Spain (Foan et al., 2010; Foan, 2012).

724

725 **Figure 3.** General structural formula of dioxin, furan, PCB and PBDE.

726



727 **Table 1.** POPs included in the Protocol of the LRTAP Convention and the Stockholm  
 728 Convention. Note: some substances have been grouped.

729

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

730

731

732 **Table 2.** Average PAH concentrations (ng g<sup>-1</sup>, dry wt) and ranges (in brackets) measured in mosses sampled in rural areas; BQL = below  
 733 quantification limit.

	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)	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)		
Dibenzo[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)				
<b>ΣPAHs</b>	<b>609.1</b>	<b>(&lt;0.3 - 4700)</b>	<b>604.5</b>	<b>(587 - 622)</b>	<b>120</b>		<b>137</b>	<b>(120 - 730)</b>	<b>512</b>	<b>(183 - 1629)</b>	<b>172</b>	<b>(86 - 372)</b>

734  
735

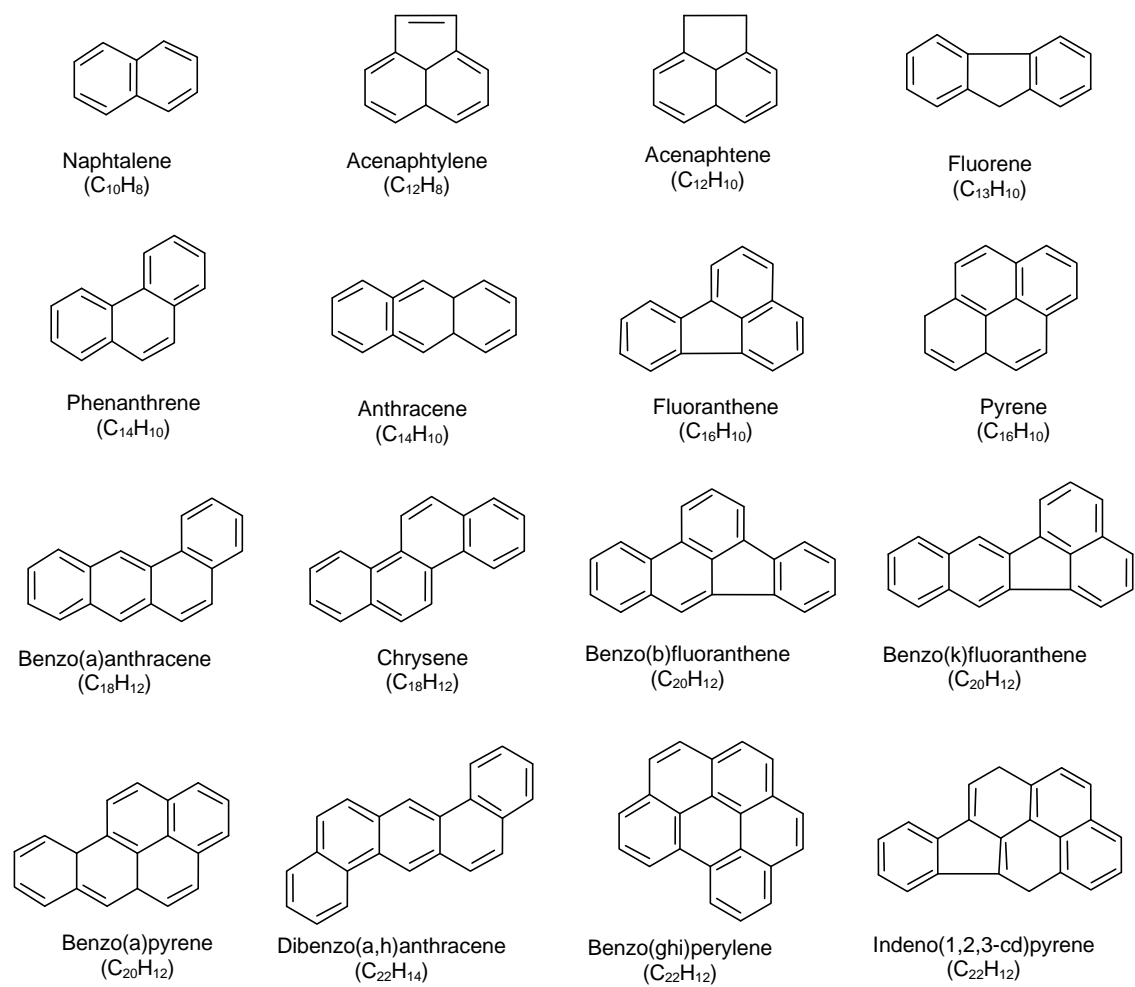
**Table 3.** Moss species used as passive biomonitors of atmospheric PAH deposition.

	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>Sanionia uncinata</i>	<i>Scleropodium purum</i>	<i>Thamnobryum alopecurum</i>	<i>Thuidium tamariscinum</i>	<i>Dicranum scoparium</i>
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 (2011)		▲		▲						
Cabrerizo et al. (2012)						▲				
Domeño et al. (2012)			▲							
Foan and Simon (2012)		▲	▲							

