HIGHER BROMINATED DIPHENYL ETHERS IN EARTHWORMS AND REFERENCE AND SEWAGE-SLUDGE AMENDED SOILS

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Introduction

Polybrominated diphenyl ethers (PBDE) are widely used flame retardants in plastics, textiles and electronics[1]. Decabrominated diphenyl ether (DeBDE) is the most used PBDE (56000 tons/year in 2001) and consists primarily of the fully brominated congener, BDE-209 with small amounts of octa- and nonaBDEs. For soils, SPBDE (BDE-47, -99, -100, -153, –154) range from 0.07 to 12 ng/g dry weight (dw) in U.K. and Norwegian background soils[2] and not detected and 13.6 ng/g dw (BDE-47, -99, –100) downwind of a polyurethane foam production plant[3]. No published data are available for concentrations of the higher brominated diphenyl ethers such as BDE-209 in soils. A source of PBDEs to soils is atmospheric deposition, which is particularly important for BDE-209[4]. Sewage-sludge amendment has also been shown to be a source of tetra-heptaBDEs to Swedish soils and contributes much more to soil concentrations than atmospheric deposition[5]. SPBDE concentrations for the tetra-heptaBDEs ranged from 0.03 to 0.11 ng/g dw in the reference soils and 0.08 to 840 ng/g dw in amended soils. Significant bioaccumulation of PBDEs, PCBs and PCDD/Fs was also seen in earthworms from these soils.

Sewage sludge from Swedish sewage treatment plants contains BDE-209 as the predominant congener[6] and sewage-sludge amendment may also contribute to significant increases in soil BDE-209 burdens. Therefore, soil and earthworm samples from the previous study were analyzed for higher brominated BDEs, including BDE-209, in order to determine soil background levels, the effect of sewage sludge amendment, and bioavailability and bioaccumulation from soil to earthworms. The environmental behaviors of the higher brominated BDEs are also compared to those of the lower brominated BDEs, PCBs and PCDD/Fs.

Methods

Samples of soil and earthworms were taken from three research stations (Petersborg, Igelösa, Lanna) and two private farms (Horred, Björketorp) in southern Sweden in 2000[5]. At the research stations, the soils were amended with controlled amounts of sewage sludge (last applications in 1997 or 1998). Some plots were never treated with sludge and were used as reference areas. In Björketorp, sewage sludge from a plant receiving waste water from PBDE-using textile industries was spread between 1978 – 1982. In Horred, no sludge was applied, but the adjacent river Viskan, containing sediments known to be polluted by PBDEs[7], almost annually floods part of the field, including the summer preceding the sampling. Reference samples from these two farms were a field that had not received any sludge (Björketorp), and a part of the field not known to have been flooded recently (Horred). Each soil sample was a pool of 30 to 40 smaller samples from each plot or site, from 0 to 20 cm depth. The samples were sieved (500 μm) to remove stones and other larger items before dry weight and loss on ignition was determined. The extraction method for the soil samples is described in detail elsewhere[8] and was used with only minor modifications. Earthworms were collected from the same areas as the soil samples, and were allowed to clear the gut and then washed with water before they were killed. This procedure, as well as the extraction and clean-up are described in more detail by Matscheko et al.[5].

Samples were analysed by GC-MS run in the chemical ionisation mode, measuring the negative ions formed (ECNI) [7]. MS conditions: electron energy 70 eV, ion source temperature 180^{o}C, reaction gas ammonia, set at a pressure of 7000-8000 millitorr. Mass fragments monitored for quantitative analysis: *m/z* -79 and -81 for PBDE, and -237 and -239 for dechlorane (internal standard). For BDE-209 the phenolate ions -487 and -489 were also measured. The GC was equipped with a constant flow, split-splitless injector (280^{o}C). DB-5MS columns (30 m for tri-heptaBDE and 15 m for octa-decaBDE) were used. Single congeners of a range of commercially available tri-decaBDEs were used as reference standards.

Ratios between the concentrations in the sludge-treated soils and reference soils at the same site were calculated using concentrations on a dry weight (dw) basis (S/R ratios). Biota-soil accumulation factors (BSAFs) were calculated using the worm concentrations on a lipid weight (lw) basis divided by the soil concentrations on an ignition loss basis.

