

## ABSTRACT

Title of Thesis: ENVIRONMENTAL FATE OF  
POLYBROMINATED DIPHENYL ETHERS  
IN AGRICULTURAL SOILS WHICH HAVE  
RECEIVED BIOSOLIDS APPLICATION

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Polybrominated diphenyl ethers (PBDEs) are used as additives in consumer products for their fire-retardant properties. While scientists observe PBDEs in various environmental media, little is known of their fate in soils. This study examines the potential fate of PBDEs in soils treated with biosolids. Surface soil samples were collected from commercial farms in the Mid-Atlantic region. Biosolids samples from the source wastewater treatment plant were collected to evaluate PBDE levels and trends. Results show that mean concentration of PBDEs in biosolids from this plant is  $1496 \pm 158 \mu\text{g/kgd.w.}$ , mean concentration in soil from fields that had not received biosolids was  $6.8 \mu\text{g/kgd.w.}$ , fields with a single application had a mean of  $18 \mu\text{g/kgd.w.}$ , and fields with multiple applications had a mean of  $52 \mu\text{g/kgd.w.}$  Statistical analysis revealed that concentrations in the multiple application group were significantly higher than those in the single application group. This work suggests that PBDEs are relatively persistent in agricultural soils.

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APPLICATION

By

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## Dedication

I would like to dedicate this thesis to my family. Thanks to my dad, Fernando, who gave me the opportunity to come to the U.S., therefore being directly responsible for my career path. He loves in his unique way; giving, with no thought of return. My mom, Sandra, has heard as many complaints as one could ever hear and she still calls me for more. Her love has been the one thing that has kept me on track. She worries, she cares, she loves. My brother, Rafael, is my best friend. I miss talking to him everyday, I miss hugging him when I'm in my annoying mood, but I really just miss being around him. Rafael, you make me a better me. Por voce, eu sinto a maior saudade de todas. Eu te amo.



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# **Chapter 1 – Introduction**

## **1.1 *Biosolids***

Biosolids are the nutrient-rich organic materials resulting from the treatment of urban sewage at a wastewater treatment plant (WWTP). The term sludge is generally used before beneficial recycling treatment criteria have been achieved. Biosolids are generated when sludge produced are treated further to meet regulatory requirements mostly to reduce or eliminate pathogens and to produce a beneficial product as specified by 40 CFR Part 503 (U.S. EPA, 1993). In the following sections we will present an overview of WWTPs, generation of sludge and biosolids' regulations.

### **1.1.1 Overview of Biosolids**

WWTPs treat sewage sludge and produce biosolids. The name “biosolids” is only given to solids that meet the criteria set by EPA for land application and are reused. A wastewater treatment plant consists of a continuous set of processes designed to treat wastewater collected from residential, commercial, and industrial areas. The different processes are named treatments and they can be classified as preliminary, primary, secondary, and tertiary treatments (Figure 1.1). A preliminary screening procedure that removes large particles from the water precedes the primary treatment. Primary treatment itself removes smaller solids that are suspended in the wastewater. This process is conducted in tanks that are called clarifiers. Ferric chloride was added to the process for

the studied biosolids to improve phosphorus removal. The solids removed from the primary treatment are further treated. The secondary treatment reduces biological oxygen demand and removes additional suspended solids. Plants use activated sludge, trickling filters, and rotating biological contactors to achieve this goal and the solids removed in this step are added to the primary sludge to be further treated. The tertiary treatment kills the majority of pathogens remaining in the wastewater. Plants use chlorination, ozonation, or ultra-violet light for tertiary treatment. Once the sludge is gathered, it receives additional treatment. The sludge goes through thickening, stabilization, disinfection, and dewatering before it can be disposed of. Stabilization can be achieved by lime addition, composting, or by aerobic or anaerobic digestion. Once treated, the sewage sludge can be called biosolids and the quality of the biosolids produced is dependant on the treatment it receives along with the origin of the sewage sludge.

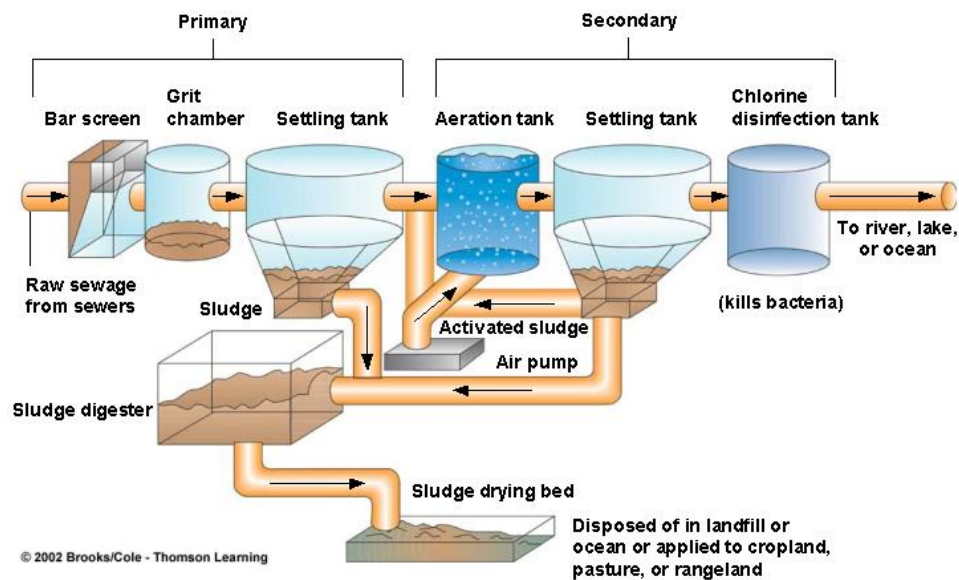


Figure 1.1 – General layout of a WWTP showing primary and secondary treatments with chlorine disinfection. A dechlorination step would be added in the end of the process if the plant has tertiary treatment. Source: Brooks/Cole – Thomson Learning (2002)

Biosolids contain high levels of nutrients and are used as fertilizer, for soil remediation projects, or as a soil conditioner. According to the National Biosolids Partnership biosolids are land applied in all 50 states (Annual Report – 2007). Beneficial use programs for land application of biosolids are important avenues for disposal of solids outflows from WWTPs. In a recent study, Singh and Agrawal (2008) provide a summary on the potential benefits and risks of application of biosolids to agricultural lands. Their report mentions beneficial soil conditioning properties of biosolids along with changes in the physical, chemical, and biological properties of soils (Singh and Agrawal, 2008). The risks for the soil and crops were mainly accumulation of heavy metals after biosolids' application. Increase in yield was observed in a number of studies and the extent of yield increase was dependent upon soil type, application rates, and crop (Singh and Agrawal, 2008). Mantovi et al. (2005) confirmed that the crop as well as the type of biosolids applied influences the yield and in general yields are increased with biosolids application. Biosolids can be effectively used for land remediation efforts (Brown et al., 2003) and they reduce dramatically the use of chemical fertilizers by farmers. This decrease in the use of fertilizers provides an important economical benefit for farmers. Estimates that the savings can be from US\$60 to US\$160 per acre (Obreza and O'Connor, 2003) were reported, and the Commonwealth of Virginia provides that farmers in that State can save up to US\$140 per acre of biosolids applied (VA Department of Health, Division of Wastewater). These savings vary according to the type of biosolids being applied, the application rate of the biosolids, the type and properties of the soil receiving the biosolids, the crop being planted, and the expected yields. Muraro et

al. (2001) estimated that a farmer could save from 12% to 63% of the total costs of fertilizers (total costs for fertilizers alone would be US\$100.65).

U.S. EPA estimates that 6.9 million dry tons of sewage sludge were produced in 1998 and 60% of the sewage sludge was considered biosolids that were beneficially used, with 41% being land applied. The 40% of the sewage sludge produced that were not beneficially used were disposed through incineration, surface disposal, and other methods. Also, the U.S. EPA estimates that the amount of sewage sludge will increase to 8.2 million dry tons by 2010, which represents a 19% increase from 1998 to 2010. In addition, it is expected that the land application percentage will increase to 48% and the total percentage of biosolids being beneficially used will increase to 70% by 2010 (U.S. EPA).

Domestic and industrial wastewaters contain a variety of synthetic compounds in trace amounts that are only partially removed from the liquid phase by conventional treatment processes. Most of their removal is through their incorporation into the solids portion of the waste stream, i.e., biosolids. Thus there is an increased concern that along with nutrients, biosolids contain organic pollutants which may have toxic or bioaccumulative properties. Some of these chemicals have been labeled Emerging Organic Pollutants (EOP), those chemicals which have recently been identified in environmental compartments and may have significant negative effects on ecosystem health. The research community and environmental groups are concerned that many of the EOPs such as antibacterials, pharmaceuticals, and flame retardants are not currently being regulated by EPA, FDA, or others. According to the literature (Oros et al., 2005, de Boer et al., 2003, Hassanin et al., 2004, Ikonomidou et al., 2002, Knoth et al., 2004, North.



2004), these chemicals have been detected in the environment and it has been postulated that land application of biosolids may represent a major source of these pollutants.

### **1.1.2 Regulatory Status**

The U.S., European Union, and Canada regulate land application of biosolids. The U.S. biosolids regulations are contained in 40 CFR Part 503 (U.S. EPA, 1993). Part 503 specifies rules for maximum metal concentrations (Table 1.1), pathogens concentrations, and vector attraction reduction. U.S. EPA did not consider background levels of heavy metals to set the ceiling concentrations. In general, levels of heavy metals in U.S. soils are lower than the ceiling concentrations resulting in accumulation of heavy metals over time, although leaching processes can be an important removal pathway for pollutants (Harrison et al., 1999). It was estimated that since the ceiling concentrations allowed in the U.S. are much higher than the concentrations allowed in the European Union, the cumulative levels of heavy metals would be approximately an order magnitude higher in the U.S. (McGrath et al, 1994).

Although Part 503 regulates the application of biosolids on a federal level, states are allowed to have their own regulations which may exceed requirements of Part 503. The regulations in the U.S. were established using a risk assessment approach. Some have suggested that this risk assessment performed should now be revised (Harrison et al., 1999) and have questioned if risk assessment alone is enough to create regulations (Schoof and Houkal, 2005). U.S. regulations also do not regulate any organic pollutant.

