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Environmental occurrence of emerging and legacy brominated flame retardants near suspected sources in Norway

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HIGHLIGHTS

- A method using LC--APPI--MS/MS was developed for analysis of emerging BFRs.
- BDE209 was found in highest levels in most samples.
- TBECH was found in seepage water, waste water and sewage sludge.
- TBBPA DBPE was found in highest levels among emerging BFRs in seepage water.

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ABSTRACT

The environmental occurrence of potentially emerging brominated flame retardants (BFRs) was investigated near suspected source zones in Norway, within seepage water, sewage waste water, sewage sludges, and sediments. Analyzed emerging BFRs included 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (TBECH), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenylethane (DBDPE), ethylene bis(tetrabromophthalimide) (EBTPI), tetrabromobisphenol A diallyl ether (TBBPA AE), and tetrabromobisphenol A bis(2,3-dipropyl ether) (TBBPA DBPE). In addition selected polybrominated diphenylethers (PBDEs) were analyzed, so that findings could be compared to legacy BFRs. An analytical method based on liquid chromatography atmospheric pressure photoionization tandem mass spectrometry was developed for analysis of EBTPI, TBBPA AE, and TBBPA DBPE. The legacy BFRs were in general found in higher levels and abundances than the studied emerging BFRs. However, BTBPE was detected in most of the studied matrices (sewage sludge, seepage water and sediment). DBDPE was detected in sewage sludge, waste water, seepage water and in sediment taken close to a combined metal recycling and car dismantling site. TBECH was found in seepage water, waste water and sewage sludge. EBTPI was identified in one seepage water sample; TBBPA AE was detected both in seepage water and sediment, and TBPPA DBPE in waste water and seepage water. Of the emerging BFRs, the highest levels in water samples were quantified for TBBPA DBPE (81 ng/L, seepage water from a combined metal recycling and car dismantling site) and in sediment for BTBPE (6.5 ng/g, taken close to landfill). The findings of current-use BFRs in seepage water, sediment and in sewage suggest that further investigations are needed of the environmental fate and effects of these flame retardants.

1. Introduction

Brominated flame retardants (BFRs) have been used commercially for several decades to fire-proof plastics, textiles and electronics. Environmental concern related to the use of BFRs has been growing in recent years since some BFRs have shown to be persistent, bioaccumulative, toxic, and undergo long-range atmospheric transport (Birnbaum and Staskal, 2004; de Wit, 2002; de Wit et al., 2010). BFRs such as the polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) have been restricted in the European Union since 2006 and industries in the US have voluntarily phased-out the penta- and octa-BDE mixtures (Cleet, 2004). Among the current-use flame retardants decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (TBECH), ethylene bis(tetrabromophthalimide) (EBTPI), tetrabromobisphenol A diallyl ether (TBBPA AE) and tetrabromobisphenol A bis(2,3-dipropyl

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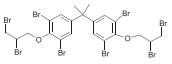
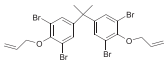
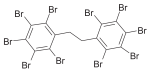
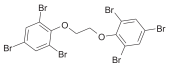
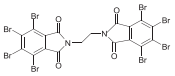
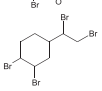
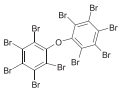
ether) (TBBPA DBPE) have been identified as probable persistent and bioaccumulative chemicals in a recent screening (Howard and Muir, 2010). All of these BFRs are used as additives in different polymeric materials (e.g. polystene, polypropylene, high impact polystyrene) and in textiles. TBBPA AE is also used as a reactive BFR. More information on production volumes and use of these BFRs are available in a review by Covaci et al. (2011), where they are also identified as the most important novel BFRs. These BFRs were also discussed by Harju et al. (2009) as BFRs of environmental concern (excluding TBECH). Though there is some concern for these current use BFRs, there are no or only limited data on the environmental occurrence of these potentially persistent and bioaccumulative BFRs (Covaci et al., 2011; de Wit et al., 2010; Harju et al., 2009).

DBDPE, BTBPE, TBBPA AE and TBBPA DBPE are low production volume chemicals (LPVC) in the EU, referring to market volumes of 10 and 1000 t per year and per distributor (esis.jrc.ec.europa.eu). EBTPI is a high production volume chemical (HPVC) in the EU, referring to volumes above 1000 t per year. TBECH is used as an additive flame retardant, and the technical product contains two major diastereomers, α- and β-TBECH, and also traces of two minor diasteromers, γ-, and δ-TBECH. The production volume in the United States was between 4 and 225 t in 2002 (epa.gov), but no information was found on its use in the EU (where it is not registered as a HPVC or a LPVC). However, it can be anticipated that the production of these non-regulated BFRs will increase in the future, as a consequence of tighter restrictions on legacy BFRs.