Results and Discussion

Previously, it was shown that sewage sludge adds directly to the load of tri-heptaBDEs to soil and that this is more pronounced than for PCBs and PCDD/Fs[5]. In this study, a similar relationship was found for the octa-decaBDEs as well. The more sludge that is used, the more the BDE concentrations increase, including for BDE-196, -197, -206, -207 and -209. The reference soils contained low concentrations, with BDE-209 concentrations ranging from 0.015-0.75 ng/g dw (0.46-10 ng/g IG). The S/R ratios for all BDEs are greater than 1, with BDE-209 generally having the highest ratio at each site. The highest overall S/R ratios were found at the two farms. Figure 1 shows the S/R ratios for BDE-47, -100, -99 and -209 in soils and worms from one of the experimental stations (Petersborg) and at the farm, Horred, where the River Viskan floods the fields each year. As can be seen, addition of sewage sludge increases the lower brominated BDE concentrations 3-4 times, but increases BDE-209 8-fold at Petersborg. At Horred, BDE-209 concentrations are more than 200 times higher in the flooded field than at the reference site. The BDE concentrations found in the worms reflect those found in the soils, and the S/R ratio patterns are similar to those seen in the soils (Fig. 1). The highest PBDE levels were found at the farm Björketorp, with SPBDE for the tetra-hexaBDEs of 1300 ng/g dry weight (20 000 ng/g IG) in amended soil and 32 000 ng/g lw in worms, and for BDE-209, 2200 ng/g dw (34 000 ng/g IG) in soil and 5200 ng/g lw in worms. The high PBDE concentrations in the amended soil at Björketorp, more than 20 years after last sludge use, indicates high persistence of PBDEs, including BDE-209 in soils.

BSAFs were quite similar independent of soil PBDE concentrations, except from the flooded field at Horred, where BSAFs were lower. The BSAFs of the BDEs declined in the following order: BDE-47>BDE-100>BDE-99>BDE-153>BDE-154>BDE-207>BDE-196>BDE-209>BDE-206 and were 4-5 for the Te-PeBDEs, 2-3 for the

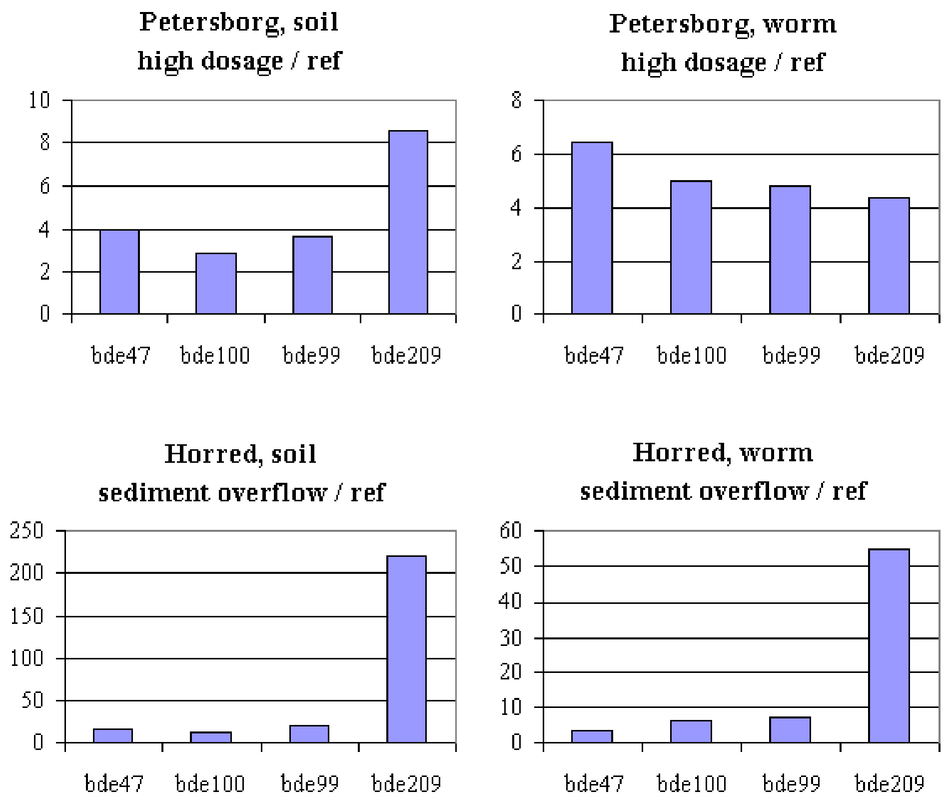

Figure 1. S/R ratios for some PBDEs in soil and worm samples from an experimental station (Petersborg) or the farm with the field flooded by River Viskan annually (sediment overflow) (Horred).

HxBDEs and ranged from 0.3-2 for the Oc-DeBDEs. When BSAFs for PBDEs are compared to those for PCBs and PCDD/Fs, the order is Te-PeBDEs>Pe-HxCBs>HxBDEs>OcBDEs>Te-PeCDFs>NoBDEs>Hp-OCDF=OCDD=DeBDE>Hx-HpCDD. Thus, higher brominated PBDEs, including BDE-209 are bioavailable from the sewage-sludge treated soils. It is generally accepted that the Te-OCDD/Fs bioaccumulate in organisms and this would indicate that octa- to decaBDEs also bioaccumulate. Thus, past and current use of sewage sludge as a fertilizer has increased concentrations of PBDEs in agricultural soils in Sweden and these will remain in the soil for a long time. This in turn leads to higher concentrations in worms, including for BDE-209. Earthworms are at the base of the terrestrial food web, thus the animals that eat them will be exposed to the contaminants they have accumulated from soil. In comparison to PCBs and PCDD/Fs, atmospheric deposition of PBDEs does not seem to be as important a source to soil as sewage sludge amendment.

In conclusion, use of sewage sludge as a fertilizer leads to increased PBDE concentrations in soils and the terrestrial food web.

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