

DETERMINATION OF LEGACY AND ALTERNATIVE FLAME RETARDANTS IN WATER – METHOD DEVELOPMENT AND INFLUENCE OF DOC

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Introduction

Flame retardants (FRs) are chemical substances that are added to materials in order to provide fire protection. They are widely used in many different materials like textiles and plastics and are present in products such as furniture, carpeting, televisions, computers and building insulation^{1, 2}. Since FRs are not always chemically bonded to the material, pollution of the environment can occur not only from point sources (e.g. landfills) but also from diffuse sources (e.g. households). As a result, many FRs are ubiquitously spread in the environment. For example, polybrominated diphenyl ethers (PBDEs) have been detected in numerous abiotic (e.g. soil, water, and sediment) and biotic (e.g. seabirds and mammals) matrices in the Arctic³. The use of three common technical PBDE products (PentaBDE, OctaBDE and DecaBDE) is nowadays forbidden in new materials within the European Union (EU)³. This restriction has increased the need of alternative FRs to be developed and used. For example, the use of tris(1,3-dichloroisopropyl) phosphate (TDCIPP) in American couches has increased since the ban of PentaBDE⁴. These new FRs often have similar properties as the banned FRs, and many of them have been found in the environment.

This study focuses on the development of a multi-compound analysis method for >100 FRs in natural waters including brominated (PBDEs and alternative FRs), chlorinated (CFRs), chlorinated and brominated (CBFRs), and organophosphorous (OPFRs) compounds. The three main objectives are: *i*) to develop a large volume extraction method for dissolved FRs in water to be conducted as a complement to large volume filtration of the particulate fraction, *ii*) to investigate the influence of dissolved organic carbon (DOC) on the extraction efficiency, and *iii*) to compare the performance of three instrumental methods including gas chromatography coupled to mass spectrometry using electron impact ionization (GC-(EI)MS), GC-MS using chemical ionization (GC-(CI)MS), and GC-tandem MS with EI ionization (GC-(EI)MS/MS).

Materials and methods

Chemicals

The target compounds ($n=101$) represent a broad hydrophobicity range (log Kow 2 to 17) and includes brominated (PBDEs, TBBPA, HBCDD, DBDPE, BTBPE, PBT, TBCO, DBE-DBCH (TBECH), OBTMPI, BEHTBP, EHTBB, ATE, TBP-DBPE, BATE, HBB, 246-TBP, 24-DBP, 26-DBP, 4'-PeBPO-BDE208, 4-BP, DBNPG, DBS, HEEHP-TEBP, PBB-Acr, PBBBr, PBEB, PBP, PBPAE, TBBPA-BDBPE, TBBPA-DHEE, TBBPA-BAE, TBBP-DBPE, TBNPA, TBX, TDBP-TAZTO, TEBP-Anh, and TTBP-TAZ), chlorinated (DP and TCBA), chlorinated and brominated (DBHCTD, PBCH and TBCT) and organophosphorus compounds (EHDPP, TBOEP, TCEP, TCIPP, TCP, TDCIPP, V6, T2CPP, T3CPP, TEHP, TEP, TNBP, TPHP, TPP, TBPP, TMP, DMP, mDEP/dDEP, TiPP, TPeP, TiPPP, IDP, CDP, RDP, BADP, TTNPP, and bBDPP). In addition to the native (¹²C) compounds, 10 ¹³C-labeled alternative FRs and 12 ¹³C-labeled PBDEs were included as internal standards (IS) and Mirex was used as recovery standards (RS).

Sample treatment

An analytical method was developed for analyzing the dissolved fraction of the selected FRs in water samples. The following sample preparation steps were optimized: *i*) elution of FRs from sorbents with different organic solvents, and *ii*) large volume (12 L) extraction using five commercially available sorbents.

Five commercially available sorbents were tested including Amberlite XAD-2 (25 g, Supelco), Amberlite IRA-743 (25 g, Supelco), Chromabond HR-X (4 g, Macherey-Nagel), Chromabond HR-P (4 g, Macherey-Nagel), and Oasis HLB (4 g, Waters).

