Knowledge gaps in the analysis of “novel” Brominated Flame Retardants

Adrian Covaci¹, Nadeem Ali¹, Mohamed A-E Abdallah², Stuart Harrad², Robin J. Law³, Dorte Herzke⁴

¹-Toxicological Centre, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium
²-Division of Environmental Health and Risk Management, School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, UK
³-The Centre for Environment, Fisheries and Aquaculture Science, CEFAS Lowestoft Laboratory, Pakefield Road, Lowestoft, Suffolk NR33 0HT, UK
⁴-Norwegian Institute for Air Research, The Polar Environmental Centre, N-9296 Tromsø, Norway

Introduction

The implementation of strict bans on the use of some widely-used BFRs (penta, octa, and deca BDE formulations) and their voluntary withdrawal from the market has paved the way for the use of “novel” BFRs as replacement for the banned formulations. Decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 2-ethylhexyl 2,3,4,5 tetrabromobenzoate (TBB), bis(2-ethylhexyl)-3,4,5,6-tetramethylphthalate (TBPH), hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO) and tetrabromobisphenol A-bis(2,3-dibromopropylether) (TBBPA-BDPE) belong to the group of “novel” BFRs (Figure 1).

Currently, there are few reports concerning the “novel” BFRs in the environment (de Wit et al., 2009; Law et al., 2006; Harrad et al., 2008). However, the detection of “novel” BFRs was mostly as collateral information resulting from the analysis of major BFRs (PBDEs). Few analytical procedures have been optimised and validated for detecting “novel” BFRs (Kolic et al., 2009). Here, we discuss these analytical techniques that have been successfully applied for the detection and quantification of “novel” BFRs in various matrices. This abstract is part of a larger piece of work studying the environmental fate and human exposure to these “novel” BFRs (Law et al., 2010; Covaci et al., 2010).

Extraction of “novel” BFRs

Abiotic samples: Soxhlet extraction was the method of choice for extracting novel BFRs (BTBPE, DBDPE and HCDBCO), alongside PBDEs from air and dust samples (Pettersson et al., 2004;
Takigami et al., 2009; Harrad et al. 2008; Zhu et al., 2008). Soxhlet was also used to extract BTBPE, DBDPE and TBBPA-bdpe from sediment and sewage sludge samples (Hoh et al., 2005; Konstantinov et al., 2006; Shi et al., 2009). Sjödin et al. (2001) used ultrasonic extraction for BTBPE from air samples. Recently, accelerated solvent extraction (ASE) was used for extracting DBDPE, TBBPA-bdpe (Sawal et al., 2008), or TBB and TBPH (Stapleton et al., 2008) from dust samples. ASE was also applied for extraction of TBB and TBPH from effluent discharge (Klosterhaus et al., 2009), as well as DBDPE from sewage sludge (Ricklund et al., 2008). Different solvent combinations were used for extraction of novel BFRs, e.g., toluene (Sawal et al., 2008), dichloromethane (DCM) (Sjödin et al., 2001; Klosterhaus et al. 2009), petroleum ether (Zhu et al., 2008), hexane-acetone (1/1, v/v) (Hoh et al., 2005; Shi et al., 2009), DCM/hexane (1/1, v/v) (Stapleton et al., 2008), acetone-toluene (1/1, v/v) (Konstantinov et al., 2006; Takigami et al., 2009), and hexane (Ricklund et al., 2008).

**Biotic samples:** ASE, with DCM/hexane (1/1, v/v), was used for extraction of BTBPE, DBDPE, TBB and TBPH from rainbow trout samples (Tomy et al., 2007). Lam et al. (2009) used Soxhlet, with DCM/hexane (3/1, v/v), for extraction of HCDBCO, TBB and TBPH from blubbers of marine mammals. Soxhlet extraction, with acetone/hexane (1/1, v/v), was also used for determination of BTBPE and DBDPE in birds tissue and eggs (Gao et al., 2009; Gauthier et al., 2009). SPE was applied for extracting DBDPE and BTBPE from blood samples (Karlsson et al., 2007).

**Clean-up**

**Abiotic samples:** Both destructive and non-destructive methods have been successfully applied. Sulphuric acid washing was reported for clean-up of air, dust, sewage sludge, sediment and tree bark samples (Kierkegaard et al., 2004; Konstantinov et al., 2006; Eljarrat et al., 2005; Zhu et al., 2006; Qiu et al., 2007). Sulphur removal was achieved using activated copper (Konstantinov et al., 2006; Law et al., 2006), silver nitrate on silica (Konstantinov et al., 2006) and TBA. Interestingly, TBA caused debromination of DBDPE in standard solutions, but this problem was less pronounced in real samples, which was attributed to a protective effect of the matrix (Kierkegaard et al., 2004). Diluted KOH in warm ethanol has been used for fat removal from sewage sludge samples with a recovery of ~60% for DBDPE (Ricklund et al., 2008). Several sorbents have been applied successfully as secondary clean-up steps including deactivated Florisil (Law et al., 2006), GPC (Julander et al., 2005), activated silica (Kierkegaard et al., 2004), aminopropyl silica (Ricklund et al., 2008), while Stapleton et al. (2008) used a column containing 8.0 g of 2.5% deactivated Florisil for DBDPE, TBB, TBPH and silica Sep-Pak cartridges for BTBPE in dust samples. Multilayer silica columns consisting of KOH and H₂SO₄ treated silica were reported for the clean-up of indoor air and dust samples (Takigami et al., 2009; Konstantinov et al., 2006; Pettersson et al., 2004) as well as sewage sludge (Konstantinov et al., 2006). Sulphuric acid silica columns were also used for clean-up of air, dust and sewage sludge samples (Sawal et al., 2008; Sjödin et al., 2001; Ricklund et al., 2008).