The aim of the present study was to screen for the presence of these current-use BFRs in environmental samples from suspected source zones in Norway. The suspected sources in the present study are sites where BFRs in consumer and end-of-use products can enter the environment. These sites include a combined metal recycling and car dismantling site, a municipal waste landfill and three waste water treatment plants. Recently, analytical methods based on liquid chromatography atmospheric pressure photoionization tandem mass spectrometry (LC–APPI–MS/MS) have been developed for a wide range of halogenated flame retardants (Bacaloni et al., 2009; Debrauwer et al., 2005; Lagalante and Oswald, 2008; Zhou et al., 2010). In this study a similar method was developed for TBBPA DBPE, TBBPA AE and EBTPI. For comparison, levels of selected PBDEs were also measured. The chemical structures of the studied BFRs are shown in Table 1.

Table 1
Chemical names, abbreviations, CAS registry numbers and molecular structures of the investigated brominated flame retardants (BFR).

BFR	CAS	Structure
Tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBPA DBPE)	21850-44-2	
Tetrabromobisphenol A diallyl ether (TBBPA AE)	25327-89-3	
Decabromodiphenylethane (DBDPE)	84852-53-9	
1,2-Bis(2,4,6-tribromophenoxy) ethane (BTBPE)	37853-59-1	
Ethylene bis(tetrabromophtalimide) (EBTPI)	32588-76-4	
1,2-Dibromo-4-(1,2-dibromoethyl) cyclohexane (TBECH)	3322-93-8	
Decabromodiphenylether (BDE 209)[a]	1163-19-5	

[a] Presented as representative of analyzed brominated diphenylethers.

2. Material and methods

2.1. Environmental sampling

Sampling was performed in suspected source zones in Norway where BFRs could possibly be discharged, in the late summer and autumn of 2009. The sampling is described in detail in Arp et al. (2011) and in the report published by Klif (2010). In brief, seepage water from a metal recycling factory was taken at the discharge point in the Loselva River (3 replicate samples taken during 1 week, 1 L per day), and sediment samples were taken 10 m from the discharge point (3 replicates). Seepage water samples were taken from a municipal waste landfill near Drammen (3 replicate samples taken during 1 week), along with sediments (3 replicates). Waste water, sewage sludge and sediment samples were collected from three municipalities, viz., Tromsø, Drammen, and Lillehammer. Sampling at WWTPs was conducted as follows: 1 L water samples were obtained daily from the inlet and outlet monitoring stations within each WWTP. Combined weekly samples (7 L) were stored in amber glass containers wrapped in aluminum foil to avoid photodegradation of BFRs. Outlet sludge was sampled daily and combined and homogenized to obtain weekly samples. Sampling, in triplicate, was done over three consecutive weeks to reach three inlet samples, and outlet and sludge samples per WWTP (in total 9 inlet water samples, 9 outlet water samples and 9 sludge samples). Sediment samples in diverse locations from the receiving water body of the WWTPs (either a lake or marine harbor) were also obtained (in total 27 sediment samples).

2.2. Chemicals

Analytical standard BDEs 47, 100 and 153 were obtained from AccuStandard (New Haven, CT, USA), and BDEs 85 and 100 were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). BTBPE and DBDPE were bought from Wellington Laboratories (Guelph, ON, Canada) and BDEs 28, 183, and 209 were synthesized at Stockholm University, Sweden. Technical grade EBTPI was obtained from Chiron (Trondheim, Norway), TBBPA AE and TBECH from Sigma-Aldrich (Stockholm, Sweden), and TBBPA DBPE from TCI (Tokyo, Japan). Stock solutions of neat chemicals were prepared in toluene.

Labeled (^{13}C) internal standards of BTBPE were bought from Wellington Laboratories (Guelph, ON, Canada) and ^{13}C-labeled BDE 28 and 209 were bought from Cambridge Isotope Laboratories (Andover, MA, USA). These internal standards were added to the samples before extraction and were used to correct for losses during the clean-up procedure. In the quantification procedure ^{13}C-labeled BDE 28 was used as internal standard for TBECH and BDEs 28, 47, 85, 99, 100, 153 and 183, ^{13}C-labeled BTBPE was used for BTBPE, TBBPA DBPE, and TBBPA AE, and ^{13}C-labeled BDE 209 was used for BDE 209 and EBTPI. Stock solutions of the BFRs were prepared in toluene. Labeled (^{13}C) PCB 208 was used as recovery standard (added to samples prior to injection) and was bought from Cambridge Isotope Laboratories (Andover, MA, USA). Methanol (SupraSolv), diethyl ether (SeccoSolv) and ethyl acetate (LiChrosolv) were bought from Merck, Germany. Hexane (Picograde) and acetone (Picograde) were bought from Promochem, and dichloromethane (glass distilled), cyclohexane (glass distilled) and toluene (glass distilled) were bought from Fluka, Switzerland.

2.3. Physical–chemical properties and statistics

Various physical–chemical properties of the studied emerging BFRs have yet to be determined experimentally, and thus estimation methods are the only existing means of assessing these properties. For BFRs it was noted previously that of the available estimating