Human Exposure to Novel Brominated Flame Retardants

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Introduction

The most extensively used and studied brominated flame retardants (BFRs) are polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and tetrabromobisphenol A (TBBP-A). These BFRs are persistent and can accumulate in the environment (de Wit, 2002; Law et al., 2006; Kierkegaard et al., 2007). Recently, PBDEs have been restricted and banned in Europe, North America and Japan (Renner, 2004; Zhou, 2006; Law et al., 2008), increasing the market demand for replacement BFRs.

Decabromodiphenyl ethane or 1,2-*bis*(pentabromodiphenyl)ethane (DBDPE), 1,2-*bis*(2,4,6-tribromophenoxy)ethane (BTBPE), tetrabromobisphenol A-*bis*(2,3-dibromopropylether) (TBBPA-BDPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH), belong to this group of "novel" BFRs used as replacements for the banned BFRs. While recent studies have shown the environmental presence of some "novel" BFRs (de Wit et al., 2010; Ismail et al., 2009; Law et al., 2006; Shi et al., 2009), the database remains very limited. Furthermore, no reliable information is available about their production volumes or uses. Although the presence of "novel" BFRs in our environment is now established (Law et al., 2010 – presented at BFR2010), more information is required to define a way forward in relation to these BFRs. In the present paper, we consider the human exposure to these "novel" BFRs.

Human exposure

Routes of exposure. BFRs accumulate in humans primarily via food intake, indoor air inhalation and dust ingestion. Few studies are available on exposure to "novel" BFRs, but most probably they follow similar exposure routes to the PBDEs. Various studies have shown their presence in the environment and human food chain, e.g. fish (Lam et al., 2009; Tomy et al., 2007; Shi et al., 2009), indoor dust (Pettersson et al., 2004; Karlsson et al., 2006; Stapleton et al., 2008; Stapleton et al., 2009; Kierkegaard et al., 2004; Sjödin et al., 2001; Harrad at al., 2008; Goosey at al., 2009). The presence of "novel" BFRs in homes and work environments may cause considerable exposure of humans to these chemicals. However, few reports exist of their presence in humans.

Dietary exposure. Dietary intake is considered the major exposure pathway of adults to PBDEs (Jones-Otazo et al., 2005), HBCDs and TBBP-A (Abdallah et al., 2008), and "novel" BFRs are probably behaving similarly. "Novel" BFRs have been reported in aquatic food webs e.g. Law et al. (2006) observed DBDPE at 1 ± 0.5 µg kg^{-1} lipid weight (lw) in fish (walleye) and BTBPE at 1.3 µg kg^{-1} lw in mussels from Lake Winnipeg, Canada. Shi et al. (2009) determined BTBPE, DBDPE and TBBPA-bdpe in farmed fish collected near an e-waste facility. DBDPE and TBBPA-bdpe were below the detection limit, while BTBPE was present at up to 0.15 µg kg^{-1} lw. Likely due to their lower level of production and use, the concentrations were lower than those of PBDEs (Shi et al.,

2009, Lam et al., 2009). Lam et al. reported concentrations of TBB and TBPH in finless porpoises from Hong Kong, China to range from <0.04-70 and <0.04-3859 μg kg^{-1} lw, respectively (Lam et al. 2009).

Another potential route of indirect human exposure to "novel" BFRs is the application of treated biosolids to agricultural fields, and DBDPE (Kierkegaard et al., 2004; Konstantinov et al., 2006; Eljarrat et al., 2005; Ricklund et al. 2008), BTBPE (Shi et al., 2009), TBBPA-bdpe (Shi et al., 2009) and TBB and TBPH (Klosterhaus et al., 2008) are present in sewage sludge. Concentrations ranged from 266 to 1995 μg kg^{-1} dw, 0.31-1.66 μg kg^{-1} dw, 238 to 8946 μg kg^{-1} dw, 40 to 1412 μg kg^{-1} dw and 57 to 515 μg kg^{-1} dw, respectively.

Exposure via dust ingestion. The significance of indoor dust ingestion as a pathway for human exposure to PBDEs has been highlighted recently (Jones-Otazo et al, 2005; Lorber, 2008). However, far fewer data are available on concentrations of "novel" BFRs in indoor dust and its implications for human exposure. DBDPE and BTBPE were measured in 5 house dust samples from Sweden at average concentrations of 47 and 5 μg kg^{-1}, respectively. However, both BFRs were below LOD in plasma samples of the house owners (Karlsson et al., 2007).

