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Dynamics of brominated flame retardants removal in contaminated wastewater sewage sludge under anaerobic conditions

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HIGHLIGHTS

- Indigenous microorganisms can significantly biodegrade PBDEs and HBCD in sludge under methanogenic conditions.
- Higher brominated DEs were removed faster than lower brominated congeners.
- The congener distribution has changed after 15 months of cultivation in favour of higher proportion of lower brominated DEs.

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ABSTRACT

Disposal of solid waste to landfills from waste water sewage treatment plants (WWTPs) serves as a potential source of contamination by polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD). Native microbial communities have been found to degrade a variety of xenobiotics, such as PBDEs and HBCDs. This study investigates the potential of autochthonous microflora to remove 11 PBDE congeners and HBCDs in waste water sludge under anaerobic conditions. Laboratory microcosms were constructed with sewage sludge from the WWTPs of Hradec Kralove and Brno. BDE 209 was detected as the prevailing congener in concentrations 685 and 1403 ng/g dw and the total amounts of 10 lower PBDEs (BDE 28, 47, 49, 66, 85, 99, 100, 153, 154, 183) were 605 and 205 ng/g dw in sludge from Hradec Kralove and Brno, respectively. The levels of HBCD were detected in both sludge lower than 24 ng/g dw. The experiment was carried out for 15 months. After three months of incubation, HBCD was completely degraded to below detection limits. In sewage from both WWTPs, the higher brominated DEs were removed faster than the lower brominated congeners. One exception was tri-BDE, which was degraded completely within 15 months of cultivation. A significant increase in congener tetra-BDE 49 concentrations was observed over the course of the experiment in all tested sewage. The relative distribution of individual congeners among all PBDEs changed after 15 months of the incubation in favour of lower brominated congeners. This indicates that debromination is the major mechanism of anaerobic biodegradation. Despite of the increase of BDE 49, the overall removal of all 11 PBDEs achieved the levels of 47.4 and 68.7% in samples from WWTPs Hradec Kralove and Brno, respectively.

1. Introduction

The large scale synthesis and use of xenobiotic compounds has resulted in worldwide contamination of air, water and terrestrial ecosystems. Brominated flame retardants (BFRs) are a class of chemicals which increase the fire resistance of industrial and commercial products.

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) are BFRs that are not covalently bounded to the material such as textile, polyurethane foams, plastics and electronic components, and therefore can leach into the environment from the products during usage or disposal. The rapid accumulation of PBDEs in the environment, and humans, has resulted in restrictions of further production and applications of PBDEs and their replacement by other compounds (Ali et al., 2011; Bocio et al., 2003; Davis et al., 2012; Law et al., 2006; Vonderheide et al., 2008).

Commercially available PBDE mixtures (PentaBDE, OctaBDE and DecaBDE) which were used in industry are divided into three groups according to the average number of bromine atoms in the molecule. In Europe in 2004, and in the USA in 2006, PentaBDE and OctaBDE mixtures were phased out from production due to concern over observed toxic effects (EPA U, 2006; EU, 2003). This led to temporarily increases in the production of DecaBDE mixtures, resulting in elevated concentrations of BDE 209 (the major congener in DecaBDE mixture) and decreasing concentrations of BDE 154 and BDE 183 (representative of

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PentaBDE and OctaBDE mixtures) in environmental samples (Law et al., 2014; Venkatesan and Halden, 2014). Following the restriction of the use of PBDE mixtures, there was also an increase in the production and usage of HBCD (Al-Odaini et al., 2015; Law et al., 2006). Based on the subsequent evidence of HBCD persistence, toxicity and bioaccumulation in the environment, it has also been recently listed for global elimination (C&EN, 2013).

The hydrophobic nature of PBDEs and HBCD causes these chemicals to be strongly bound to solid particles in sewage sludge and soil (Law et al., 2006). Sewage treatment plants have been reported as one of the major sources of BFR pollution through the discharge of wastewater effluents and subsequent usage of sewage sludge (Gorga et al., 2013; Venkatesan and Halden, 2014). The most common methods of sludge use and disposal are agriculture, compost, landfilling and incineration. Before land application, sludge is treated to reduce odour and pathogens (Stiborova et al., 2015b). Furthermore, the land-applied sludge needs to meet the regulatory criteria for the amount of heavy metals. However, no guidelines currently exist for BFRs such as PBDEs and HBCD (86/278/EEC, 1986; Davis et al., 2015) so the amount of these compounds in land-applied biosolids is not regulated. In the USA, it was estimated that 24,000–36,000 kg/year of PBDEs and 50–76 kg/year of HBCD were released through land applications (Venkatesan and Halden, 2014). Similar quantities are also estimated to be deposited through land application of contaminated sewage sludge in Europe and Asia (Dong et al., 2014; Gorga et al., 2013; Knoth et al., 2007; Vrkoslavova et al., 2010).

Biodegradation is an effective strategy for the removal of contaminants in the environment (Demnerova et al., 2002; Mackova et al., 2010; Uhlik et al., 2013). The degradation of both xenobiotic HBCD and PBDEs were also described under both aerobic and anaerobic conditions. Davis et al. (2005) found that the degradation of HBCD was faster in anaerobic compared to aerobic conditions. Recently, there has been increasing attention on the degradation of PBDEs under both aerobic and anaerobic conditions (Deng et al., 2011; Huang et al., 2014; Stiborova et al., 2015a; Tokarz et al., 2008; Vrkoslavova et al., 2011).

