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Critical review of soil contamination by polybrominated diphenyl ethers (PBDEs) and novel brominated flame retardants (NBFRs); concentrations, sources and congener profiles[☆]

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A B S T R A C T

Polybrominated diphenyl ethers (PBDEs) have been used in a broad array of polymeric materials such as plastics, foams, resins and adhesives to inhibit the spread of fires since the 1970s. The widespread environmental contamination and well documented toxic effects of PBDEs have led to bans and voluntary withdrawals in many jurisdictions. Replacement novel brominated flame retardants (NBFRs) have, however, exhibited many of the same toxic characteristics as PBDEs and appear to share similar environmental fate. This paper presents a critical review of the scientific literature regarding PBDE and NBFR contamination of surface soils internationally, with the secondary objective of identifying probable pollution sources. An evaluation of NBFR distribution in soil was also conducted to assess the suitability of the newer compounds as replacements for PBDEs, with respect to their land contamination potential. Principle production of PBDEs and NBFRs and their consequent use in secondary polymer manufacture appear to be processes with strong potential to contaminate surrounding soils. Evidence suggests that PBDEs and NBFRs are also released from flame retarded products during disposal via landfill, dumping, incineration and recycling. While the land application of sewage sludge represents another major pathway of soil contamination it is not considered in this review as it is extensively covered elsewhere. Both PBDEs and NBFRs were commonly detected at background locations including Antarctica and northern polar regions. PBDE congener profiles in soil were broadly representative of the major constituents in Penta-, Octa- and Deca-BDE commercial mixtures and related to predicted market place demand. BDE-209 dominated soil profiles, followed by BDE-99 and BDE-47. Although further research is required to gain baseline data on NBFRs in soil, the current state of scientific literature suggests that NBFRs pose a similar risk to land contamination as PBDEs.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardants (BFRs) that have been used in a broad array of polymeric materials such as plastics, foams, resins and adhesives to inhibit the spread of fires (WHO, 1997). PBDEs have been manufactured since the 1970's and have become known as significant global contaminants (de Wit et al., 2006; Brits et al., 2016; Yu et al., 2016). Decades of research has documented the accumulation of PBDEs in a range of environmental matrices and biota (Law et al., 2014), while toxic effects including endocrine disruption and developmental neurotoxicity are well evidenced (Linares et al., 2015). PBDEs have historically been sold in three major commercial formulas known as Penta-BDE, Octa-BDE and Deca-BDE, which each contain a range of the 209 mono-through deca-brominated congeners (La Guardia et al., 2006). Specific congeners have dominated within the commercial mixtures and are therefore typically analysed in environmental samples as indicators of the individual formulas. In particular, the tetrabrominated congener BDE-47, pentabrominated BDE-99 and -100, and hexabrominated BDE-153 and -154 are each representative of Penta-BDE formulas, while Octa-BDE products are indicated by heptabrominated BDE-183 and Deca-BDE products by the decabrominated BDE-209. Penta- and Octa-BDE formulas have been banned from use in many jurisdictions (EU, 2003; NICNAS, 2007; Stapleton et al., 2012)

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while the tetra-through hepta-brominated homologues most common to these mixtures were listed as Persistent Organic Pollutants (POPs) under the United Nations Stockholm Convention in 2009 (UNEP, 2009). The addition of Deca-BDE commercial mixtures to the Convention has been officially proposed (UNEP, 2013) and a range of restrictions and phase-out initiatives have been implemented globally (EU, 2009; USEPA, 2010). An assortment of new generation BFRs have emerged to replace the restricted compounds and are interchangeably referred to as “alternative”, “new”, “emerging” or “novel” BFRs (NBFRs). The physicochemical characteristics of NBFRs are generally analogous to those of PBDEs, and similar patterns of environmental contamination and toxicity have been indicated (Covaci et al., 2011; Ezechiáš et al., 2014). Among the most common NBFRs are decabromodiphenyl ethane (DBDPE), which replaces Deca-BDE formulas, bis(2,4,6-tribromophenoxy) ethane (BTBPE), being used in place of Octa-BDE and bis(2-ethylhexyl) tetrabromophthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), which constitute replacements of Penta-BDE mixtures (Covaci et al., 2011; Ezechiáš et al., 2014). Hexabromobenzene (HBB), 2,3,4,5,6- pentabromotoluene (PBT) and 2,3,4,5,6-pentabromoethylbenzene (PBEB) are each general use flame retardants replacing PBDEs in a range of polymers (Covaci et al., 2011; Ezechiáš et al., 2014).

