

NEW BROMINATED FLAME RETARDANTS IN DUTCH SEDIMENTS AND SUSPENDED PARTICULATE MATTER

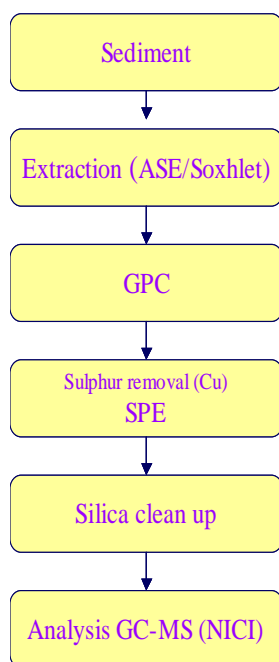
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Introduction

There are more than seventy-five different types of commercially available brominated flame retardants (BFRs) (1). Until now most attention of environmental chemists has been paid to polybrominated diphenylethers (PBDE's), hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBP-A). However, based on the combination of carbon and halogens, it may be assumed that several other BFRs would also be present in various environmental compartments. Some have been identified already, e.g. decabromodiphenylethane (DBDPE) (2), 1,2-bis(2,4,6-tribromo-phenoxy)ethane (BTBPE) and pentabromotoluene (PBT) (3). In the present study a method for a selection of "new" BFRs was developed. It was used to identify and quantify concentrations of these compounds, in addition to PBDE's, in sediment and suspended particulate matter samples from the river Western Scheldt, The Netherlands.

Materials and methods



Standards of the following BFRs were obtained as 98% pure: Pentabromochlorocyclohexane (PBCCH) (congeners A, B, C and D), 2,3,5,6-tetrabromo-*p*-xylene (*p*TBX), Tetrabromo-*o*-chlorotoluene (TBoCT), Pentabromotoluene (PBT), 1,2-bis(2,4,6-Tribromo-phenoxy)ethane (BTBPE), Decabromo-diphenylether (BDE209), and Decabromodiphenylethane (DBDPE). Commercial standards of Tetrabromophthalic anhydride (TBPPhA) and Tris(2,3-dibromopropyl)phosphate (TDBPP) were also supplied by AccusStandard with a minimum of 80% of purity. All solvents used were suitable for organic residue analysis. Figure 1 shows the method that was designed in order to "catch" a maximum number of analytes. Accelerated solvent extraction (ASE) or Soxhlet extraction was followed by gel permeation chromatography (GPC): PL-Gel 50A 300x25 m 10µm 50A(x2), mobile phase: dichloromethane 10 mL/min. One minute fractions from 14 min (15 mL) to 28 min (29 mL) were collected. Sulphur was removed by shaking the key GPC fraction with copper powder. Solid phase extraction (SPE) and silica gel column chromatography (1.8 g, 1.5 % w/w of water, elution: 12 mL iso-octane, 24 mL 15% (v/v) diethyl ether in iso-octane, 16 mL diethylether) were used for a final clean up of the extracts. A number of experiments were carried out to find the optimum SPE cartridge. Oasis HLB (500 mg) was finally selected (5 mL dichloromethane for cleaning, 0.5

Figure 1: Analytical method flow scheme.

mL methanol for conditioning, 0.5 mL methanol for removal part of the remaining lipids and elution with 5 mL dichloromethane/iso-octane (3:1, v/v)). The results of the fractionation experiments are given in Figure 2. The final analysis was carried out by GC/ECNI-MS (Agilent, Amstelveen, The Netherlands) using a CP Sil8CB column (60m x0.25mm x 0.25µm) and a J&W DB5 column (15m x0.25mm x 0.25µm), the latter for a proper determination of decaBDE and DBDPE. BDE58, ¹³C-decaBDE and ¹³C-BTBPE were used as internal standards. ¹³C-DBDPE was not suitable as internal standard due to a very low response. Samples were obtained from four location in the Western Scheldt, from the Belgium border (Ouden Doel) until Wielingen at the very end of the estuary, over a stretch of ca. 80 km.

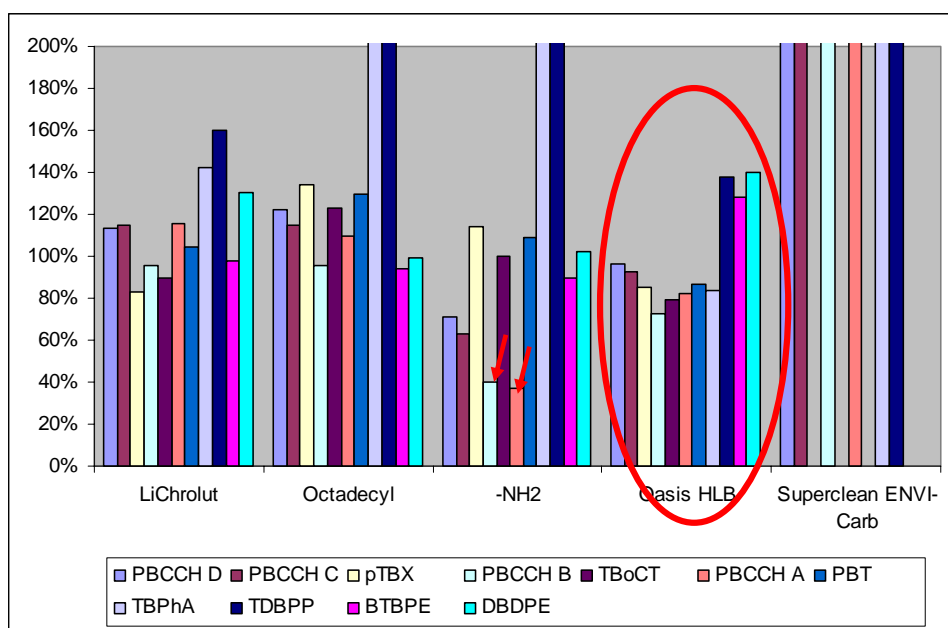


Figure 2. Result of SPE optimization experiments.