It was documented that several factors could stimulate BDE 209 debromination under anaerobic conditions, such as: i) additional co-substrates (Huang et al., 2014; Lee and He, 2010); ii) priming debromination by other halogenated compounds (Gerecke et al., 2005) or iii) additional different electron donors which had also impact on the overall microbial community (Qiu et al., 2012; Xu et al., 2012). An interesting approach was also described by Yang et al. (2013) who enhanced BDE 209 degradation by microbial electricity generation.

Various redox zones exist in freshwater or saline sediments and soils and thus nitrate-reducing, sulphate-reducing, iron-reducing or methanogenic conditions can be found within different layers (Haggblom et al., 1993; Voordeckers et al., 2002). There have been many observations of reductive dehalogenation under methanogenic conditions (Voordeckers et al., 2002; Ye et al., 1995). As the molecular methods have further advanced, not only have been methanogens described to be highly abundant during anaerobic sludge digestion but also in various terrestrial and aquatic environments (Brablcova et al., 2015; Praeg et al., 2014). In the anaerobically stabilized sludge from WWTPs Brno and Hradec Kralove methanogenic populations were detected previously (Stiborova et al., 2015b).

BFRs were detected in subsurface layers of the soil and sediment compartments (Kwan et al., 2014a) and thus, it is essential to understand potential degradation of these compounds under limited oxygen condition. As majority of studies had focused on the debromination of individual BDE congeners (Gerecke et al., 2005; Nyholm et al., 2010; Qiu et al., 2012; Xu et al., 2012; Zhu et al., 2014) or the research was conducted using microbial enriched culture or pure strains (Huang et al., 2014; Xu et al., 2014) we decided to study the removal of wide spectrum of PBDE congeners (PBDEs No. 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, 209) and HBCD directly in industrially contaminated sewage sludge by autochthonous microflora. The degradation in slurries was monitored over the course of 3, 6 and 15 months of cultivation under anaerobic conditions.

2. Methods

2.1. Chemicals

An analytical set of standard solutions containing PBDE congeners (concentration 50 μg/ml in nonane): 4,4′-diBDE (BDE15); 2,4,4′-triBDE (BDE 28); 3,4,4′-BDE (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′,3,4,4′,5′,6-heptaBDE (BDE 183) and deca-BDE (BDE 209) and HBCD standard (50 μg/ml in toluene), all with declared purity 98%, was obtained from Cambridge Isotope Laboratories (CIL, Andover, USA).

The organic solvents (cyclohexane, dichloromethane, ethylacetate and isooctane) declared for "organic trace analyses" grade were all supplied by Merck (Darmstadt, Germany). Anhydrous sodium sulphate supplied by Penta Chrudim (Chrudim, Czech Republic) was heated at 600 °C for 5 h and then stored in dessicator prior use. Styrene-divinylbenzene gel (Bio Beads S-X3, 200–400 mesh) was purchased from Biorad Laboratories (Hercules, CA, USA). Sulphuric acid (98%) was obtained from Merck (Darmstadt, Germany). The redox indicator resazurin was obtained from Sigma-Aldrich.

2.2. Sludge collection and microcosm preparation

Two industrially sewage sludge samples contaminated by BFRs were collected in WWTPs Hradec Kralove and Brno (WWTP Hradec Kralove — the amount of cleaned wastewater: 16 million m^3; the total length of sewerage net: 496 km; the number of sewage connection: 16,775; WWTP Brno — the amount of cleaned wastewater: 31 million m^3; the total length of sewerage net: 1350 km; the number of sewage connection: 49,930). Samples were collected in May, 2007 (Stiborova et al., 2015a). The samples were pooled in jars and stored on ice during the transport and then stored at 4 °C for no longer than 2 weeks. The sludge was not additionally spiked by PBDEs or HBCD.

The homogeneity of PBDEs and HBCD distribution which were present as contamination in the sludge, was ensured by thoroughly mixing and the uniformity of samples was confirmed before slurry preparation. Sewage sludge samples were resuspended in the medium described by Shelton and Tiedje (1984) used for dehalogenators in volume ratio 40:60. Thirty millilitre of suspension was filled up to 50 ml glass serum bottles. Starch (20 mg) and yeast extract (50 mg) were added into each bottle under the atmosphere of nitrogen and carbon dioxide (80:20). The redox indicator reasuzurin was added into the bottles to ensure that conditions in the anaerobic microcosms were reducing. The bottles were tightly capped and incubated in the incubator at 28 °C for 15 months in the dark. Fifteen months was chosen due to previously documented persistence of PBDEs (Gerecke et al., 2005, 2006; Nyholm et al., 2010).

Control experiments with heat-sterilized sludge were performed simultaneously. Three parallel bottles for each condition were always determined for analysis of PBDEs and HBCD contents.

2.3. Analysis

Samples were transferred into Soxhlet extraction thimbles, dried at 40 °C and then mixed with anhydrous sodium sulphate to form a free flowing powder. As a recovery standard PCB 112 was used. Extraction was performed by 170 ml of dichloromethane in Soxhlet apparatus for 7 h. After solvent evaporation, the sample was dissolved in 10 ml of solvent mixture cyclohexane–ethylacetate (1:1, v/v) and then purified