"Novel" Brominated Flame Retardants in the Environment: a Review

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Introduction

To date, at least 75 different brominated flame retardants (Leonards et al., 2008) have been produced. So far, studies have been primarily restricted to three groups: PBDEs, HBCDs, and TBBP-A. Recently some information has become available for other "novel" BFRs, although little is known about their uses or production volumes. A recent paper by de Wit et al. (in press) indicated that a number of these "novel" BFRs are of particular concern as they are being found in the Arctic, indicating long-range transport. We aim to gather together the available data and to try to identify directions for further research.

Environmental Occurrence

Abiotic matrices

Seawater

BFRs are seldom determined in seawater as they are very hydrophobic and rapidly become particle-bound. López et al. (2009) determined twelve "novel" BFRs (brominated phenols, toluenes, anilines and anisoles, primarily), in seawater samples from the Western Scheldt, finding them to occur at concentrations up to 25 ngL^{-1}.

Sewage Sludge

DBDPE (decabrominated diphenyl ethane) was found in 25 out of 50 sewage sludge samples from Swedish WWTP (Kierkegaard et al., 2004), at concentrations up to 100 μgkg^{-1} dry weight (dw). The fate of DBDPE and BDE209 on passage through a wastewater treatment plant (WWTP) was studied by Ricklund et al. (2008a). Fate of the two BFRs was similar: 99% was found in the digested sludge, at 81 and 800 μgkg^{-1} dw, respectively. Ricklund et al. (2008b) also detected DBDPE in sewage sludge from all 42 WWTPs in 12 countries worldwide, suggesting that this is now a widespread contaminant, in Europe at least. The highest concentration observed (216 μgkg^{-1} dw) was in a sample from the Ruhr area of Germany. BTBPE (1,2-*bis*(2,4,6-tribromophenoxy)ethane), DBDPE and tetrabromobisphenol A-*bis*(2,3-dibromopropylether) (TBBPA-DBPE) were determined in sewage sludge samples from southern China (Shi et al., 2009). Maximum concentrations were 1.7, 2,000 and 8,950 μgkg^{-1} dw, respectively. The high concentrations of DBDPE and TBBPA-DBPE are consistent with their use in the electronics industry in the Pearl River Delta region of China. TBPH and TBB were also detected in two sludges from the San Francisco Bay area, at concentrations ranging from 40 - 1412 μgkg^{-1} dw and 57 - 515 μgkg^{-1} dw, respectively (Klosterhaus et al., 2008).

Sediment and Soil

BTBPE was detected in a sediment core from Lake Michigan taken in 2004 (Hoh et al., 2005). BTBPE first appeared in the sediment record around 1973 and increased rapidly until 1985 (ca. 8 μgkg^{-1} dw), then stabilised. In 1987, the concentration of BTBPE was ca. 10 x higher than the sum of BDE47, BDE99 and BDE100, major components of the penta-PBDE formulation. Production volumes in the USA were 4,500 - 22,500 t/y from 1986 - 1994, but decreased to 450 - 4,500 t/y after 1998 (Hoh et al., 2005). BTBPE has been proposed as a replacement for the octa-PBDE formulation.

BTBPE was determined in a sediment core from Lake Ontario in 2004 (Qiu et al., 2007). The highest concentration, found at the surface, was 6.7 μgkg^{-1} dw, about half that of BDE209. Neither BTBPE nor DBDPE were detected in sediments taken from Lake Winnipeg in 2003 (Law et al., 2006).

Maximum concentrations of BTBPE, DBDPE and TBBPA-DBPE in sediments from southern China were 22, 364 and 2,300 μgkg^{-1} dw, respectively (Shi et al., 2009). In farmland soils, the respective maximum concentrations were 0.11, 36 and 60 μgkg^{-1} dw. DBDPE was detected in all surface sediment samples and sediment cores taken in 2006 from southern China at concentrations from 19 to 430 μgkg^{-1} dw (Zhang et al., 2009). In the core samples, concentration trends suggested that use of DBDPE was replacing that of the deca-PBDE formulation.

