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Review

Review of contamination of sewage sludge and amended soils by polybrominated diphenyl ethers based on meta-analysis☆

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are still present in sewage sludge and sludge-amended soil, even though commercial PBDEs were prohibited or voluntarily phased out several years ago. In this study, levels and compositional profiles of seven major PBDE congeners in sludge are assessed in relation to their usage patterns in commercial products, and years of being banned and phased out in North America, Europe, and Asia. Annual accumulations and future long-term changes of PBDE in sludge-amended soil are estimated. BDE-209 has the highest concentration, followed by BDE-99 and BDE-47. The highest concentrations, up to 23,500 ng g^{-1}, of PBDEs in sludge were found in North America until 2004–2007, whereas since then sludge PBDE concentrations, up to 6600 ng g^{-1} have been higher in Asia than on the other two continents. The amount of sludge applied and the soil organic matter content play important roles in determining PBDE concentrations in sludge-amended soil. The estimated concentrations of BDE-47, -99, and -209 in soils receiving sludge applications during the past 15 years are 40–300 times higher than in soils after the initial sludge application. The accumulated concentrations of BDE-47 and BDE-99 are expected to decrease by 99% between 2016 and 2100, whereas the decrease in the BDE-209 concentration is predicted to be approximately 87%.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of industrial aromatic organobromine chemicals that have been used since the 1970s as flame retardants in a wide range of consumer products and articles, such as plastics, computers, textiles and upholstery (Cincinelli et al., 2012; Daso et al., 2012; Hites, 2004). PBDE molecules contain up to 10 bromine atoms attached to two carbon rings ($C_{12}H_{(10-x)}Br_xO$ ($x = 1, 2, \ldots, 10$)). The nomenclature and numbering system are based on the number and position of attached bromine atoms. The chemical structure results in 209 PBDE congeners, divided into 10 homologue groups (mono- to deca-BDE) according to the number of bromine atoms in the molecule. Three commercial mixtures of PBDE congeners were produced and sold industrially: commercial pentabromodiphenyl ether (c-PentaBDE), commercial octabromodiphenyl ether (c-OctaBDE), and commercial decabromodiphenyl ether (c-DecaBDE) (Andrade et al., 2015).

Due to their physicochemical properties, including hydrophobicity and lipophilicity, PBDEs are persistent and bioaccumulative in the environment, leading to adverse effects on human health and the ecosystem (de Wit et al., 2010; Eens et al., 2013; Law et al., 2014). Therefore, c-PentaBDE and c-OctaBDE were added to Annex A of the Stockholm Convention as persistent organic pollutants (POPs) in May 2009, and their production and uses have been widely eliminated, except for certain exemptions (Stockholm Convention on Persistent Organic Pollutants, 2009). c-DecaBDE is not listed in the Stockholm Convention, but it is being evaluated by the POP Reviewing Committee for listing (UNEP, 2014). The total amounts of c-PentaBDE and c-OctaBDE used in the world were around 100,000 tonnes each by 2005. More than 1.1 million tonnes of c-DecaBDE had been distributed by 2005, and it is still being produced and consumed (Li et al., 2009; Schenker et al., 2008; UNEP, 2014).

PBDEs continue to enter municipal wastewater treatment plants (WWTPs) due to washing and cleaning of rags, carpets, and laundry, as well as shower gray water and human waste (Gevao et al., 2011; Zeng et al., 2010). Most conventional wastewater

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treatment processes are not designed to effectively remove PBDEs (Gevao et al., 2008). Owing to their low solubility, high hydrophobicity, and limited biodegradability, over 60–90% of total PBDEs detected in influent wastewater accumulate in sewage sludge in WWTPs (Deng et al., 2015; North, 2004; Peng et al., 2009; Song et al., 2006; Xiang et al., 2013). PBDE concentrations in sewage sludge have been determined in global ranges. For example, concentration levels ranging from 1000 to 2290 ng g^{-1} for tri- to hexa-BDEs and from 85 to 4890 ng g^{-1} for deca-BDE were determined in the U.S. (Davis et al., 2012; Hale et al., 2003). The concentrations of PBDEs in sludges generated from wastewater treatment plants in China and South Korea were found in the ranges of 150 to 24,000 ng g^{-1} and 17 to 67,000 ng g^{-1}, respectively (Hwang et al., 2012; Peng et al., 2009). In sludge collected in Italy, PBDE concentrations ranged from 150 to 9430 ng g^{-1} (Cincinelli et al., 2012).

Land application of sewage sludge has been adopted worldwide as an option for sludge disposal (Gorgy et al., 2012; Olofsson et al., 2012). The sewage sludge acts as an organic matter supplement and improves soil physical properties (Clarke and Smith, 2011; Li et al., 2009; Martinez et al., 2003). The percentage of sewage sludge applied to agricultural land was as high as 50% in Germany, 65% in France, 71% in the U.K., 60% in the U.S., and 26% in South Korea (Eljarrat et al., 2008; Hale et al., 2012; Ministry of environment, 2012). As a result, application of sewage sludge contaminated with PBDEs may contribute significantly to increased soil burdens of PBDEs. Gorgy et al. (2012, 2013) showed that the PBDE concentrations on agricultural soil in Canada increased from 0.08 to 0.3 ng g^{-1} to 300–600 ng g^{-1} after sludge application. Gaylor et al. (2014) found that sludge-amended soils in the U.S. contained ~17,600 ng g^{-1}, but no PBDEs were detected in reference soil. Levels of ~200 ng g^{-1} were determined in sludge-amended soils from China (Li et al., 2015), and ~1300 ng g^{-1} for soil samples collected in Spain (Eljarrat et al., 2008). These studies also revealed that the levels and distributions of PBDEs in sludge-amended soils may depend on the levels and distribution of PBDEs in sewage sludge.