The inclusion of some organic pollutants (PCBs, dioxins, and furans) to Part 503 has been discussed but not finalized (Harrison et al., 1999).

In Canada, the regulations are at a territorial level rather than at the federal level. Some provinces in Canada use the U.S. regulations as basis for their regulations while others have developed their own. In the European Union, the regulations for land application of biosolids can be found in 18 articles from a 1986 Directive (Council of the European Communities) that has been amended many times. The European Union has a more conservative approach in determining the ceiling concentrations of pollutants allowed in the sewage sludge and is planning on regulating many organic pollutants that the U.S. is not considering. However, the pathogen limits in the European laws are not as well established as set by Part 503 (Iranpour et al., 2004).

Table 1.1 – Comparison between heavy metals ceiling concentrations in the U.S. and the European Union.

<b>Pollutant</b>	<b>Ceiling Concentrations for U.S. (mg/kg d.w.)</b>	<b>Ceiling Concentrations for EU (mg/Kg d.w.)</b>
Arsenic	75	-
Cadmium	85	40
Chromium	3,000	-
Copper	4,300	1,750
Lead	840	1,200
Mercury	57	25
Molybdenum	75	-
Nickel	420	400
Selenium	100	-
Zinc	7,500	4,000

## **1.2 Polybrominated Diphenyl Ethers**

### **1.2.1 Nomenclature, chemical structure, and physical properties**

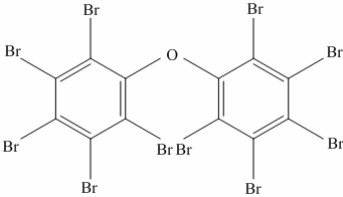
Polybrominated diphenyl ethers (PBDEs) are a class of chemical compounds in which up to 10 bromine atoms are attached to a diphenyl ether molecule. There are 209 different possible combinations, forming different compounds depending on the number and position of the bromine atoms. Each one of the 209 possible compounds is called a congener and a set of these compounds can also be called homologs if they contain the same number of bromine atoms (Table 1.2). PBDEs are hydrophobic (Table 1.3) and resistant to degradation. For these compounds, water solubility and vapor pressure decrease with increasing degree of bromination. Also, a large number of bromine atoms contributes more to the hydrophobicity of the molecule; the molecule increases in size without a gain in polarity. A study measured the Henry's law constants for congeners BDE-28, BDE-47, BDE-100, BDE-99, BDE-154, BDE-153, and BDE-209 and found that there is a strong dependence in temperature, and this dependence varies with degree of bromination and the structural position of bromines (Cetin and Odabasi, 2005). Values varied from 0.04 to 4.83  $\text{Pam}^3\text{mol}^{-1}$  at 25°C, where BDE-209 held the lowest value and BDE-28 held the highest.

Table 1.2 – Chemical name, abbreviation, CAS#, molecular formula, and molecular weight of PBDEs analyzed in this study.

<b>General Term</b>	<b>Name of Compound</b>	<b>Abbreviation</b>	<b>CAS#</b>	<b>Molecular Formula</b>	<b>Molecular Weight</b>
Tri-BDE	2,4,4' - tribromodiphenyl ether	BDE - 28	41318- 75-6	C <sub>12</sub> H <sub>7</sub> Br <sub>3</sub> O	406.89
Tetra-BDE	2,2',4,4' - tetrabromodiphenyl ether	BDE - 47	5436- 43-1	C <sub>12</sub> H <sub>6</sub> Br <sub>4</sub> O	485.79
Penta-BDE	2,2',4,4',5 - pentabromodiphenyl ether	BDE - 99	60348- 60-9	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	564.69
Penta-BDE	2,2',4,4',6 - pentabromodiphenyl ether	BDE - 100	189084- 64-8	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	564.69
Hexa-BDE	2,2',4,4',5,5' - hexabromodiphenyl ether	BDE - 153	68631- 49-2	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	643.58
Hexa-BDE	2,2',4,4',5',6 - hexabromodiphenyl ether	BDE - 154	207122- 15-4	C <sub>12</sub> H <sub>4</sub> Br <sub>6</sub> O	643.58
Hepta-BDE	2,2',3,4,4',5',6 - heptabromodiphenyl ether	BDE - 183	207122- 16-5	C <sub>12</sub> H <sub>3</sub> Br <sub>7</sub> O	722.51
Deca-BDE	decabromodiphenyl ether	BDE - 209	1163- 19-5	C <sub>12</sub> Br <sub>10</sub> O	959.21

Table 1.3 – Physical and chemical properties of the compounds of interest for this study ( $\pm$  standard errors). Koa = n-octanol/air partition coefficient;  $P_L$  = supercooled liquid vapor pressure (Pa); H = Henry's Law constant measured at 25°C ( $\text{Pa m}^3 \text{mol}^{-1}$ ); Kow = n-octanol/water partition coefficient. References: (1) Hui-Ying et al, 2007; (2) Wania et al., 2002; (3) Wong et al., 2001; (4) Cetin and Odabasi, 2005; (5) Braekveelt et al., 2003.

Abbreviation	Structure	logKoa	logP <sub>L</sub>	H	logKow
BDE - 28		9.7 <sup>(1)</sup>	-2.93 <sup>(1)</sup>	4.83 $\pm$ 0.67 <sup>(4)</sup>	5.94 $\pm$ 0.15 <sup>(5)</sup>
BDE - 47		10.34 <sup>(2)</sup>	-3.5 <sup>(3)</sup>	0.85 $\pm$ 0.35 <sup>(4)</sup>	6.81 $\pm$ 0.08 <sup>(5)</sup>
BDE - 99		11.28 <sup>(2)</sup>	-4.17 <sup>(3)</sup>	0.6 $\pm$ 0.11 <sup>(4)</sup>	7.32 $\pm$ 0.14 <sup>(5)</sup>
BDE - 100		11.40 <sup>(1)</sup>	-4.47 <sup>(1)</sup>	0.24 $\pm$ 0.06 <sup>(4)</sup>	7.24 $\pm$ 0.16 <sup>(5)</sup>
BDE - 153		12.15 <sup>(2)</sup>	-5.07 <sup>(3)</sup>	0.26 $\pm$ 0.08 <sup>(4)</sup>	7.90 $\pm$ 0.14 <sup>(5)</sup>
BDE - 154		12.18 <sup>(1)</sup>	-5.18 <sup>(1)</sup>	0.08 $\pm$ 0.04 <sup>(4)</sup>	7.82 $\pm$ 0.16 <sup>(5)</sup>
BDE - 183		12.89 <sup>(1)</sup>	-5.84 <sup>(1)</sup>	logH= 1.535 <sup>(1)</sup>	8.27 $\pm$ 0.26 <sup>(5)</sup>

					
BDE - 209		15.73 <sup>(1)</sup>	-8.4 <sup>(1)</sup>	0.04 ± 0.01 <sup>(4)</sup>	10.33 <sup>(5)</sup>

Polybrominated diphenyl ethers receive commercial names in addition to their IUPAC names by industry and consumers. Usually, these compounds are produced as a mixture of congeners; rarely are they sold separately. The most important mixtures that are commercialized are the penta-BDE (mixture of tri-BDE, tetra-BDE, penta-BDE, and hexa-BDE), the octa-BDE (mixture of hexa-BDE, hepta-BDE, octa-BDE, and nona-BDE), and the deca-BDE (mixture of octa-BDE, nona-BDE, and deca-BDE). The mixtures have different compositions depending on the manufacturer.

### 1.2.2 Production and uses

PBDEs belong to a group of chemicals known as brominated flame retardants (BFRs). Industry uses BFRs globally in hundreds of products, such as foam mattresses, televisions, computers, plastics, textiles, and more, in order to reduce their flammability (de Wit, 2002). The global production of BFRs increased from 107,000 metric tons in 1989 to 203,000 metric tons in 1999 (Alaee *et al.*, 2003) with a large percentage of the global production directed to North America (de Wit, 2002). As the use of plastics increases so will the demand for these chemicals. There are three major types of BFRs:

- (a) Tetrabromobisphenol A (TBBPA) is added during the production of epoxy and polycarbonate resins used in circuit boards and other products. It becomes part of the polymer backbone, making it less available for loss to the environment.

(b) Polybrominated diphenyl ethers (PBDEs) are added to different polymers, but they are not chemically bound to the polymer backbone and thus are easily released to the environment.

(c) Hexabromocyclododecane (HBCDD) is added to polystyrene foam used in building construction.

The world demand for BFRs is difficult information to obtain. The latest data is for 2001 (Table 1.4) but since 2004 the production of penta-BDE and octa-BDE mixtures has ceased in the U.S. In Massachusetts, 16 companies used approximately 2.4 million pounds of deca-BDE for the year 2000.

Table 1.4 – Global demand for BFRs

<b>Global Market Demand for BFRs in 2001 (metric tons)</b>					
	<b>America</b>	<b>Europe</b>	<b>Asia</b>	<b>Rest of World</b>	<b>Total</b>
TBBPA	18,000	11,600	89,400	600	119,700
HBCD	2,800	9,500	3,900	500	16,700
Deca-BDE	24,500	7,600	23,000	1,050	56,100
Octa-BDE	1,500	610	1,500	180	3,790
Penta-BDE	7,100	150	150	100	7,500
<i>Source: Bromine Science and Environment Forum, 2003</i>					

### 1.2.3 Toxicity and endocrine disruptor effects

PBDEs have similar structure to polychlorinated biphenyls (PCBs), which are well known pollutants with adverse effects on biota. The levels of PBDEs in biota have been rising as opposed to PCBs' levels which have been decreasing (ES&T Science News). PBDEs could present health risks for humans because they are hydrophobic and partition to fatty tissue in humans and animals. The low brominated congeners are known

to bioaccumulate (accumulation in the same trophic level), biomagnify (accumulation in different trophic levels) (Voorspoels et al., 2007), to easily absorb, and to be more bioactive than the deca-BDE (McDonald, 2002). It is reported that all PBDE products can potentially cause thyroid effects and neurobehavioral effects, while the deca-BDE presented some carcinogenic potential in female and male rats (McDonald, 2002). PBDEs' structures are similar to the thyroid hormone, therefore once inside the organism, PBDEs can mimic the role of the hormone, deregulating the production of the same, which later causes the disruption of the endocrine system. Lilienthal et al. (2006) showed that offspring of female rats that received penta-BDE (10 mg/kg body weight) during pregnancy had a decrease in sex steroids and feminization of adult males. Rats and mice are usually the choice of toxicology effect studies for they could be used to represent effects in humans. Staskal et al. (2005) shows that metabolic capacity and exposure for different species (rats and mice) may significantly influence the congener profile inside the body, which raises the question of which species would better represent humans in toxicological studies.

