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A first European scale multimedia fate modelling of BDE-209 from 1970 to 2020

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ABSTRACT

The European Variant Berkeley Trent (EVn-BETR) multimedia fugacity model is used to test the validity of previously derived emission estimates and predict environmental concentrations of the main decabromodiphenyl ether congener, BDE-209. The results are presented here and compared with measured environmental data from the literature. Future multimedia concentration trends are predicted using three emission scenarios (Low, Realistic and High) in the dynamic unsteady state mode covering the period 1970–2020. The spatial and temporal distributions of emissions are evaluated. It is predicted that BDE-209 atmospheric concentrations peaked in 2004 and will decline to negligible levels by 2025. Freshwater concentrations should have peaked in 2011, one year after the emissions peak with sediment concentrations peaking in 2013. Predicted atmospheric concentrations are in good agreement with measured data for the Realistic (best estimate of emissions) and High (worst case scenario) emission scenarios. The Low emission scenario consistently underestimates measured data. The German unilateral ban on the use of DecaBDE in the textile industry is simulated in an additional scenario, the effects of which are mainly observed within Germany with only a small effect on the surrounding areas. Overall, the EVn-BTER model predicts atmospheric concentrations reasonably well, within a factor of 5 and 1.2 for the Realistic and High emission scenarios respectively, providing partial validation for the original emission estimate. Total mean MEC:PEC shows the High emission scenario predicts the best fit between air, freshwater and sediment data. An alternative spatial distribution of emissions is tested, based on higher consumption in EBFRIP member states, resulting in improved agreement between MECs and PECs in comparison with the Uniform spatial distribution based on population density. Despite good agreement between modelled and measured point data, more long-term monitoring datasets are needed to compare predicted trends in concentration to determine the rate of change of POPs within the environment.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are additive flame retardant chemicals used in a wide range of products including electrical and electronic (E&E) equipment, textiles and foams. The three most commonly used commercial PBDE mixtures (PentaBDE, OctaBDE and DecaBDE) have been produced in large amounts with recent global production rates of more than 50 kilotons/year (BSEF, 2012). Historically, DecaBDE has been produced in the largest volumes of any commercial PBDE (1.3 million tonnes globally 1970–2010 (Earnshaw et al., 2013)). Due to their toxicity the PentaBDE and OctaBDE products were banned in the EU in 2004 (Stockholm Convention on POPs). In 2008, DecaBDE was banned from use in E&E equipment in the EU Restriction of Hazardous Substances Directive 2008/95/EC (RoHS Directive (European Council, 2008)) and production looks likely to cease by 2014 globally although many manufacturers are already switching to alternatives (European Environmental Bureau, 2008). Another step toward removing DecaBDE from the European market is the recent agreement of the European Chemicals Agency (ECHA) Member State Committee on the identification of decabromodiphenyl ether as a Substance of Very High Concern (SVHC) (ECHA, 2012). The agreement identifies DecaBDE as a substance which is persistent, bioaccumulative and toxic (PBT), and very persistent and very bioaccumulative (vPvB) in accordance with Articles 57 (d) and (e), respectively, of Annex XIII of the REACH Regulation 1907/2006.

Despite the bans, a legacy of products containing PBDEs continues to release these PBT/vPvB chemicals into the environment from a wide range of sources (Kumari et al., 2014). Assuming sales of PBDE products cease in 2015, it may take until the 2030s before PBDEs in the

Abbreviations: ADV, aerosol deposition velocity; DecaBDE, decabromodiphenyl ether; E&E, electronic and electrical; EBFRIP, European brominated flame retardant industry panel; ECHA, European Chemicals Agency; EVn-BETR, European Variant Berkeley Trent; LRAT, long range atmospheric transport; MEC, measured environmental concentration; PBDE, polybromodiphenyl ether; PEC, predicted environmental concentration; POP, persistent organic pollutant; RoHS, Restriction of Hazardous Substances Directive 2002/95/EC; RSR, rain scavenging ratio; SFA, substance flow analysis; SVHC, Substance of Very High Concern; VECAP, voluntary emissions control action programme; WWTP, wastewater treatment plant.

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anthroposphere reach negligible levels and emissions cease (Earnshaw et al., 2013). It is also recognised that DecaBDE is transformed in the environment to, among other substances, the lower bromodiphenyl ethers with PBT/vPvB properties, and also precursors to substances classified as PBT/vPvB (ECHA, 2012).

PBDEs and in particular BDE-209, are reported to be widespread in the European environment, occurring in the atmosphere (Castro-Jiménez et al., 2011; Cetin and Odabasi, 2008; Egebäck et al., 2012; Tlili et al., 2012; Vives et al., 2007; Wilford et al., 2008), sediment (Christensen and Platz, 2001; Guerra et al., 2010; Van Ael et al., 2012; Vives et al., 2007), freshwater (Cristale et al., 2013; Harman et al., 2013; Teil et al., 2012) and snowpack in remote regions (Arellano et al., 2011). BDE-209 is also present in Spanish pine tree needles (Ratola et al., 2011), Spanish white stork eggs (Munoz-Arnanz et al., 2011), Danish blue mussels (Christensen and Platz, 2001), Swedish peregrine falcon eggs (Johansson et al., 2011), Spanish peregrine falcon eggs (Guerra et al., 2012), Mediterranean sandhoppers (Ungherese et al., 2012) and a range of biota in the Scheldt estuary, Netherlands (Van Ael et al., 2012). PBDEs, including the congener BDE-209, have been found in liver and kidney cells of East Greenland polar bears at concentrations of tens of ng/g, demonstrating their capacity for long-range transport to remote regions (Sonne et al., 2012). Elevated levels of BDE-209 are reported in the sewage sludge of wastewater treatment plants (WWTPs) and can be a significant source to freshwater catchments via discharge of effluents, and agricultural soils through use as fertiliser (Cincinelli et al., 2012; Eljarrat et al., 2008; Ricklund et al., 2009; Sellström et al., 2005).

