WATER RESEARCH 47 (2013) 6496–6505

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Polybrominated diphenyl ethers in sewage sludge and treated biosolids: Effect factors and mass balance

M. Kim, P. Guerra, M. Theocharides, K. Barclay, S.A. Smyth, M. Alaee*

Science and Technology Branch, Environment Canada, 867 Lakeshore Rd., P.O. Box 5050, Burlington, ON L7R 4A6, Canada

ARTICLE INFO

Article history:
Received 12 December 2012
Received in revised form
1 August 2013
Accepted 17 August 2013
Available online 2 September 2013

Keywords:
Polybrominated diphenyl ethers
Sewage sludge
Biosolids
Mass balance
Solids-liquid distribution coefficient
Sludge treatment

ABSTRACT

Polybrominated diphenyl ether (PBDE) flame retardants have been consistently detected in sewage sludge and treated biosolids. Two hundred and eighty-eight samples including primary sludge (PS), waste biological sludge (WBS) and treated biosolids from fifteen wastewater treatment plants (WWTPs) in Canada were analyzed to investigate the factors affecting accumulation of PBDEs in sludge and biosolids. Factors examined included environmental/sewershed conditions and operational parameters of the WWTPs. PBDE concentrations in PS, WBS and treated biosolids were 230–82,000 ng/g, 530–8800 ng/g and 420–6000 ng/g, respectively; BDE-209,-99, and -47 were the predominant congeners. Concentrations were influenced by industrial input, leachate, and temperature. Several examinations including the measurement of BDE-202 indicated minimal debromination during wastewater treatment. Estimated solids-liquid distribution coefficients were moderately correlated to hydraulic retention time, solids loading rate, mixed liquor suspended solids, solids retention time, and removal of organic solids, indicating that PBDE partitioning to solids can be optimized by WWTPs' operational conditions. Solids treatment type strongly affected PBDE levels in biosolids: 1.5 times increase after solids digestion, therefore, digestion efficiency could be a potential factor for variability of PBDEs concentration. In contrast, alkaline treatment reduced PBDE concentrations in biosolids. Overall, mass balance approaches confirmed that PBDEs were removed from the liquid stream through partitioning to solids. Variability of PBDE levels in biosolids could result in different PBDEs burdens to agricultural land, and different exposure levels to soil organisms.

1. Introduction

One of the most highly prioritized topics in environmental science is water quality. Wastewater treatment plants (WWTPs) play an important role in converting used water from households and industry into environmentally acceptable water by removing biodegradable carbon, nitrogen and phosphorous compounds, and microorganisms. Biosolids are a major by-product of wastewater treatment as a result of solids separation from influent wastewater and the generation of excess biomass during biological treatment. The term biosolids refers to the treated stabilized product of sewage sludge treatment obtained for further use, such as land application (Madan, 2009). Biosolids are also sent to a landfill

* Corresponding author. Tel.: +1 905 336 4752; fax: +1 905 336 6430.
E-mail address: Mehran.Alaee@ec.gc.ca (M. Alaee).
0043-1354/$ – see front matter
http://dx.doi.org/10.1016/j.watres.2013.08.022

or incinerated. Due to their nutrient and organic carbon content, biosolids contribute positively to recycling nutrients, soil properties and fertility (Clarke and Smith, 2011). In Canada annual production of biosolids is more than 660,000 tonnes (Bonte-Gelok, 2012) and a third of the biosolids are used for land application (UN-HABITAT, 2008). However, land-applied biosolids may be contaminated with organic compounds that were not removed during wastewater treatment (WEAO, 2010).

Polybrominated diphenyl ether (PBDE) flame retardants are organic compounds that can enter the environment through biosolids land application (Clarke and Smith, 2011). PBDEs have low water solubility and high lipophilicity (Environment Canada, 2006; USEPA, 2010a); they have been detected worldwide in humans, wildlife and environmental media (USEPA, 2010a). In addition, PBDEs are identified as bioaccumulative, persistent and toxic chemicals (Environment Canada, 2006; USEPA, 2010a). Three commercial mixtures of PBDEs were used in commerce: Penta-, Octa- and Deca-BDEs (Alaee et al., 2003), by 2004 there was significant changes in the global production and use of Penta- and Octa-BDEs through various regulatory and voluntary initiatives. In addition, by 2013 USA companies will phase out the production and use of Deca-BDEs (USEPA, 2010a).

