

## THE PRESENCE OF A 'NEW' FLAME RETARDANT, DECABROMODIPHENYL ETHANE, IN ENVIRONMENTAL SAMPLES

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### Introduction

Among the brominated flame retardants in use, the polybrominated diphenyl ethers, PBDEs, have received attention because of their ubiquitous appearance in biota both from remote areas as well as near user sites<sup>1</sup>. While DecaBDE (BDE209) is the major PBDE product in use, the most abundant congeners reported in biota are the lower brominated PBDEs (up to hexaBDE). High concentrations of BDE209 have previously been reported in e.g. sediment and sewage sludge<sup>2,3,4</sup>. Due to its high molecular weight (mw 959.2) BDE209 was assumed not to be bioavailable. However, lately BDE209 has been detected in human blood<sup>5</sup> and more recently in significant amounts in peregrine falcons<sup>6</sup>.

Decabromodiphenyl ethane (DeBDethane) was introduced in the early 1990s under the trade name 'SAYTEX® 8010' by Albemarle Corporation. The applications are the same as for BDE209 but in contrast to BDE209 it produces no PBDD and only minor quantities of 2,3,7,8-DBDF under pyrolysis conditions<sup>7</sup>. DeBDethane has a molecular weight of 971.2 and a calculated logP of about 11. To our knowledge it has never been identified in environmental samples.

### Materials and methods

The DeBDethane (SAYTEX® 8010, lot#8721-21, Albemarle Corporation, USA) was dissolved in acetone, tetrahydrofurane and toluene, 20:30:50 %. The sewage sludge samples (collected in year 2000) were part of a Swedish survey including 50 sewage treatment plants of different sizes, geographically distributed all over Sweden. Two samples were selected for quantification on basis of a high DeBDethane/BDE209 ratio. Both plants are of medium size (approx. 15000 person equivalents). The sediment sample (sieved and freeze dried) originates from Western Scheldt in the Netherlands. The area is highly contaminated with respect to DecaBDE<sup>4</sup> and was used in the feasibility study in the EU project BROCC, Biological Reference Materials for Organic Contaminants (2001-2003). Sediment and sewage sludge were solvent extracted with toluene:acetone (1:1). Sulphur removal and sulphuric acid treatment were made according to previously described method<sup>8</sup>. The extracts were further cleaned up on a SiO<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub> column (1g, 2:1 w/w) and for high resolution MS (HRMS) identification fractionated on an activated silica column (1g). Air samples were collected indoors in an electronics dismantling facility in Stockholm using personal air sampling pumps<sup>9</sup>. The samples represent approximately 2 m<sup>3</sup> of air. The filter extracts was cleaned up on an amino-SPE cartridge (1 g).

The samples were quantified with GC/MS (Finnigan SSQ) in ECNI mode, recording the bromine ions using an ion source temperature of 230°C. Dechlorane was used as internal standard. HRMS/EI (Finnigan MAT95, source temp. 250°C) was used for identification by single ion recording of the ions 482.6054, 484.6034, 486.6014 and 488.5994 in the most abundant fragment, [C<sub>6</sub>Br<sub>5</sub>CH<sub>2</sub>]. The extracts were injected on-column and the resolution was 15000. In addition, the molecular ion cluster was scanned (m/z 964-978) with a resolution of 1500. Full scan mass spectra in low resolution MS (EI and ECNI) were recorded using a TSQ7000 (FinniganMAT, source temp. 170°C). A DB-5 MS (J & W, 15m, 0.25mm, 0.10µm) column was used in all systems.

### Results and Discussion

A brominated compound eluting after BDE209 was found in sediment from the Western Scheldt in the Netherlands, in sewage sludge from various parts of Sweden and in air samples from an electronics dismantling facility in Stockholm (Fig 1). The retention time matched that of the DeBDethane standard solution.

