# Measurement of flame retardants and triclosan in municipal sewage sludge and biosolids

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## ABSTRACT

As polybrominated diphenyl ethers (PBDEs) face increasing restrictions worldwide, several alternate flame retardants are expected to see increased use as replacement compounds in consumer products. Chemical analysis of biosolids collected from wastewater treatment plants (WWTPs) can help determine whether these flame retardants are migrating from the indoor environment to the outdoor environment, where little is known about their ultimate fate and effects. The objective of this study was to measure concentrations of a suite of flame retardants, and the antimicrobial compound triclosan, in opportunistic samples of municipal biosolids and the domestic sludge Standard Reference Material (SRM) 2781. Grab samples of biosolids were collected from two WWTPs in North Carolina and two in California. Biosolids samples were also obtained during three subsequent collection events at one of the North Carolina WWTPs to evaluate fluctuations in contaminant levels within a given facility over a period of three years. The biosolids and SRM 2781 were analyzed for PBDEs, hexabromobenzene (HBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), di(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH), the chlorinated flame retardant Dechlorane Plus (syn- and anti-isomers), and the antimicrobial agent 5-chloro-2-(2,4-dichlorophenoxy)phenol (triclosan). PBDEs were detected in every sample analyzed, and ΣPBDE concentrations ranged from 1750 to 6358 ng/g dry weight. Additionally, the PBDE replacement chemicals TBB and TBPH were detected at concentrations ranging from 120 to 3749 ng/g dry weight and from 206 to 1631 ng/g dry weight, respectively. Triclosan concentrations ranged from 490 to 13,866 ng/g dry weight. The detection of these contaminants of emerging concern in biosolids suggests that these chemicals have the potential to migrate out of consumer products and enter the outdoor environment.

## 1. Introduction

For over a decade, a great deal of attention has been focused on polybrominated diphenyl ethers (PBDEs; Fig. 1), a group of additive brominated flame retardants (BFRs) that have historically been widely used to decrease the flammability of a variety of consumer products. However, the persistence, bioaccumulation potential, and toxicity of PBDEs have resulted in several restrictions on their use in recent years. Two of the three commercial mixtures, PentaBDE and OctaBDE, were banned in Europe and voluntarily phased out in the United States in 2004 (Tullo, 2003). Additionally, components of both commercial mixtures (i.e., tetra–heptabromodiphenyl ethers) are now listed as persistent organic pollutants under the Stockholm Convention on Persistent Organic Pollutants (2009). The third commercial mixture, DecaBDE, will undergo a voluntary phase out by manufacturers in the United States by 2013 (EPA, 2009a).

PBDEs continue to be detected worldwide in humans, wildlife, and environmental media (Chen and Hale, 2010; de Wit, 2002; de Wit et al., 2006; Hale et al., 2003; Hites, 2004; Law et al., 2006). Some of the highest concentrations of PBDEs in North America have been measured in sewage sludge and biosolids, and these concentrations commonly exceed 1 mg/kg dry weight (dw) (EPA, 2009b; Hale et al., 2001; Hale et al., 2006; La Guardia et al., 2007; North, 2004). The presence of high levels of PBDEs in municipal wastewater influent is likely due in large part to contaminated residential wastewater from homes that contain PBDE-treated products. PBDEs in the wastewater stream sorb to wastewater solids (Song et al., 2006), thereby resulting in high concentrations in sewage sludge and also in biosolids, which are defined by the US Environmental Protection Agency (EPA) as "the nutrient-rich organic materials resulting from the treatment of sewage sludge" (EPA, 2011). This is of particular concern because the disposal of these treated biosolids on agricultural and other soils as a nutrient-rich amendment is a growing trend (EPA, 1999). An estimated 4 million dry tons of biosolids were land-applied to soils in the United States in the year 2004 alone (NEBRA, 2007). Little is known about the ultimate environmental fate and

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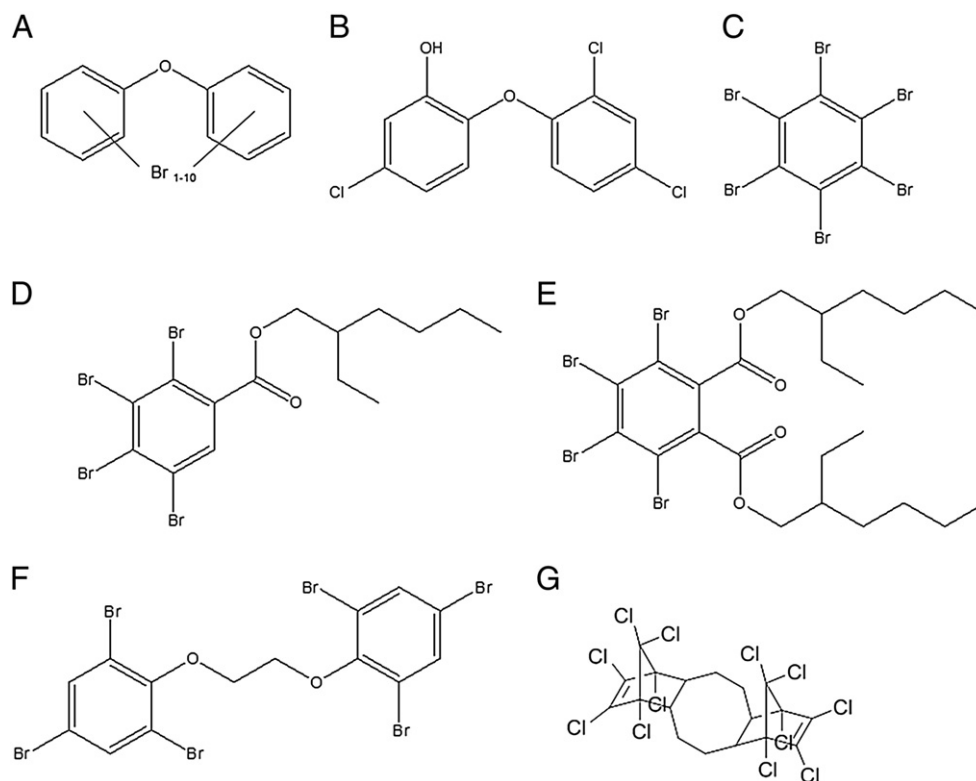E-mail address: heather.stapleton@duke.edu (H.M. Stapleton).