Toxicity in humans is not well studied and limited data are available. Two studies on skin sensitization proved no sensitization for deca-BDE, which was the only congener analyzed (Darnerud et al, 2001 and Hardy, 2002). Workers from factories that manufacture PBDEs presented higher levels of hypothyroidism, but the effects could not be attributed to PBDEs (Darnerud et al, 2001). Although there are a few studies with humans and many studies with animals, the risk for human health offered by PBDEs can not be well established at this time, and more studies in this area are needed.



#### **1.2.4 Sources, fate, distribution, and concentrations**

PBDEs are generally released to the environment in two different ways: volatile release from consumer products or with wastewater effluents or solids. Release from consumer products occurs because PBDEs are used as additives and are not incorporated into the polymer backbone. There are many studies demonstrating that PBDEs are volatilized from consumer products. PBDEs have been reported in house dust and indoor air (Stapleton et al., 2005, Harrad et al., 2006, Harrad et al., 2008, Hazrati and Harrad, 2006, Jones-Otazo et al., 2005, Mandalakis et al., 2007, Schecter et al., 2005), illustrating that humans are susceptible to ingestion of these chemicals in different environments.

The average concentration in dust inside a house varies according to the microenvironment analyzed. Allen et al. (2008) concluded that the concentrations in the main living areas of houses were higher than the concentrations in bedrooms. In Southern Ontario, window organic films from outside and inside of houses were analyzed and concentrations in the indoor films were higher than the outdoor films (Butt et al., 2004). A recent report by Mandalakis et al. (2007) shows concentration of PBDEs in indoor air from computer/electronics shops are usually higher than the concentrations found in indoor air from houses or furniture stores. In addition, Hazrati and Harrad, (2006) showed that when a computer constructed in 1998 was substituted by one constructed in 2003, PBDE concentrations in indoor office air decreased considerably. It was hypothesized that the computer was the cause of the concentration decline since PCB levels remained approximately constant.

Another study indicates that electronics are a bigger source of PBDEs to indoor air than furniture (Chen et al., 2008). Lorber (2008) suggests that the majority of the

intake of PBDEs by humans is derived from the use and the presence of electronics rather than food ingestion. He mentions, as part of the possible exposure pathways, that direct contact with house dust and furniture containing PBDEs plays a role in the total human intake. Dermal exposure was also cited by Staskal et al. (2005); in their study they confirmed that approximately 62% of the BDE-47 administered to female mice was absorbed through skin.

Once PBDES are free from commercial products they reach wastewater and eventually enter a WWTP or are directly discharged into a body of water. These compounds will enter WWTPs and it is expected that will subsequently concentrate in sewage sludge. After land application, potential loss processes from soil are microbial degradation, photolysis, volatilization, leaching, and movement with soil during storm events. Little information is currently available on the relative importance of any of these processes.

Since scientists have detected PBDEs in many compartments of the environment, we know a fair amount regarding their fate. However, their transformation in the environment is still largely unknown. Besides its toxicity, the potential to bioaccumulate, persistence in the environment, and the potential for long-range atmospheric transport are used to assess appropriate restrictions for use of these chemicals (Gouin and Harner, 2003). BDE-209 is believed to be unavailable for bioaccumulation although some studies show that seals (Thomas et al., 2005) and fish (Stapleton et al., 2006) accumulate in blood, tissue, and liver. Distilled water, a 20% methanol solution, and a dissolved humic solution were tested as leachants for plastics containing PBDEs (Kim et al., 2006). The results showed that when methanol and humic solution was present, the leaching was

greatly increased, which is of importance when taking in consideration that plastic products usually have a landfill as their final destination. Studies show that the transport of PBDEs is difficult to model accurately (Gouin and Harner, 2003). It appears that there are parameters that are not in current models governing the partitioning of PBDEs in the many compartments of the environment.

The photodegradation of BDE-209 has been observed (Ahn et al, 2006; Sanches-Prado et al. 2005, Eriksson et al., 2004) and is considered important for the environmental fate of this compound because deca-BDE formulation is the major industrial PBDE product. Results from Ahn et al. (2006) have shown that the photodegradation depends on the amount of light received, the type of soil where the PBDEs are present and the amount of PBDEs that are adsorbed into organic matter. Another study shows dependency on the solvent (Rayne et al., 2006). While the formation of brominated 2-hydroxybiphenyls and brominated dibenzofurans occurred in acetonitrile, these compounds were not identified in the experiments with distilled water and seawater. The half-life ( $t_{1/2}$ ) of BDE-153 in acetonitrile was found to be 1.6 min while the half –life in seawater (both rates were for observed first order reactions) was calculated as 4.6 min and the half-life in distilled water could not be calculated (Rayne et al., 2006). The half-life calculated for BDE-209 in methanol/water was 0.5h and for BDE-47 was 12d, indicating that the bromination level of the molecule affects its photolysis (Eriksson et al., 2004). This was also observed by Fang et al. (2008); the calculated a half-life for BDE-183 in hexane was 0.26h while the half-life for BDE-28 in hexane was 4.9h. Since PBDEs can be found in many compartments of the environment it is important to know the behavior of these chemicals in the presence of water as well as

organic matter (represented in the studies by some organic solvents). Also, since PBDEs have been analyzed in many environmental samples, it is important to know of any type of degradation to prevent its occurrence when samples are being analyzed in the laboratory.

The products of the photodegradation of deca-BDE are less brominated congeners (Ahn et al., 2006). The products found by Rayne et al., (2006) when they analyzed the photodegradation products of the hexa brominated congener, BDE-153, were seven different penta and tetra-brominated congeners. The many congeners that can result from the photodegradation of a single PBDE leads to the question of pathway and reaction mechanism. While analyzing the photodegradation products of BDE-209, Bezares-Cruz et al. (2004) found that the products were a wide range of PBDEs, from nona brominated to tetra brominated congeners. This experiment was conducted using hexane as solvent for the PBDE mixture. Eriksson et al. (2004) found that the products of BDE-209 photodegradation were the three nona brominated congeners and seven octa brominated congeners.

There is not one specific pathway that explains the photodegradation of PBDEs, rather, there are many pathways that can occur depending on the environment (amount and wavelength of light reaching the PBDEs and the material where PBDEs are present, among other factors). Consecutive reductive debromination seems to be the major pathway for the photodegradation of PBDEs (Fang et al., 2008, Sanchez-Prado et al., 2005, and Eriksson et al., 2004). So far, direct photolysis (sun's photons directly interact with the chemical) was studied but it is difficult to mimic the environmental conditions to understand the role of indirect photolysis (sun's photons interact with dissolved organic

molecules causing them to become reactive and in turn react with the chemical) for these chemicals (Eriksson et al., 2004). Proposed pathways for the photodegradation of the BDE-153 can be compared (Figure 1.2, Figure 1.3, and Figure 1.4). For lower brominated compounds, the photoreactivity decreased depending on the position of the bromine atoms (ortho > para) but for higher brominated compounds, the position of the bromine atoms does not seem to have an effect (Fang et al., 2008).

Figure 1.2 – BDE-153 photodegradation primary and secondary products obtained in hexane (Fang et al., 2008).

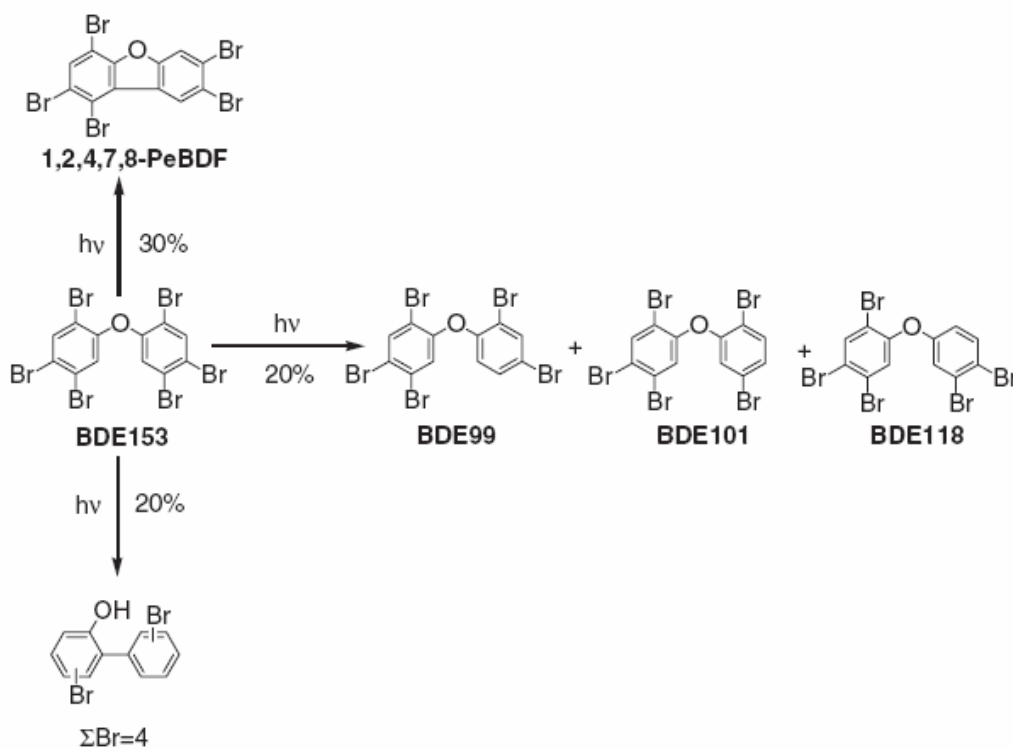


Figure 1.3 – Primary products, including not only PBDEs but also brominated dibenzofurans and 2-hydroxybiphenyls, observed in photodegradation experiments utilizing acetonitrile, distilled water, and seawater as solvents (Rayne et al., 2006).

