Occurrence of the "new" brominated flame retardant, decabromodiphenyl ethane, in sewage sludge from Spain

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Introduction

Among the brominated flame retardants (BFRs) in use, polybrominated diphenylethers (PBDEs) were the most studied. A considerable number of works reported levels of PBDEs in environmental and biotic samples. However, only sparse data are available on other BFRs. Decabromodiphenyl ethane (DeBDethane) is a relatively new BFR with similar applications to that of Deca-BDE. It was introduced in the early 1990s under the trade name SAYTEX® 8010 by Albemarle Corporation. Although currently is not as widely used as Deca-BDE due to their higher cost, it is predicted that their use will increase considerably.

The objective of this study was to determine the occurrence of the “new” BFR, DeBDethane in sewage sludge samples from different waste-water treatment plants in Spain. To the knowledge of the authors, only two previous studies reported environmental data related to this compound. Kierkegaard et al.[1] identified DeBDethane in some Swedish environmental samples, such as sewage sludge, sediment and indoor air. On the other hand, McCrindle et al.[2] determined DeBDethane in sewage sludge from Ontario (Canada).

Materials and Method

Sample collection:Sewage sludge was sampled in eight waste-water treatment plants, during 2002 year at different locations throughout Spain. Operating conditions were based on physicochemical treatment of activated sludge, followed by stabilisation and final drying on a belt filter press device. According to type of influent stream and number of inhabitants, different facilities were divided into the following categories: “urban” refers to waste-water from highly-populated/low-industrialised sites; “industrial”, zones with high industrial activities cores, “mixture”, mixed urban and industrial activities, and “rural”, zones with agricultural activities.

Samples were taken by plant staff, air-dried (or at 40^{o}C) until constant weight to avoid lack of volatile congeners, ground to a fine powder, poured into sealed amber-glass flasks to prevent highly brominated congeners from photodegradation and sent to the laboratory. Upon receiving, they were stored at –20^{o}C reducing as much as possible time between collection and analysis.

Extraction and cleanup:A 2.5-gram of dried sludge sample was extracted using a Dionex ASE100 at the following conditions: hexane:DCM (1:1), 100ºC, 1500 psi, 90% flush volume and three static cycles. Resulting extracts were transferred into a separation funnel and liquid-extracted with concentrated sulphuric acid to remove organic matter. Clean-up stage was then performed in an automated purification Power Prep^{TM} System (FMS, Inc., USA) including acidic silica gel and basic alumina columns. Different mixtures of hexane:DCM were used to recover target analytes while retaining interfering compounds. The extracts obtained were concentrated avoiding dryness and further analysed by GC-MS.

Instrumental analysis: Analyses were carried out by GC-NCI-MS in a Gas Chromatograph Agilent 6890 connected to a Mass Spectrometer Agilent 5973 Network (Agilent Technologies, Madrid, Spain). A DB-5ms capillary column (15 m., 0,25 mm. of i.d., 0,25 µm film thickness) containing 5% phenylmethylsiloxane was used with helium as the carrying gas at a constant pressure of 10 psi. The temperature program was from 140^{o}C (held for 1 min.) to 325^{o}C (held for 10 min.) at 10^{o}C/min., using splitless injection during 1 min. Other operating conditions were 250ºC ion source temperature and ammonia as chemical ionisation moderating gas at an ion source pressure of 1.9 x 10^{-4} Torr. Identification and quantification was carried out using the technical product SAYTEX® 8010 as external

standard. However, quantitative data should be regarded as estimated levels since the method was not optimized for this compound, and recovery studies were in course.