**Fig. 1.** Structures of (A) PBDEs, (B) triclosan, (C) HBB, (D) TBB, (E) TBPH, (F) BTBPE, and (G) DP.

effects of flame retardants in these land-applied biosolids, but possible environmental impacts could include uptake by agricultural crops, introduction into terrestrial food webs, runoff into waterways, and enhanced long-range transport potential.

As the use of PBDEs becomes increasingly restricted worldwide, the use of alternate and new flame retardants is expected to increase due to efforts to comply with fire safety standards. Among these potential replacements are hexabromobenzene (HBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), 2-ethylhexyl 2,3,4,5-tetrabromo-benzoate (TBB), and di(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH) (Fig. 1). HBB has historically been used as an additive flame retardant in materials such as paper and plastics. Information on the production volumes of HBB is limited. Its production/import volume was between 10,000 and 500,000 lbs in EPA Inventory Update Reporting year 1998, with no available information for other reporting years (EPA, 2006). BTBPE, another additive BFR, is a high production volume chemical (EPA, 2006) and is sold by Chemtura Corporation under the name Firemaster® 680 (FM 680). FM 680 has been in production for over 25 years but recently has been marketed as an OctaBDE replacement product (Chemtura, 2004; Chemtura, 2007b). Both BTBPE and HBB were recently detected in sewage sludge from Toronto, Canada (Kolic et al., 2009), and BTBPE was recently detected in sewage sludge from a mid-Atlantic WWTP (La Guardia et al., 2010).

The commercial mixture Firemaster® 550 (FM 550) contains the brominated components TBB and TBPH. Approximately 50% of FM 550 is a mixture of isopropylated triaryl phosphates and triphenyl phosphate. The remainder of the mixture is composed of Firemaster® BZ-54, which contains TBB and TBPH (Bearr et al., 2010; Stapleton et al., 2008). TBPH is also present in the commercial mixture DP-45, which is used as a flame retardant plasticizer for polyvinylchloride (PVC) applications (Chemtura, 2007a). FM 550 is marketed as a replacement for PentaBDE and is used primarily in polyurethane foam in products such as furniture and baby products (Stapleton et al., 2009, 2011). All three commercial products are manufactured by Chemtura. TBB and TBPH have recently been detected in indoor dust and sewage sludge

as well as in marine mammals from Hong Kong, South China (La Guardia et al., 2010; Lam et al., 2009; Stapleton et al., 2008). Little is known about the environmental fate of TBB and TBPH, although their potential for bioaccumulation and toxic effects and their photodegradation potential have recently been reported (Bearr et al., 2010; Davis and Stapleton, 2009). Notably, TBPH is a tetrabrominated analog of di(2-ethylhexyl)-phthalate (DEHP), a common plasticizer that is now restricted in children's toys because of its endocrine disrupting properties (CPSC, 2008; Swan, 2008).

In addition to BFRs, some current-use chlorinated flame retardants have been detected in sewage sludge. Dechlorane Plus (DP; Fig. 1) is a chlorinated flame retardant that is composed of the two stereoisomers syn- and anti-DP. DP, a replacement for the banned pesticide Mirex, is now used as an additive flame retardant in a variety of electrical applications such as wire cable coatings (Sverko et al., 2007). Both syn- and anti-DP have recently been detected in sewage sludge in North America and Europe (de la Torre et al., 2011; Kolic et al., 2009; La Guardia et al., 2010). Additionally, the chlorinated antimicrobial agent 5-chloro-2-(2,4-dichlorophenoxy)phenol (triclosan), while not a flame retardant, bears structural similarities to PBDEs and other flame retardants (Fig. 1) and is widely used in personal care products. One study reported an average triclosan concentration of $30,000 \pm 11,000$ ng/g dw in biosolids from the mid-Atlantic United States (Heidler and Halden, 2007). These high concentrations, together with its potential for toxicity to aquatic biota and bioaccumulation potential in earthworms and other species (Kinney et al., 2008; Veldhoen et al., 2006), make triclosan a contaminant of concern in biosolids.

The objective of this study was to measure the concentrations of PBDEs, HBB, BTBPE, TBB, TBPH, syn- and anti-DP, and triclosan in biosolids from two WWTPs in North Carolina, two WWTPs in California, and a Standard Reference Material (SRM) domestic sludge sample. The SRM was included in this study because biosolids matrices can present significant analytical challenges, and concentrations of flame retardant chemicals in control materials such as SRMs can be

useful for future method development efforts. We also examined, to a limited extent, some temporal trends in four biosolids samples obtained from a single North Carolina WWTP between the years 2006 and 2010.

## 2. Materials and methods

### 2.1. Materials

HPLC-grade dichloromethane (DCM) was purchased from Honeywell Burdick & Jackson (Muskegon, MI, USA). Ultra resi-analyzed hexane and concentrated sulfuric acid were purchased from J.T. Baker (Phillipsburg, NJ, USA). GR ACS grade methanol was purchased from EMD Chemicals (Gibbstown, NJ, USA). The internal and surrogate standards 2,2′,3,4,5,5′-hexachloro[$^{13}C_{12}$]diphenyl ether ($^{13}$C CDE-141), decabromo[$^{13}C_{12}$]diphenyl ether ($^{13}$C BDE 209), 5-chloro-2-(2,4-dichloro[$^{13}C_6$]phenoxy) [$^{13}C_6$]phenol ($^{13}$C triclosan), and 2,2′,4,4′-tetrabrominated 6-hydroxy[$^{13}C_{12}$]diphenyl ether ($^{13}$C 6-OH BDE 47) were purchased from Wellington Laboratories (Guelph, Ontario, Canada). 4′-Fluoro-2,3′,4,6-tetrabromodiphenyl ether (F-BDE 69) was purchased from Chiron (Trondheim, Norway). Quantification standards for TBB, TBPH, BTBPE, HBB, syn- and anti-DP, and triclosan were purchased from Wellington Laboratories (Guelph, Ontario, Canada).

