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Pleurozium schreberi as an ecological indicator of polybrominated diphenyl ethers (PBDEs) in a heavily industrialized urban area

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are toxic contaminants with a persistent character and adverse effects on humans and wildlife. Therefore, the deposition of these chemicals in vegetation must be carefully controlled. Our objective was to determine PBDE concentrations (BDEs 28, 47, 66, 85, 99, 100, 153, 154, 183 and 209) in *Pleurozium schreberi* collected in a heavily industrialized urban agglomeration. High PBDE concentrations in the moss confirm the presence of active sources of atmospheric pollution in an area tested. The distribution of these xenobiotics was related to the vegetation cover being lower in sites surrounded by forests which indicates that PBDEs may have a tendency to be trapped from the air by tree leaves and needles. Congener profiles in *P. schreberi* were dominated by BDE 209 which was for 79% (in case of the coke smelter) to 95% (in case of the chemical plant) part of the total PBDE burden in this moss. The principal component and classification analysis classifying the concentration of PBDEs in *P. schreberi* allowed us to distinguish the pattern of these compounds characteristic for the origin of pollution. *P. schreberi* may be used as a bioindicator for PBDEs in areas contaminated with these chemicals.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of widespread and ubiquitous contaminants whose concentrations in the environment have been increasing in several regions worldwide (Prevedouros et al., 2004). According to Schuster et al. (2010) a reduction in primary emissions and a rate of decline for these compounds in Europe may be observed. However there still are remnants of PBDEs in soil and biota forming a pool which may influence the regulation of distribution of these xenobiotics in the environment and control the trends in ambient levels (Schuster et al., 2010). Recent studies have shown that lower brominated PBDEs have a toxic potential similar to that of PCBs with a similar chemical structure and physicochemical properties (Mariussen et al., 2008a; Wang et al., 2011). Atmospheric transport is believed to be a major vector for the long-range transfer of these compounds away from their sites of origin. Therefore, the deposition of these chemicals in soils and vegetation must be carefully controlled (de Wit et al., 2006; Mariussen et al., 2008b; Yogui et al., 2011; Tarcau et al., 2013). The source of PBDEs is fire-preventive additives in various products including textiles, furniture, electronics, and cars (Mariussen et al., 2008b; Huang et al., 2011; Tian et al., 2012). PBDEs are divided into three main groups: penta-, octa-, and deca-BDEs, of which deca-BDE mixtures are used in the highest quantities (de Wit et al., 2006). The compounds, discovered in environmental samples in the late 1970s, have attracted great attention because of their potentially harmful and persistent character and adverse effects on humans and wildlife (Klánová et al., 2009; Mariussen et al., 2008a; Tian et al., 2012). Mueller et al. (2006) revealed that several PBDEs, especially those with less than eight bromine atoms, had a potential for bioaccumulation. Relatively little information is available on PBDEs in terrestrial mosses and it is summarized in Mariussen et al. (2008b); Yogui and Sericano (2008); Harmens et al. (2013). With their low vapor pressures,

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very low water solubility and high log octanol/water ratios, PBDEs when entering the environment are expected to tend to bind to the organic fraction of particulate matter. Lower brominated PBDEs (tetra- to hepta-BDEs) are slightly more soluble in water and have a greater tendency for volatilization and atmospheric transport than highly brominated PBDEs. In the atmosphere, these homologs would also tend to partition to particulates (Gouin and Harner, 2003). For this investigation we selected the Kędzierzyn-Koźle urban area with i.a. chemical plants involved in heavy organic synthesis. The industry is a source of various organic compounds probably also including polybrominated diphenyl ethers (Kiedik et al., 2002; Krzyżanowska and Jazienicka, 1997). To gain an insight into the bioaccumulative properties of these chemicals in plants we selected the terrestrial, carpet forming, pleurocarpous and ectohydric moss *P. schreberi* because it occurs widely in the Northern Hemisphere, including Poland. The species has been used successfully in the last decades and has proved to be a suitable bioindicator widely used to map and control metal pollution in Europe (Pesch and Schroeder, 2006; Niemelä et al., 2007; Kosior et al., 2010). Mosses provide complementary information to conventional passive air samplers and may indicate the actual congener pattern to which other biota are exposed and concentration levels in the environment (Mariussen et al., 2008b).

The aim of this work was to study the concentration of 10 congeners of PBDEs in the terrestrial moss *P. schreberi*. The tested hypothesis was whether the ubiquitous *P. schreberi* may be a suitable bioindicator of PBDE pollution.

