BROMINATED FLAME RETARDANTS IN SLUDGE FROM 50 SWEDISH SEWAGE TREATMENT PLANTS: EVIDENCE OF ANAEROBIC DEGRADATION OF HBCD AND TBBPA

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Abstract
Sludge samples from 50 Swedish sewage treatment plants collected in 2000 were analyzed for tetra-decabrominated diphenyl ethers, hexabromocyclododecane, tetrabromobisphenol A and decabromobiphenyl. STPs represented major cities, towns with potential point sources and different-sized STPs scattered randomly around Sweden. Except where there were point sources, PentaBDE-related congeners (BDE47, 99, 100, 153, 154 or Σ5PBDE), BDE209, HBCD and TBBPA concentrations did not vary much and concentrations were independent of STP size or latitude. This indicates similar, diffuse inputs per person equivalent into wastewater, possibly from domestic sources such as house dust, washing textiles and cleaning surfaces. Comparison of raw and organic-matter adjusted digester sludge concentrations showed statistically significantly lower HBCD and TBBPA concentrations in digester sludge, indicating anaerobic biodegradation in the digester process.

Introduction
Flame retardants such as polybrominated diphenyl ethers (PBDE), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA) are used in plastics, rubber and textiles to prevent fires. The contaminant load in sewage sludge is a reflection of what products are being used in society. Wastewater entering a sewage treatment plant (STP) undergoes several steps and the raw sewage sludge from these steps is used/disposed of as such, for example as fertilizer or is further processed anaerobically in a digester (digester sludge). Earlier studies in Sweden have shown the presence of BDE47, 99, 100 and TBBPA in digester sewage sludge from a few STPs.[1, 2] Digester sewage sludge samples from three sewage treatment plants (STP) in Stockholm collected in 1997-98 contained measurable amounts of these BFRs but also of BDE153, 154, 209, and HBCD.[3] Öberg et al. presented summary statistics for BDE47, 99, 100, 153, 154 and 209 and TBBPA in sludge from 22 STPs in Sweden, but gave no ancillary information on the size or locations of these STPs or the type of sludge analyzed.[4] Remberger et al. analysed sludge from several STPs in or near Stockholm and found HBCD in primary sludge samples before digestion but not in digester sludge, possibly indicating biodegradation.[5] Biodegradation has also been seen experimentally for HBCD, TBBPA and BDE209 under anaerobic conditions (digester sludge) but not under aerobic conditions (activated sludge).[6-9] A preliminary study suggests that this also occurs in STP digesters as well.[7]

Based on the previous scattered results showing the presence of BFRs in sewage sludge from Stockholm STPs, the Swedish Environmental Protection Agency initiated a larger study to determine the extent of the problem in Sweden. Sewage sludge samples were collected for analysis of BDE47, 99, 100, 153, 154 (PentaBDE congeners), BDE209 (DecaBDE), HBCD and TBBPA from 50 representative STPs spread randomly around the country. Samples included raw and digester sludges, allowing a study of possible anaerobic biodegradation of BFRs.

Materials and Methods
The 412 sewage treatment plants (STPs) in Sweden were ranked into three size classes: large – > 75 000 person equivalents (pe) (5% of the total); medium – 20 000 to 75 000 pe (13%); and small – < 20 000 pe (82%). Eight STPs from the three major Swedish cities (Stockholm, Gothenburg, Malmö) and seven additional STPs that had suspected or known sources connected were to be included. Of these, 8 were large, 4 were medium and 3 were small. To obtain a representative number of STPs in proportion to their size, an additional 2 medium and 33 small STPs were chosen at random and checked to see that they were spread geographically throughout the entire country. Sludge samples from the final step at each STP were collected in 2000. Sludge samples were extracted according to Nylund et al. for PBDEs and HBCD with modifications for TBBPA.[1, 2] Single congeners of BDEs 47, 99, 100, 153, 154 (99 % purity, Cambridge Isotope Laboratories, Andover, MA, USA) were used as

reference standards. HBCD (Michigan Chemical, St. Louis, MI, USA), BDE209 (Dow Chemicals, FR-300BA) was analysed using a technical product as reference standard. Dechlorane®603 (previously Hooker Chemical Comp., now Occidental Chemicals, Dallas, TX, USA) and 3,3',5'-tribromo-5-chlorobisphenol A (TrBCBPA) (kind gift of Department of Environmental Chemistry, Stockholm University) were used as internal standards. CB189 (kind gift of Department of Environmental Chemistry, Stockholm University) was used as injection standard. Half of each extract was used for analysis of BDE47, 99, 100, 153, 154, 209 and HBCD (neutral fraction) and the other half was used for the analysis of TBBPA (phenolic fraction). TBBPA was derivatized using diazomethane before final analysis. Samples were analysed using GC-MS run in the chemical ionisation mode, measuring the negative ions formed (ECNI).[10] The reaction gas was ammonia (pressure 7000-8000 millitorr). Mass fragments monitored: *m/z* -79 and -81 for all brominated compounds as well as TrBCBPA, *m/z* -237 and -239 for dechlorane (internal standard), and *m/z* –394 and –396 for CB189. A chromatographic peak was considered quantifiable when the signal-to-noise (S/N) ratio was equal to or greater than five. If present in the blank, the detection limit was set to five times that value. The recoveries for dechlorane and TrBCBPA were 40-90% and 30-120%, respectively. Principal components analysis was performed using SIMCA 10 P (Umetri, Umeå, Sweden). Variables with non-normal distributions were log-transformed before analysis, and all variables were scaled to unit variance. Differences between concentrations in raw and digester sludge were tested statistically using the Mann-Whitney U-test due to the presence of outliers. TBBPA concentrations that were below the limit of quantitation were set to half that value before statistical analyses were performed.