### 2.2. Biosolids sample collection

Digested and dewatered cake sewage sludge (i.e., biosolids) were collected in the fall of 2006 from one advanced secondary wastewater treatment facility in Durham, North Carolina and one tertiary waste-water treatment facility in Cary, North Carolina, referred to here as NC WWTP #1 and NC WWTP #2, respectively. Biosolids were also collected in February 2008 from an advanced secondary WWTP in California (CA WWTP #1) and another large secondary WWTP in California (CA WWTP #2). At NC WWTPs #1 and #2, the annual aver-age flow rates are approximately 34,000 and 19,000 cubic meters per day ($m^3$/d), respectively. CA WWTPs #1 and #2 have annual average flow rates of approximately 83,000 and 260,000 $m^3$/d, respectively. Concentrations of PBDEs in the effluent and sludge of CA WWTP #1 have previously been reported (North, 2004). To examine temporal differences in contaminant levels, additional biosolids were collected from NC WWTP #1 in June 2009, December 2009, and February 2010. All samples were stored at −20 °C in baked amber glass jars until analysis (with the exception of the CA WWTP #2 biosolids, which were stored in baked clear glass jars). The 2006 samples from NC WWTPs 1 and 2 were freeze-dried prior to storage. Moisture content was determined gravimetrically by drying triplicate subsamples of each matrix at 100 °C for 24 h. SRM 2781, a domestic sludge material produced by the National Institute of Standards and Technology (Gaithersburg, MD, USA), was analyzed alongside the biosolids. SRM 2781 was generated from partially dehydrated sewage sludge that was collected in Denver, CO in 1991. The SRM was stored at room temperature in the laboratory.

### 2.3. Extraction and analysis of PBDEs, HBB, BTBPE, TBB, TBPH, and DP

Triplicate 0.5 g subsamples of each biosolids material were ho-mogenized with sodium sulfate and were loaded into stainless steel extraction cells with 2 glass fiber filters on each end, spiked with two internal standards (F-BDE 69 and $^{13}$C BDE 209) and extracted via pressurized fluid extraction (ASE 300, Dionex Inc.). Samples were extracted 3 times with 50:50 DCM:hexane at a temperature of 100 °C and a pressure of 1500 psi. Extracts were then concentrated to a volume of 1 mL using a rapid evaporation system with ultra-high purity nitrogen gas, syringe-filtered to remove particulates (0.45 μm PTFE, VWR International), and then cleaned by elution

through a GPC column (Envirogel™ GPC Cleanup 90 × 300 mm) at a flow rate of 5 mL/min using DCM as the mobile phase. The first 60 mL of each sample were discarded and the following 40 mL were collected. The eluate was then reconcentrated to 1 mL and further cleaned via treatment with 1 mL of concentrated sulfuric acid, and the mixture was briefly vortexed. The mixture was extracted in triplicate with 3 mL aliquots of hexane. The organic fractions were collected and reconcentrated to a volume of 0.5 mL. The samples were then spiked with the recovery standard, $^{13}$C CDE 141, immedi-ately prior to instrumental analysis.

Samples were analyzed for a suite of PBDEs as well as BTBPE, TBB, TBPH, and syn- and anti-DP via gas chromatography/mass spectrom-etry operated in negative ionization mode (GC/ECNI–MS; Agilent 6890N/5975) using previously published methods (Stapleton et al., 2008). Syn- and anti-DP were quantified using $m/z$ 654 and 652 as the quantitative and qualitative ions, respectively. Sample extracts were analyzed for HBB via gas chromatography/electron impact mass spectrometry (GC/EI–MS) using $m/z$ 552 and 471 as the quanti-tative and qualitative ions, respectively. In addition, because the pentaBDE congener BDE 99 (2,2′,4,4′,5-pentabromodiphenyl ether) coelutes with TBB in GC/ECNI–MS mode, sample extracts were also analyzed for BDE 99 via GC/EI–MS. BDE 99 was quantified by moni-toring $m/z$ 562 (quantitative) and 486 (qualitative) ([M−H]$^+$ and [M−Br]$^+$, respectively).

### 2.4. Extraction and analysis of triclosan

Triplicate 1.0 g subsamples of each biosolids material (with the exception of the November 2006 NC WWTP #1 biosolids, in which case n = 2 and the mass extracted for each replicate was 0.4 g due to limited material) were homogenized with sodium sulfate, spiked with the internal standard $^{13}$C triclosan, and extracted via pressurized fluid extraction as described above, again using 50:50 DCM:hexane as the extraction solvent. Extracts were concentrated to a volume of 1 mL and purified via treatment with 1 mL of concentrated sulfuric acid, and the mixture was briefly vortexed. The mixture was extracted in triplicate with 5 mL aliquots of 50:50 DCM:hexane. The organic fractions were collected and then reconcentrated to a volume of 1 mL. The samples were then loaded onto Sep-Pak Plus Silica solid phase extraction (SPE) cartridges (55–105 μm particle size, Waters Corporation, Milford, MA, USA) that had been preconditioned with 10 mL of 50:50 DCM:hexane. A further 10 mL of 50:50 DCM:hexane was used to elute the sample. The extracts were then reconcentrated to a volume of 0.5 mL and solvent-switched to methanol under a gentle $N_2$ stream, syringe-filtered to remove particulates (0.20 μm nylon, VWR International), and spiked with the recovery standard, $^{13}$C 6-OH BDE 47, immediately prior to instrumental analysis.

