Environment International 35 (2009) 303–309

Contents lists available at ScienceDirect

Environment International

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

Concentrations, transport, fate, and releases of polybrominated diphenyl ethers in sewage treatment plants in the Pearl River Delta, South China

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ARTICLE INFO

Article history:
Received 12 May 2008
Accepted 31 July 2008
Available online 5 September 2008

Keywords:
PBDEs
Wastewater
Sewage treatment plants
Pearl River Delta

ABSTRACT

Wastewater has proved to be a significant source of polybrominated diphenyl ethers (PBDEs) in the environment. Seventeen congeners from tri- to deca-BDEs were determined to characterize the occurrence, fate, and transport of PBDEs in two sewage treatment plants in the Pearl River Delta, South China. The PBDE concentrations varied substantially from 13.3 to 2496.4 ng L^{-1} in the raw wastewater, depending on the wastewater types and contents of the suspended particulate matter (SPM). The concentrations declined to 0.9 to 4.4 ng L^{-1} in the treated effluent and were closely associated with SPM contents. BDE-209 was the predominant congener in the wastewater and sewage sludge. Most of PBDEs might have ended up in the sewage sludge, with <4.7% being discharged with the treated effluent. The results revealed that PBDEs were not significantly degraded by biological treatment and chlorination in the STPs. An annual release of PBDEs was estimated at 2280 kg/year through wastewater from the Pearl River Delta.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of flame retardants that are added to thousands of consumer products, such as thermoplastics, electronic equipment, and textiles (Hale et al., 2001). The global demand for PBDEs was estimated at 70,000 tonnes in 2001, of which penta-, octa-, and deca-formulation represented approximately 24%, 4%, and 72%, respectively (Hale et al., 2003; North, 2004). The Asian shares of the global market for penta-, octa-, and deca-BDE products are 0%, 52%, and 42%, respectively (Wang et al., 2007a). PBDEs are now ubiquitous in the environment and previous research has revealed that municipal sewage could be a significant source of PBDEs contamination that is ubiquitous throughout the environment. Concentrations of PBDEs were detected at 265 to 51,232 ng L^{-1} and 26 to 39 ng L^{-1} in the raw wastewater and the treated effluent from sewage treatment plants (STPs) in North America, which meant that generally less than 10% of PBDEs input in municipal sewage may be discharged into receiving waters with treated wastewater. However, the mass loading to natural waters could be quite significant given the high volumes of municipal sewage (North, 2004; Rayne and Ikonomou, 2005a,b; Song et al., 2006). PBDEs were found to be closely associated with particles due to their strong hydrophobicity and therefore the predominant portion (i.e. >90%) was observed to end up in sewage sludge during treatment in STPs (De Boer et al., 2003; North, 2004). Concentrations of PBDEs in STP sludge ranged from several nanograms to several micrograms per gram dry weight worldwide (Eljarrat et al., 2008; Gevao et al., 2008; Hagenmaier et al., 1992; Hale et al., 2001, 2003, 2008; Harrison et al., 2006; Knoth et al., 2007; North, 2004; Rayne and Ikonomou, 2005a; Song et al., 2006; Wang et al., 2007c). PBDEs absorbed in sludge may find path into the environment through landfills, use as soil amendments, and emission to the atmosphere during incineration (Eljarrat et al., 2008; North, 2004; Rayne and Ikonomou, 2005b).

China is the most important production base of deca-BDE in Asia. The domestic production of commercial deca-BDE mixture in China has increased by 200% from 10,000 to about 30,000 tonnes between 2000 and 2005 due to the rapid growth of manufacturing activities, e.g., electronic products and automobiles (Chen et al., 2007). Concentrations of PBDEs were reported at 0.84 ng L^{-1} in the treated effluent from an STP in Beijing (Wang et al., 2007b) and 5.1 to 1114.9 ng g^{-1} in sewage sludge from several provinces in China (Wang et al., 2007c). However, the occurrence of PBDEs in municipal wastewater in China, their fate and transport during treatment in STPs, and subsequently potential releases into the environment are not yet fully understood.

The Pearl River Delta (PRD) is one of the largest manufacturing bases of electronic products and also one of the largest dumping sites of e-wastes in China. Previous reports have demonstrated significant PBDE pollution in air, sediment, water, biota, and soil in the PRD (Chen et al., 2006; Mai et al., 2005; Guan et al., 2007; Guo et al., 2007; Wu et al., in

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doi:10.1016/j.envint.2008.07.021

press; Zou et al., 2007). In this study, a detailed investigation of tri- to deca-BDEs was conducted in two STPs from the PRD to (1) characterize the occurrence of PBDEs in municipal sewage in China and their fate and transport during typical wastewater treatment, and (2) estimate the potential discharges of PBDEs through wastewater from the PRD into the Pearl River. The chosen two STPs represent typical wastewater treatment techniques that are currently used in China.