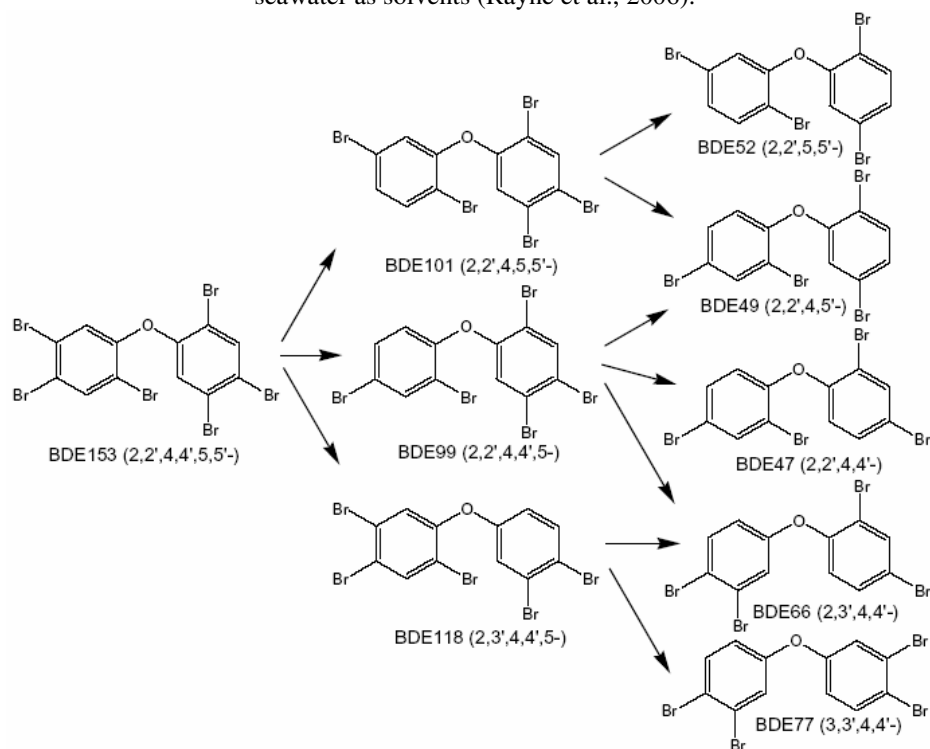
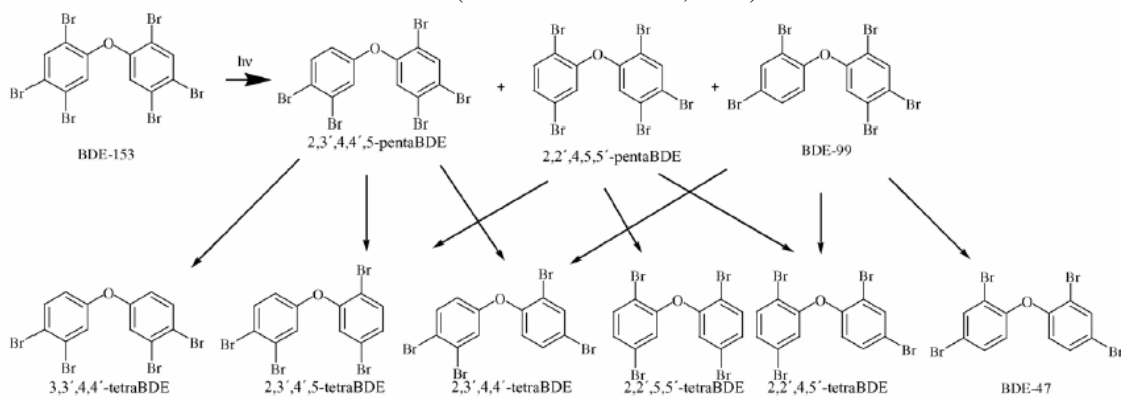


Figure 1.4 – Primary and secondary photodegradation products found in a solution of water and acetone (Sanchez-Prado et al., 2005).



Anaerobic biodegradation studied by Gerecke et al. (2005) indicates that deca-BDE biodegrades to nona and octa-BDEs “within a period of 238 days in experiments with sewage sludge as the inoculum”. The calculated half-life for BDE-209 by this group was 700 days. Another study (Welsh, 2008) shows that bacteria present in sewage sludge was capable of performing anaerobic debromination of BDE-209 at environmental relevant levels (40ppb), but does not mention rate of degradation. A comparison between biodegradation in a sediment environment and in a biomimetic environment (a laboratory procedure that mimics the natural environment) was performed by Tokarz et al. (2008). This study investigated BDE-209, BDE-47, and BDE-99. The debromination of BDE-209 to mainly hexa brominated compounds occurred fast in the biomimetic system (five minutes), while the debromination in sediment occurred and significant increase in the products was observed after 3.5 years of incubation. This study also used the biomimetic acquired reaction rate to predict the reaction rate in an environment where sorption is an important factor. The predicted values are near to the values obtained by the sediment experiments, although the rates for the latter varied by an order of magnitude. This experiment shows that the anaerobic degradation of BDE-209 could play an important role in the presence of lower brominated BDEs in the environment (Tokarz et al., 2008). Studies conducted by He et al. (2006) showed that a species of bacteria that anaerobically debrominated deca-BDE to lower congeners did not have the ability to debrominate lower congeners further. In contrast, another species could not break down deca-BDE but successfully debrominated congeners present in an octa-BDE mixture. The products of the biodegradation were lower brominated congeners such as BDE-154, BDE-99, and BDE-47. In the environment, selective degradation by different strains of bacteria could

either hinder total degradation or amplify it. Anaerobic degradation was also observed by Rayne et al. (2003). The analyzed BDE was 4, 4'-dibromodiphenyl ether (BDE-15) and the debromination products observed were 4-bromodiphenyl ether (BDE-3) and the parent compound: diphenyl ether (DE). Their research shows that the rate-limiting step is the transformation of BDE-15 to BDE-3. This observation could be of environmental importance since the majority of PBDEs that reach the environment are higher brominated ones. If the transformation of the higher brominated compounds into the lower brominated compounds is slow, then the persistence of these chemicals could be relatively large. A mixed culture extracted from soil contaminated with a penta-BDE commercial mixture was able to perform degradation of some congeners in less than five minutes (Vonderheide et al., 2006). This fast disappearance of BDEs occurred in a water based environment and not in a soil environment, therefore we can not assume the same rate of degradation, especially since in a soil environment, sorption will play a more important role than biodegradation (Vonderheide et al., 2006). The pathway of debromination had never been systematically studied, due to difficulties in detecting some of the congeners and co-elution in GC columns, until a different method of analysis was used (Robrock et al., 2008). Seven congeners (main components of an octa-BDE mixture and BDE-47 and BDE-99) underwent degradation by three dehalogenating cultures. The preferred pathway of bromine removal observed was para and meta. Also noteworthy was that the extent of removal of bromines from the BDE molecules was orders of magnitude smaller than the removal of chlorines from PCBs (Robrock et al., 2008).



Many publications show the presence of PBDEs in biota, especially fish (Johnson-Restrepo et al., 2005; Li et al., 2006; Luo et al. 2007; Jacobs et al., 2002). Studies that analyzed mammals like polar bears (Dietz et al., 2007; Gebbink et al., 2008) and even humans (Sjodin et al., 2001) also show PBDEs in their system. For humans the highest concentration is found in breast milk (Antignac et al., 2008), which increases the concern that children may be exposed as infants. There are many studies that show concentrations for the different compartments of the environment. These studies combined give scientists a better understanding of the environmental behavior of PBDEs.

Hassanin et al. (2005) analyzed pasture samples in the United Kingdom to identify time trends in air concentrations. The basic trend discovered by this group was that the concentrations began to rise in the 1970s, reached the highest level in the year 2000 and then concentrations started to decline in response to restrictions on the use of PBDEs in Europe (Hassanin et al. 2005). Another study (Hassanin et al. 2004) completed in United Kingdom and Norway analyzed soil samples and found that concentrations could reach up to 12 µg/kg d.w. ( $\Sigma$  all PBDEs congeners). It is important to notice that these samples were collected in remote areas representing background soil concentrations. The same study also concluded that the congener distribution found matched that of the penta-BDE commercial mixture and that the higher brominated congeners were retained more easily and more efficiently than the lower brominated compounds. Wang et al., (2005) analyzed soil and sediment samples collected in the area surrounding an electronic waste disposal and recycling facility in China. The highest concentration found was 824 µg/kg d.w. for hepta-BDE in one type of soil but penta-BDE had a high consistent concentration in the two types of soil and sediment.

Recent studies have also examined the presence of deca-BDE in the environment, but the data for this compound is limited because of challenges in accurate analysis at environmentally relevant concentrations. Sample processing must be carried out under specific light conditions, and analytical standards are extremely expensive. Most of the studies completed consider only one matrix and rarely analyze for all the congeners that are expected in the environment.