PBDEs make their way to WWTPs through the disposal of wash water from contaminated indoor dust, leachate from landfilled PBDE-containing products, and discharge from industrial sites processing PBDE containing material (USEPA, 2010a). Therefore, PBDE levels in wastewater can vary with different geographical uses and industrial discharges. In North America, some of the highest concentrations of PBDEs were measured in sewage sludge and biosolids at concentrations exceeding the low ng/g dry weight (dw) range ($<10^3$ ng/g) (USEPA, 2009). Since sewage sludge and biosolids are complex sample matrices, few studies have focused on these matrices. However, information on the fate of PBDEs in the solid stream is needed to generate mass balances and fully understand chemical partitioning, transformation, and persistence of PBDEs during wastewater treatment. The few mass balances that have been completed in the past have shown that PBDEs are largely associated with biosolids (>96%) (Clarke et al., 2010; North, 2004). These studies indicated that partitioning to sludge was the predominant mechanism of PBDE removal in WWTPs. However, to the best of our knowledge, no studies have analyzed the effect of different WWTP operational conditions on the fate of PBDE in sludges and biosolids. Considering that biosolids are produced from raw sludge through physical, chemical and biological processes, it is necessary to investigate the potential effect of the applied treatment on PBDE levels. Moreover, to understand the sorption mechanism of PBDEs in WWTPs, the distribution of PBDEs in the solids-liquid stream need to be delineated. It is also important to determine mass loading to terrestrial environments via land application of biosolids. This information will help determine their chemical loading to streams and soils receiving treated effluents and biosolids, respectively (Heidler and Halden, 2008).

This study investigated the effects of operational conditions on PBDE concentrations in raw sludge and the effects of solids treatment on PBDE levels in biosolids. Overall 288 solid samples, consisting of 107 primary sludge (PS), 75 waste biological sludges (WBS) and 106 biosolids samples, were collected from 15 Canadian WWTPs, reflecting differences in seasons, community size, contributions from the industrial sector, and various wastewater and solids treatment types. The obtained data was integrated with information on PBDEs in the liquid stream of WWTPs (Kim et al., 2013). This study provides a comprehensive understanding of PBDE levels and fate during sewage and sludge treatment in relation to operational parameters in WWTPs using the largest number of samples reported to date.

2. Materials and methods

2.1. *Sampling*

A total of 15 WWTPs (4 chemically-assisted primary treatment, 1 gravity primary treatment, 8 secondary biological treatment, and 2 advanced biological nutrient removal treatment) participated in this study. Grab samples of PS, WBS and biosolids were collected from the underflow of the primary clarification tanks, the underflow of secondary clarification and after solids treatment/dewatering, respectively. The use of grab samples of sludge and biosolids is adequate because clarifier underflow and digester retention times at WWTPs reduce variability in sludge characteristics and produce a more homogeneous mixture. Accordingly, for short-term period sampling, a grab sample can be comparable to a composite (USEPA, 1988). However, it should also be noted that among different solids types, the composition of PS is subject to a higher degree of fluctuation since it is generated from solids in influent wastewater that is highly variable (Metcalf and Eddy, 2003). Grab samples were collected for 3 consecutive days to provide a measure of the variability in the sampling and analytical system. The sampling campaign was done twice a year (winter and summer) and moreover, four WWTPs i.e. plants B, C, R, L were sampled during two consecutive project years to study annual variation. Samples were collected using 8 L stainless steel buckets; then, collected samples were transferred to 500 mL Amber Glass jars (Systems Plus etc. Baden, ON), and kept at 4 °C while being transported to AXYS Analytical Services (Sidney, BC, Canada) on ice, by overnight courier, for analysis. Details of WWTP operational conditions such as sludge treatment, digestion type, community size and biosolids production rate are shown in Table 1.

2.2. *Sample and data analysis*

PBDEs were analyzed according to USEPA method 1614A (USEPA, 2010b). A detailed description of sample and data analysis is presented in the Supporting Information. To examine the influence of sampling and analytical system variability on PBDE levels, the three results from each sampling point at every sampling campaign were treated as triplicates. Median relative standard deviation (RSD) of the concentrations in PS was 28% (3–76%, $n = 36$) across all congeners at all WWTPs with six instances exceeding an RSD of 50%. Less variability was found in WBS concentrations, with a