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Parameters affecting the occurrence and removal of polybrominated diphenyl ethers in twenty Canadian wastewater treatment plants

M. Kim [a], P. Guerra [a], M. Theocharides [a], K. Barclay [a], S.A. Smyth [a], M. Alaee [b,*]

[a] Emerging Priorities Division, Science and Risk Assessment Directorate, Science and Technology Branch, Environment Canada, Burlington, Canada

[b] Aquatic Contaminants Research Division, Water Science and Technology Directorate, Science and Technology Branch, Environment Canada, 867 Lakeshore Rd., P.O. Box 5050, Burlington, ON L7R 4A6, Canada

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ABSTRACT

This study determined PBDE levels in influent, primary effluent, and final effluent collected from diverse treatment processes including four aerated lagoons, two facultative lagoons, four primary treatments, eight secondary biological treatments and two advanced treatments. Parameters examined for correlation included seasonal temperature, community sizes, industrial inputs, and operational conditions. PBDE levels in influent were 21–1000 ng/L (median 190 ng/L). Higher concentrations in influent samples were found during summer, and in WWTPs which treated leachate and higher proportions of industrial wastewater vs. residential wastewater. Final effluent levels ranged between 3 and 270 ng/L (median 12 ng/L). Among all congeners, the sum of BDE-209, -47 and -99 accounted for 79 and 71% of total PBDEs in influent and final effluent, respectively, with BDE-209 having the highest proportion. Median removal efficiencies for all process types exceeded 90% except primary treatment at 70%. PBDE levels and removals were correlated to the levels and removals of conventional parameters that represent wastewater strength, such as chemical oxygen demand and total suspended solids. The role of the primary clarifier was significant (~82% removal) and removal was associated with hydraulic retention time (HRT) and surface loading rate. Best removal of PBDEs was achieved at greater than 2000 mg/L mixed liquor suspended solids (MLSS), longer than 10 h of HRT, and 9 days of solids retention time.

1. Introduction

Municipal wastewater treatment plants (WWTPs) collect and treat wastewater streams containing a variety of pollutants generated from industrial discharges, domestic/commercial wastes, leachate from landfills, and precipitation (Petrovic et al., 2003). They can efficiently remove large proportions of contaminants, including nutrients and biodegradable organics (Metcalf and Eddy, 2003). However, some persistent organic pollutants (POPs) have low removal efficiencies because WWTPs were not originally designed to remove them. Therefore, via effluents and biosolids disposal, WWTPs are a potential point source of POP discharge to the environment (Vogelsang et al., 2006; Clarke and Smith, 2011).

One group of POPs widely detected in the environment is polybrominated diphenyl ethers (PBDEs) (Clarke and Smith, 2011). They are used as additive flame retardants in consumer products such as plastics, textiles, and polyurethane

* *Corresponding author*. Tel.: +1 905 336 4752; fax: +1 905 336 6430.
E-mail address: Mehran.Alaee@ec.gc.ca (M. Alaee).

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foam, because they suppress the spread of fire; and were commercially formulated in three different mixtures: Penta-, Octa- and Deca-BDEs (Alaee et al., 2003). However, they are not bonded to the products, therefore, will be released to the environment during the time that the product is in use. This may be harmful because PBDEs were identified as persistent, bioaccumulative, and toxic, resulting in the development of worldwide regulations. In North America, Octa- and Penta-BDEs mixtures ceased production and use in 2005, while Deca-BDEs will be phased out by 2013 (Environment Canada, 2010b). These regulations will protect the environment from further contamination. However, PBDEs cannot be fully eliminated from the environment because they will continue to be released from in-use products.

The major route of PBDEs' introduction to the environment is via WWTP effluents. WWTPs receive PBDEs through discharge from manufacturing sites, leachates, and industrial and residential wastewater (Environment Canada, 2010b). However, due to the implementation of regulations, the PBDEs burden from manufacturing sites should be minimal. Furthermore, historically, PBDEs were never manufactured in Canada. Thus, domestic wastewater and leachate are the primary sources of PBDEs to WWTPs. Vaporization from, and wear-out of day to day products containing PBDEs can allow PBDEs to be emitted into the air (Hazrati and Harrad, 2006; Webster et al., 2009). Once released, PBDEs' high octanol–water coefficients and strong affinity to organic particles assist PBDE attachment to indoor particles such as dust (USEPA, 2010a; Richardson and Ternes, 2011). Then PBDEs are discharged to the sewer system through wash water from contaminated indoor dust, furniture and textiles (Environment Canada, 2010b).