### **1.2.6 Concentration in wastewater and biosolids**

Levels of PBDEs in sewage sludge have been measured in a few studies. Nylund *et al.*, (1992) investigated sewage sludge as a source of PBDEs to the Baltic Sea and observed the tetra and penta-brominated PBDEs at concentrations ranging from 3.4-19 µg/kg d.w. per congener. Effluent from a landfill used by the plastics industry was found to increase the levels of TBBPA in sludge from the receiving WWTP by approximately 50% (56 µg/kg d.w. vs. 31 µg/kg d.w.) over another plant with no known sources of TBBPA (Sellstrom and Jansson, 1995). However, both of these studies only included a very small number of samples. A more extensive study in the Netherlands measured PBDEs in solids associated with the influent and effluent waters from 4 different WWTPs (de Boer *et al.*, 2003). Surprisingly, suspended particle PBDE concentrations in the effluent waters were often higher than in the influent, especially for the most hydrophobic decabrominated PBDE. The authors speculated that the effluent contained only the finest particles with the highest organic carbon content and the highest concentrations of PBDE. This may indicate that the influent water contained more

inorganic material that “diluted” the particle phase PBDE concentrations. Biosolids samples from 22 wastewater treatment plants in Sweden resulted in concentrations from 0.3 to 11  $\mu\text{g/kg}$  w.w. for different (BDE-47, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, and BDE-209) congeners, with BDE 209 having the highest concentrations and BDE 138 having the lowest (Oberg et al. 2002). In Germany, samples were collected and analyzed from 11 wastewater treatment plants (Knoth et al. 2004). The concentration for the sum of BDE 28, 47, 99, 100, 153, 154, and 183 congeners ranged from 12.5 to 288  $\mu\text{g/kg}$  d.w., and the concentration of BDE 209 ranged from 97.1 to 2217  $\mu\text{g/kg}$  d.w. In Spain, sewage sludge samples were collected in five WWTPs and concentrations found were between 197 and 1185  $\mu\text{g/kg}$  d.w. and the mean value was established at 572  $\mu\text{g/kg}$  d.w. (Eljarrat, 2008). A more recent study in Kuwait, analyzed sludge samples from three WWTPs and reported mean concentrations ( $\Sigma\text{PBDEs}$ ) in the range of 5.7-1599  $\mu\text{g/kg}$ . This study showed a high concentration variability and the authors also observed a seasonal trend related to temperature effects (Gevao et al., 2008). In Australia, 16 WWTPs were surveyed for PBDEs and the average sludge concentration was 1137  $\mu\text{g/kg}$  (Clarke et al., 2008). The same study collected samples in 2005 and 2006 to analyze for seasonal variations, but samples presented differences only between WWTPs and not between years.

In the U.S., Hale et al., (2001a), found PBDEs in biosolids in eleven samples from WWTPs in Virginia, Maryland, New York, and California. The concentrations ranged from 1100-2290  $\mu\text{g/kg}$  d.w. for the penta-brominated PBDEs and 85-4890  $\mu\text{g/kg}$  d.w. for the decabrominated PBDE congener indicating that input was high. Hale et al., (2001b) linked land-applied biosolids to high levels of these chemicals in fish in Virginia. In

California, reported concentrations from one plant ranged from 0.06 to 1.44 µg/kg d.w. for different congeners, showing that the congeners from the penta-BDE commercial formulation corresponded to 88% of the total PBDE concentration in the effluent while BDE-209 contributed to 6% of the total PBDE concentration (North. 2004). Overall, PBDE concentration in sludge from North America exceeds that reported from European countries.

### **1.2.7 Regulatory status**

In the U.S., some of the commercial mixtures of PBDEs (penta and octa) are no longer in production or are being phased out soon in many states. California passed a state-wide ban in 2003 on penta and octa PBDEs; the initial date for a ban was set to 2006 but was later pushed to 2008 (Official California Legislative Information). In April of 2007 Washington State passed a ban on PBDEs including penta, octa, and deca formulations that goes into effect in 2008 with some exceptions, such as televisions and computers that can still receive the deca-BDE until 2011 (Peele, 2004). In Europe, electronics containing deca-BDE were banned in July of 2006. Penta and octa formulations were phased out in 2003. In Canada the laws for PBDEs are considered weak by some environmental groups and deca-BDE is still widely used. The Canadian Environmental Law Association and David Suzuki Foundation filed a formal call for the federal government to ban all PBDEs in February of 2007 according to the David Suzuki Foundation website.

### **1.3 Study Objectives**

PBDEs are in production and are used in many consumer products. They find their way into WWTPs and they have been detected in many environmental matrices. While inside the WWTPs, PBDEs partition to organic matter and are released mostly through biosolids. However, we do not fully understand the fate of these chemicals after they leave the WWTP. The main objective of this work was to improve our understanding of the environmental fate of PBDEs after land application of biosolids. We characterized the nature of the temporal changes in PBDE concentrations in biosolids from one large WWTP and examined the effect of biosolids applications on PBDE concentrations in soils of commercial farms. The results of this work provide important new information on PBDE concentrations in biosolids and their fate in agricultural soils.

#### **1.3.1 Presence in biosolids**

The concentrations of the PBDE congeners in biosolids were measured every two months for two years (July 2005 to August 2007). The goal was to evaluate PBDE's trends to identify whether the congener distribution or magnitude varies as a function of temperature or with precipitation prior to sampling and to estimate variability in PBDE concentrations of the source material to farms. We hypothesized that the PBDEs concentrations would remain relatively constant throughout the year even though warmer weather could lead to faster degassing and more sunlight could lead to faster photodegradation of the higher-brominated PBDE congeners. Photodegradation might not play an important role on the variability of the PBDE concentrations since they are

attached to particles and the transparency of the wastewater may provide an obstacle to photodegradation.

### **1.3.2 Commercial Farm Soil Survey**

The objectives of this task were to determine the background levels of PBDE congeners in commercial farms in the mid-Atlantic region of the U.S. and to establish if land application of biosolids has an effect on the concentration of PBDEs in the soils. The hypothesis was that levels of PBDEs will increase with more biosolids application due to their incorporation and adsorption to the soil. To achieve the objective of this task, commercial farms of Virginia that have already received biosolids amendments or that will receive in the future were sampled.

## **Chapter 2: Sampling and Analytical Methods**

### ***2.1 Sample Collection***

#### **2.1.1 Biosolids**

Biosolids samples were collected every two months for over two years (July 2005 to March 2008) from a large wastewater treatment plant in the Mid-Atlantic region of the U.S. In this plant, biosolids, after the removal of excess water, receive lime (approximately 15% on a dry weight basis) for stabilization. After the addition of lime,

biosolids are transferred to large size tanks where they are stored until they are loaded on to trucks. These trucks transport the biosolids to farms that receive land application. The samples analyzed for this task were collected from the transfer lines that direct the biosolids to the tanks for storage. Samples for PBDE analysis were obtained using the plant's sampling system and were then transferred to 250mL amber, wide-mouth jars and were kept frozen (-30°C) until processing. Duplicate samples were collected and sent to a contract laboratory where they were analyzed by standard methods for calcium content and total percentage of solids (Appendix A).

### **2.1.2 Commercial Farms**

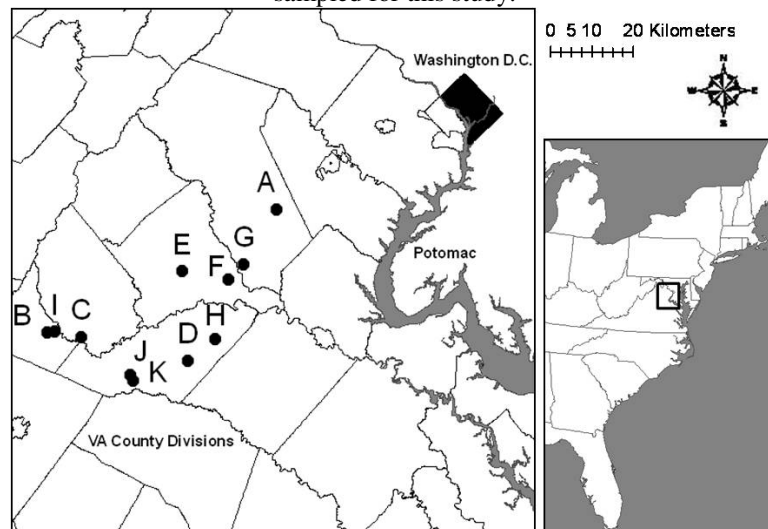
Soil samples were collected between March 30 and April 01 of 2006 from farms in Virginia. A total of 30 fields were targeted for sample collection (Appendix B). As part of the experimental design, three types of sites were selected:

1. 10 sites that had never received biosolids application but will receive application in the next two years
2. 10 sites that had received no more than one biosolids application in the past 3 ½ years
3. 10 sites that have received more than one biosolids application in the past 5 to 10 years

All selected fields, except for two (field 2 of farm A and field 12 of farm H which were planted with corn), were pasture fields for cattle to graze. All the fields have received or will receive biosolids application from the same wastewater treatment plant

where the biosolids samples were collected. Sample collection points were geolocated and recorded using a field GPS instrument (Trimble, Westminster, GeoExplorer Series) (Figure 2.1). The sample collection sites were selected using a spatial relationship according to the size and shape of the field. The spatial analysis was performed using ArcMap (ESRI GIS and Mapping Software, Vienna, VA). All the satellite imagery was obtained from USDA Geospatial Data Gateway.

Figure 2.1 – Map of Virginia counties (black lines) and DC (black square). Location of commercial farms sampled for this study.



Surface soil samples were collected to a depth of approximately 10 cm using a N-2 Handle (Clements Associates Inc. (JMC Soil Samplers), Newton, JMC N-2 Handle PN003) sampler with attached zero-contamination tube (Clements Associates Inc. (JMC Soil Samplers), Newton, PN014) (Figure 2.2, 2.3). Soil samples were a composite of three cores that were each collected in a 30 cm diameter area around the collection site. The number of samples collected per field varied with the size and shape of the field. The zero contamination plastic liners were labeled appropriately and were stored temporally



on ice until they could be transferred to a freezer (-30°C). The soil samples were kept frozen until processing.

Figure 2.2 – N2-Handle sampler used to collect the soil samples in this study.



Figure 2.3 – The zero-contamination plastic tube is inserted in the metal bottom part of the sampler to hold the composite soil samples.



## ***2.2 Analytical Methods***

This section describes the laboratory methods used to analyze the field samples.

### **2.2.1 Target Compounds**

Eight PBDE congeners were selected as target analytes ranging from the tribrominated BDE-28 to the decabrominated BDE-209 (Table 1.2). Some of the compounds are the major components of commercial formulations and others are products of degradation that have been reported in environmental samples (Oros et al., 2005, de Boer et al., 2003, Hassanin et al., 2004, Ikonomou et al., 2002, Knoth et al., 2004, North., 2004).

### **2.2.2 Method Development**

The process of method development included comparisons of extraction and clean-up methods to achieve efficient recovery of the target analytes. Two different extraction methods were tested in this study using sand and soil samples as matrix: accelerated solvent extraction and vortex mixing extraction. Initially, the Accelerated Solvent Extractor 200 (ASE) (Dionex, Sunnyvale, ASE 200) was used with two solvents (dichloromethane (DCM) and hexane) and two solvent mixtures (DCM:Hexane 4:1 and DCM:Hexane 1:1) under typical pressure and temperature parameters (Table 2.1) utilized by other researchers (Oros et al. 2005, Saito et al. 2004). The ASE method did not offer consistent results and the equipment did not work reliably (Appendix C).