Stapleton et al. (2008) reported DBDPE (<10-11,070; median = 201 μg kg^{-1}) and BTBPE (2-789; median = 30 μg kg^{-1}) in 19 domestic dust samples from Boston, USA. In addition, 2 components of the commercial flame retardant FM550 namely, TBB (<6.6-15,030; median = 133 μg kg^{-1}) and TBPH (1.5-10,630; median = 142 μg kg^{-1}) were reported (Stapleton et al., 2008).

Dust from Birmingham, UK contained average concentrations of 120, 7, and 8 μg kg^{-1} (BTBPE) and 270, 170, and 400 μg kg^{-1} (DBDPE) in homes (n = 30), offices (n = 18), and cars (n = 20) respectively. On average, UK adults and toddlers were exposed to 5 and 14 ng day^{-1} (DBDPE) and 2 and 6 ng day^{-1} (BTBPE) respectively. BTBPE exposure was lower than for PBDEs, while DBDPE exposure was similar to Σtri-hexa-BDEs, but less than for BDE-209 and HBCDs (Harrad et al, 2008). DBDPE, BTBPE and TBBPA-bdpe were detected in dust samples from primary school classrooms and daycare centres (n = 43) in Birmingham, UK at average concentrations of 380, 1600 and 210 μg kg^{-1}, respectively (Goosey et al., 2009). Hexachlorocyclopentadienyl-dibromocyclooctane (HBCDCO) was reported in residential indoor dust (n=69; median = 2; maximum = 93,000 μg kg^{-1}) and air (n = 55; median = 92; maximum = 3,000 pg m^{-3}) from Ottawa, Canada (Zhu et al., 2008). The detection of" novel" BFRs in the indoor environment may raise concerns about the potential implications of human exposure to these chemicals, although very little is known about their toxicological effects so far.

Occupational exposure. Ingestion of dust particles and inhalation of contaminated air is considered a major exposure pathway for occupationally-exposed workers, especially those working in computer recycling facilities. However, few reports exist on the levels of "novel" BFRs in workers. Venier and Hites, 2008 observed high concentrations of DBDPE (1 to 22 pg m^{-3}) and BTBPE (0.5 to 1.2 pg m^{-3}) in the particulate phase in air around the Great Lakes. High levels of BTBPE (0.1-10 pg m^{-3}) were reported in air from the east central USA, with highest levels close to a BTBPE manufacturing site (Hoh and Hites, 2005).

Karlsson (2006) reported BTBPE and DBDPE at 29 ng m^{-3} and 6.6 ng m^{-3} respectively (n = 8) during an 8 h working day at an electronic dismantling facility after a production increase in the spring of 2005. However, neither BFR was detected in the serum of exposed workers (Sjödin et al., 2003; Karlsson et al., 2006). Petersson-Julander et al. (2004) reported that indoor air in Swedish houses contained BTBPE at 4-40 pg m^{-3}, while an electronics dismantling plant contained 10,000 pg m^{-3}. Levels of BTBPE and DBDPE were ca. 1,900 and 9 times higher in the recycling facility air compared to household air (Pettersson-Julander et al., 2004). Shi et al (2009) observed high

concentrations of BTBPE up to 232 μg kg^{-1} dry wt and DBDPE up to 139 μg kg^{-1} dry wt in dust samples (n = 5) collected near an e-waste area. Such high levels of BTBPE and DBDPE in air from electronics recycling plants indicate the potential for high exposure to "novel" BFRs of workers in such facilities.

Levels of new BFRs in humans. Very few human risk assessments and biomonitoring studies of "novel "BFRs have been conducted. Karlsson et al. (2006) and Sjödin et al. (2003) studied DBDPE and BTBPE alongside PBDEs in serum samples collected from workers in Swedish electronic recycling plants. BTBPE and DBDPE were not detected in the workers' serum. The presence of BTBPE in air samples and its absence in serum samples may be due to rapid metabolism of BTBPE, as indicated in rats when given orally (Nomeir et al., 1993). Alternatively, the apparent absence of BTBPE and DBDPE could be due to sub-optimal analytical methods, as those used to date are designed for PBDEs.

Research gaps related to human exposure. "Novel" BFRs are present in a range of environmental samples, e.g. sewage sludge, dust, air, sediments, tree bark and fish. However, few studies have focused primarily on "novel" BFRs, and their analysis requires optimisation. Concentrations of "novel" BFRs in samples relevant for human exposure (e.g. food, dust, air) are generally lower than those of PBDEs, but they are already present and may be expected to increase if use of "novel" BFRs grows in response to restrictions on PBDEs.

Consequently, concerns about human exposure and possible environmental impacts are growing. Although no risks have yet been identified, this is based on a very scant database on human exposure. Consequently, biomonitoring programmes e.g. of breast milk and blood are required, as well as studies designed specifically to monitor levels and delineate pathways of exposure. Coupled with toxicological studies, such programmes will facilitate risk assessment of "novel" BFRs.