Since WWTPs were not designed to remove PBDEs, their presence can present a challenge for wastewater engineers and operators (Metcalf and Eddy, 2003). Several studies showed that PBDEs were present in both effluents and sludge, although the levels in effluent were much lower (North, 2004), mainly due to PBDEs' high partitioning to solids (Rayne and Ikonomou, 2005; Song et al., 2006). This indicates that PBDEs in the liquid stream of WWTPs are generally removed, but the overall fate of PBDEs during wastewater treatment requires more clarity. Previous studies have focused their attention only on PBDE concentrations in a limited number of influent and final effluent samples. However, WWTP performance is strongly affected by environmental and operational parameters such as season, treatment time, and process complexity (Metcalf and Eddy, 2003). To date, those parameters have not been examined for PBDEs; therefore, the effect of operational conditions on the removal of these compounds is unknown.

In order to investigate the potential relationship between PBDEs removal and operational conditions during wastewater treatment a total of 377 liquid samples was collected from 20 Canadian WWTPs: 145 influent, 86 primary effluent, and 146 final effluent samples, encompassing lagoon, primary, secondary, and advanced treatment processes. Different seasons, configurations, sizes and operational conditions were also studied. To date, this is the first investigation addressing the parameters influencing PBDEs removal using the largest dataset published in the literature. This study offers a comprehensive understanding of the occurrence and removal of PBDEs in various types of WWTPs. A companion paper discusses PBDEs in the solid stream and mass balance during wastewater treatment (Kim et al., submitted for publication).

2. Materials and methods

2.1. WWTPs and sampling

A total of 20 WWTPs participated in this study, representing 15% of the Canadian population, different geographic regions, and widely-used typical wastewater treatment processes. Table 1 summarized the features of these WWTPs that included 4 aerated lagoons (AL), 2 facultative lagoons (FL), 4 primary treatments (PT), 8 secondary biological treatments (ST) and 2 advanced biological nutrient removal treatments (AT). ST processes included conventional activated sludge, trickling filter and biological aerated filter. The 20 plants varied widely in population served (1500–>1,000,000) and flow rate (0.8–>700,000 m^3/day). Sampling from all plants was conducted seasonally (summer and winter), constituting three days per season to investigate seasonal differences. Samples from five WWTPs i.e. B, C, J, R, and L were collected during two consecutive project years to study annual variation.

Sampling points included influent wastewater and final effluent for lagoon and primary treatment processes. Primary clarifier effluent was also included for secondary and advanced treatment processes. Samples from final effluents were taken prior to chlorine disinfection in order to reduce potential chemical interferences in sample analysis (plants A, L, P, Q). However, where ultraviolet light (UV) was used for disinfection, effluent samples were collected after UV treatment (plants B, C, E, F, H, R, T, W). All samples were collected as 24 h equal volume composites (400 mL every 30 min) using Hach Sigma 900 refrigerated autosamplers (Hach Company, Loveland CO, USA), kept at 4 °C and transported to AXYS Analytical Services (Sidney, BC, Canada) on ice, by overnight courier, for analysis.

2.2. Sample and statistical analysis

All detailed sample analysis is described in the supporting information. PBDEs were analyzed according to USEPA (2010b) method 1614A. Analyzed data were statistically evaluated by non-parametric methods such as Mann–Whitney test and Spearman coefficients since the datasets were not normally distributed. All statistical analyses were performed using Minitab 16 Software (Minitab Inc., PA, USA).

3. Results and discussion

3.1. Variability in measurement of PBDEs

Because of the relatively small datasets reported to date, there is little information in the literature on the variability in measurement of PBDEs in wastewater treatment systems. Three samples were collected at each WWTP sampling point