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Novel brominated flame retardants and dechlorane plus in Greenland air and biota

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ABSTRACT

Following the ban of polybrominated diphenyl ethers, other halogenated flame retardants (FRs) might be used increasingly. This study has analyzed hexabromocyclododecane (HBCD), 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) and dechlorane plus (DP) in Greenland air over the course of a year. Moreover, BTBPE, DPTE, DP, 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), bis(2-ethylhexyl)tetrabromophthalate (TBPH) and decabromodiphenyl ethane (DBDPE) were analyzed in samples of polar bear, ringed seal, black guillemot and glaucous gull from Greenland. HBCD in air appeared low, while mean concentrations of *syn*- and *anti*-DP were 2.3 and 5.2 pg/m^3, respectively. BTBPE and DPTE were undetectable in air. Detection frequencies in biota were <50% for BTBPE, TBPH and DBDPE, but near 100% for the remaining compounds. Ringed seals from East Greenland had highest mean concentrations of TBB, DPTE, *syn*- and *anti*-DP (1.02, 0.078, 0.096 and 0.42 ng/g wet weight, respectively). Our study documents the long-range transport and, to some extent, bioaccumulation of these novel FRs.

1. Introduction

Brominated flame retardants (BFRs) have been widely used to increase fire safety of construction materials and consumer products, but have also become an environmental and human health issue (Frederiksen et al., 2009). Several BFRs, such as polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs) and hexabromocyclododecane (HBCD) have been shown to be sufficiently persistent to be transported to the Arctic and to accumulate in Arctic animals (de Wit et al., 2010). Combined with increasing awareness of their potential toxicity, these compounds are now regulated through the Stockholm Convention on Persistent Organic Pollutants (POPs).

In order to maintain fire safety levels, unregulated halogenated flame retardants might be used increasingly. The term novel BFRs (NBFRs) is often used to summarize a group of chemically diverse compounds assumed to replace the banned BFRs. Covaci et al. (2011) provide a careful estimate of a production volume of 100,000 to 180,000 tons/year, which is roughly twice the combined production volumes of the three PBDE mixtures before their ban (de Wit et al., 2010). However, information on production volumes, trade patterns and industrial applications of NBFRs is sparse, and data of environmental occurrence and fate of some NBFRs are only just emerging. Recent studies have documented the presence of some NBFRs in the indoor environment (e.g. Stapleton et al., 2008), in sewage sludge (e.g. Gorga et al., 2013), and consequently, in the outdoor environment including biota (e.g. Guerra et al., 2012). Some studies have also shown long-range transport to the Arctic and bioaccumulation in Arctic wildlife for NBFRs (Vorkamp and Rigét, 2014).

Based on initial evidence of their occurrence in Arctic biota, bis(2-ethylhexyl)tetrabromophthalate (TBPH), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), 1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE), decabromodiphenyl ethane (DBDPE) and 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) were chosen for this study. A mixture of TBPH and TBB has been marketed as Firemaster® 550 to replace PentaBDE, but TBPH has also been used individually in, for example, polyvinylchloride (PVC) (Stapleton et al., 2008). TBPH and TBB have been found to exhibit endocrine disrupting potential, furthermore, the TBPH metabolite mono(2-ethylhexyl) tetrabromo phthalate (TBMEHP) showed thyro- and hepatotoxicity in rodents (Saunders et al., 2013; Springer et al., 2012). BTBPE and

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DBDPE are replacement products of OctaBDE and DecaBDE, respectively, and production sites in the USA and, for DBDPE, in China have been described (Covaci et al., 2011). DPTE was produced in Germany until 1985, but it is unclear whether or not it is still being produced for use as a flame retardant (Vetter et al., 2010).

In addition to these NBFRs, dechlorane plus (DP) might be increasingly used as a flame retardant. It was originally introduced in the 1960s as a replacement product of the insecticide Mirex (Hoh et al., 2006), but has also been reported to replace DecaBDE in the EU (Möller et al., 2010). Two recent reviews concluded that DP was a ubiquitous global pollutant with the potential for long-range transport and bioaccumulation (Feo et al., 2012; Sverko et al., 2011). Chemical structures and physical–chemical properties of the NBFRs and DP are given as Supporting information.

Our objective was to address the transport of these compounds to Greenland in terms of their atmospheric concentrations and to study their accumulation in selected wildlife species. Besides NBFRs and DP, the atmospheric analyses included HBCD, which had previously been found in increasing concentrations in Greenland biota (Vorkamp et al., 2011, 2012).

2. Materials and methods

2.1. Air samples

Samples were collected at Station Nord (81°36′N 16°40′E) in North-East Greenland as described by Bossi et al. (2013). The samples were collected on a weekly basis in 2012 using a High Volume Sampler (Digitel, Hegnau, Switzerland) at a flow rate of 0.5 m^3/min, resulting in a total sample volume of 5000 m^3 for each sample. The sampler was equipped with a pre-cleaned quartz fiber filter (15 cm in diameter) in front of a pre-cleaned cartridge of PUF/XAD-2/PUF. After sampling, the filters and PUF/XAD-2/PUF cartridges were stored at −20 °C.