Results and Discussion

A brominated compound eluting after BDE-209 was detected in all the samples analysed. The retention time of this compound matched that of technical product SAYTEX® 8010, and thus the compound was identified as the "new" BFR DeBDethane (Figure 1). Table 1 show the quantitative data obtained for DeBDethane, as well as the corresponding level of BDE-209 (data from Fabrellas et al.[3]). As can be seen, DeBDethane levels ranged from 0.2 to 15 ng/g dry weight (dw), whereas BDE-209 was found at higher levels (from 32 to 541 ng/g dw) probably reflecting the higher usage of Deca-BDE. Our results were lower than those reported for samples from Sweden (from not detected to 100 ng/g dw)[1], and similar to those found in Canada (from 6 to 32 ng/g dw)[2]. DeBDethane/BDE-209 ratios were calculated, obtaining results from 0.001 to 0.07. Similar ratios were found in Canadian sludge (from 0.01 to 0.03)[2], and higher values were observed in Swedish sludge (from 0.02 to 0.7)[1]. Although all samples in which DeBDethane was detected also contained BDE-209, the differences in DeBDethane/BDE-209 ratios seems to indicated that the products are used independently.

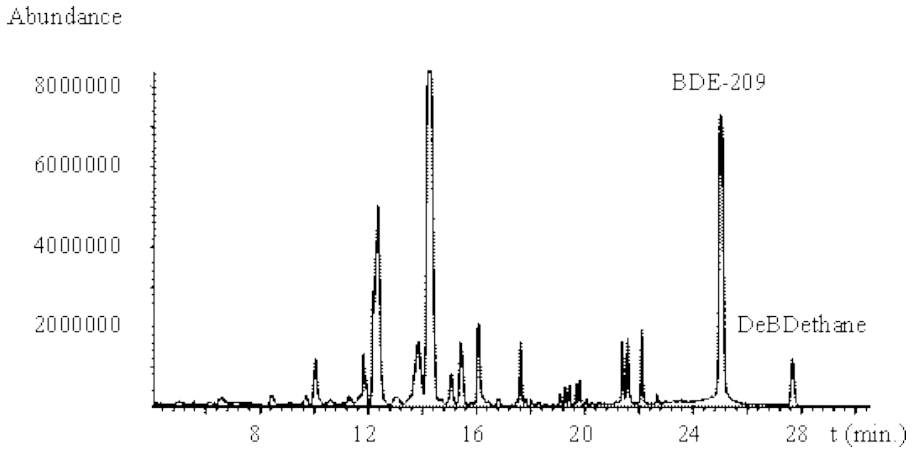

Figure 1. GC-NCI-MS (*m/z* 79) chromatogram obtained for SS2 sample in a DB-5ms (15m x 0.25 mm i.d., 0.25 µm film thickness).

Table 1: DeBDethane and BDE-209 concentrations in ng/g dw of sludge samples analysed.

	SS1	SS2	SS3	SS4	SS5	SS6	SS7	SS8
Type of influent	Mixture	Industrial	Urban	Urban	Industrial	Mixture	Mixture	Rural
Nº of inhabitants*	Low	Low	Low	High	Low	Medium	Low	Low
DeBDethane	15.2	7.64	11.5	9.06	0.81	1.03	2.48	0.21
BDE-209	271	110	251	292	541	94.3	72.2	32.0
$R_{DeBDethane/BDE-209}$	0.06	0.07	0.05	0.03	0.001	0.01	0.03	0.01

* Low: < 500000; Medium: 500000 – 1000000; High: > 1000000

The variation in DeBDethane values evidences considerable influence of different local sources, having particular operational conditions as type of influent entering the plant and/or the number of inhabitants related to that area. However, no correlation between DeBDethane levels and characteristics of treatment plants was observed. It seems that urban impact leads to relatively high levels of this compound (9 and 12 ng/g dw), perhaps as a consequence of the prominent use of thermoplastics, as housing for televisions and computers, or textile stuffs.

Debromination of BDE-209 in environmental systems is discussed controversially, leading to the occurrence of lower brominated diphenylethers with known adverse effect for the environment. The same behaviour could be expected for DeBDethane. Therefore, and before using DeBDethane to replace BDE-209, clarifying this effect as well as assessing features such as half-life and bioavailability is desirable, particularly when sewage sludge is intended for land application under high sun radiation conditions, as in most Mediterranean countries. From the view of these results it may be concluded that a better knowledge of this “new” BFR in the environment, and especially in sewage sludge for land application would be desired. Current data only constitute a first approach. Observations need to be confirmed by enlarging number of samples and facilities evaluated.

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