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Polybrominated diphenyl ether in sewage sludge in Germany

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Abstract

Sewage sludge samples from 11 municipal waste water treatment plants in Germany were collected from March 2002 to June 2003. Total Tri- to HpBDE concentrations (sum of significant congeners BDE 28, 47, 99, 153, 154 and 183) ranged from 12.5 to 288 (median 108) and DeBDE (BDE 209) concentrations from 97.1 to 2217 (median 256) ng/g d.m. BDE 209 dominated the congener profile. A significant change of the Tri- to HpBDE congener profile (% of total BDE 28, 47, 99, 153, 154, 183 without 209) in sludge from different stages of the waste water treatment process (primary sludge, secondary excess sludge and (dewatered) digested sludge), indicating a degradation of DeBDE to these congeners, was not observed.

Keywords: Polybrominated diphenyl ether; PBDE; Waste water treatment plant; WWTP; Sewage sludge; Degradation

1. Introduction

With the rapidly growing use of combustible polymer material, e.g. for IT/TV casings, mattresses, upholstered furniture, the use of flame retardants like polybrominated diphenyl ethers (PBDE) has also increased strongly.

PBDE are available as three commercial mixtures of BDE congeners named after their principal component: PeBDE (European and North American usage in 2001 150 and 7.100 t/a), OcBDE (610 and 1.500 t/a) and DeBDE (7.600 and 24.500 t/a). North America accounts for approximatively 95% of the global demand for PeBDE based on this data (BSEF, 2005). PBDEs can release into the environment during their production, use or after disposal and have become ubiquitous. Because of exponentially increasing levels of the dominating congeners of technical Pe- and OcBDE in human blood and milk, the use and sale of preparations and articles containing these two flame retardants in concentrations >0.1% by mass are prohibited from August 15, 2004 in the European Union (EU, 2003). PBDE are subject to regulation and legislation in many countries (BSEF, 2005; NCEL, 2005). The main North American manufacturer of PeBDE flame retardant has voluntarily ceased production by the end of 2004 (Tullo, 2003). DeBDE EU risk assessment was closed on May 26, 2004. It will be reviewed, if after voluntary emission reduction new data from a monitoring programme lasting for 6 years with a possible extension to 10 years, are available (EU, 2004). It was concluded that there is a need for further information on the possible degradation of DeBDE to more toxic and bioaccumulative compounds. In a paper recently presented on BFR 2004, the anaerobic degradation of DeBDE to No- and OcBDE in incubation experiments with sewage sludge over a period of 114 days was studied (Gerecke et al., 2004, 2005).

The objective of this study is to get more information about the actual levels and time trend of PBDE in sewage sludge in Germany to ascertain whether there is degradation of DeBDE to lower brominated congeners during waste water treatment process.

2. Materials and method

2.1. Sampling

Thirty-nine sewage sludge samples from different stages of the waste water treatment process (primary sludge,

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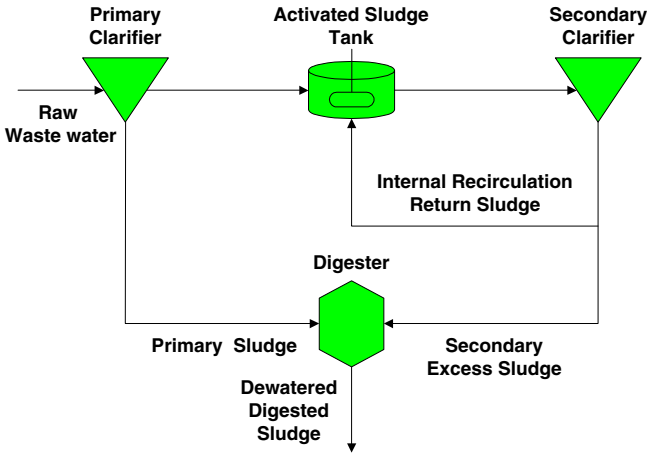

Fig. 1. Flow scheme of the biological part of a WWTP.

