Sewage Treatment Processing:An Investigation of Brominated Dipheny Ether Levels

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Over the last few years, there has been heightened awareness globally regarding the environmental presence of the group of chemicals classified as endocrine disruptors[1]. One particular group of such chemicals that has posed great concern is brominated flame retardants (BFRs). The concern for BFRs is largely due to the large amount produced (60,000 tonnes annually) globally and is driven by an increasing need for stringent fire standards[2,3,]. BFRs are found to be involved in the manufacturing of plastics, polymers, resins, textiles, and paint[1,4]. They are known to have low water solubility and have a strong tendency to bind to particulates[1].

A major source of BDEs to the environment is fugitive emission from consumer products like textiles and computers. These emissions make their way into wastewater treatment plants (WWTP) and subsequently into the environment. The sewage treatment process and resulting emission to the environment of BFRs is indicative of the usage of products containing BFRs by society[5]. Treated sewage sludge is used in agricultural land application in many areas. This study involves the investigation of BrominatedDiphenylether (BDE) levels found in the influents and effluents of the sewage treatment process. BDE congener profiles and levels are compared in WTP influent, effluent, and biosolid (sludge) from related areas.

Experimental

Sample Preparation

A 1 to 2 gram sample was used for the analysis of BDEs in biosolids and a 1-2 L sample was extracted for the water analysis. Samples were fortified with $^{13}C_{12}$ BDE quantification standards with at least one congener for each homologue group (BDE 28, 47, 99, 153, 154, 183, 209). All biosolid samples were Soxhlet extracted overnight in toluene for approximately 12-16 hours. Water samples were fortified with quantification standards and later extracted via Empore ® speed disk. After extraction, the sample was eluted off the disk with a mixture of ethanol/toluene. Complete details of cleanup and analysis methodology are listed in MOE Method E3430 (Analysis of BrominatedDiphenyl Ethers in Environmental Matrices) [6]. All BDE standards were purchased from Wellington Laboratories Inc. (Guelph, Canada).

Instrumentation

All analyses were performed using HRGC/HRMS. Brominateddiphenyl ethers were analyzed on a HP6890 Plus gas chromatograph (GC) interfaced to a VG Autospec - Ultima NT High Resolution Mass Spectrometer. Split/Splitless was used with a direct injection sleeve - 1.5 mm I.D. (Supelco). Chromatographic separation for the tri-BDEs to hepta - BDEs were carried out on a DB-5HT 30m X 0.25 mm X 0.10mm (J & W Scientific, USA) decaBDEs was analyzed on a DB-5HT 15m X 0.25mm X 0.10 mm (J&W Scientific, USA) column. All water samples were run only on the 15m DB-5HT column. The GC-HRMS system was tuned to greater that 10,000 RP (10% valley definition). A calibration series of BDE-CS1 to BDE-CS5 were used to quantify the tri to decaBDEs.

Results

The following results are a comparison of BDE levels found in sewage plant influent and effluent samples. These samples were also compared to levels found in biosolids in the same sample area. In Figure 1 below, the expected trends of BDE levels, Biosolid > Influent > Effluent (Pre and Post Disinfection) are depicted. In general, the overall congener distribution that was noted was BDE 47 > BDE 99 > BDE 209 at all stages of the sewage processing. There was a significant decrease in the BDE 209 found in the effluent.

Figure 1: BDE Profiles Found During Sewage Processing at Site 1

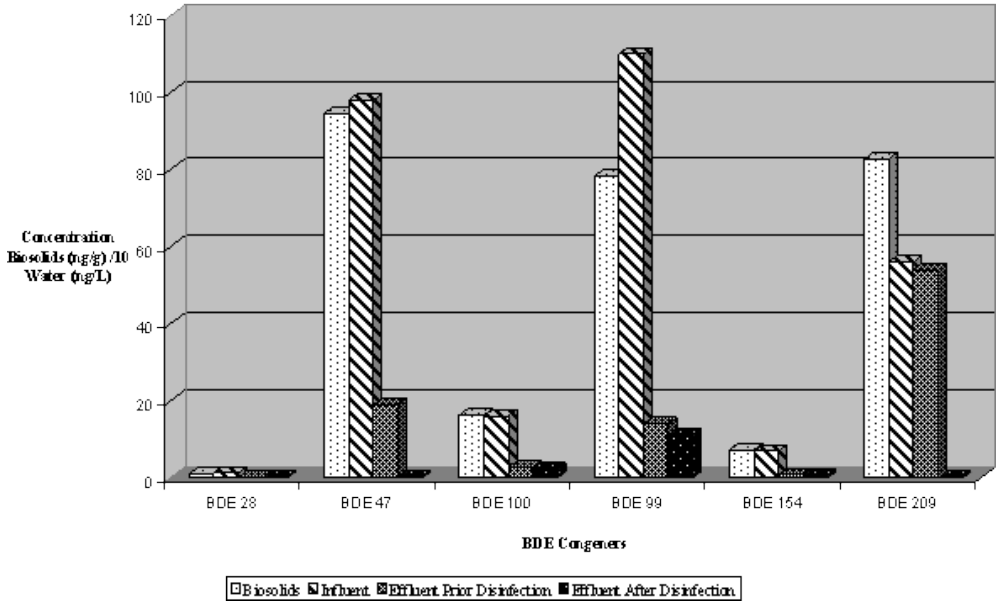
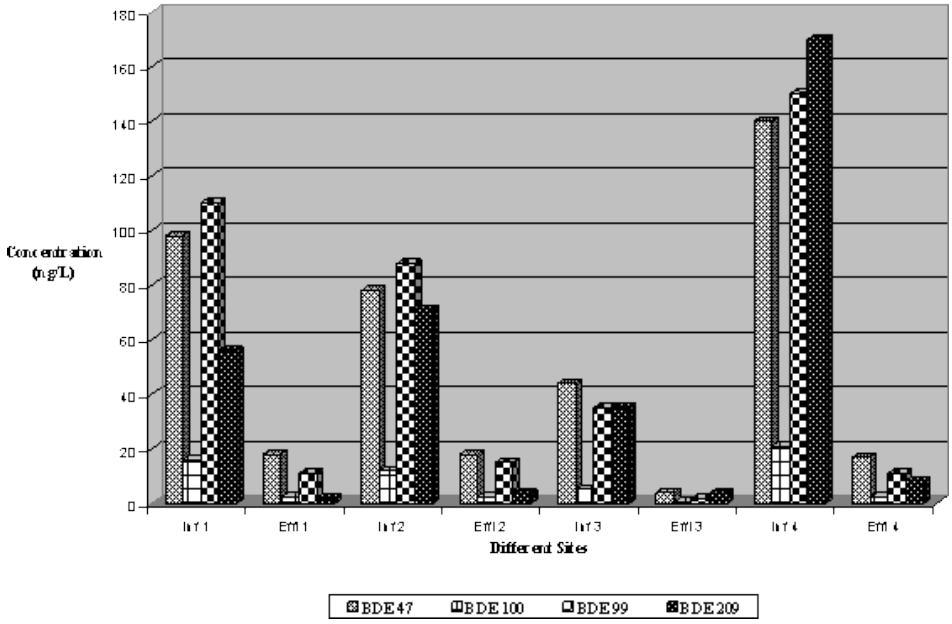