Results and discussion

The method was successfully developed for a number of target compounds: PBCCH (all isomers), p-TBX, TBoCT, PBT, TBPhA, TDBPE, BTBPE and DBDPE. Recoveries were between 70 and 140%. Acid treated silica was tried as an alternative for GPC, but did not result in good recoveries for TDBPP and BTBPE. Table 1 shows that most of the “new” BFRs are present in the Western Scheldt samples, although some of them at relatively low concentrations. Only TBPhA and TDBPP were not detected. PBT and BTBPE have maximum concentrations around 0.3 ng/g dw. PBCCH D is present at concentrations up to 14 ng/g, although absent at the location Ouden Doel. DBDPE shows a maximum of 10 ng/g dw. This is in line with an earlier report of Kierkegaard et al. (2). The high decaBDE concentration in this area, most likely due to textile and plastic industries upstream the river Scheldt in Belgium have been reported before (4).

<i>Compound</i>	<i>Terneuzen</i>	<i>Wielingen</i>	<i>Ouden Doel</i>	<i>Hansweert</i>	<i>Terneuzen*</i>
PBCCH D	3.8	0.13	n.d.**	14	13
PBT	0.12	0.01	0.33	0.25	0.29
PBCCH C	0.16	0.03	n.d	0.51	n.d
TBPhA	n.d	n.d	n.d	n.d	n.d
pTBX	0.01	0.001	0.02	0.01	0.06
PBCCH B	0.12	n.d	0.70	0.35	n.d
TBoCT	0.003	n.d	0.02	0.01	0.05
PBCCH A	0.11	n.d	0.52	1.0	n.d
TTBPP	n.d	n.d	n.d.	n.d	n.d
BTBPE	0.25	n.d	0.31	n.d	n.d
BDE 3	4.8	0.86	5.2	11	17
BDE 7	0.01	n.d	n.d	0.04	n.d
BDE 15	0.06	0.02	0.30	0.24	6.3
BDE 17	0.01	n.d	0.18	0.19	0.03
BDE 28	n.d	0.01	0.62	0.49	0.47
BDE 47	0.16	0.04	1.9	1.2	1.6
BDE 49	0.36	0.08	3.0	1.6	2.3
BDE 66	n.d	n.d	0.04	0.04	n.d
BDE 71	0.18	0.05	2.0	1.1	1.3
BDE 77	n.d	n.d	n.d	n.d	n.d
BDE 85	0.01	n.d.	n.d.	n.d	0.10
BDE 99	0.15	0.04	1.2	0.70	2.0
BDE 100	0.06	0.01	0.44	0.32	0.50
BDE 119	n.d	n.d	0.07	n.d	n.d.
BDE 126	0.02	0.01	0.05	n.d	0.80
BDE 138	n.d	0.02	n.d	n.d	0.29
BDE 153	0.09	0.02	0.44	0.20	0.92
BDE 154	0.02	0.004	0.18	0.13	1.2
BDE 156	n.d	0.01	n.d	n.d	n.d
BDE 183	0.04	0.01	0.05	0.04	0.10
BDE 184	0.01	0.01	0.06	0.01	n.d.
BDE 191	n.d	n.d	0.01	n.d	n.d
BDE 196	0.04	0.01	0.13	0.09	0.27
BDE 197	0.04	0.01	0.12	0.08	0.28
BDE 206	0.96	0.28	5.8	5.2	5.7
BDE 207	0.47	0.11	2.4	1.9	3.8
BDE 209	44	4.7	240	260	83
DBDPE	1.1	0.65	9.8	8.8	3.4

* SPM; first four samples are sediments.

** n.d. non detected

Table 1. BFR concentrations in Western Scheldt sediment and suspended matter in ng/g dw.

Interesting is also the concentration of the monobrominated diphenylether BDE 3: up to 11 ng/g dw. Clearly, Wielingen, the most westerly location in the Scheldt estuary, in fact in coastal water, is the location with the lowest BFR levels, while Hansweert (east from Terneuzen) and Ouden Doel (at the Belgium border), so the most upstream locations, compete for the highest degree of contamination. At Terneuzen, both a sediment and an SPM sample have been taken. On a dry weight basis almost all PBDE and other BFR concentrations are higher in the SPM sample. Although peak values can occur in SPM, a more likely explanation is an increase in concentration with time of these compounds: the sediment sample is a more time-integrated sample, even while only the top layer was sampled, while the SPM reflects the actual situation at the moment of sampling. The present data suggest an increasing trend for most of the BFRs analysed in this area. Obviously more measurements will be needed to underpin this suggestion.

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