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Absorption and translocation of polybrominated diphenyl ethers (PBDEs) by plants from contaminated sewage sludge

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are used as additive flame retardants. PBDEs are persistent, bioaccumulative and toxic compounds. They are often detected in sewage sludge which is applied on agricultural soils as fertilizer. The objective of this study was to find out whether plants are able to accumulate and translocate PBDEs. Tobacco (*Nicotiana tabacum*) and nightshade (*Solanum nigrum*) were planted in pots containing contaminated sewage sludge and uncontaminated substrate. After 6 months of plant cultivation in sewage sludge up to 15.4 ng g^{-1} dw and 76.6 ng g^{-1} dw of PBDE congeners – BDE 47, BDE 99 and BDE 100 were accumulated in the nightshade and tobacco tissue, respectively. Corresponding values in plants vegetated in the control garden substrate were 10 times lower. The bioconcentration factors (BCFs) of accumulated congeners were calculated. Tobacco exhibited higher BCFs values and for both plants BCFs values of BDE 47, BDE 99, BDE 100 and BDE 209 negatively correlated with their octanol–water partition coefficients (log K_{ow}). The exception was decaBDE (BDE 209) which was accumulated only in tobacco tissue in the concentration of 116.8 ng g^{-1} dw. The majority of PBDEs was detected in aboveground plant biomass indicating that both plants have the ability to translocate PBDEs. To our knowledge this is one of the first studies reporting the accumulation of both lower PBDEs and BDE 209 in plants. Our results suggest that absorption, accumulation and translocation of PBDEs by plants and their transfer to the food chain could represent another possible risk for human exposure.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been widely used as flame retardants in many countries throughout the world for more than 30 years, although they are known to present health and environmental risks. They are lipophilic with bioaccumulative properties (Rahman et al., 2001) and despite their low acute toxicity the low-brominated congeners act as endocrine disruptors, carcinogens and/or neurodevelopment toxicants (Hardy, 2002; McDonald, 2002). Three technical mixtures of PBDEs are industrially manufactured: Deca-, Octa- and PentaBDE. PBDEs are used as additive flame retardants in plastics products, electrical components, textiles, building materials and other products (Rahman et al., 2001; McDonald, 2002). They enter the environment more easily than the reactive BFRs and therefore entrance into the food chain is facilitated (Alaee and Wennig, 2002; McDonald, 2002). The main sources of PBDEs in the environment are effluents from factories producing BFRs and flame-retardant polymers, flame-resistant products and the waste that contains PBDEs. PBDEs are released into the environment in various of forms: associated with particles, by leaching, and by volatilization from flame-resistant products during their use and waste disposal such during incineration of municipal waste (Watanabe and Sakai, 2003; Hites, 2004).

PBDEs have been found in both abiotic samples and biota. These compounds have been detected in the air, sewage sludge, sediments, soils, water, aquatic organisms (marine mammals – e.g. whales, dolphins, seals and fishes), birds that feed on fish (e.g. ospreys, cormorants and gulls) (Hites, 2004; Hajšlová et al., 2007; Knoth et al., 2007) and also birds of prey family (kestrel, sparrow hawk and owl) (Chen et al., 2007). Studies have also confirmed the presence of PBDEs in human blood, adipose tissue and breast milk. There is proof that PBDEs concentrations are rising in human tissues and in biota (Hites, 2004; Pulkrabová et al., 2009). The primary route of human exposure to PBDEs is *via* ingestion of food with the high content of fat (e.g. fatty fish, meat and diary products) (Darnerud et al., 2001; Vonderheide et al., 2008; Frederiksen et al., 2009). The other significant source of PBDEs in human tissues

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is inhalation of compounds in the gas phase or dust particles and direct dermal exposure to flame-resistant product (Hites, 2004; Frederiksen et al., 2009). Inhalation of house dust presents unwanted source of PBDEs during all life stages (Jones-Otazo et al., 2005; Allen et al., 2008).

Due to the hydrophobic character of PBDEs, these chemicals are strongly bound to solid particles such as soil, sediments and sewage sludge (Hites, 2004; Hale et al., 2006). With regards to abiotic samples, such as atmosphere and aqueous media, the occurrence of pentaBDE congeners is higher than decaBDE due to their physico-chemical properties (Vonderheide et al., 2008).

In the biotic samples low-brominated congeners (BDE 47, BDE 99, BDE 100, BDE 153 and BDE 154) appear to be the most predominant congeners because of their high bioavailability (de Wit, 2002; Watanabe and Sakai, 2003; Mariottini et al., 2008). This predominance could be caused by their higher potential for bioaccumulation and according the study Wan et al. (2008) the predominance of BDE 47 in high trophic level animals could be also contributed by the debromination of higher brominated PBDEs and its relatively high biomagnification potential in food webs.

Some studies suggest that PBDEs concentrate at different trophic levels within aquatic ecosystems and have a biomagnification potential in the food chain (Hajšlová et al., 2007). In contrast, much less is known about terrestrial systems and there are only two reports describing the plant uptake of PBDEs from soil and their translocation to above-ground part of plant. Mueller et al. (2006) showed that plants such as radish and zucchini have the ability to take up and accumulate pentaBDEs from contaminated soil. Huang et al. (2010) described the uptake, translocation and metabolism of BDE 209 in six plant species. Plants could therefore play an important role for the transfer of PBDEs into the food chain. Pirard and De Pauw (2007) found that PBDEs can be accumulated in the liver and the abdominal fat of chickens, and consequently they can be transferred to eggs. Kierkegaard et al. (2007) have described that there is an accumulation of BDE 209 in the body fat and meat of cows and its further metabolic debromination leads to formation of low-brominated congeners nonaBDE (BDE 207), octaBDEs (BDE 196 and BDE 197) and heptaBDE (BDE 182). People may be thus exposed to PBDEs by consuming of herbivore meat.