For the elution test, the following solvents were tested: dichloromethane (DCM), acetone/cyclohexane (Ac:Chex) 1:1 (v/v), and Ac:Chex 1:4 (v/v). The selected native FRs (10-40 ng) were spiked directly onto the respective sorbent packed in glass columns before elution with the different solvents. Several fractions were collected in order to find the optimal elution volume. Extracts were concentrated, dried with sodium sulfate, and finally solvent exchanged into 0.5 mL isooctane before analysis. Recoveries were calculated based on a single point external calibration using a recovery standard.

Extraction performance of the five sorbents was tested by spiking the selected native and mass-labeled FRs (10-40 ng) directly onto the respective sorbent packed in glass columns. River water (12 L; pre-filtered through glass fiber filters, 0.7 μ m pore size) sampled in the city center of Uppsala (Sweden) was then pumped through the sorbents. One column per sorbent was spiked with 13 C-labeled internal standards only for control of background levels in the river water. Blanks were prepared by spiking 13 C-labeled internal standards onto the sorbents after addition of 2-3 mL Millipore water.

Influence of DOC

The influence of DOC on the extraction efficiency was investigated by adding different amounts of fulvic acid (Nordic aquatic fulvic acid reference, International Humic Substances Society), to 12 L natural water samples resulting in DOC concentrations between 15 and 60 mg/L. The water samples were spiked with mass-labeled FRs and extracted using pre-packed HLB SPE-cartridges (6g, Waters). For elution, the previously determined optimal solvent was used.

Instrumental analysis

Three instrumental methods were developed for the analysis of the selected FRs. The GC parameters were kept constant, while the ionization and detection technique of the mass spectrometer were varied. GC-(EI)MS, GC-(CI)MS and GC-(EI)MS/MS methods were all developed by injection of individual standards and mixtures. The performance of the instrumental methods was examined by preparing an extract from a 12 L river water sample (Fyris River, Uppsala, Sweden). The final extract was spiked with different levels of selected FRs and analyzed with all three instrumental methods. The resulting chromatograms were evaluated in terms of selectivity, sensitivity, limit-of-detection (LOD) and limit-of-quantification (LOQ).

Results and discussion

Sample treatment

The results from the elution tests using three different solvents (3x60 mL for IRA743 and XAD-2, and 3x10 mL for HR-P, HR-X and HLB) show that the recoveries depend on which solvent that was used (Figure 1 and 2). The recoveries were biased towards high recoveries, and this was presumably due to chromatographic effects caused by mixed solvents in the calibration standards. This effect does, however, not impact the relative recoveries between experiments, and the results could be used for selection of elution solvents. For PBDEs on the XAD sorbent, DCM was less efficient for elution than the two mixtures of acetone and cyclohexane (Figure 1). The Ac:Chex 1:4 mixture provided the highest recoveries of PBDEs for both XAD (on average 165%) and IRA (on average 154%). For HR-P and HR-X, DCM resulted in the highest recoveries (on average 170% and 162%, respectively), while the recoveries using Ac:Chex were more similar for the HLB sorbent (on average around 160%).