Results and Discussion

Highest mean concentrations were found for BDE209 (120 ng/g dw), followed by BDE99 (60 ng/g dw), BDE47 (49 ng/g dw), HBCD (45 ng/g dw) and TBBPA (32 ng/g dw). Lowest mean concentrations were found for BDE153 (6.1 ng/g dw), BDE154 (4.1 ng/g dw), and BDE100 (11 ng/g dw). The concentrations for the five PentaBDE congeners are similar to results found in other studies of sewage sludge in Sweden and Europe, but are 10 times lower than concentrations seen in North America.[1, 3, 4, 11-17] The congener pattern for these five BDEs is similar across the 50 STPs and is essentially identical to the composition of Bromkal 70-5DE.[18] Mean BDE209 concentrations were similar to those seen in sludge samples from other Swedish studies[4,11], were similar or somewhat lower than seen in Europe[12, 13] but were 10 times lower than in North America[14,15]. Concentrations of HBCD were similar to those found in digester sludge from three Stockholm STPs and in primary sludge from two Swedish STPs but were 3-30 times lower than in European sludges.[5, 11, 19] TBBPA concentrations were below the limit of quantitation for 12 samples (24%). Mean TBBPA concentrations were similar or higher than those seen in previous Swedish studies of sewage sludge and were similar to those seen in Canada, but were 2-3 times lower than in Europe.[2-4, 11, 19, 20]

None of the sludge samples had unexpectedly high Σ5PBDE congener concentrations, suggesting diffuse leakage of the technical product to wastewater entering the STPs as the source of these. This concurs with the discontinuation of use of PentaBDE in Sweden during the early 1990s and thus no current point sources. Higher concentrations of BDE209, HBCD and/or TBBPA were found in a few sludge samples from STPs with known or suspected point sources (textile industries, extruded polystyrene production) but in some cases the point source was unknown. Otherwise, BDE209, HBCD and TBBPA concentrations did not vary much between STPs, also indicating diffuse leaching of technical products into wastewater streams.

The diffuse entryways for BFRs to sewage sludge remain to be determined. One possibility could be emissions to air, long range transport and deposition of BFRs, which then enter the STP from storm drains as runoff from large surface areas. If this were significant, latitudinal trends should be present, with higher concentrations in southern Sweden than in northern Sweden and shifts towards a higher percentage of lower brominated BDE congeners in the Σ5PBDEs in northernmost samples. However, no correlations were found between any BFR concentrations and latitude, nor was there any evidence of latitudinal fractionation for the five BDEs of PentaBDE. No correlations were seen between concentrations of brominated flame retardants in sludge and the size of the STP indicating a similar input per person equivalent connected. A potential domestic source for diffuse emissions could be house dust entering wastewater streams from washing floors and surfaces. House dust from Sweden also has a PBDE pattern for the lower brominated BDEs that is similar to Bromkal 70-DE.[21, 22]

TBBPA concentrations were below the limit of quantification in 10 of 24 digester sludge samples (42%) compared to only 2 of 26 (8%) raw sludge samples. Statistical comparisons were made between raw sludge and digester sludge after correcting the digester sludge BFR concentrations for the reduction of organic matter content that occurs during the digester process (Fig. 1). The concentrations of PBDEs, including BDE209 were not significantly different between the two sludge types. However, HBCD and TBBPA concentrations were significantly lower in the digester sludge samples than in the raw sludge samples. This indicates that anaerobic biodegradation of HBCD and TBBPA does occur in the digester process, supporting previous laboratory studies. Thus, if digester sludge is used for monitoring inputs and sources of BFRs to STPs, biodegradation will hinder identifying point sources.

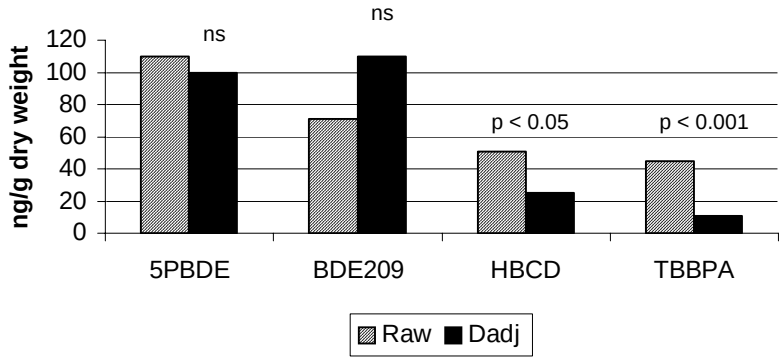

Fig. 1. Mean BFR concentrations for raw and organic-matter-adjusted digester sludge (Dadj).

Principal component analysis of the data indicates the independent use of at least four BFR products: PentaBDE (BDE47, 99, 100, 153, 154), DecaBDE (BDE209), HBCD and TBBPA in Sweden, of which DecaBDE, HBCD and TBBPA are or have been in use recently.

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