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References

Abdallah MA, Harrad S, Covaci A. 2008. Environ Sci Technol 42: 6855.
de Wit CA. 2002. Chemosphere 46: 583.
de Wit CA, Herzke D, Vorkamp K. 2010. Sci Tot Environ, doi:10.1016/j.scitotenv.2009.08.037
Eljarrat E, Labandeira A, Martinez A, Fabrellas B, Barceló D. 2005. Organohalogen Comp 67: 459.
Goosey E, Abdallah MA, Roosens L, Harrad S, Covaci A. 2009. Organohalogen Comp 71: 452.
Harrad S, Ibarra C, Abdallah MA, Boon R, Neels H, Covaci A. 2008. Environ Int 34: 1170.
Hoh E, Hites RA. 2005. Environ Sci Technol 39: 7794.
Ismail N, Gewurtz S, Pleskach K, Whittle D, Helm P, Marvin C, Tomy G. 2009. Environ Toxicol Chem 28: 910.
Jones-Otazo HA, Clarke JP, Diamond ML, Archbold JA, Ferguson G, Harner T, Richardson GM, Ryan JJ, Wilford B. 2005. Environ Sci Technol 39: 5121.
Karlsson M. 2006. PhD thesis.
Karlsson M, Julander A, van Bavel B, Hardell L. 2007. Environ Int 33: 62.

Kierkegaard A, Asplund L, de Wit CA, McLachlan MS, Thomas GO, Sweetman AJ, Jones KC. 2007. Environ Sci Technol 4: 417.
Kierkegaard A, Bjorklund J, Friden U. 2004. Environ Sci Technol 38: 3247.
Klosterhaus S, Konstantinov A, Stapleton HM. 2008. www.sfei.org/rmp/posters/08BFR_Poster_klosterhaus_shrunk.pdf
Konstantinov A, Arsenault G, Chittim B, Kolic T, MacPherson K, McAlees A, McCrindle R, Potter C, Reiner EJ, Tashiro C, Yeo B. 2006. Chemosphere 64: 245.
Lam JCW, Lau RKF, Murphy MB, Lam PKS. 2009. Environ Sci Technol. 43: 6944.
Law K, Halldorson T, Danell R, Stern G, Gewurtz S., Alaee M, Marvin C, Whittle M, Tomy G. 2006. Environ Toxicol Chem 25: 2177.
Law K, Halldorson T, Danell R, Stern G, Gewurtz S, Alaee M, Marvin C, Whittle M, Tomy G. 2007. Environ Toxicol Chem 25: 190.
Law RJ, Allchin CR, Mead LK. 2005. Mar Poll Bull 50: 344.
Law RJ, Covaci A, Harrad S, Herzke D, Ali N, Abdallah MAE. 2010. 'Novel' BFRs in the environment: a review. BFR2010.
Lorber M. 2008. J Exp Sci Env Epidemiol 18: 2.
Nomeir AA, Markham PM, Ghanayem BI, Chadwick M. 1993. Drug Metab Dispos 21: 209.
Pettersson-Julander A, Van Bavel B, Engwall M, Westberg H. 2004. J Environ Monit 6: 874.
Renner R. 2004. Environ Sci Technol 38: 14A.
Ricklund N, Kierkegaard A, McLachlan MS, Wahlberg C. 2008. Chemosphere 74: 389.
Sawal G, Feibicke M, Meinecke S, Warmbrunn-Suckrow E, Lepom P. 2008. Organohalogen Comp 70: 2029.
Shi T, Chen S, Luo X, Zhang X, Tang C, Luo Y, Ma Y, Wu JP, Peng X, Mai B. 2009. Chemosphere 74: 910.
Sjödin A, Bergman A, Pattersson Jr DG. 2003. Environ Int 29: 829.
Sjödin A, Carlsson H, Thuresson K, Sjolin S, Bergman A, Ostman C. 2001. Environ Sci Technol 35: 448.
Stapleton HM, Allen JG, Kelly SM, Konstantinov A, Klosterhaus S, Watkins D, McClean MD, Webster TF. 2008. Environ Sci Technol 42: 6910.
Stapleton H, Klosterhaus S, Eagle S, Fuh J, Meeker J, Blum A, Webster T. 2009. Environ Sci Technol 43: 7490.
Takigami H, Suzuki G, Hirai Y, Ishikawa Y, Sunami M, Shin-ichi S. 2009. Environ Int 35: 688.
Venier M, Hites RA. 2008. Environ Sci Technol 42: 4745.
Zhou ZM. 2006. Flame Retard Mat Technol 4: 15.