Samples were analyzed for triclosan via liquid chromatography/ electrospray ionization tandem mass spectrometry (LC/ESI–MS–MS) using an Agilent 1200 series binary pump SL and autosampler and an Agilent 6140 triple quadrupole tandem mass spectrometer. An Agilent Eclipse XDB-C18 column (4.6 × 50 mm, 1.8 μm particle size) was used to separate the analytes. The isocratic mobile phase consisted of 5% deionized water and 95% methanol at a flow rate of 0.4 mL/min. The column temperature was controlled at 30 °C, the injection volume was 5 μL, and the run time was 5 min. The MS/MS parameters included a gas temperature of 350 °C, a gas flow rate of 10 mL/min, a nebulizer pressure of 40 psi, and a capillary voltage of 4000 V. The fragmentor energy was 80 V for $^{13}$C triclosan, triclosan, and $^{13}$C 6-OH BDE 47. The collision energies for $^{13}$C triclosan, triclosan, and $^{13}$C 6-OH BDE 47 were 10 V, 10 V, and 20 V, respectively. The LC/MS–MS was operated in negative electrospray ionization mode. Data was acquired using multiple reaction monitoring (MRM). The MRM transitions used to quantify $^{13}$C triclosan, triclosan, and $^{13}$C 6-OH BDE 47 were 301 35.1, 289 35.1, and 512.7 78.9, respectively.

## 2.5. Quality assurance

All biosolids samples were extracted in triplicate unless otherwise noted. In addition, for each extraction procedure, analyte levels were measured in laboratory blanks consisting only of sodium sulfate (n = 3) and also in SRM 2781 (National Institute of Standards and Technology, Gaithersburg, MD, USA; n = 3). In the PBDE and alternate BFR extraction procedure, recoveries of the F-BDE 69 and $^{13}$C BDE 209 internal standards were 79 ± 12% and 73 ± 31%, respectively. Recovery of the $^{13}$C triclosan internal standard from the triclosan extraction procedure was 53 ± 17%. All analyte values were corrected for recovery. In addition, a matrix spike experiment was performed to evaluate the recovery of selected analytes (specifically, TBB, TBPH, and triclosan), the properties of which may not be accurately represented by currently available labeled standards. Triplicate 0.1 g samples of SRM 2781 were spiked and were then extracted, treated, and analyzed as described in the methods above. Percent recoveries of TBB, TBPH, and triclosan in the matrix spike samples were 63 ± 4%, 63 ± 2%, and 97 ± 9%, respectively.

When a given analyte was present in the laboratory blanks, the method detection limit (MDL, ng/g dw) was calculated as three times the standard deviation of the amount of the analyte in the blank, normalized to the average dry weight mass extracted for a given biosolids sample matrix. Sample values were blank corrected using the average amount of a given analyte in the laboratory blanks. When a given analyte was not present in the laboratory blanks, the MDL was calculated by dividing the instrument detection limit (IDL, ng; three times the noise of the baseline where the peak elutes) by the average dry weight mass extracted for that biosolids matrix.

## 2.6. Data analysis

GC/ECNI–MS data acquisition and analysis was performed using Agilent MSD Chemstation software, and LC/MS–MS data acquisition and analysis was performed using Agilent MassHunter software. A Student's $t$-test (Microsoft Excel 2007) was used to evaluate differences between contaminant concentrations in biosolids collected in North Carolina compared to California. Temporal variations within NC WWTP #1 were evaluated with analysis of variance (ANOVA) using the software JMP 9.0.0. Statistical significance was defined at α = 0.05.

## 3. Results and discussion

Table 1 presents the concentrations of the flame retardants and triclosan measured in the biosolids and SRM 2781. Results are given in terms of average concentrations ± one standard deviation from triplicate analyses in ng/g dry weight (dw) unless otherwise noted.

### 3.1. PBDEs

Of the 40 PBDE congeners for which authentic standards were available (BDEs 17, 25, 30, 28/33 (co-eluting), 47, 49, 66, 71, 75, 99, 100, 116, 119, 88/155 (co-eluting), 138, 153, 154, 156, 171, 176, 179, 181, 183, 184, 188, 190, 191, 196, 197, 201, 202, 203/200 (co-eluting), 205, 206, 207, 208, and 209), the following 13 BDE congeners were detected in at least 50% of the biosolids samples analyzed: 28/33, 47, 66, 99, 100, 85/155, 153, 154, 183, 206, 207, 208, and 209. These congeners comprised greater than 99% of the ΣPBDE concentration in every sample. BDEs 28/33, 47, 66, 99, 100, 85/155, 153, and 154, which are components of the PentaBDE mixture, contributed 40–73% of the ΣPBDE concentrations in the biosolids. The DecaBDE technical mixture typically consists of >97% BDE 209 but also contains minor contributions from the three nonaBDEs 206, 207, and 208 (La Guardia et al., 2006). These four congeners contributed 27–59% of the ΣPBDE concentrations in the biosolids. Therefore, nearly the entire PBDE burden measured in biosolids in this study was due to congeners associated with the PentaBDE and DecaBDE commercial mixtures. The ΣPBDE concentrations in the biosolids ranged from 1750 to 6358 ng/g dw and are comparable to literature values for North American biosolids and sewage sludges, which have commonly reported ΣPBDE concentrations in excess of 1 mg/kg dw (EPA, 2009b; Hale et al., 2001, 2006; La Guardia et al., 2007; North, 2004). In addition, the average ΣPBDE concentration in CA WWTP #1 was 2140 ± 83 ng/g dw, which is lower than the average

ΣPBDE concentration of 3381 ± 335 ng/g dw that was reported for treated sewage sludge collected four years earlier from this same facility (North, 2004).

### 3.2. TBB and TBPH

Both TBB and TBPH were detected in biosolids samples. TBPH was detected in every sample except SRM 2781 at concentrations ranging from 206 to 1631 ng/g dw. TBB was detected in the biosolids collected from NC WWTP #1 in November 2006 and CA WWTP #2 at average concentrations of 128 ± 11 and 2941 ± 776 ng/g dw, respectively, but was not detected in the other biosolids samples. The range of TBB concentrations was 120 to 3749 ng/g dw. In the North Carolina WWTPs, TBPH concentrations were an order of magnitude lower than ΣPBDE concentrations. However, in CA WWTP #2, TBPH concentrations were comparable to ΣPBDE levels. In particular, TBPH levels in CA WWTP #2 very closely resembled the summed concentrations of all PBDE congeners associated with the PentaBDE commercial mixture (i.e., the sum of all tetra–hexabrominated congeners detected). The TBPH and PentaBDE concentrations in CA WWTP #2 were 1340 ± 275 and 1373 ± 376 ng/g dw, respectively. In the November 2006 NC WWTP #1 biosolids, the TBB concentration was an order of magnitude lower than the ΣPBDE concentration. However, in CA WWTP #2, the only other biosolids matrix in which TBB was detected, the TBB concentration was higher than the ΣPBDE concentration (2941 ± 776 versus 2036 ± 306 ng/g dw, respectively), although the difference was not significant.