Eljarrat et al. (2004) reported DBDPE concentrations ranging from 2 - 132 μgkg^{-1} dw in river and marine sediments taken in 2002. In a sediment sample from the Western Scheldt, the Netherland, taken in 2001, DBDPE concentration was 24 μgkg^{-1} dw, compared to 1,280 μgkg^{-1} dw for BDE209 (Kierkegaard et al. 2004). Leonards et al. (2008) reported concentrations of three "novel" BFRs in sediments from two locations in the Western Scheldt. Maximum concentrations of DBDPE, BTBPE and octabromo-1-phenyl-1,3,3-trimethylindan (OBIND) were 10, 0.3 and 1.0 μgkg^{-1} dw. In a separate study, López et al. (2008) reported maximum concentrations of pentabromochloro-cyclohexane (PBCH), pentabromotoluene (PBT), tetrabromophthalic anhydride (TBPhA), 2,3,5,6-tetrabromo-*p*-xylene (*p*TBX), tetrabromo-*o*-chlorotoluene (TB*o*CT), (*tris(*2,3-dibromopropyl)-phosphate (TTBPP), BTBPE and DBDPE at 15, 0.3, nd, 0.06, 0.05, nd, 0.3 and 9.8 µg/kg dw, respectively. Ruan et al. (2009) identified *tris*(2,3-dibromopropyl)isocyanurate (TBC) in surface sediments downstream of a manufacturing plant in southern China. Concentrations ranged from 9.8 - 79 μgkg^{-1}dw and there was a linear decline in concentration with distance from the source.

Air

Low concentrations of BTBPE (0.03-70 pg m^{-3}) were detected in outdoor air samples from 5 sites in east –central U.S. with the highest levels in Arkansas, near a production site (Hoh and Hites, 2005). Similar levels (0.1-10 pg m^{-3}) were reported later in air samples collected at five sites around the Great Lakes (Venier and Hites, 2008) and from Guangzhou city, China (n=4; mean=30.7 pg m^{-3}) (Shi et al., 2009). BTBPE was also measured at higher concentrations (600-67000 pg m^{-3}) in indoor air from various electronic dismantling sites in Sweden (Pettersson-Julander et al., 2004, Sjodin et al., 2001, Julander et al., 2005).

DBDPE was detected at median concentrations of 1-22 pg m^{-3} in air samples from 5 sites around the great lakes (Venier and Hites, 2008). Higher concentrations (10-1200 pg m^{-3}) were reported in indoor air from e-waste recycling sites from Sweden (Kierkegaard et al., 2004, Pettersson-Julander et al., 2004, Julander et al., 2005). However, DPDPE was only detected in 1 (23 pg m^{-3}) out of 5 air samples collected from houses in Sweden (Karlsson et al., 2007).

Low levels of PBEB were detected in outdoor air samples from various U.S. sites except for a Chicago sample with a relatively high concentration of 550 pg m^{-3}. Unlike BTBPE and DBDPE, PBEB was present mainly in the vapour phase (Hoh et al., 2005). PBEB was also found at low levels (8.9-90 pg m^{-3}) in outdoor air samples collected near Oxford, UK (Lee et al., 2002).

Recently, hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO) was detected in residential indoor air samples from Toronto, Canada (n=55; average=240 pg m^{-3}) (Zhu et al., 2008).

Aquatic Biota

Fish, Mussels and others

Concentrations of BTBPE and PBEB were determined in lake trout from Lake Ontario between 1979 and 2004 (Ismail et al., 2009). Concentrations of PBEB showed no overall trend, while BTBPE concentrations peaked around 1993 and then declined. Peak concentrations were around 300 and 2.5 μgkg^{-1} lipid weight (lw), respectively. BTBPE and DBDPE were determined in a Lake Winnipeg food

web (Law et al., 2006). Maximum BTBPE and DBDPE concentrations (in fish and mussels) were 3.7 and 3.3 μgkg^{-1} lw, respectively. The maximum concentration of BTBPE in fish from southern China was 0.15 μgkg^{-1} lw; DBDPE and TBBPA-DBPE were not detected (Shi et al., 2009). Munschy et al. (2007) reported concentrations of HBB, BB153, BTBPE and DBDPE in muscle tissue of common sole from French waters. Maximum concentrations were 4.3, 1.1, 2.2 and 3.9 μgkg^{-1} lw, respectively.