Table 2.1 – ASE parameters utilized for tests.

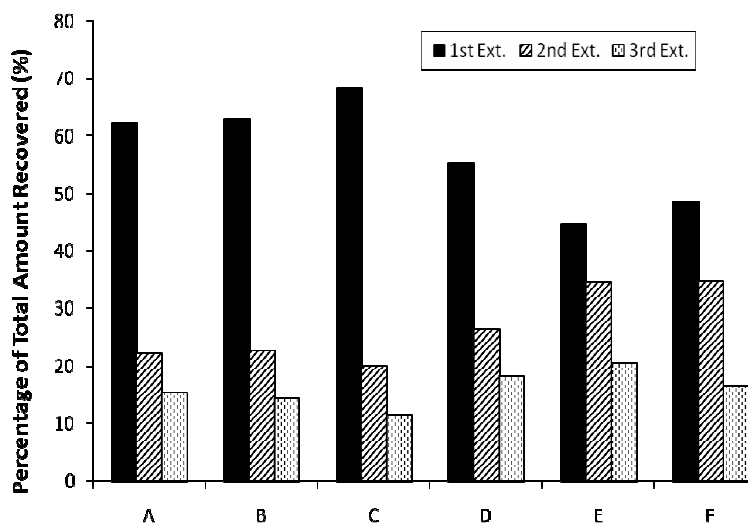
<b>Preheat</b>	0 minutes
<b>Static</b>	5 minutes
<b>Flush</b>	40% volume
<b>Purge</b>	180 seconds
<b>Cycles</b>	3
<b>Pressure</b>	2000 psi
<b>Temperature</b>	125°C

The vortex mixing extraction method extracted a 10g soil (1g biosolids) sample repeatedly with 50mL of solvent at room temperature in a 50mL Teflon centrifuge tube (Nalgene, Rochester, NY). This method is a modified QuEChERS (Quick, Easy, Cheap, Effective and Safe) method (Lehotay, 2005; Anastassiades and Lehotay, 2003), and we tested it for extraction time, number of extractions, and different solvents to optimize for the extraction of PBDEs from soil. For the extraction time experiment, the same sample was divided into three sub-samples that were extracted once with a DCM:Hexane 1:1 mixture for different times: one minute, two minutes, and five minutes. The recovery for the surrogate standard, 2,2',3,3',4,4',5,5',6,6' – decachlorobiphenyl (PCB-209), for the one minute extraction was 50.5%, recovery for the two minutes extraction was 55.5%, and recovery for the five minutes extraction was 56.3%. We determined that two minutes was an adequate extraction time since there was not a significant increase in recovery from two minutes to five minutes.

In another experiment the number of extractions needed was tested by extracting six samples three times with 20mL of DCM and collecting the extracts in separate tubes for analysis. The recoveries for the two first extractions were responsible for at least 70% of the total recovery obtained with three extractions (Figure 2.4), therefore two

extractions were considered optimum for this study. Two extractions of two minutes each using DCM as the solvent were chosen for providing the best recoveries.

Figure 2.4 – Results for the experiment of number of extractions needed for PBDEs in soil with the modified QuEChERS method.

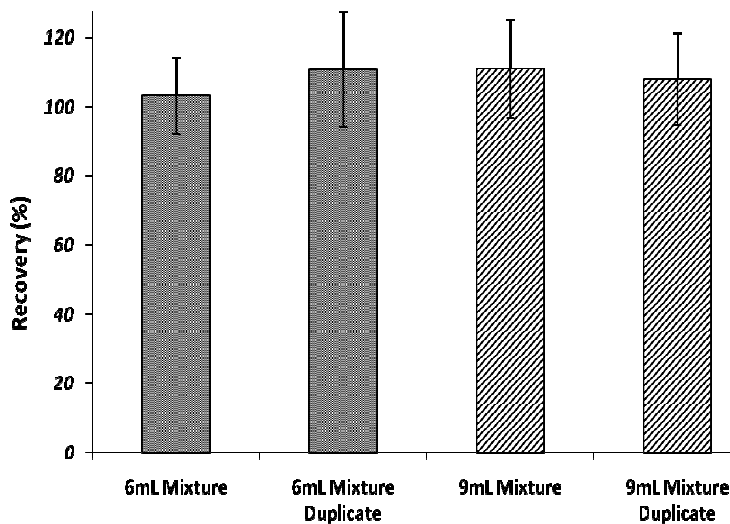


The clean-up procedure development included the comparison between the alumina glass column method and the alumina solid phase extraction (SPE) cartridge method. We also tested two elution solvents (DCM and hexane). The (1cm i.d. x 25cm length) glass columns contained 4g of deactivated alumina with a 1cm layer of anhydrous sodium sulfate on top. The columns were pre-rinsed with 25mL of solvent. The sample was then added to the head of the column and eluted with 35mL of solvent. The SPE cartridges contained 2g of alumina (Superclean LC-Alumina-N , Supelco, Bellefonte, PA). The cartridge was pre-rinsed with 25mL of solvent and eluted with 35mL of solvent. Recoveries from the SPE method ranged from 58% – 81% with hexane and from 77% - 84% with DCM, while recoveries from the glass column method were 54% - 58% and

56% - 63% with hexane and DCM respectively. Therefore, the cartridge method using DCM as solvent was chosen as the clean up method for this study.

Another experiment was completed to optimize the amount of solvent needed for the clean-up procedure. Sand samples spiked with a PBDE mixture were prepared and did not go through the extraction procedure. Half of the samples were cleaned-up with 6mL while the other half was cleaned-up with 9mL of DCM:Hexane 1:4 (by volume) and they were all concentrated to 1mL. The results showed that there was not a significant difference in recoveries using different volumes of solvent when using the mixture of solvent (Figure 2.5). The extraction volume chosen for this study was 6mL.

Figure 2.5 – Recoveries of experiment for different volumes of clean-up solvent. No significant difference was found between the volumes tested. Error bars represent the standard deviation on the recoveries of all BDE congeners analyzed.



### 2.2.2 Sample Processing

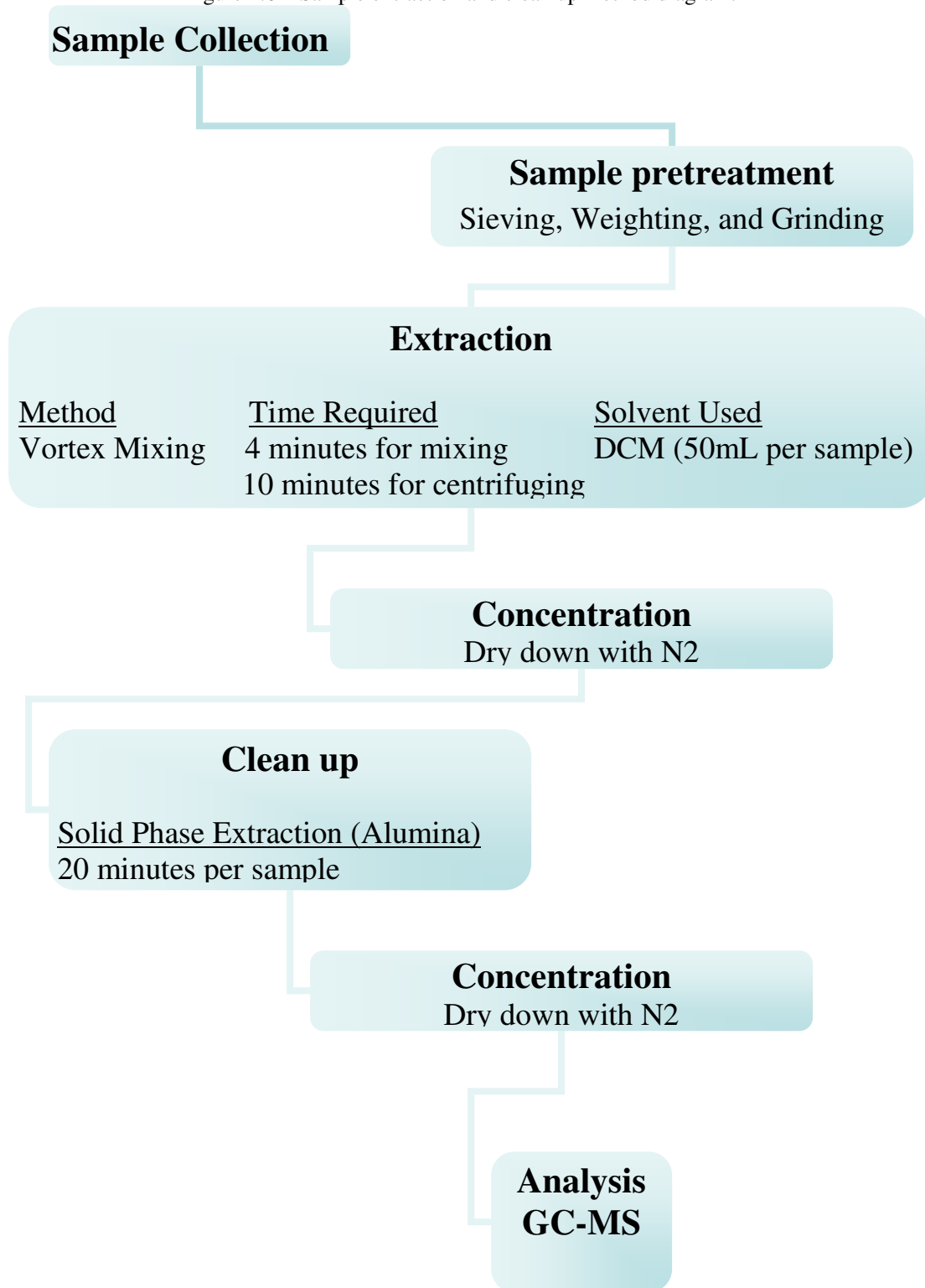
Soil and biosolids samples were kept frozen and in the dark until preparation for extraction. The laboratory lights (overhead and hood) were covered with a light filter that blocks light with wavelengths below 240nm and the windows were kept covered so minimal natural light would come into the lab. Samples were thawed in a refrigerator (4°C) over night and then allowed to reach room temperature. The samples were then sieved to remove grass, rocks, worms, etc (Figure 2.6). Two aliquots were removed from the sample jar. A 5.0 g soil sample (1g for biosolids samples) was pre-weighed, transferred to an aluminum tray, baked at 100 °C for 4 hours, and then re-weighed to determine moisture content. A second 10 g soil aliquot (1g for biosolids samples) was weighed, dried with approximately 30 g of anhydrous sodium sulfate (J.T. Baker, Phillipsburg, NJ). A mortar and pestle was used to grind the sample with the sodium sulfate and make it as homogeneous as possible. We split the dried sample in two approximately equal parts and placed into two 50 mL Teflon centrifuge tubes. Each tube (soil and biosolids) received 15 mL of DCM and 5µL of a 4 ppm solution of PCB 209 that was used as extraction surrogate.