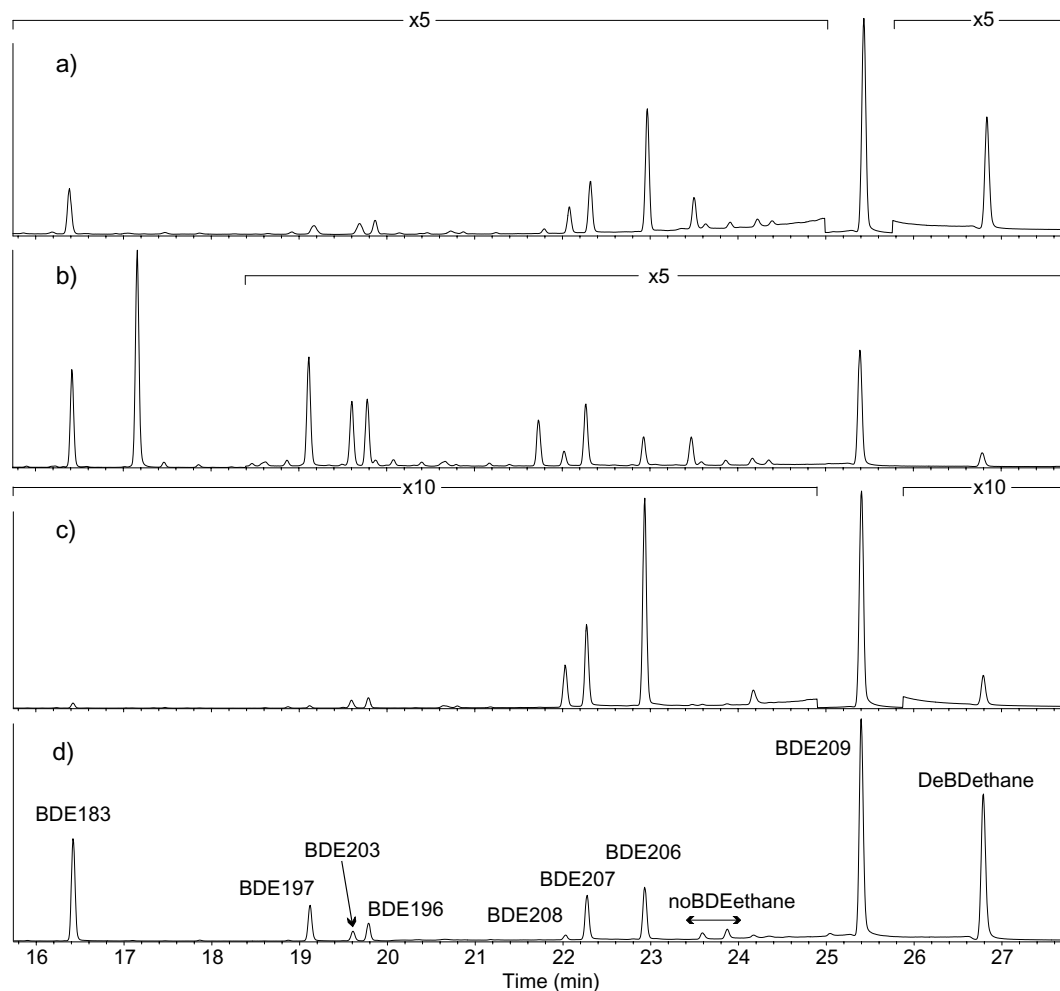


Figure 1. Mass chromatogram ( $m/z$  79+81) of a) sewage sludge B, b) an air sample, c) sediment and d) a reference standard mixture of the technical products Bromkal 79-8DE (octaBDE product), DecaBDE and decabromodiphenyl ethane.

Figure 2A shows an EI fullscan mass spectrum of a DeBDethane standard solution. The molecular ion is present at  $m/z$  971 [ $M+10$ ] and fragments at  $m/z$  891, 811, 731, 651 and 571 are also detected, corresponding to the loss of 1 to 5 bromine atoms respectively. The high abundance fragment at  $m/z$  485 with an isotopic pattern indicating 5 bromine atoms, is most likely formed by the cleavage of the ethyl bond yielding the  $[C_6Br_5CH_2]$  fragment. Fragments at  $m/z$  405 [ $C_6Br_4CH_2$ ] and 324 [ $C_6Br_3CH_2$ ] would then correspond to the ethyl cleavage together with the loss of one or two bromine atoms. The dominating fragments in ECNI mode are the bromine ions ( $m/z$  79, 81) (Fig. 2B). Low abundance fragments are detected at  $m/z$  around 891, 811, 731, 651, 571, 491, 411 and 331, indicating

fragments formed by the loss of 1 to 8 bromine atoms. No trace of the molecular ion was observed. Three additional fragments were detected at  $m/z$  472, 392 and 312, possibly suggesting the formation of the  $[C_6Br_3]$ ,  $[C_6Br_4]$  and  $[C_6Br_5]$  respectively.