2. Materials and methods

2.1. Sewage treatment plants studied

The two STPs are located in Guangzhou, the biggest city in the PRD. The GZSTP-A has a designed capability of 30,000 $m^3\ d^{-1}$ and serves a population of about 0.45 million. It consists of primary settlement followed by activated sludge treatment and a secondary clarifier and treats a mixture (~6:4) of domestic and industrial wastewater mainly from chemical, food, automobile, and electronic manufacturers. The GZSTP-B has three parallel treatment systems and serves a population of 2.5 million. The systems 1 and 2 use an identical treatment process that consists of a sequence of anaerobic, anoxic, and aerobic tanks (A_2O) and handle the same type of wastewater from household (>90%) and business, with a total capacity of 330,000 $m^3\ d^{-1}$. Therefore, only the system 1 (GZSTP-B1) was sampled in this work. The system 3 (GZSTP-B3) uses inverted A_2O technique, i.e., anoxic → anaerobic → aerobic treatment, and processes industrial wastewater mainly from plastic/rubber, leather, electronic/electric, and pharmaceutical industries with a capacity of 220,000 $m^3\ d^{-1}$. About 200 $m^3\ d^{-1}$ of leachate from municipal landfills in the north of Guangzhou city is also introduced into the GZSTP-B3. All treatment systems in GZSTP-B employ a secondary clarifier followed by chlorine disinfection before release into the Pearl River. Industrial wastewaters are pretreated prior to being discharged into the STPs for further treatment. A flow chart of the two STPs with the location of the sampling points and sample types is shown in Fig. 1.

2.2. Sampling

Sampling campaigns were conducted once in the GZSTP-A in March 2007 and twice in the GZSTP-B in September 2006 and March 2007, respectively. Wastewater and returning sludge were sampled hourly from 14:00 to 17:00 and were combined to build a composite sample respectively. Pretreatment solids, thickened and dewatered sludge were collected as grab samples. Samples were collected in pre-cleaned amber glass bottles (for wastewater) and jars (for sludge) without headspace and kept on ice during transit to the laboratory. Sodium azide was added to each sample (0.5 g L^{-1}) immediately after collection to suppress potential bacteria activities. Upon arriving at the laboratory, pretreatment solids and dewatered sludges were wrapped with pre-baked (450 °C) aluminum foil, sealed in Ziplock bags, and stored at −18 °C until further treatment. The effluent from anaerobic and aerobic tanks, returning, and thickened sludge samples were centrifuged (3000 rpm, 4 °C, 5 min) immediately to separate solid from liquid phase. The solid fractions were then wrapped and stored as described above. All liquid samples were stored at 4 °C in the dark until extraction within a week.

2.3. Extraction and analysis

The extraction of wastewater and sludge samples followed the procedures described in detail previously (Mai et al., 2005). Briefly, a water sample (20 L) was filtered through 0.7 μm glass fiber filters (Whatman, Maidstone, England), spiked with ^{13}C PCB 141, and passed through a glass column packed with XAD-2:XAD-4 resin (1:1 in volume) at a flow rate of ~10 mL min^{-1}. The resin was eluted three times with methanol, followed by three ultrasonic extractions with a mixture of dichloromethane (DCM) and methanol (1:1 in volume). The extracts were combined and then liquid–liquid extracted using DCM. The DCM extract was concentrated, solvent-exchanged to hexane, and cleaned up on a complex acidic–basic–neutral silica/alumina column. The PBDEs were eluted with a mixture of hexane and DCM (1:1). The eluent was finally reduced to 200 μL under a gentle nitrogen stream. The suspended particulate matter (SPM) collected on glass fiber filters and sludge samples were freeze-dried. The SPM and homogenized sludge samples were accurately weighed before being spiked with ^{13}C PCB 141 and Soxhlet-extracted with a mixture of acetone and hexane (1:1). Activated copper flakes were used to remove elemental sulfur. The extracts were concentrated and cleaned up as described above. A known amount of ^{13}C-PCB 208 was added as internal standard prior to instrumental analysis.