The sample was mixed rapidly with the extraction solvent using a vortex mixer (Fisher Scientific, Fairlawn, NJ) at a speed of 2500 rpm for 2 minutes (Figure 2.6). The samples were centrifuged for 5 minutes at the speed of 5000 rpm, and the solvent was decanted. The samples received an additional 10 mL of DCM, were extracted as before, centrifuged, and the solvent combined with that from the first extraction. The extract was concentrated to a 1mL using a gentle stream of N<sub>2</sub>. The extract was cleaned up using a 2g alumina Superclean N-alumina SPE cartridge (pre-rinsed with 6mL of DCM). The

analytes were eluted with 6mL of DCM and the extract was concentrated to 1mL. The extract was exchanged to hexane and the samples were further concentrated to 500 $\mu$ L. The extracts were quantitatively transferred to 2mL amber glass vials. An internal standard (10 $\mu$ L of a 4-ppm solution) of  $^{13}\text{C}_{12}$  2,2',3,4,4',5' – hexachlorobiphenyl ( $^{13}\text{C}_{12}$  PCB 138) was added to the GC vial.

The carbon content of the soil was determined by a Laboratory Equipment Corporation (LECO) WR-12 Analyzer (St. Joseph, Michigan). The soil sample undergoes pyrolysis and the product of the reaction ( $\text{CO}_2$ ) is measured using a gas chromatograph equipped with a thermal conductivity detector.

Figure 2.6 – Sample extraction and clean up method diagram.

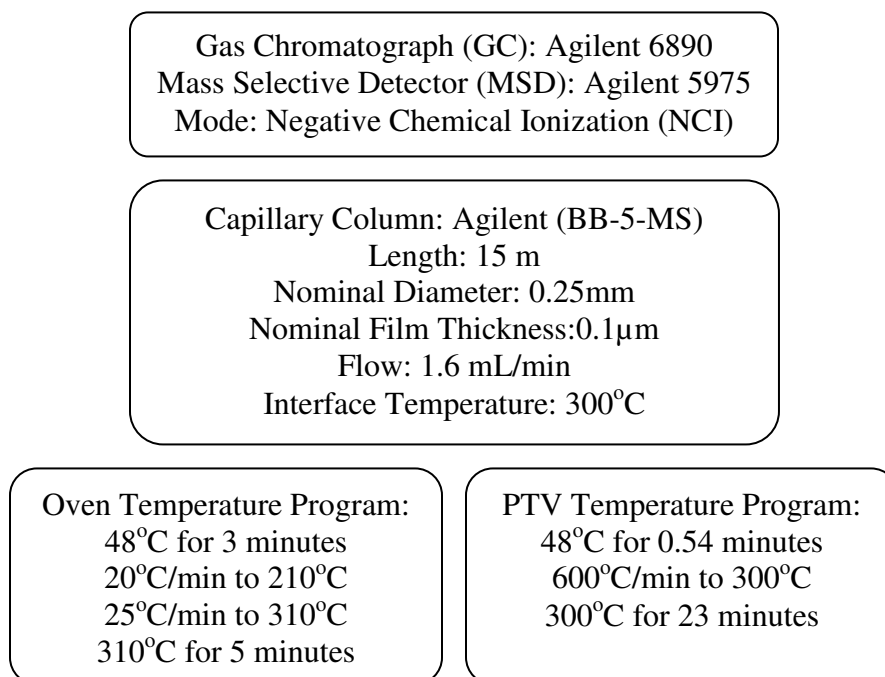




### 2.2.3 GC-MS analysis

Samples extracts were analyzed using an Agilent 6890 gas chromatograph (GC) coupled with an Agilent 5975 mass selective detector (MSD) in negative chemical ionization (NCI) mode (Figure 2.7). An Agilent capillary column (DB-5-MS) had a length of 15m, nominal diameter of 0.25mm, and nominal film thickness of 0.1 $\mu$ m (J&W Scientific, Folsom, CA). This column was preceded by a fused silica capillary deactivated column (5m, 0.25mm i.d.). The carrier gas used was helium with a constant flow of 1.6 mL/min. The oven temperature program was as follows: 48°C for 3 minutes, 20°C/min to 210°C, 25°C/min to 310°C, 310°C for 5 minutes. Extract injection volume was 1 $\mu$ L and the syringe volume was 10 $\mu$ L. A PTV (Programmable Temperature Vaporizing) inlet was used with the following temperature program: 48°C for 0.45 minutes and then ramped at a rate of 600°C/min to 300°C and held for 23 minutes. The GC-MS interface was kept at a temperature of 300°C. Sample concentrations were quantified using the internal standard method and a five point calibration curve. We monitored each compound using at least two ions (Appendix D). We successfully identified the compounds using specific ion proportions with a relative 30% window for error and a 0.1 minute retention time window.

Figure 2.7 – Summary of gas chromatography-mass spectrometry parameters used for PBDE analysis.



## 2.2.4 Quality Control

For each of the farm fields analyzed, we processed, along with the field samples, one blank sand sample (spiked with 10µL of  $^{13}\text{C}_{12}$  BDE 209) and a second sand sample that was spiked with 10µL BDE solution that contained a known amount of the BDE congeners to be analyzed. Also, for each of the farm fields, a random field sample was chosen to receive 10µL of the BDE solution in order to calculate BDE recoveries with the matrix influence accounted for. The blank samples were included to account for any laboratory contamination. Surrogate recoveries were based on the known amount spiked in each sample processed. For example,

$$\text{Recovery (\%)} = \frac{\text{PCB 209 Response (ng)} \times 100\%}{\text{Amount spiked (ng)}}$$

Equation 1

Surrogate recoveries (PCB-209) averaged 72% (n=338). Mean PBDE congener recoveries for sand spikes was  $91 \pm 16\%$ , while the labeled BDE-209 had a mean recovery in sand of  $80 \pm 29\%$ . In soil samples (to account for matrix interference) mean PBDE congener recovery was  $81 \pm 34\%$  and the labeled BDE-209 recoveries were  $107 \pm 46\%$ . Final concentration values were not adjusted for recovery values.

Each farm field had one random sample chosen to be a laboratory duplicate (the same collected sample analyzed twice). During the collection of the samples, 13 out of the 30 fields sampled were randomly chosen to have one field duplicate sample (the same sampling site was sampled twice). Both laboratory and field duplicates had average results with less than 10% difference. The change between duplicates was calculated as follows:

$$\% \text{ Change} = \frac{ABS(c_1 - c_2)}{c_1 + c_2} \times 100\%$$

Equation 2

The instrument detection limit (IDL) is set to 2ppb for all PBDE congeners except for BDE-209, which had the IDL set to 20 ppb for this was the lowest detectable concentration given the parameters used. The method detection limit was calculated using EPA 40 CFR Part 136 Appendix B (Table 2.2 and Table 2.3) and sand as a matrix.

Congener	Soil MDL (µg/kg)
BDE-28	0.57
BDE-47	0.56
BDE-100	0.38
BDE-99	0.50
BDE-154	0.60
BDE-153	0.62
BDE-183	0.50
BDE-209	6.02

Table 2.2 – Soil detection limit.

Congener	Biosolids MDL (µg/kg)
BDE-28	15.33
BDE-47	15.00
BDE-100	10.20
BDE-99	13.42
BDE-154	15.93
BDE-153	16.46
BDE-183	13.28
BDE-209	160.62

Table 2.3 – Biosolids detection limit.

## Chapter 3: Results and Discussion

BDE concentrations were calculated using the GC/MS responses and the dry weight of the samples:

$$c_n = \sum \frac{\text{BDE Response } (\mu\text{g})}{\text{dry weight of sample (kg)}} \quad \text{Equation 3}$$

$$C \left( \frac{\mu\text{g}}{\text{kg d.w.}} \right) = \sum_{n=1}^8 c_n \quad \text{Equation 4}$$

C (Equation 4) is the total BDE soil or biosolids concentration in one sample in  $\mu\text{g/kg d.w.}$ ,  $c_n$  is the concentration of the individual BDEs in each sample, and n is the number of congeners analyzed in each sample (eight congeners were analyzed). The contribution from each of the congener was calculated in percentage following this equation:

$$\text{Contribution } (\%) = \frac{c_n \times 100\%}{C} \quad \text{Equation 5}$$

### 3.1 Biosolids

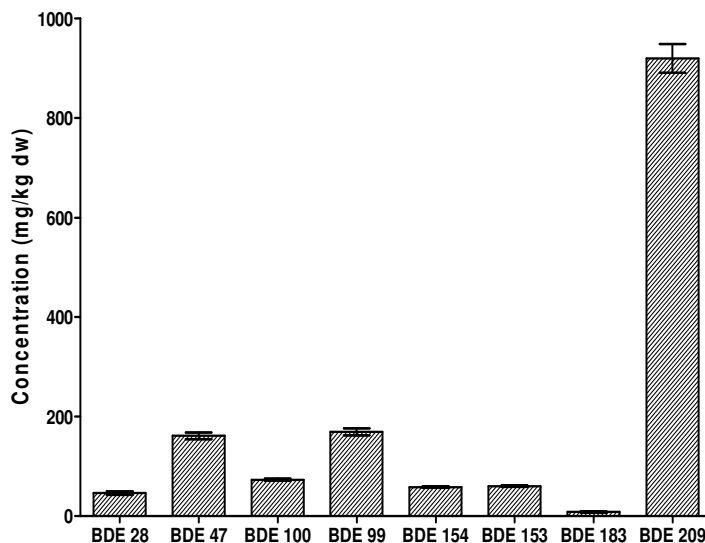
Results show that concentrations of total PBDEs in biosolids from this plant are in the range of 1325-1820  $\mu\text{g/kg d.w.}$  (Table 3.1), with a mean value of  $1496 \pm 158 \mu\text{g/kg d.w.}$  (congener concentration for each of the biosolids samples is available – Appendix E). With the exception of BDE-183 (which was detected in only one sample), all of the

congeners analyzed in this study were present in all of the biosolids samples. BDE-47, BDE-99, and BDE-209 together represent 82-87% of the total concentration; this pattern of congeners in biosolids suggests that the commercial formulations of Penta-BDE and Deca-BDE as PBDE sources to the WWTP (Figure 3.1). An equivalent trend was recently reported by Eljarrat et al., (2008), where sewage sludge samples were collected and analyzed in Spain.