Table 1
Capacity of the WWTP

WWTP	Population equivalent
A	1820000
B	45000
C	45000
D	45000
E	75000
F	350000
G	75000
H	63500
I	240000
J	48000
K	50000

secondary excess sludge and (dewatered) digested sludge) (Fig. 1) were collected from 11 municipal waste water treatment plants (WWTP) of the Rhine-Main area in Germany from March 2002 to June 2003. The capacity of the WWTP investigated ranged from 45000 to 1820000 population equivalents (Table 1).

2.2. Analysis

The complete sewage sludge sample was sterilized in an autoclave for 20 min at 121 °C, an aliquot freeze-dried, 2 g spiked with six $^{13}C_{12}$-BDE standards (20 ng BDE 28, 47, 99, 153, 183 and 200 ng BDE 209), one of each degree of bromination and extracted by Soxhlet extraction (Knöfler–Böhm hot extractor) with toluene. The extract was cleaned by a four column clean-up (1. Multi layer SiO_2–$AgNO_3$, H_2SO_4, NaOH. 2. Macro Al_2O_3. 3. GPC Bio-Beads S-X3. 4. Mini Al_2O_3), spiked with the injection standard (20 ng 4,4′-dibromoctafluorbiphenyl) and reduced to 100 µl. 1 µl was injected on-column (guard column 2 m × 0.32 mm, uncoated, deactivated) and analysed by GC-SIM(EI+)LRMS (GC 8000Top-MS Voyager, ThermoQuest) using a DB-5MS (15 m × 0.25 mm, 0.1 µm). The two most intense masses of the bromine cluster (Tri- and TeBDE: M^+. Te- to DeBDE: M^+-2Br) were measured for each homologue group. The identification of PBDE was based on retention time and correct isotope ratio for both fragments recorded. Quantification was performed by means of the $^{13}C_{12}$-labelled internal standards. All congeners except BDE 100 and BDE 154 were quantified based on their corresponding $^{13}C_{12}$-labeled analogues used as internal standards. BDE 100 was quantified using the $^{13}C_{12}$-BDE 99 and BDE 154 using the $^{13}C_{12}$-BDE 153 internal standard (Knoth et al., 2002, 2003). The method is described in detail in the new analytical standard ISO/DIS 22032 (ISO, 2004). The laboratory took part in the BSEF/QUASIMEME interlaboratory study on brominated flame retardants December 2001 to March 2002. Method blanks were analysed every four samples.

3. Results and discussion

The total concentration of BDE 28, 47, 99, 100, 153 and 154 the dominating congeners of technical PeBDE and BDE 183, the dominating congener of technical OcBDE, ranges from 12.5 to 288 (median 108) ng/g d.m. (Table 2). With the increasing use of flame retardant polymer material the median level has risen 13 fold since the report from Germany in 1992 (total Tri- to HpBDE 0.5 to 17.7 (median 8.4, $n = 13$), not designated which congeners) (Hagenmaier et al., 1992). An increasing time trend was also observed in other actual studies from Germany and Sweden whereas in Switzerland the concentrations have decreased. In North America, where about 95% of technical PeBDE is used, levels 10–100 times those in Europe were detected (Table 3 and Fig. 4).

Levels of DeBDE (BDE 209) varied more between WWTP than total Tri- to HpBDE, ranging from 97.1 to 2217 (median 256) ng/g d.m. Although the German polymer and textile industries voluntarily phased out the use of PBDE including DeBDE as early as 1986 (UBA, 2001), in two WWTP (G and K, Table 2) surprisingly high levels of BDE 209 were detected probably from landfill leachates or industrial discharges. Such high DeBDE contamination was also found in Spain, Switzerland, and with an increasing time trend from 1993 to 2002 in North America (Table 3 and Fig. 5). In this study there was no relationship between PBDE burden and capacity of the WWTP (Tables 2 and 1).

The BDE 28–209 congener profile (% of total BDE 28, 47, 99, 100, 153, 154 and 209) is dominated by BDE 209 (Fig. 2). The total retention time of sludge in a WWTP is 11–13 days. No significant change of the congener profile (% of total BDE 28, 47, 99, 153, 154 without 209) in sludge samples from different stages of the waste water treatment process for a given plant (primary sludge, secondary excess