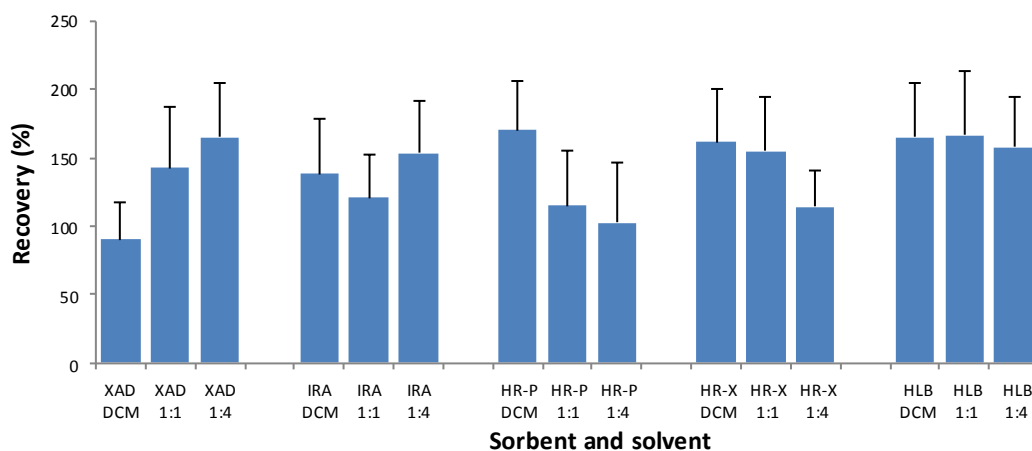


Figure 1 Average recoveries and standard deviations ($n=2$) for SPBDEs in the elution test using different sorbents and solvents. (XAD=Amberlite XAD-2, IRA=Amberlite IRA743, HR-P=Chromabond HR-P, HR-X=Chromabond HR-X, HLB=Oasis HLB, DCM=dichloromethane, 1:1=acetone:cyclohexane ratio 1:1, 1:4=acetone:cyclohexane ratio 1:4).

For the alternative FRs, Ac:Chex 1:4 eluted the compounds more efficiently from XAD and IRA (on average 154 and 134%, respectively) than DCM and the Ac:Chex 1:1 mixture (Figure 2). In contrast to the results for XAD and IRA, DCM provided the highest recoveries for HR-P and HR-X. For HLB, the differences were small between the different solvents but with slightly higher recoveries for DCM (on average 153%) and the 1:1 Ac:Chex mixture (154%) than for the 1:4 mixture.

Overall, all solvents performed similarly for the elution from HLB. However, not only FRs were included in the present test but also other persistent organic compounds (results not shown). It was concluded that DCM gave the highest recoveries for the elution of polycyclic aromatic hydrocarbons (PAHs) from HLB, and this solvent was therefore selected for further tests even though the Ac:Chex 1:1 mixture performed just as well for eluting the FRs. The extracts eluted from HR-P and HR-X had high background levels of PAHs, and these sorbents were therefore excluded from further tests. Considering all aspects, XAD and IRA eluted with Ac:Chex 1:4 and HLB eluted with DCM were selected for further testing, since these showed the best overall suitability.

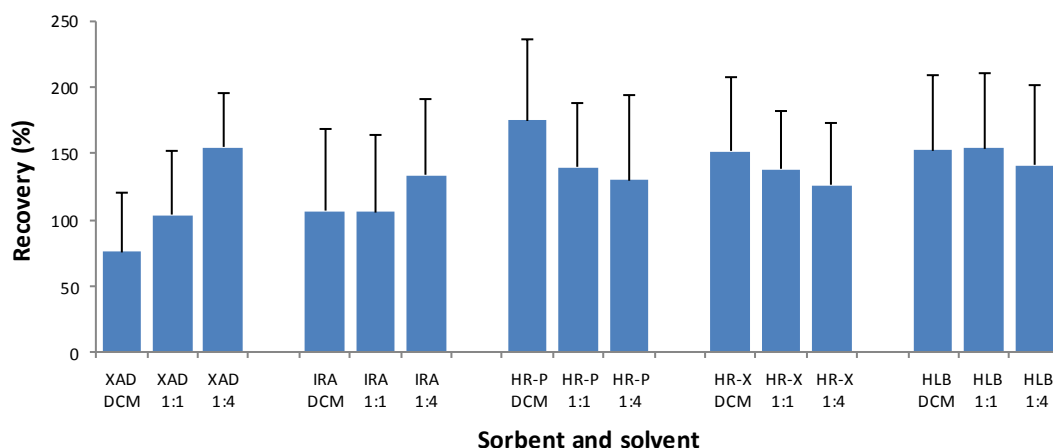


Figure 2 Recoveries with standard deviations ($n=2$) of alternative FRs in the elution test using different sorbents and solvents. (XAD=Amberlite XAD-2, IRA=Amberlite IRA743, HR-P=Chromabond HR-P, HR-X=Chromabond HR-X, HLB=Oasis HLB, DCM=dichloromethane, 1:1=acetone:cyclohexane ratio 1:1, 1:4=acetone:cyclohexane ratio 1:4).