At least three commercial formulations are known to contain TBB, TBPH, or a mixture of the two compounds. TBPH is a high production volume chemical and has been in use for over 20 years, and annual production and/or import volumes of TBPH in the United States were between 1 and 10 million lbs in EPA Inventory Update Reporting years 1990, 1994, 1998, 2002, and 2006 (EPA, 2006). TBPH is the sole component of DP-45, which is used as a flame retardant plasticizer for PVC applications (Chemtura, 2007a). In addition, both TBB and TBPH are found in FM 550, an additive flame retardant that also contains triaryl phosphate isomers and triphenyl phosphate. Other formulations may contain TBB and/or TBPH, but to date FM 550, BZ-54, and DP-45 are the only reported commercial mixtures that contain these compounds. TBB and TBPH have been measured in North American house dust at concentrations comparable to those of hexabromocyclododecane (HBCD), another widely used brominated flame retardant (Stapleton et al., 2008). As with other flame retardants, a likely source of TBB and TBPH to the wastewater treatment stream is the leaching of these chemicals from consumer products treated with commercial flame retardant mixtures.

In the commercial FM 550 mixture, the TBB/TBPH ratio is approximately 2.5:1 (Bearr et al., 2010). When the TBB/TBPH ratio in environmental samples differs from the commercial mixture ratio, it implies contributions from sources other than FM 550 and/or potentially different fate and transformation behaviors. Due to the low detection frequency of TBB in this study, the calculation of this ratio was possible only for the November 2006 NC WWTP #1 samples and the CA WWTP #2 samples. The average TBB:TBPH ratios for these samples were 0.35 and 2.18, respectively. The TBB:TBPH ratio in biosolids collected in 2008 from CA WWTP #2 closely resembles that of the FM 550 commercial mixture, which was promoted as a replacement for PentaBDE when PentaBDE was phased out in 2004 (Chemtura, 2004). It is possible that FM 550 is being used as a replacement for PentaBDE in polyurethane foam to meet the California TB117 flammability standard (California, 2000b), which may explain why the TBB:TBPH ratio in the California biosolids more closely reflects the ratio of the commercial mixture. In contrast, the TBB:TBPH ratio in biosolids collected from NC WWTP #1 in 2006 was considerably lower and suggests that at the time of sampling in 2006, TBPH contributions to the NC WWTP #1 wastewater treatment stream may have come from commercial mixtures other than FM 550. The other known possible alternative source of TBPH is the flame retardant plasticizer DP-45. As discussed above, TBPH is a high production volume chemical that has been in use for over two decades. Therefore, past use of TBPH in DP-45 or other unknown commercial products could have contributed to the TBPH levels in the biosolids. Alternatively, this finding could suggest differential migration or degradation of TBB relative to TBPH out of consumer products and during the wastewater treatment process.

### 3.3. HBB, BTBPE, and DP

BTBPE was detected in the November 2006 biosolids from both NC WWTP #1 and #2, both of the CA WWTPs, and SRM 2781. All BTBPE values reported in this study were found to be 2–3 orders of magnitude lower than ΣPBDE values and are comparable to the levels reported in Toronto sewage sludge by Kolic et al. (2009). In contrast to BTBPE, HBB was not detected in any of the biosolids analyzed in this study or in SRM 2781.

Both DP isomers were detected in all biosolids samples analyzed as well as in SRM 2781. Concentrations of syn-DP ranged from 2 to 24 ng/g dw with an average concentration of 10 ng/g dw, while anti-DP concentrations ranged from 5 to 29 ng/g dw with an average concentration of 15 ng/g dw. DP has been in use for decades but was first reported in environmental samples in 2006 (Betts et al., 2006; Hoh et al., 2006). Hoh et al. (2006) measured total DP in sediment cores from Lake Erie and Lake Michigan and found concentrations at or below 10 ng/g dw. Since 2006, DP has been measured in a variety of abiotic and biotic matrices in North America including sediment (Qiu et al., 2007; Shen et al., 2011; Sverko et al., 2008; Tomy et al., 2007), tree bark (Qiu and Hites, 2008; Salamova and Hites, 2010), air samples (Venier and Hites, 2008), indoor dust (Zhu et al., 2007), aquatic food webs (Tomy et al., 2007), herring gull eggs

**Table 1**

Mean concentrations and standard deviations (n = 3, with the exception of *, where n = 2) of chlorinated and brominated flame retardants and triclosan in biosolids samples and SRM 2781 (ng/g dry weight).