Birds

The maximum concentrations of BTBPE and DBDPE in watercock from southern China were 2.4 (liver) and 124 (kidney) μgkg^{-1} lw (Shi et al., 2009). Both BFRs were detected at relatively higher concentrations in the liver and kidney than in muscles. The BFR profile for all bird tissues was as follows: BDE209 > DBDPE > penta-BDEs = BDE183 > BTBPE.

DBDPE and BB153 were determined in five waterbird species, collected between 2005 and 2007 in Qingyuan, south China with maximum concentrations of 800 and 2,800 μgkg^{-1} lw, respectively (Luo et al., 2009). DBDPE was detected in all samples except one, at levels ~ 1 order of magnitude lower than those of BDE209. In samples from north China, concentrations of DBDPE and BB-153 in aquatic birds were up to 1.7 and 0.7 μgkg^{-1} lw (Gao et al., 2009).

In Northern Fulmar eggs from the Faroe Islands, BTBPE was measured at concentrations up to 0.11 μgkg^{-1} lw (Karlsson et al., 2006). Verreault et al. (2007) examined hexabromobenzene (HBB), BTBPE, pentabromoethylbenzene (PBEB) and PBT in plasma and egg yolk of glaucous gulls from the Norwegian Arctic. Maximum concentrations were (HBB) 0.15 and 2.6; (BTBPE) 0.26 and 1.0; (PBEB) nd and 0.23; (PBT) 0.15 and 0.12 μgkg^{-1} ww, respectively. Detection frequencies and levels of all four BFRs were generally higher in the lipid-rich egg yolk. However, in the egg yolk samples, BTBPE, PBT, HBB, and PBEB constituted a very small percentage of the combined concentrations of the brominated compounds.

Egg pools of herring gulls collected in 2004 from six sites in the Great Lakes of North America were considered in two studies (Gauthier et al., 2007 & 2009). In the first study, maximum concentrations of PBEB, PBT, BTBPE and HBB were 1.4, 0.02, 0.7 and 0.53 μgkg^{-1} ww, respectively. Pentabromobenzyl acrylate (PBBA) and pentabromobenzyl bromide (PBBB) were not detected. In the second study, maximum concentrations of HBB, BTBPE, DBDPE and 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH) were 3.9, 1.8, 288 and 3.4 μgkg^{-1} ww, respectively and were present in eggs from all the colonies. In comparison, maximum concentrations of ΣPBDE (7 congeners) and BDE-209 were 1,140 and 20 μgkg^{-1} ww. In eggs from 2005 and 2006, the concentrations of DBDPE were highest at three of the seven colonies (1.3 to 288 μgkg^{-1} ww) and surpassed BDE-209. HBB (0.10 to 3.92 μgkg^{-1} ww), BTBPE (0.06 to 1.82 μgkg^{-1} ww), and TBECH were detected at lower concentrations. Spatial trends were observed, although temporal trends were not obvious in most cases.

Marine Mammals

Tomy et al. (2008) detected the β- isomer of TBECH (not the α-isomer) in Canadian Arctic beluga whales, at 1.1 to 9.3 μgkg^{-1} lw. 2,3-dibromopropyl-2,4,6-tribromophenylether (DPTE) was detected in seal blubber and brain tissue from the Barents and Greenland Seas (von der Recke & Vetter, 2007). Maximum concentrations were 470 and 340 μgkg^{-1} ww, respectively. Lam et al. (2009) reported concentrations of "novel" BFRs in blubber of dolphins and porpoises from Hong Kong: 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), and bis-(2-ethylhexyl)-tetrabromophthalate (TBPH), with maximum concentrations of TBB and TBPH being 5.3 and 3,860 μgkg^{-1} lw, respectively. Hexachlorocyclopentadienylbromocyclooctane (HCDBCO) was not detected.

Terrestrial biota

Recently, in China, DBDPE was detected in 87% of captive giant and 71% of red panda tissues at

conc. up to 863 μgkg^{-1} lw.(Hu et al., 2008).

Conclusions

A wide range of "novel" BFRs has been detected, broadly across matrices and locations. Much more data is needed before their significance can be assessed, and further monitoring is encouraged.

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