2. Material and methods

2.1. Sampling design

The study site was selected in the urban agglomeration of Kędzierzyn-Koźle with chemical industry, nitrogen fertilizer industry and a coke smelter (Fig. 1, Supplementary file). Thirty sites were selected and divided into six groups: (1) the coke smelter (no. 1–4), (2) the chemical plant (no. 5–8, 11–12), (3) the nitrogen fertilizer plant (no. 21–24), (4) urbanized areas (no. 13–20), (5) forest clearings (no. 9–10, 25–28) and (6) the control sites (no. 29–30). At each site within a 50 m × 50 m square, two replicates of moss were collected randomly to yield $N = 30$ samples. Each sample consisted of a mixture of five subsamples. As required by the rules set by the Environmental Monitoring and Data Group (Markert et al., 1996) and within the European Heavy Metal Survey (ICP Vegetation, 2005), the collected moss had not been exposed directly to canopy throughfall. Dead material, soil particles and litter were manually removed from the moss (green parts of gametophytes). Mosses were transported to the laboratory wrapped in aluminum foil (Klánová et al., 2009).

2.2. Chemical analyses

All moss samples were dried at ambient temperature and ground. Moss samples were extracted with dichloromethane in a Büchi System B-811 automated Soxhlet extractor unit

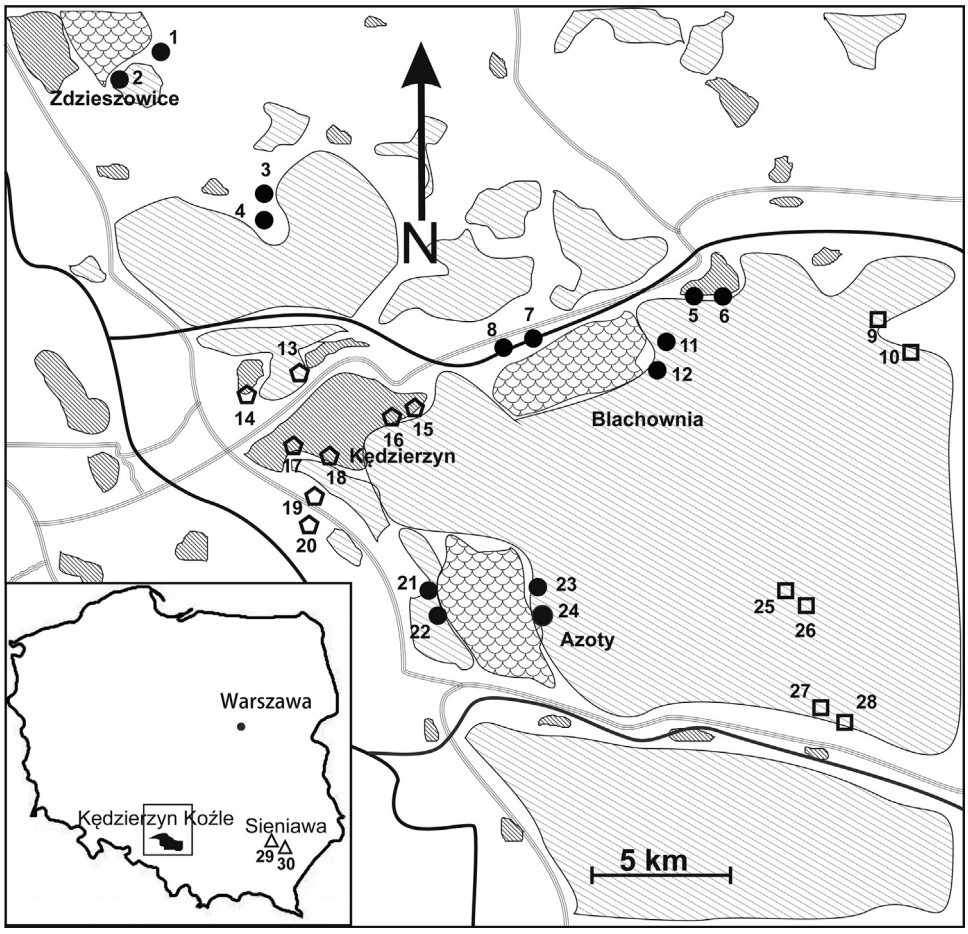

Fig. 1. Location of the investigation area: urbanized areas; sampling sites of urbanized areas; forest clearings; sampling sites of forest clearings; industrial areas; sampling sites of industrial areas; control; roads, rivers.