| Name | SRM 2781 | NC WWTP #1, 11/2006 | NC WWTP #1, 6/2009 | NC WWTP #1, 12/2009 | NC WWTP #1, 2/2010 | NC WWTP #2, 12/2006 | CA WWTP #1, 2/2008 | CA WWTP #2, 2/2008 |
|---|---|---|---|---|---|---|---|---|
| % Moisture | 0.00% | 7.64% | 81.68% | 81.59% | 84.60% | 6.78% | 75.98% | 73.56% |
| BDE 30 | <0.5 | <1 | <2 | <2 | <3 | <0.5 | <2 | <2 |
| BDE 17 | 8 ± 1 | 13 ± 1 | <2 | <2 | 9 ± 6 | <0.5 | <2 | <2 |
| BDE 25 | <0.5 | 4 ± 1 | <1 | <1 | <1 | <0.5 | <1 | <1 |
| BDE 28,33[a] | 24 ± 5 | 41 ± 1 | 73 ± 8 | <8 | <9 | 8 ± 0.5 | 16 ± 9 | <5 |
| BDE 75 | <0.5 | <1 | <3 | <4 | <3 | <1 | <2 | <2 |
| BDE 49 | <1 | <2 | <5 | <5 | <5 | <1 | <4 | <3 |
| BDE 71 | <2 | <3 | <9 | <9 | <10 | <2 | <7 | <6 |
| BDE 47 | 586 ± 85 | 1046 ± 26 | 1133 ± 165 | 711 ± 73 | 770 ± 18 | 613 ± 10 | 730 ± 72 | 685 ± 141 |
| BDE 66 | 17 ± 3 | 23 ± 2 | <1 | <2 | <2 | 18 ± 2 | <1 | 20 ± 7 |
| BDE 100 | 147 ± 20 | 283 ± 2 | 311 ± 55 | 190 ± 26 | 193 ± 13 | 135 ± 3 | 170 ± 26 | 173 ± 27 |
| BDE 119 | <1 | <2 | <5 | <5 | <6 | <1 | <4 | <3 |
| BDE 99 | 389 ± 57 | 810 ± 44 | 759 ± 94 | 396 ± 52 | 427 ± 4 | 348 ± 22 | 274 ± 159 | 341 ± 116 |
| BDE 116 | <0.5 | <1 | <2 | <2 | <2 | <0.5 | <1 | <1 |
| BDE 85,155[a] | 31 ± 4 | 46 ± 3 | 57 ± 9 | <4 | <5 | 24 ± 2 | <3 | 19 ± 10 |
| BDE 154 | 81 ± 11 | 106 ± 4 | 128 ± 20 | 74 ± 12 | 71 ± 14 | 50 ± 3 | 59 ± 9 | 61 ± 15 |
| BDE 153 | 78 ± 9 | 120 ± 4 | 145 ± 26 | 68 ± 10 | 83 ± 7 | 58 ± 2 | 76 ± 10 | 73 ± 15 |
| BDE 138 | <0.5 | 7 ± 5 | <2 | <2 | <2 | <0.5 | <2 | <1 |
| BDE 156 | <1 | <2 | <5 | <5 | <6 | <1 | <4 | <3 |
| BDE 188 | <2 | <3 | <8 | <8 | <9 | <2 | <6 | <5 |
| BDE 184 | <1 | <3 | <7 | <7 | <8 | <1 | <6 | <5 |
| BDE 179 | <4 | <7 | <20 | <20 | <23 | <4 | <16 | <13 |
| BDE 176 | <1 | <3 | <8 | <8 | <9 | <1 | <6 | <5 |
| BDE 183 | 17 ± 3 | 24 ± 5 | 24 ± 21 | 13 ± 11 | 14 ± 12 | 10 ± 1 | <1 | 16 ± 6 |
| BDE 191 | <1 | <3 | <7 | <7 | <8 | <1 | <6 | <4 |
| BDE 181 | <1 | <3 | <7 | <7 | <8 | <1 | <6 | <5 |
| BDE 171 | <1 | <3 | <7 | <7 | <8 | <1 | <5 | <4 |
| BDE 190 | <1 | <2 | <5 | <5 | <6 | <1 | <4 | <3 |
| BDE 202 | <2 | <5 | <12 | <13 | <14 | <2 | <10 | <8 |
| BDE 201 | <3 | <5 | <13 | <14 | <15 | <3 | <11 | <9 |
| BDE 197 | 5 ± 1 | 7 ± 3 | <9 | <9 | <10 | <2 | <7 | <6 |
| BDE 203,200[a] | <1 | 2 ± 2 | <2 | <2 | <2 | <0.5 | <1 | <1 |
| BDE 196 | 4 ± 1 | 7 ± 4 | <8 | <9 | <10 | <2 | <7 | <6 |
| BDE 205 | <0.5 | <0.5 | <1 | <1 | <1 | <0.5 | <1 | <0.5 |
| BDE 208 | 11 ± 2 | 36 ± 7 | 10 ± 8 | <2 | <2 | 7 ± 3 | <1 | <1 |
| BDE 207 | 17 ± 3 | 53 ± 9 | 26 ± 15 | <8 | <8 | 15 ± 4 | <6 | <5 |
| BDE 206 | 22 ± 4 | 120 ± 3 | 78 ± 20 | 19 ± 6 | 24 ± 17 | 46 ± 4 | 28 ± 22 | 12 ± 8 |
| BDE 209 | 560 ± 23 | 2933 ± 346 | 2722 ± 933 | 1091 ± 131 | 1215 ± 342 | 1416 ± 244 | 744 ± 125 | 636 ± 21 |
| ΣPBDEs | 1999 ± 216 | 5680 ± 348 | 5473 ± 1171 | 2588 ± 37 | 2806 ± 325 | 2757 ± 245 | 2140 ± 83 | 2036 ± 306 |
| Penta[b] | 1329 ± 187 | 2441 ± 36 | 2533 ± 331 | 1455 ± 121 | 1544 ± 36 | 1248 ± 11 | 1328 ± 268 | 1373 ± 326 |
| Octa[c] | 27 ± 3 | 37 ± 3 | 30 ± 30 | 13 ± 11 | 14 ± 12 | 13 ± 2 | all<MDL | 16 ± 6 |
| Deca[d] | 610 ± 23 | 3142 ± 355 | 2837 ± 967 | 1110 ± 133 | 1239 ± 359 | 1485 ± 254 | 797 ± 180 | 648 ± 29 |
| Triclosan | 5993 ± 68 | 2269 ± 101* | 551 ± 61 | 4370 ± 281 | 6504 ± 870 | 1429 ± 15 | 11,843 ± 225 | 12,876 ± 1016 |
| TBB | <31 | 128 ± 11 | <161 | <165 | <184 | <30 | <131 | 2491 ± 776 |
| TBPH | <5 | 368 ± 24 | 925 ± 67 | 603 ± 91 | 624 ± 45 | 220 ± 13 | 273 ± 50 | 1340 ± 275 |
| HBB | <2 | <3 | <9 | <9 | <10 | <2 | <7 | <6 |
| BTBPE | 25 ± 6 | 27 ± 10 | <1 | <1 | <2 | 10 ± 1 | 9 ± 7 | 10 ± 3 |
| syn-DP | 22 ± 3 | 11 ± 5 | 11 ± 2 | 8 ± 2 | 9 ± 2 | 7 ± 3 | 6 ± 1 | 3 ± 1 |
| anti-DP | 26 ± 3 | 11 ± 2 | 39 ± 45 | 7 ± 2 | 7 ± 3 | 14 ± 7 | 10 ± 1 | 6 ± 2 |

Values less than method detection limit (MDL) are shown as <the MDL value in ng/g dw for that biosolids material.