Palm et al. (2002) performed a first and screening level analysis to estimate the environmental distribution and behaviour of PBDEs and concluded, among other things, that "more accurate emission and monitoring data" are needed "to more fully understand their fate". Over a decade on, we aim to improve on their estimates for BDE-209 with the use of a European emission inventory for 1970–2020, updated physical–chemical properties and monitoring data for the European environment. The European Variant of the Berkeley-Trent model (EVn-BETR) has previously been used to model emissions of Benzo[α]pyrene (Hauck et al., 2008), Lindane (Prevedouros et al., 2004b) and PentaBDE (Prevedouros et al., 2004a). These studies generally underestimated MECs largely due to underestimated emission rates.

1.1. Study outline and aim

This study uses the EVn-BETR multimedia fate model and a previously estimated emission inventory (Earnshaw et al., 2013) to predict BDE-209 concentrations in European environmental media for the period 1970–2020. The emission inventory was derived for compatibility with the EVn-BETR model and several emission scenarios are used to estimate predicted environmental concentrations (PECs). Focus is weighted toward the compartments of lower air (atmosphere), freshwater and sediment due to the available measurement data. PECs are compared with monitoring data and temporal data sets for validation of the emissions estimates and spatial distribution of emissions.

2. Methods

2.1. Model structure and parameterisation

The EVn-BETR model consists of inter-connected environmental compartments and uses the fugacity approach (Prevedouros et al., 2004b). The European continent is split into 50 regions by way of a 5° × 5° grid with four additional external regions to represent neighbouring continents (Fig. 1). The multimedia environment within each region is described by inter-connected homogenous and discrete compartments. Vertically segmented air compartments simulate long-range atmospheric transport of chemicals in the troposphere; a freshwater compartment simulates rivers separately to coastal water; soil, sediment and vegetation complete the mass balance (Fig. S1). The compartments are represented as matrices of volumetric flow rates describing the movement of air and water across regional boundaries and control chemical transport between regions. Chemical fate and behaviour are described using fugacity (f, Pa), which is related to concentration (C, mol/m^3) by the proportionality constant, Z (mol/m^3·Pa) the fugacity capacity specific to the chemical, environmental compartment and temperature. Full details of model description can be found in Mackay (2001), MacLeod et al. (2001) and Woodfine et al. (2001). The model uses the physical–chemical properties of BDE-209; molecular weight, vapour pressure, aqueous solubility and partition coefficients, compiled from the scientific literature and presented in Table S1. A previous modelling study by Schenker et al. (2008) provides an almost complete physical–chemical data set. Estimated emissions are released to the lower atmosphere, freshwater and soil compartments of the model according to three scenario conditions, described in Section 2.3. Predictive capability of the EVn-BETR model is tested here for BDE-209. Both steady-state and dynamic runs were used to assess PECs against measurement data and historical time trends of BDE-209 in Europe. Steady-state runs used emission data for 2010 when atmospheric emission rates approximately peak. The dynamic runs cover the period 1970–2020 and we assume that production and consumption of new DecaBDE product are phased-out by 2015. An extended run to 2050 is included to assess when concentration of the chemical in the environment falls to negligible levels.

2.2. Gas and particle phase emissions

Gas phase emissions represent releases of BDE-209 via volatilisation whereas emissions occurring from physical abrasion and weathering represent the particle bound phase. Emission estimates from Earnshaw et al. (2013) split atmospheric emissions in to gaseous and particle bound pathways over the period 1970–2020. The fraction of each pathway varies slightly over time with gas and particle pathways representing a mean 7% (±5%) and 92% (±4%) respectively. Gas phase emissions increase slightly during the 2010s as emissions from the legacy of BDE-209 in landfill sites become more important. Gas phase and particle bound BDE-209 will behave differently once released to the environment; gas phase BDE-209 will behave according to the physical–chemical properties of the molecule, whereas the behaviour of particle bound BDE-209 will be largely influenced by the particle properties (i.e. size, weight, composition, etc.). It is not possible to run the EVn-BETR model simultaneously for both phases therefore, emissions are separated into the two pathways and the model is run individually using different physical–chemical properties, half-lives and environmental parameters to mimic the two phases.

A recent study found that the larger BDE congeners (Br_{7-10}) generally sorb to larger sized particles than their lower brominated counterparts (Wilford et al., 2008). Sorption to smaller sized particles increases the potential for LRAT and longer atmospheric residence times and also has important implications for human respiratory system exposure and health (Mandalakis et al., 2009). However, smaller particles have a lower solar light shielding capacity in the atmosphere, but once deposited from the atmosphere to surface soils tend to pack more closely and limit light scattering and permeation of the soil to lower depths, resulting in shorter atmospheric half-life and longer soil half-life (Ahn et al., 2005). BDE-209 may permeate into the matrix of porous soil and sediment particles and be further stabilised by organic carbon that can non-covalently bind to polar organic compounds (Söderström et al., 2003). The presence of humic acid in soil has been shown to decrease the degradation rate when irradiated with UV light (Hua et al., 2003), although clay minerals can provide a catalysing effect enhancing the photo-degradation of BDE-209 by electron donation (Ahn et al., 2005). Clearly particle complexity and composition are important factors affecting chemical stability, however, this cannot be simulated in the EVn-BETR model.