The extraction test was performed using 12 L water sample together with the elution solvent which was optimal for each sorbent (Ac:Chex 1:4 for XAD and IRA, DCM for HLB). Again, recoveries were biased towards high values, but relative recoveries were not affected. In general, XAD and HLB performed better than IRA (Figure

3). HLB resulted in the highest recoveries for most compounds, especially for the less hydrophobic compounds (not shown). HLB was therefore selected for further experiments.

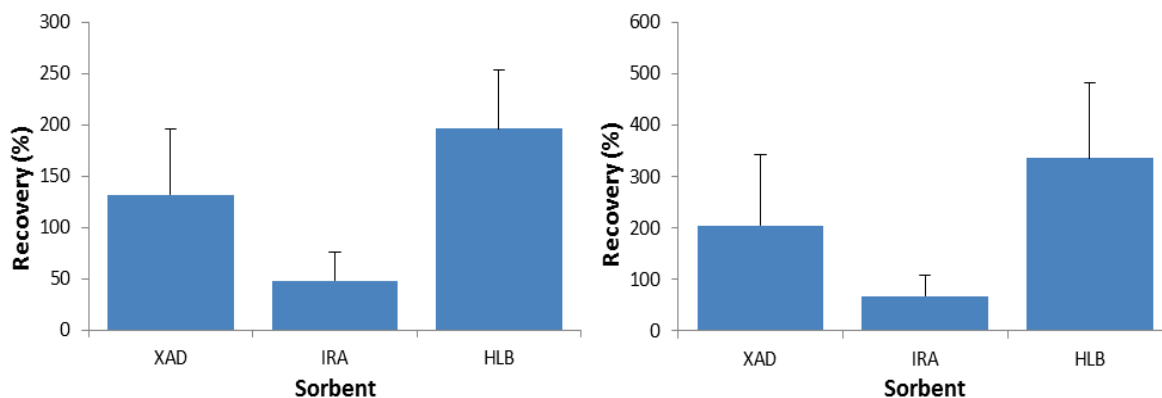


Figure 3 Average recoveries with standard deviations ($n=2$) of PBDEs (left) and alternative FRs (right) obtained in the extraction test using 12 L of water. (XAD=Amberlite XAD-2, IRA=Amberlite IRA743, HLB=Oasis HLB).

Influence of DOC

The results from the DOC test are currently under evaluation. It will be presented at the conference in August.

Instrumental analysis:

Out of the 101 FRs included in this study, 31 showed good MS responses in all of the three instrumental techniques (GC-(EI)MS), GC-(CI)MS), and GC-(EI)MS/MS). In total 13 FRs could not be detected with any of the setups either because of poor retention on the short column, too high boiling point, or poor ionization. A few FRs had to be excluded from further tests due to interfering impurities in the standard solution. The GC-(EI)MS/MS showed good responses for 87 of the selected FRs, while GC-(EI)MS and GC-(CI)MS detected somewhat fewer (83 and 78 FRs, respectively). As expected, the background noise was lower for the techniques with high selectivity (GC-(EI)MS/MS and GC-(CI)MS) as compared to GC-(EI)MS, and non-halogenated FRs proved less suitable for GC-(CI)MS analysis. Degradation in the injector was observed for a few compounds when using a split/splitless injector at temperature 320°C. This was avoided by using a multimode inlet (MMI) injector with a programmed temperature ramp.

After finalizing the method development, the optimized methods will be applied to water samples collected at different contaminated sites. This includes surface water sampled downstream waste water treatment plants, run-offs from airports and urban storm water.

Acknowledgements:

This study was financed by the Swedish Research Council Formas under the contract Dnr 216-2011-427. Henrik Jernstedt (SLU, Sweden) is acknowledged for instrumental maintenance.

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