[a] Co-eluting PBDE congeners.
[b] Tetra–hexabrominated diphenyl ether congeners.
[c] Hepta–octabrominated diphenyl ether congeners.
[d] Nona–decabrominated diphenyl ether congeners.

(Gauthier and Letcher, 2009; Gauthier et al., 2007), and bald eagle plasma (Venier et al., 2010). Syn- and anti-DP were recently detected in Spanish sewage sludge at average concentrations of 8 and 24 ng/g dw, respectively, which are comparable to the concentrations detected in our samples (de la Torre et al., 2011). La Guardia et al. reported average syn- and anti-DP concentrations in sewage sludge of 15 and 14 ng/g dw, respectively (La Guardia et al., 2010). Additionally, Kolic et al. (2009) detected syn- and anti-DP in Toronto sewage sludge at concentrations of approximately 100 ng/g dw each, which is higher than the range obtained for our samples.

The anti-DP isomer has been reported to comprise 65% (Tomy et al., 2007) to 80% (Hoh et al., 2006) of the commercial DP mixture. In this study, anti-DP comprised 36% to 69% of total DP with a mean value of 55%. The average fractions of total DP represented by the anti-stereoisomer ($f_{anti}$) in NC WWTP #2, CA WWTP #1, and CA WWTP #2 are 0.66, 0.64, and 0.66, respectively, close to ratios observed in the commercial mixture. In contrast, the average $f_{anti}$ across all time points examined in NC WWTP #1 was 0.47, which suggests either alternative sources of DP to this facility or different chemical transformations of the isomers under certain circumstances. It has been hypothesized that syn-DP could be more stable as a result of greater chlorine shielding of the four interior carbon atoms relative to the anti-DP isomer (Hoh et al.,

2006). The average $f_{anti}$ in SRM 2781 is 0.55. The lower contribution of anti-DP in the SRM could be a result of anti-DP degradation in the years since the production of the SRM in 1991 or a result of DP contributions from sources other than the commercial mixture.

### 3.4. Triclosan

Triclosan was detected in every biosolids sample analyzed and in SRM 2781. Concentrations ranged from 490 to 13,866 ng/g dw with an average value of 5880 ng/g dw. Our values fall within the range of available data for triclosan in North American biosolids and sewage sludge. For instance, the 2009 EPA Targeted National Sewage Sludge Survey, which statistically selected 74 WWTPs and screened sludge samples for 145 analytes, reported triclosan concentrations ranging from 430 to 133,000 ng/g dw (EPA, 2009b). Additionally, McAvoy et al. (2002) collected digested sludge from five WWTPs in Ohio and found that triclosan concentrations ranged from 500 to 15,600 ng/g dw. In a more recent study, triclosan concentrations in biosolids from three Michigan WWTPs ranged from 90 to 7060 ng/g dw (Cha and Cupples, 2009), and both of these papers report triclosan concentrations that are comparable to our

data. Heidler and Halden (2007) reported an average triclosan concentration of 30,000 ± 11,000 ng/g dw in biosolids collected from a WWTP in the mid-Atlantic region of the United States. The facility sampled in their study was designed to treat approximately 680,000 m³/d, which is a considerably larger flow rate than any of the facilities sampled in the present study. However, the significantly higher concentrations detected there could also be the result of other factors, including possible industrial sources of triclosan or different treatment processes that may have resulted in decreased degradation of triclosan in that facility relative to the ones sampled in our study. In addition, the triclosan extraction method used in this study should be viewed as preliminary due to the approximately 50% recovery of ¹³C triclosan that was observed on average. However, this apparent low recovery may also be attributed in part to ion suppression due to the presence of matrix interferences in the electrospray ionization source, especially when considered in light of the high recovery of triclosan found in our matrix spike experiment using SRM 2781 (97 ± 7%). The extraction and analytical methods for triclosan that are described here possess the significant advantage of allowing the direct measurement of triclosan using liquid chromatography techniques, but in the future, these methods should undergo further development in order to eliminate complications from matrix effects.

### 3.5. Temporal variations

Because we had access to four different biosolid samples collected from NC WWTP #1 at four separate time points (November 2006, June 2009, December 2009, and February 2010) we examined some temporal trends in the data. While only four samples were available, which considerably restricted our ability to observe significant trends, it was of interest to examine temporal variations given the recent phase-out of PBDEs and change in flame retardant use in products. Overall, PBDE levels appeared to follow a declining trend over time. The ΣPBDE concentrations declined significantly (p<0.05) between June and December of 2009. The same pattern was also observed in concentrations of the PentaBDE congeners (i.e., all tetra–hexabrominated congeners detected) and DecaBDE congeners (i.e., all nona–decabrominated congeners detected), although congeners associated with the OctaBDE mixture did not change significantly over the time period of interest.

Temporal variations were also examined for TBPH, triclosan, s-DP, and a-DP. TBPH concentrations in NC WWTP #1 were lowest in November of 2006. TBPH levels had increased significantly by June of 2009 (p<0.05) and then dropped significantly by December of 2009, while remaining significantly higher than the 2006 levels. TBPH levels then increased again by February of 2010 although the concentrations were not significantly different than those in December of 2009. Although a great deal of temporal variability was observed in TBPH concentrations in NC WWTP #1, the levels appear to follow an overall upward trend. More extensive temporal monitoring of TBPH in biosolids should be conducted in light of its increased use in PentaBDE replacement products (e.g., FM 550). Triclosan concentrations at every time point were significantly different from one another (p<0.05), but no overall upward or downward trend could be discerned. Additionally, no significant differences in s- or a-DP concentrations were observed over time. Evaluations of temporal variability were not possible for TBB, HBB, and BTBPE due to the low detection of these analytes in some or all of the time points analyzed.