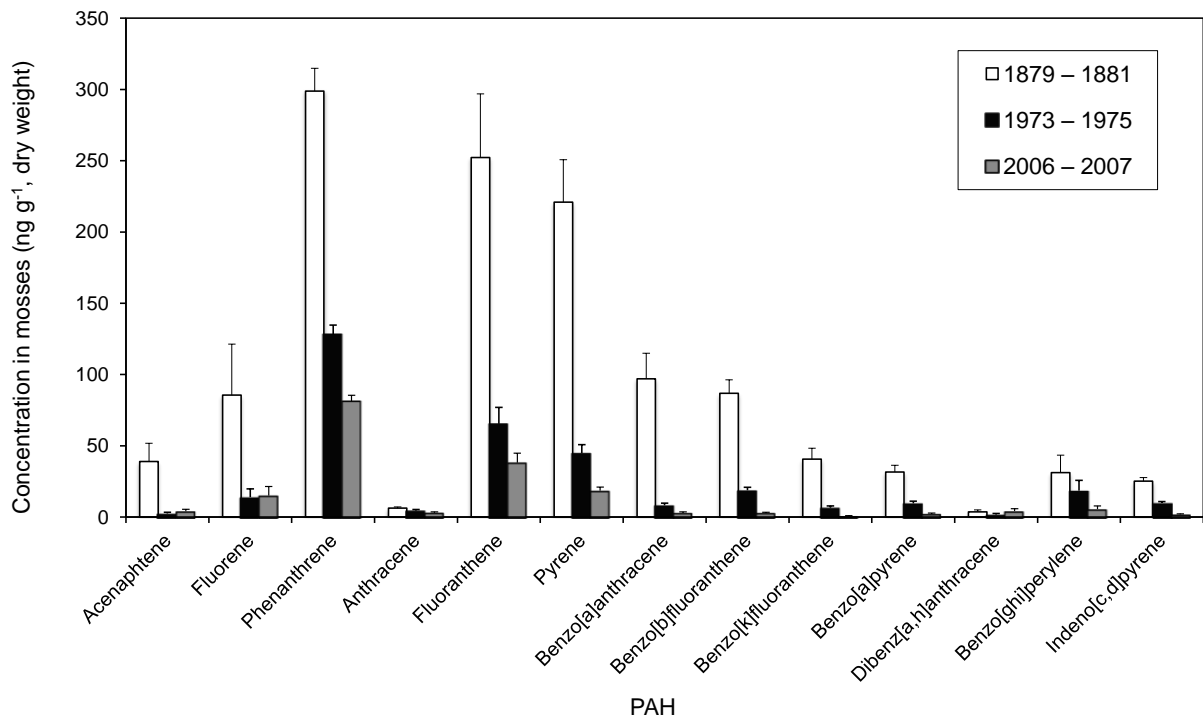
736

737 **Table 4.** Mean or ranges of OCs concentrations (ng g<sup>-1</sup>, dry wt) in mosses. Except for Singapore (a mixture of rural and urban sites), samples  
 738 were collected in rural or remote areas; BQL: below quantification. limit, x = number of compounds determined.  
 739

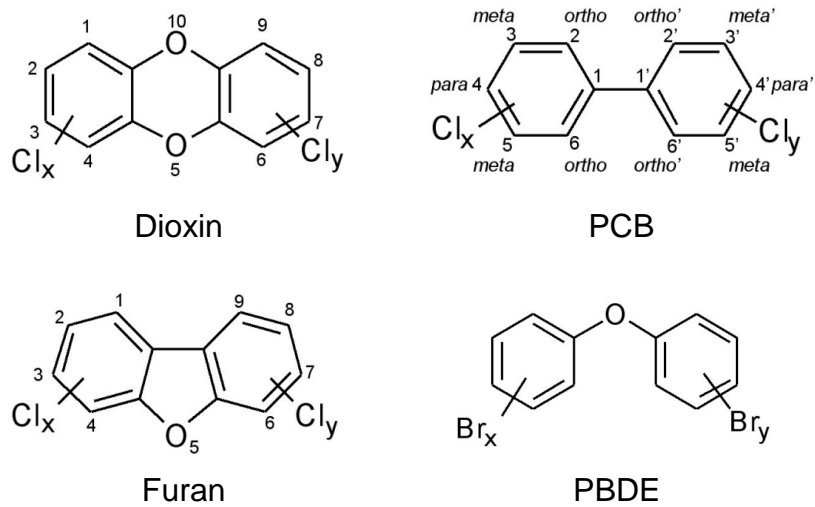
	Sampling period	Country	Σ <sub>x</sub> PCBs	HCB	α-HCH	β-HCH	γ-HCH	δ-HCH	Σ <sub>x</sub> HCH	p,p'-DDE	p,p'-DDT	pp'-DDD	Σ <sub>x</sub> DDT	PCBz
Carlberg et al. (1983)	1979	Norway	10-35	0.4-22	9-49		3-43			0.1-1.4	0.4-6.6			
Bacci et al. (1986)		Antarctica	<5-12	0.30-0.68						0.17-0.53				
Focardi et al. (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	1.6	1.07	<0.1	1.28	<0.3		0.15	1.14			
			<0.3-1.1 (x=3)	<0.1-18	<0.1-3.8		<0.1-5.9			<0.1-0.4	<0.1-6.8			
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			0.65	21.19	BQL	0.574		1.86	2.08	2.08		
			31-69 (x=40)		BQL-1.78	BQL-22.57	BQL	BQL-1.53		BQL-1.56	BQL-1.56	BQL-1.96		
Holoubek et al. (2007)	1996-2005	Czech Republic	7.1	2.7					4.6				2.2	
			0.87-20 (x=7)	BQL-47					BQL-150 (x=4)				BQL-7.2 (x=3)	
Cipro et al. (2011)	2004-2005	Antarctica	7.76 - 18.6 (x=51)	0.141-1.06					BQL-1.20 (x=4)				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				



**Figure 1.**



**Figure 2.**



**Figure 3.**