The main source of PBDEs in soil is application of enormous volumes of contaminated sewage sludge to agricultural areas (Law et al., 2006; Eljarrat et al., 2008; Vonderheide et al., 2008; US EPA, 2009). Based on the median concentrations of PBDEs analyzed in 15 sewage sludge samples in the Czech Republic in 2006 it was calculated that 29.2 kg of Penta- and OctaBDE mixtures and 67.6 kg of DecaBDE mixture were land-applied per year (Stiborová et al., 2009). A similar study shows that in Germany 150 kg per year of Penta- and OctaBDE mixtures and 350 kg per year of DecaBDE were released into the environment *via* sewage sludge land-application in 2001 (Knoth et al., 2007). There are no guidelines for the content of organic pollutants such as PBDEs in sewage sludge used in agriculture (Eljarrat et al., 2008).

The aim of the present study was to investigate the uptake of PBDEs from sewage sludge into plants and their translocation to above-ground tissues. The application of sewage sludge in the fields used for the growth of the plants for human consumption represent a worst case scenario and many more studies are needed to display enough evidence to ban that on European level. We have chosen *Nicotiana tabacum* and *Solanum nigrum* for our experiment because these plants are used as the model plants in many studies (Evangelou et al., 2007; Gichner et al., 2007; Rezek et al., 2007; Wei et al., 2010) and for their known ability to accumulate PCBs (Mackova et al., 2009) which are structurally similar to PBDEs.

2. Materials and methods

2.1. Chemicals

The following set of standard solutions containing PBDE congeners (concentration 50 μg mL^{-1} in nonane) were obtained from Wellington Laboratories, Canada: 2,4,4′-triBDE (BDE 28); 3,4,4′-triBDE (BDE 37); 2,2′,4,4′-tetraBDE (BDE 47); 2,2′,4,5′-tetraBDE (BDE 49); 2,3′,4,4′-tetraBDE (BDE 66); 2,2′,3,4,4′-pentaBDE (BDE 85); 2,2′,4,4′,5-pentaBDE (BDE 99); 2,2′,4,4′,6-pentaBDE (BDE 100); 2,2′,4,4′,5,5′-hexaBDE (BDE 153); 2,2,4′,4,5′,6′-hexaBDE (BDE 154); 2 2,2′,3,4,4′,5′,6-heptaBDE (BDE 183), decaBDE (BDE 209) and ^{13}C BDE 209. Standard solution of PCB 112 (10 μg mL^{-1} in isooctane) was purchased from Gr. Ehrenstorfer GmSH (Germany). The organic solvents (cyclohexane, dichloromethane, hexane, ethylacetate and isooctane) declared for organic trace analyses grade were all supplied by Merck (Germany). Anhydrous sodium sulphate supplied by Penta Chrudim (Chrudim, Czech Republic) was heated at 600 °C for 5 h and then stored in desiccator before use. Styrene–divinylbenzene gel (Bio Beads S-X3, 200–400 mesh) was purchased from Biorad Laboratories (USA).

2.2. Analytical methods

Extraction of PBDEs was performed by Soxhlet extraction using dichloromethane as solvent for sewage sludge and a mixture of hexane:dichloromethane (1:1, *v/v*) for plants. The crude extract was carefully evaporated and the sample dissolved in solvent mixture cyclohexane–ethylacetate (1:1, *v/v*) that was used as a mobile phase in gel permeation chromatography (GPC) employing Bio Beads S-X3 column for separation of interfering co-extracts.

An Agilent 6890 (Agilent, USA) gas chromatograph equipped with a single quadrupole mass analyzer Agilent 5975 XL operated in negative chemical ionization mode (GC/MS-NCI) and DB-XLB capillary was employed for routine analyses of PBDEs in purified extracts. The GC conditions were as follows (for all analyzed PBDEs with exception of BDE 209): capillary column DB-XLB column (30 m × 0.25 mm i.d. × 0.1 μm film thickness, J & W Scientific, Folsom, USA), column temperature program: from 105 °C (hold 2 min) to 300 °C at 20 °C min^{-1} (hold 5 min); carrier gas: helium (Siad, Czech Republic) with constant flow 1.5 mL min^{-1}; injection temperature: 275 °C; injection volume: 1 μL using pulsed splitless injection mode (splitless time: 2 min). The mass selective detector with quadrupole analyzer was operated in a selective ion-monitoring mode (SIM) in a negative chemical ionization (NCI). Monitored ions (*m/z*) were 79, 81, 159 and 161. Ion *m/z* 79 was used for quantification of all target analytes. Methane, which was used as a reagent gas (purity 99.995%, Siad, Czech Republic), was set at a pressure 2×10^{-4} mbar. Ion source temperature was 150 °C and quadrupole temperature 105 °C.

The presence of BDE 209 was monitored using the same GC/MS-NCI employing a shorter capillary column BD-XLB (15 m × 0.25 mm i.d. × 0.1 μm film thickness J & W Scientific, USA). The temperature program was the following: from 80 °C (hold 2 min) to 280 °C at 20 °C min^{-1} and to 320 °C at 5 °C min^{-1} (hold 5 min); carrier gas: helium with constant flow 3 mL min^{-1}; injection temperature: 285 °C; injection volume: 1 μL using pulsed splitless injection mode (splitless time: 2 min). Monitored ions (*m/z*) were 485 and 487 for BDE 209, 495 and 497 for ^{13}C labelled BDE 209 (Stiborová et al., 2008).

2.3. Quality assurance/quality control

Analysis was carried out in an accredited testing laboratory (No. 1316.2) in the Czech Republic (current standard: EN ISO/IEC