Figure 2: BDE Profiles - Influent vs Effleunt Post Disinfection Different Sites



There was a slight decrease noticed between the pre-disinfection versus post disinfection process.

In Table 1, the following general trends were noted between BDE 47, 99, and 209. The concentration level distributions were found to be similar between the biosolids and the influent samples, BDE 47 ˜ BDE 99 ˜ BDE 209. In the effluent, BDE 47 ˜ BDE 99 but there appeared to be a difference between the pre and post disinfection processes when comparing these congeners against BDE 209. In the pre disinfection BDE 47 ˜ BDE 99 were 3 times greater in concentration than BDE 209. However, in the post disinfection, BDE 47 appeared to be 5 times BDE 209 and BDE 99 is only 3 times BDE 209.

Table 1: BDE Levels at Various Stages of Sewage Processing at Site 1

Congener	Biosolids (ng/g)	Influent (ng/L)	Effluent Pre-Disinfect (ng/L)	Effluent Post Disinfect (ng/L)
BDE 28	10	1.1	0.38	0.35
BDE 47	807	78	17	18
BDE 100	111	12	2.5	2.5
BDE 99	753	88	15	15
BDE 154	66	5.4	0.86	0.85
BDE 209	650	71	4.6	3.5
BDE 47/99	1.07	0.89	1.13	1.20
BDE 47/209	1.24	1.10	3.70	5.14
BDE 99/209	1.16	1.23	3.26	2.16

Figure 2 depicts the congener distribution profile found in both influent and effluent water samples. The predominant congeners found in the influent were BDE 47, 99, and 209. There were similarities in congener profile distributions between sites. On examining the influent samples at site location 1 to 3, the profile was BDE 209 = BDE 47 = BDE 99 and at Site 4, BDE 47 = BDE 99 = BDE 209. In the effluent, the general profile was BDE 209 = BDE 99 = BDE 47. There was approximately an 80-95% decrease noted between the influent and effluent levels.

Conclusion

A significant decrease in BDE levels were found at the final effluent discharge. The decrease in the BDE levels correlate with the decrease in amount of solid material present in the liquid phase. BDE 47 and BDE 99 were still present at the final effluent stage of the sewage processing. Is the persistence of these congeners due to breakdown of BDE 209 during the sewage treatment process or are they simply there due to their potential solubility in the liquid phase since the Log K_{OW} for BDEs range anywhere from 5 to 10[1]. Effluents are treated by chlorination or UV irradiation. Further investigative work is needed in order to fully understand and evaluate the effect of treatment and the fate of these compounds in the sewage treatment process[7].

References

1) C.A. de Wit, Chemosphere, Vol **46**, No. 5, 2002, 583-624.

2) Swedish Environmental Protection Agency, Persistent Organic Pollutants; A Swedish View of an International Problem, NaturVarsVerket Publishers, 1998.

3) Robert C. Hale, Mark J. La Guardia, Ellen Harvey, T. Matt Mainor, Chemosphere, 2002, Vol 46, 729-735.

4) A. Bergman, 20th International Symposium on Halogenated Environmental Organic Pollutants & POP, Monterey California, USA, August 13-17, 2000, Vol **47**, 36-40.

5) Birkett, J.W and Lester, J., N; (2003) Endocrine Disrupters in Waste Water and Sludge Treatment Process, Lewis Publishers, 2003.

6) Ontario Ministry of the Environment, Toronto, Canada (2004). Method BDE-E3430.