Understanding of concentrations and compositions of PBDE in sewage sludge may be addressed based on the usage patterns of commercial products in regions (i.e., geographical factors), year of ban and phase-out in various countries (i.e., temporal factors). However, there is no information on the geographical and temporal trend of PBDEs remaining in sludge controlling PBDE contamination of sludge-amended soil, and thus dictating the level and composition of PBDEs. Due to the lack of information, global changes (past and future trends) of PBDEs accumulated in sludge-amended soil have not been clearly delineated. In the past two decades, analysis of PBDEs has been challenging due to their complex composition and the high organic matter content of sewage sludge and sludge-amended soil that cause co-elution of interfering compounds and the need to remove them (EC, 2001; Król et al., 2012; Wu et al., 2012). Different procedures for the determination of PBDE congeners in sludge and sludge-amended soil are also applied in different regions, making it difficult to compare results.

In this study, we (i) provide a critical overview of common or developed analytical procedures for determining PBDE congeners in sludge and sludge-amended soil, including: pre-treatment, extraction, clean-up, and instrumental analysis; (ii) discuss geographical and temporal trends of the levels and compositional profiles of PBDE congeners in sewage sludge, based on the usage and dominant constituents of commercial PBDE mixtures, and year of ban and phase-out in different regions of the world; (iii) estimate past scenarios (2000–2015) regarding PBDE concentrations accumulated in soils during the period of sludge application, based on the trends identified in (ii); (iv) discuss the factors influencing the accumulation and loss of PBDEs in sludge-amended soil; and (v) predict future (2016–2100) levels of PBDE congeners in sludge-amended soil driven by degradation in agricultural soils after banning sludge application.

2. Background and methodology

2.1. PBDE congeners selected for special attention in sludge and sludge-amended soil

In the three commercial PBDE products, c-PentaBDE mainly contained 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47), 2,2′,4,4′,5-pentabromodiphenyl ether (BDE-99), and 2,2′,4,4′,6-pentabromodiphenyl ether (BDE-100) (La Guardia et al., 2006). c-OctaBDE consisted mainly of several hexa- to deca-brominated congeners. Congeners representative of the c-OctaBDE formulations are 2,2′,4,4′,5,5′-hexabromodiphenyl ether (BDE-153), 2,2′,4,4′,5,6′-hexabromodiphenyl ether (BDE-154), and 2,2′,3,4,4′,5′,6-heptabromodiphenyl ether (BDE-183) (Strakova, 2015). c-DecaBDE, still available in some regions, is mostly composed of 2,2′,3,3′,4,4′,5,5′,6,6′-decabromodiphenyl ether (BDE-209) (92–98%) (Bianchi and Canuel, 2011). For this reason, these seven PBDE congeners (BDE-47, -99, -100, -153, -154, -183, and -209) have been mainly detected in sewage sludge and soil (Arnold et al., 2008; Eljarrat et al., 2008; Gorgy et al., 2010; La Guardia et al., 2007; Lee et al., 2014; Li et al., 2015; Sellström et al., 2005). Moreover, these congeners have received considerable attention due to their toxic effects (Akortia et al., 2016). Therefore, BDE-47, -99, -100, -153, -154, -183, and -209 were selected for special attention in the present study. The molecular structures and key properties of these PBDEs are presented in Table S1 of Supplementary Information.

2.2. Experimental determination of PBDEs in sewage sludge and soils

The analytical procedures for the determination of PBDEs in sewage sludge and sludge-amended soil involve pre-treatment and extraction, clean-up, and measurement by analytical instruments. In this study, experimental procedures for determining PBDEs in sewage sludge and soils were collected from articles published during the last 25 years. Findings are arranged according to: (i) variation over time in analytical procedures (extraction, clean-up, and instrument method), (ii) typical non-polar solvents used in extraction methods for PBDE congeners, (iii) column types and elution solutions used in the clean-up stage, and (iv) instrument properties and methods (column length, temperature, detection technique, and separation technique) applied during the final stage of PBDE congener analysis.

2.3. Monitoring data of sewage sludge and sludge-amended soils from geographical regions

North America, Europe, and Asia have dominated the production and consumption of PBDEs and PBDE-containing goods (BSEF, 2003). These three continents consumed over 90% of the world's PBDE production in 2001 (Hale et al., 2002). Commercial PBDE mixtures have been predominantly banned and phased out in North America, Europe, and Asia. In 2004, c-PentaBDE and c-OctaBDE were banned in Europe, and the primary U.S. producer voluntarily phased out production of c-PentaBDE and c-OctaBDE. Since 2004, Sweden, Canada, and the U.S. states of Maine and Washington banned c-DecaBDE, and several other U.S. states proposed legislative bans (Vonderheide et al., 2008). In China, use of c-PentaBDE in electric products has been banned since 2007 (UNEP, 2007). Therefore, in this study, PBDE levels in sewage sludge and