**Biotic samples:** Tomy et al. (2007) used a 1.2% deactivated Florisil column for the clean-up of rainbow trout samples for BTBPE determination. Gao et al. (2009) used GPC for lipid removal and silica gel SPE as clean up to study DBDPE from bird tissue and eggs. Multilayer silica columns were reported for the clean-up of Fulmar egg samples (Karlsson et al., 2006) and human blood samples (Karlsson et al., 2007) to study DBDPE and BTBPE.

**Instrumental analysis**

While the analysis of some “novel” BFRs (e.g. HCDBCO and BTBPE) occurs without major problems alongside PBDEs, other compounds, such as DBDPE and TBB/TPBH, can present many difficulties in their analysis.

**DBDPE:** Konstantinov et al. (2006) reported that the best DBDPE response in splitless injection was achieved by initially applying a high carrier gas flow (10 ml/min) for 1 min followed by a
decreased flow (1 ml/min). On a non-polar column, DBDPE typically elutes after BDE-209. However, since DBDPE also degrades on the GC column, it is necessary to minimize its elution time. Therefore, it has been successfully analysed on 10–15 m DB-5 like stationary phases (Kierkegaard et al., 2009). DBDPE does not form any high molecular weight fragments in ECNI and therefore Br⁻ ions alone can be monitored. A lower response for DBDPE than for BDE209 has been reported in LR-ECNIMS (Kierkegaard et al., 2004) and similar results have been reported in LR-EIMS full scan and with HRGC-EIMS when the molecular ion was monitored (Konstantinov et al., 2006). In HR/LR-EIMS both the molecular ion and the base peak, i.e. the pentabromobenzyl fragment, \([C_7H_2Br_5]^+\) have been used for quantitative analysis (Kierkegaard et al., 2009). Since no high MW fragments are formed in ECNIMS, isotope-labelled DBDPE cannot be used as an internal standard (IS). However, this is possible with EIMS due to the abundance of the \([C_7H_2Br_5]^+\) fragment (Kierkegaard et al., 2004). If LR-ECNIMS is to be used, then \(^{13}\)C-labelled BDE209 is a good alternative as an IS. Although method detection limits (LOD) for the DBDPE are usually higher than for BDE209. A GC-MS/MS method was developed for the analysis of DBDPE in sewage sludge with LOD lower than that for BDE209 analysed by LR-ECNIMS (De la Torre et al., 2007).

**TBB/TBPH:** TBB and TBPH were determined in dust samples by GC-ECNIMS using a 0.25 mm × 15 m fused silica capillary column coated with 5% phenyl methylpolysiloxane (0.25 μm film thickness). While TBB was quantified using ion fragments \([m/z]\) 357 (quantitation) and 471 (qualitative confirmation) while TBPH was quantified using ion fragments \([m/z]\) 463 (quantitation) and 515 (qualitative confirmation). A significant co-elution of TBB with BDE99 was observed on a 15m DB5-MS column. However, methods that employ a 30 or 60 m column may have improved chromatographic resolution (Stapleton et al., 2008).

Recently, two LC-MS/MS methods using APPI (Zhou et al., 2009a) and APCI (Zhou et al., 2009b) ion sources were reported for determination of TBB and TBPH alongside other halogenated flame retardants. The main advantages of the LC-MS/MS methods were summarized as simplicity, speed, and high sensitivity.

**TBBPA-dbpe:** Attempts to use LC-ESI/MS or LC-APCI/MS in positive or negative ion mode for determination of TBBP-A-dbpe were unsuccessful (Koppen 2006). The samples were therefore quantified by LC–DAD using external calibration with purified substance since no native or isotopic labelled standards were available. The method was validated using matrix-spike sediment and sewage sludge samples. The LODs were 10 and 22 μg/kg in sediment and sewage sludge, respectively.

**Quality control.** There are to date no inter-laboratory comparison data available for “novel” BFRs and their analysis is still at an early stage of development.

**Concluding remarks**

Essentially, “novel” BFRs are at present being detected using methods developed for other compounds, e.g. PBDEs. As the solubility of “novel” BFRs in organic solvents might differ from those of PBDEs, the lack of extraction efficiency and solubility could be a source of concern. The data now need to be considered for significance so that purpose-made methods can be optimised for the most important “novel” BFRs. It is clear that the road to robust high quality routine analytical methods will be longer for “novel” BFRs than it was for PBDEs. However, the available evidence suggests that there are many similarities in the analytical challenges posed by these two groups of compounds. We can expect that the experience gained from PBDE analysis over the last 10 years will greatly facilitate progress in the analysis of “novel” BFRs.

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