Seventeen congeners from tri- to deca-BDEs (including BDEs-28, -47, -66, -85, -99, -100, -153, -154, -183, -196, -197, -203, -205, -206, -207, -208, and -209) were analyzed on a Shimadzu Model 2010 GC-MS equipped with an AOC-20i auto injector (Shimadzu, Japan) using negative chemical ionization (NCI) in the selected ion monitoring (SIM) mode. A DB-XLB (30 m×0.25 mm i.d., 0.25 μm film thickness) and a CP-Sil 13 CB (12.5 m×0.25 mm i.d., 0.2 μm film thickness) capillary columns were used to determine tri- to hepta-PBDEs (BDEs-28 to -183) and octa- to deca-BDEs (BDEs-196 to -209), respectively. Instrumental condition and analyte identification were detailed elsewhere (Mai et al., 2005). Ion fragments *m/z* 79 and 81 were monitored for tri- to hepta-BDEs,

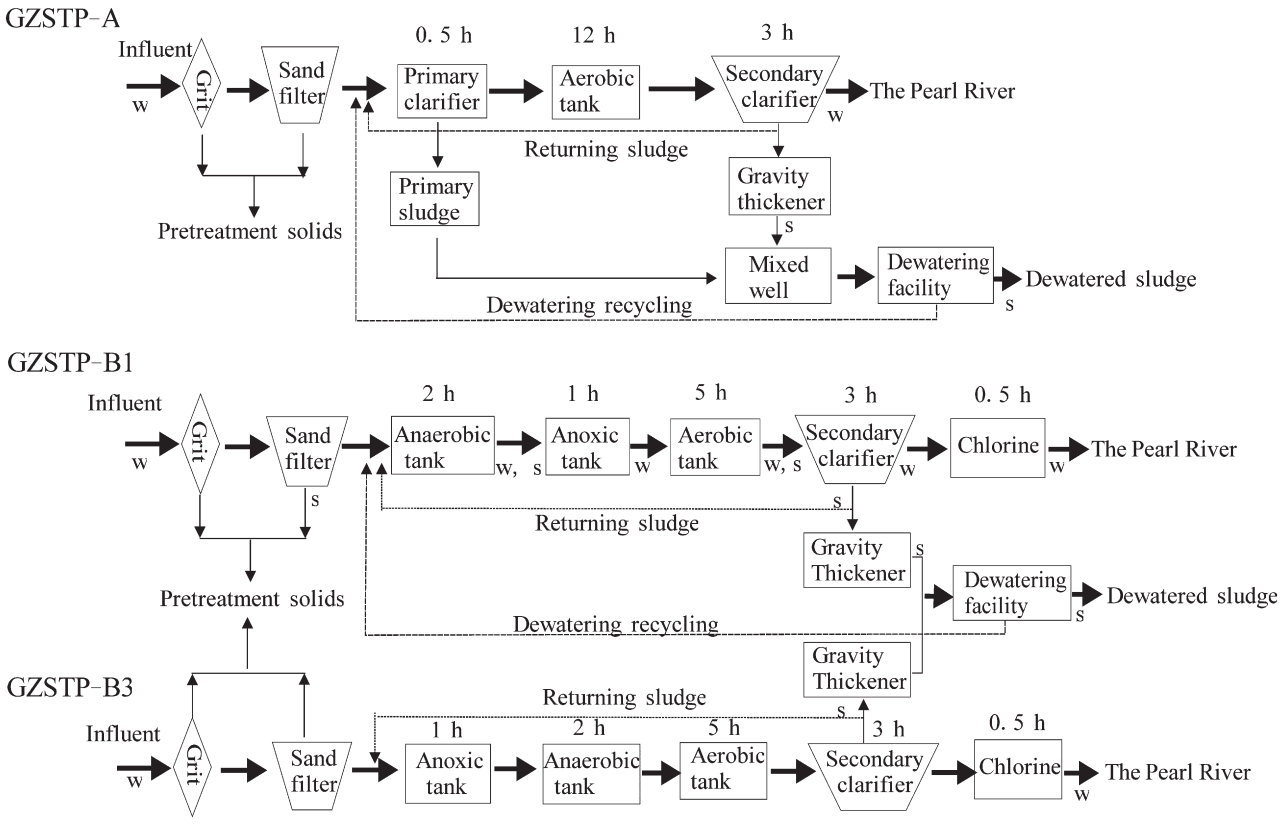

Fig. 1. Process flows, sampling sites, and sample types in the two sewage treatment plants in the Pearl River Delta, South China. w = Water sample, s = solid/sludge sample. Figures above the treatment tanks denote hydraulic retention times.