PBDEs and NBFRs enter the environment via atmospheric emission from a variety of sources including manufacturing (Gouteux et al., 2008; Li et al., 2015b), waste incineration (Wang et al., 2010b), recycling facilities (Hearn et al., 2012) and other general industrial processes (Wang et al., 2010a). Electronic and electrical waste (e-waste) recycling has proven to be among the greatest sources of atmospheric release, owing to typically high concentrations within products and processing techniques which exacerbate their dispersion (Labunska et al., 2013; Li et al., 2014). Emitted contaminants may be transported large distance in air and undergo net deposition to land (Newton et al., 2014; Cetin et al., 2016). PBDEs and NBFRs also enter soils via direct transfer from flame-retarded products in dumpsites (Hafeez et al., 2016) or via landfill leachates (Olukunle and Okonkwo, 2015). The application of sewage sludge to soil as a nutrient amendment has been demonstrated to be a significant pathway of BFR loading to agricultural land due to high levels of contamination inherent in sewage waste streams (Kim et al., 2017). The lipophilic properties of PBDEs and NBFRs cause them to bind tightly to organic matter and persist in soils where half-lives as long as ~28 y have been estimated (Andrade et al., 2010).

PBDEs and NBFRs have been shown to bioaccumulate in soil dwelling invertebrates like earthworms (Nyholm et al., 2010; Gaylor et al., 2013), allowing propagation of the contaminants into terrestrial food-chains (Nie et al., 2015). Contaminated soils may also transfer PBDEs into suspended solids and sediments of aquatic environments via precipitation run-off (Muresan et al., 2010). Bioaccumulation and trophic transfer of PBDEs and NBFRs has been observed in the ecosystems of fresh water and marine organisms (Law et al., 2006; Klosterhaus et al., 2012; Poma et al., 2014). Soils contaminated by PBDEs or NBFRs also form potential human exposure pathways for humans. Inhalation of soil fragments suspended in outdoor air or dermal absorption of settled particles may contribute to the intake of these BFRs (Abdallah et al., 2015; Akortia et al., 2017). Ingestion of soils adhered to vegetables grown on contaminated land and direct oral intake of soil by toddlers are also potential exposure routes. The ability for many plant crops to translocate PBDEs from soil into vegetative structures may also result in consistent low level exposure through the diet (Navarro et al., 2017). In light of the risks to human health posed by contaminated soils, reference screening values have been established by government agencies in some jurisdictions (NEPC, 2013; USEPA, 2017).

This review aims to summarise the published studies on PBDE and NBFR soil contamination. An interrogation of the current data regarding concentrations across different land-uses will attempt to provide an account of the most probable sources of BFRs to soils internationally. Comparisons of the congener profiles among PBDE contaminated sites will be used to identify global commercial formula usage patterns. An evaluation of NBFR distribution in soil will also be conducted with the objective of assessing the suitability of the newer compounds as replacements for PBDEs, with respect to their land contamination potential.

2. Featured studies and reporting conventions

This paper reviews soil contamination data presented in English language peer-reviewed scientific literature published up until May 2017. Studies related to soil contamination as a result of direct sewage sludge or waste-water application have not been included. Land application of sewage sludge to improve soil structure and nutrient content represents a major contribution of PBDEs and NBFRs to soils globally (Kim et al., 2017). PBDEs and NBFRs may enter wastewater streams from manufacturing, industrial waste and domestic sources and are often retained in sludges during municipal treatment processes (Clarke et al., 2008; De la Torre et al., 2012; Zeng et al., 2014). PBDE concentrations measured in sewage sludges from North America, Europe, Asia and Australia have regularly exceeded 1000 ng/g, while NBFR levels are typically orders of magnitude lower (Kim et al., 2014a; Zeng et al., 2014). In excess of 10 million tonnes of sludge are applied to land globally each year (Kim et al., 2017), creating a massive potential for PBDE and NBFR transfer to soil. However, the exact contamination impact to soils from sewage sludge is determined by complex interactions between the two media. The PBDE and NBFR concentrations in the applied sewage sludge, rate and frequency of sludge application and tilling/mixing methods employed each have a strong effect on contaminant concentrations over time (Andrade et al., 2010; Li et al., 2015a). The behavior and fate of PBDEs and NBFRs in soil from application of contaminated waste requires specific and complex consideration regarding these factors, which have been comprehensively addressed in a number of recent review articles (Clarke and Smith, 2011; Clarke and Cummins, 2015; Kim et al., 2017).

In all cases, $\sum_x$PBDEs refers to the sum of x PBDE congeners including BDE-209, unless otherwise stated. Concentration values have been reported to a maximum of three significant figures and all units of measurement have been converted to ng/g for consistency. All concentrations are reported on a dry weight basis unless otherwise stated. Concentrations on an organic matter basis are reported as ng/g OM, concentrations on an organic carbon basis are reported as ng/g OC and concentrations on a wet weight basis are reported as ng/g WW. All mean values are arithmetic means unless otherwise stated and in all cases ND abbreviates “not detected”. Data presented in Fig. 1 has been arranged into land-use categories by the authors according to sample site information provided in original data sources. Author-assigned land-use categories are provided in Table 1 as numerical superscript notations. Values reported to be below detection limits appear in Fig. 1 as half of the respective detection limit.

3. PBDE congener profiles

PBDE congener profiles in soil have been broadly representative of the major constituents in commercial mixtures of Penta-, Octa- and Deca-BDE and related to predicted market place demand. As the main component of Deca-BDE mixtures, BDE-209 has been the