2.2. Biota samples

The biota samples analyzed in this study had been collected in Central East Greenland in 2012, with additional ringed seal *(Pusa hispida)* samples from West Greenland ($N = 4$), and included black guillemot *(Cepphus grylle)* eggs ($N = 4$), glaucous gull *(Larus hyperboreus)* liver ($N = 4$), blubber of ringed seal ($N = 5$) and polar bear *(Ursus maritimus)* adipose tissue ($N = 5$). A map with the sampling locations is given in the Supporting information.

2.3. Chemical analysis of HBCD in air samples

One filter sample per month was analyzed. Because of their lipophilic character and low vapor pressure, HBCD isomers are mainly associated with particles (Hoh and Hites, 2005; Yu et al., 2008). All filters were spiked with isomer-specific ^{13}C-labelled HBCD (Cambridge Isotope Laboratories (CIL), Tewksbury, MA, USA) and Soxhlet extracted with hexane:acetone (4:1, v:v). The extracts were reduced in volume and cleaned on 2 g activated silica. After elution of other analytes with 100 ml hexane, the HBCD isomers were eluted with 20 ml hexane:dichloromethane (1:1, v:v). The eluates were dried under nitrogen, and the HBCD isomers were re-dissolved in 500 μl methanol. The analysis was performed by high performance liquid chromatography (HPLC) with electrospray ionization in negative mode and tandem mass spectrometry detection (MS/MS) as detailed by Vorkamp et al. (2012).

The procedural blank (pre-cleaned unexposed filter) contained traces of the three isomers near detection limits, which were subtracted from HBCD in the samples. Method detection limits (MDLs) were approximately 0.0047 pg/m^3 for each isomer. Filters spiked with 5.75 ng of each isomer gave recovery rates of 99.6 ± 0.4, 101.5 ± 0.5 and 98.5% ± 5.6% for α-, β- and γ-HBCD, respectively.

2.4. Chemical analysis of NBFRs and dechlorane plus in air samples

Because of the limited sample amount and the suite of compounds to be monitored in the same samples (Bossi et al., 2013), the analyses in this study only included BTBPE, DPTE, *syn*- and *anti*-DP. Analytical standards were obtained from Wellington Laboratories (Guelph, Ont., Canada). As for HBCD, samples of each month were analyzed. For February, two samples were available, which were analyzed separately and averaged in the data processing. Each sample consisted of a quartz fiber filter and a PUF/XAD-2/PUF cartridge, which were Soxhlet extracted together using hexane:acetone (4:1; v:v). The extracts were cleaned on 1 g silica (ISOLUTE® Si, Biotage, Uppsala, Sweden; 7% moisture), which had been conditioned with 5 ml hexane, and eluted with 7 ml hexane:dichloromethane (30:70, v:v) and 7 ml dichloromethane, which subsequently were combined. The instrumental analysis was performed by gas chromatography (GC) with high resolution mass spectrometry (HRMS) as described by Kolic et al. (2009) and Bossi et al. (2013).

Three unexposed filters and PUF/XAD-2/PUF were extracted as blanks along with the samples. The four compounds were detectable in at least one of the blanks, but below MDLs, which ranged between 0.4 and 2 pg/m^3.

2.5. Chemical analysis of NBFRs and dechlorane plus in biota samples

Following homogenization, sub-samples were spiked with ^{13}C-*trans*-chlordane (CIL) for recovery determination and ^{13}C-TBPH (Wellington Laboratories). The samples were Soxhlet extracted using 350 ml of hexane:dichloromethane (1:1; v:v). The extracts were divided in half for separate clean-up of TBPH and the remaining compounds. As TBPH is not stable to acid treatment (Ali et al., 2011), these extracts were cleaned by gel permeation chromatography (GPC) (Phenogel 300 × 21.20 mm; Phenomenex, Torrance, CA, USA) followed by 7 g activated silica from which TBPH and ^{13}C-TBPH were eluted with hexane:dichloromethane (1:1, v:v). The other extracts were cleaned on a column containing aluminium oxide, silica, acidified silica and Na_2SO_4 as previously used for PBDEs (Vorkamp et al., 2004a). The compounds were likewise eluted with hexane:dichloromethane (1:1, v:v). The eluates were evaporated to dryness in silicone-coated vials (Vorkamp et al., 2014), and the compounds were re-partitioned into 200 μl isooctane including BDE-71 (CIL) as a syringe standard.

The extracts were analyzed by gas chromatography (GC) and low resolution mass spectrometry (LRMS) with electron capture negative ionization (ECNI) as previously described for PBDEs (Vorkamp et al., 2004a). While DBDPE, *syn*- and *anti*-DP were separated on a 15 m DB-1 column (0.25 mm i.d., 0.25 μm film thickness; J&W Scientific, Folsom, CA, USA), a 60 m DB-5 column (0.25 mm i.d., 0.25 μm film thickness; J&W Scientific) was used for the remaining NBFRs.

The procedural blank showed low, but quantifiable levels of *syn*- and *anti*-DP, which were subtracted from the amount in the samples. MDLs ranged between 0.002 and 0.024 ng/g wet weight (ww) (Supporting information). Recoveries were >75% (mean 91%) for the method including the column clean-up (Supporting information). As some samples had lower recoveries in the GPC clean-up (>22%; mean 87%), TBPH was quantified by isotope dilution with ^{13}C-TBPH. Spiked and non-spiked duplicate samples of