Although a wide variety of factors can potentially influence the temporal variability of contaminant concentrations in wastewater treatment facilities, no significant changes in treatment process, industrial waste input, or population size occurred at this facility during the time period examined. Therefore, with caution, observed temporal trends may be interpreted as being related at least partially to concurrent changes in flame retardant usage over time. Environmental samples such as biosolids should continue to be monitored in the United States in the coming years to further evaluate temporal trends in flame retardant levels.

### 3.6. Comparisons to dust levels

Contaminated indoor dust that enters the municipal wastewater treatment stream (e.g., as effluent from washing machines) is one likely source of the contamination observed in sewage sludge and biosolids. Thus, a potential correlation exists between the flame retardant levels in biosolids and those in indoor dust. Most of the flame retardants measured in this study have previously been detected in indoor dust samples. Several studies have reported concentrations of PBDEs in residential indoor dust (Allen et al., 2008; Johnson et al., 2010; Stapleton et al., 2005; Wilford et al., 2005), and these values are often similar to or higher than values reported for sewage sludge and biosolids. For instance, in the present study, ΣPBDE concentrations in biosolids ranged from 1750 to 6358 ng/g dw with a mean value of 3185 ng/g dw. In 2005, Stapleton et al. measured PBDEs in indoor dust and reported ΣPBDE values ranging from 780 to 30,100 ng/g dw with a mean value of 5900 ng/g dw (Stapleton et al., 2005). More recently, Johnson et al. reported ΣPBDE concentrations in indoor dust ranging from 980 to 44, 546 ng/g dw with a geometric mean of 4742 ng/g (Johnson et al., 2010). In both studies, the PBDE burden in house dust was dominated by congeners from the Penta- and DecaBDE products, similar to what has been observed in biosolids and sewage sludge. Significantly less information is available on the concentrations of alternate and emerging flame retardants relative to PBDEs in both indoor dust and biosolids, particularly in the United States. However, alternate flame retardants are commonly found at lower concentrations than PBDEs in both biosolids and indoor dust.

### 3.7. Differences between North Carolina and California

It has been reported that the environmentally relevant tetra- and pentabrominated congeners 47, 99, and 100 are present at significantly higher concentrations in indoor dust samples from California than in dust samples from other parts of the United States (Zota et al., 2008). Zota et al. hypothesized that elevated levels of these PBDE congeners in California may have resulted from more stringent furniture flammability standards in that state, namely Technical Bulletins 116 and 117 (California, 2000a, 2000b). As contaminated residential indoor dust may constitute a significant source of PBDEs and other contaminants to municipal wastewater treatment streams, we compared the concentrations of PBDE and the alternate flame retardants in the few biosolids samples collected from North Carolina and California in this study.

DecaBDE was significantly higher in the North Carolina biosolids relative to the California biosolids (p<0.05). However, no significant differences were detected in our samples between regions for the PentaBDE and OctaBDE groups. In order to compare our data directly with the findings of Zota et al., comparisons were also conducted for the individual BDE congeners 47, 99, and 100. However, as with the PentaBDE group, no significant differences existed in the concentrations of any of these congeners between the California and North Carolina biosolids.

A wide range of potential factors could influence flame retardant concentrations in biosolids from different facilities in different regions of the country. In addition to the potential influence of state-specific flammability requirements such as Technical Bulletins 116 and 117 , these concentrations could be influenced by different treatment processes employed at the four facilities, with certain chemicals undergoing greater removal or transformation at some facilities relative to others. Additionally, the variety of different influent volumes treated by each facility could affect the final concentrations of flame retardants and triclosan in the biosolids. These concentrations are also likely affected by different residential and industrial sources that contribute to the influent stream of the wastewater facilities. Further research is needed to determine whether regional differences in PBDE concentrations exist and to elucidate their possible causes.

### 3.8. SRM 2781

SRM 2781 was generated from sewage sludge collected in Denver, CO in 1991 and was therefore expected to contain historically used contaminants but not the more modern replacement chemicals. We detected PBDEs, BTBPE, syn-DP, anti-DP, and triclosan in SRM 2781, and commercial use of all of these compounds is known to have predated the production of the SRM. For instance, PBDEs have been in widespread use since the 1970s, Dechlorane Plus has been in use for approximately 40 years (Hoh et al., 2006), BTBPE has been used in the form of FF 680 for over 25 years (Chemtura, 2007b), and triclosan was introduced in 1972 (Jones et al., 2000). The concentrations of all of these analytes reported here in SRM 2781 are in agreement with available literature values for sewage sludge and biosolids (Cha and Cupples, 2009; Hale et al., 2001, 2006; Heidler and Halden, 2007; Hoh et al., 2006; Kolic et al., 2009; McAvoy et al., 2002). TBB and TBPH were not detected in SRM 2781. However, as previously discussed, reports of TBPH production date back only to 1990, and FM 550 was highlighted as a PentaBDE replacement product in 2004, which provides a potential explanation for the absence of TBB and TBPH in SRM 2781.

### 3.9. Implications

In summary, a suite of brominated and chlorinated flame retardants and the antimicrobial agent triclosan were detected in North American biosolids. We also report concentrations of several brominated and chlorinated flame retardants and triclosan in SRM 2781. This study consists of grab samples of biosolids collected at different dates and times, rather than the result of a sustained monitoring effort. Therefore, it is not feasible to use these data to make rigorous comparisons across space and time. The temporal and spatial differences reported in this study may be reflections of the use patterns of these chemicals, or they may simply be caused by a given facility's flow rate, treatment processes, or influent composition. The detection of alternate flame retardants such as TBB and TBPH in biosolids, in addition to their detection in indoor dust (Stapleton et al., 2008; Stapleton et al., 2009), suggests that, like PBDEs, these replacement chemicals have the potential to migrate out of consumer products and enter the environment.

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