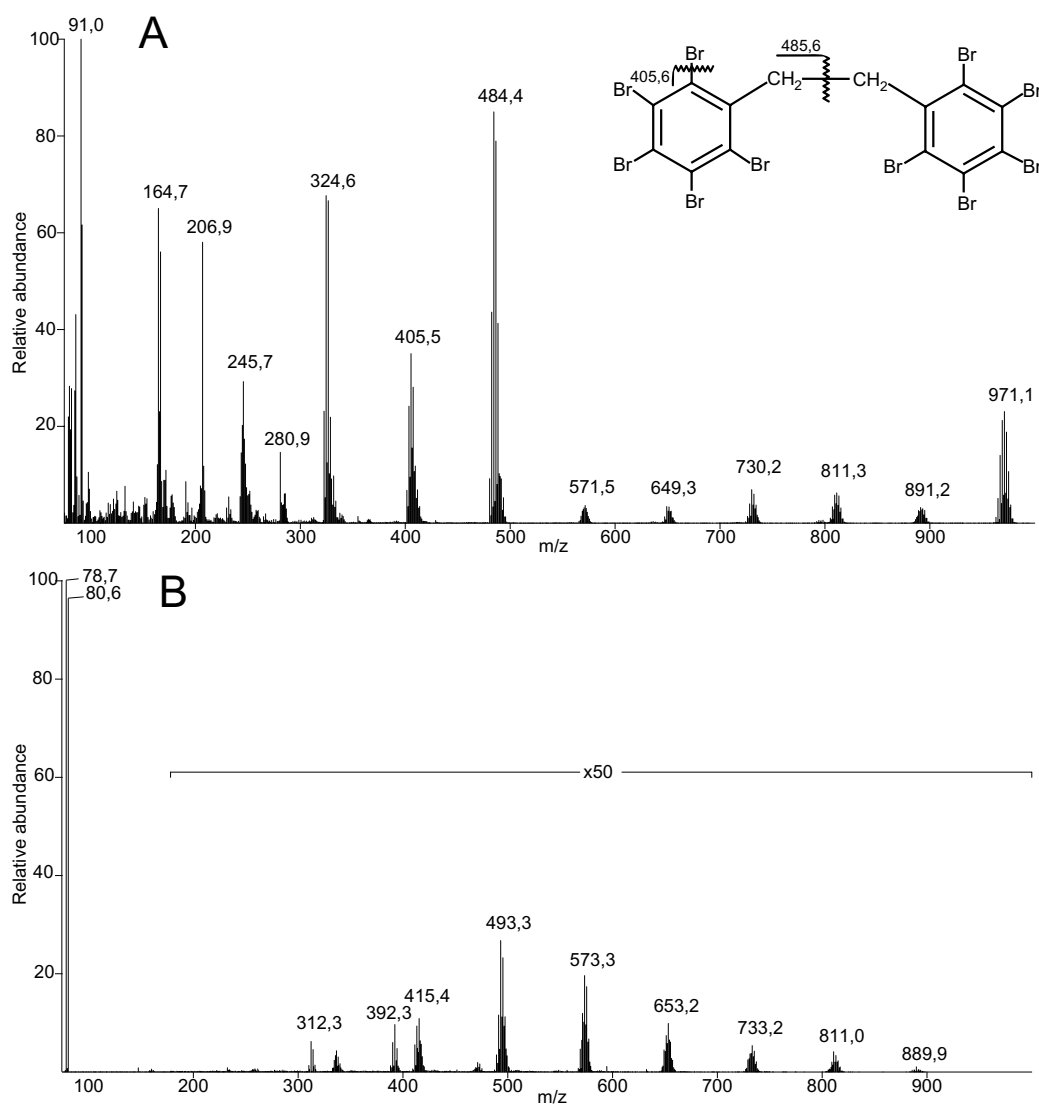


Figure 2. Mass spectra of decabromodiphenyl ethane in A) EI mode and B) in ECNI mode.

DeBDethane was identified in all samples by retention time and by HRMS recording the most abundant fragment as well as the molecular ion. DeBDethane was present in sludge from at least 25 out of the 50 sewage treatment plants. No correlation of DeBDethane to plant size or location was observed. Compared to BDE209 the concentrations of DeBDethane were low in all screened samples. The levels ranged from 24 to 51 ng/g dry weight in the quantified samples (Table 1). The results should however be regarded as minimum concentrations since the method has not been optimised for this compound. The ratio of DeBDethane to BDE209 was 0.01 in the sediment and 0.3 and 0.6 in the sewage sludge samples. The sewage sludge samples however, were selected because of the high

DeBDethane/BDE209 ratio, and therefore do not necessarily represent the samples with the highest DeBDethane concentration.

Sample	Dry weight %	BDE209 ng/g dw	DeBDethane ng/g dw
Sewage sludge A	21	89*	51
Sewage sludge B	16	99*	33
Sediment	99,8	1980**	24

Table 1. Concentrations (ng/g dry weight) of decabromodiphenyl ethane and decabromodiphenyl ether in sediment and sewage sludge. The dry weight in % of the wet weight is also given (the sediment was freeze dried). \* Quantified in a previous study <sup>10</sup> and \*\* in the feasibility study (BROC).

In analytical solutions of the product there are at least two peaks eluting before DeBDethane, indicating the presence of nonabrominated congeners as well as traces of octaBDethane. In accordance with the chemical physical behaviour of BDE209 these tentative nonaBDethane congeners increase under unfavourable treatments/conditions.

Although all samples contained BDE209 in varying concentrations, no correlation was found between BDE209 and DeBDethane concentrations, which supports the assumption that the products are used independently.

The presence of a 'new' brominated flame retardant has been confirmed in sewage sludge, sediment and air samples. So far the concentrations are low compared to BDE209, which probably reflects the higher usage of BDE209. A risk assessment of the BDE209 product is currently under evaluation in EU for a future risk reduction strategy on the use of this product. Since DeBDethane has similar applications as BDE209 it is important to investigate its environmental behaviour before substituting BDE209 with DeBDethane.

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