Table 3.1 – Biosolids total (sum of all congeners analyzed in this study) mean concentration according to date when the samples were collected. The values are the average of duplicate samples for each collection date.

<b>Total PBDE Concentration</b>	
<b>Collection Date</b>	<b>(µg/kg d.w.)</b>
July-05	1349
September-05	1725
January-06	1501
March-06	1418
May-06	1524
July-06	1403
September-06	1411
November-06	1372
January-07	1391
March-07	1488
May-07	1740
August-07	1356
October-07	1613
December-07	1325
March-08	1820

Figure 3.1 – Mean congener concentration in biosolids samples. The presence of BDE-47, BDE-99, and BDE-209 in greater amounts than other congeners is a trend seen in many parts of the U.S. and Europe. Errors bars represent standard error.



PBDE concentrations observed in biosolids in this study are similar to those in other published reports in the U.S. Hale et al., (2001a) examined eleven biosolids samples from WWTPs in Virginia, Maryland, New York, and California and concentrations ranged from 1100-2290  $\mu\text{g/kg d.w.}$  for the penta-brominated PBDEs and 85-4890  $\mu\text{g/kg d.w.}$  for the decabrominated BDE congener. PBDEs have also been reported in sewage sludge from Wisconsin (Hale et al., 2003) where means were 507, 706, and 466  $\mu\text{g/kg d.w.}$  for BDE-47, BDE-99, and BDE-209 respectively. In California, reported total PBDEs concentrations from one plant ranged from 0.06 to 1.44  $\mu\text{g/kg d.w.}$ , which is considered low for U.S. biosolids (North, 2004).

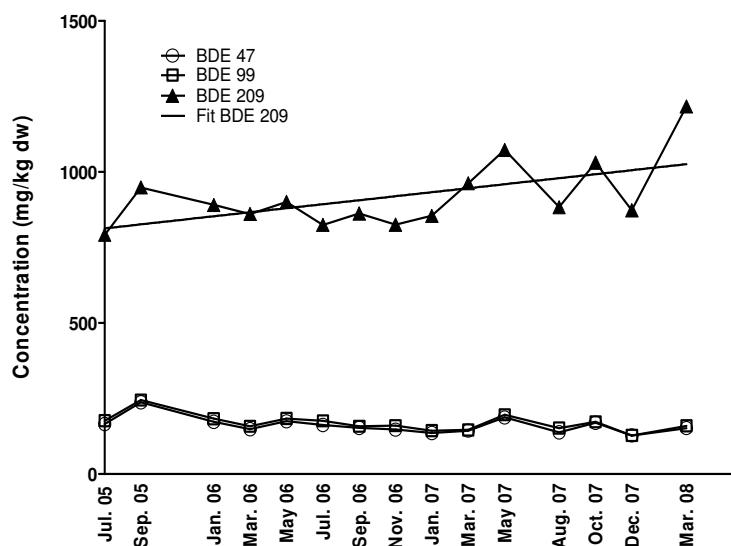
Overall, PBDE concentration in sludge from North America exceeds that reported from European countries. Nylund et al., (1992) investigated sewage sludge as a source of PBDEs to the Baltic Sea and observed the tetra and penta-brominated BDEs at concentrations ranging from 3.4-19  $\mu\text{g/kg d.w.}$  per congener. However, that study only

included a small number of samples. Biosolids samples from 22 WWTPs in Sweden resulted in concentrations from 0.3 to 11 µg/kg w.w. for eight congeners (BDE-47, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, and BDE-209), with BDE 209 having the highest concentrations and BDE 138 having the lowest (Oberg et al. 2002). In Germany, samples were collected and analyzed from 11 wastewater treatment plants (Knoth et al. 2004). The sum of BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183 congeners ranged from 12.5 to 288 µg/kg d.w., and the concentration of BDE-209 ranged from 97.1 to 2217 µg/kg d.w., showing that some places in Europe present similar concentrations as the ones found in North America, especially for BDE-209. In Spain, sewage sludge samples were collected in five WWTPs and concentrations found were between 197 and 1185 µg/kg d.w. and the mean value was established at 572 µg/kg d.w. (Eljarrat, 2008). A more recent study in Kuwait examined sludge samples from three WWTPs and reported mean concentrations ( $\Sigma$ PBDEs) in the range of 5.7-1599 µg/kg d.w. The authors observed a high degree of variability in concentration and also observed a seasonal trend related to temperature effects (Gevao et al., 2008). In Australia, 16 WWTPs were surveyed for PBDEs and the average concentration was 1137 µg/kg, matching U.S. levels (Clarke et al., 2008). The same study included samples from 2005 and 2006 to analyze for seasonal variations, but samples presented differences only between WWTPs and no temporal trend was detected.

For our study, over the collection period, an increase in BDE-209 of approximately 26% was detected ( $r^2=0.34$ ) (Figure 3.2), indicating a possible increase in source strength in the wastewater influent during the study period from mid-2005 to early-2008. This result may reflect increased usage of the deca-BDE formulation in

consumer products; however, only limited information on usage in the U.S. is available. A slight decrease of 24% and 26% in concentration was observed for BDE-47 ( $r^2=0.26$ ) and BDE-99 ( $r^2=0.31$ ) respectively (Figure 3.2), indicating essentially no change in load to the wastewater stream during the study period despite the phase-out of penta-BDE production in the U.S. This result indicates that many products treated with the penta-BDE formulation are still in use. In addition to the regression, a Mann-Kendall test was performed on the data for BDE-209 and the test result suggest that the hypothesis of no trend is rejected. There is a downward trend (BDE-209 concentration is decreasing with time) at the 95% confidence level ( $Z=-1.781$ ).

Figure 3.2 – Temporal trend observed for congeners BDE-47, BDE-99, and BDE-209 in biosolids samples. A slight increase in concentration over time was observed for BDE-209 ( $r^2=0.34$ ), while BDE-47 ( $r^2=0.26$ ) and BDE-99 ( $r^2=0.31$ ) both presented a slight decrease in concentration over time.

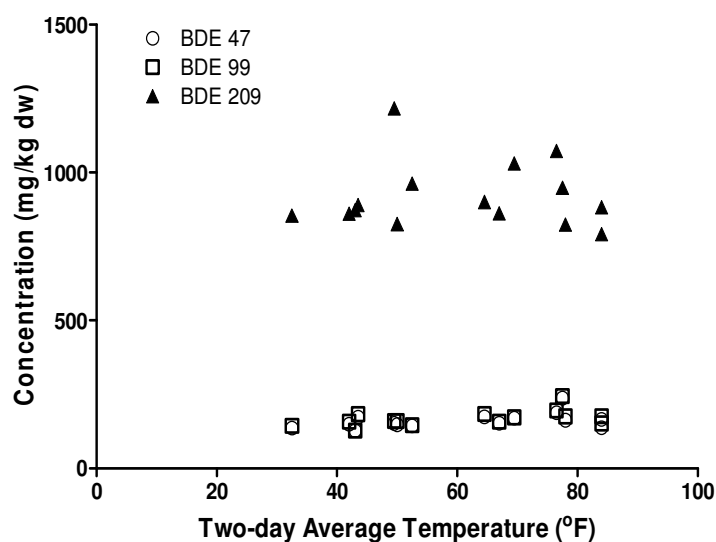


The effect of ambient temperature changes on PBDE concentrations in biosolids was examined for the 32-month sample period. Theoretically, increased temperatures could result in lower concentrations in biosolids. A higher temperature would facilitate



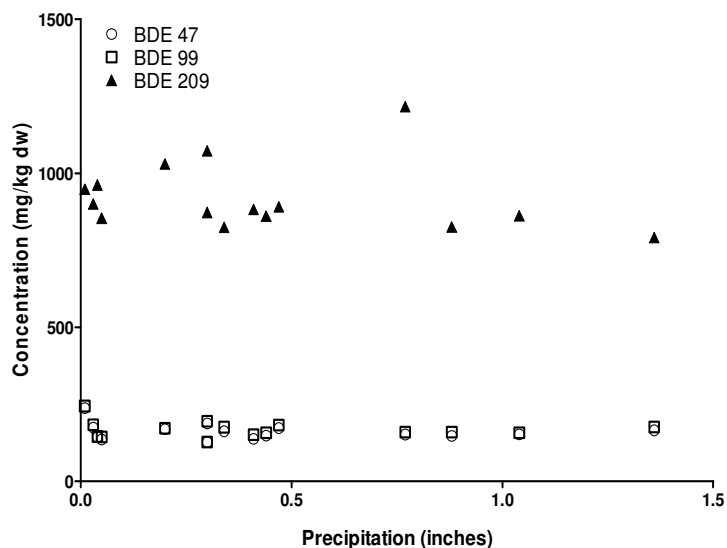
the solubility of these chemicals and they would then be available to transit from the water to the air. PBDE congener concentrations were compared with local ambient temperature data (two-day mean values) for the day of collection and the previous day (Ronald Reagan Washington National Airport – National Oceanic and Atmospheric Administration (NOAA)). No relationship was observed between temperature and concentrations of BDE-209 in biosolids samples ( $r^2=2.6 \times 10^{-4}$ ). BDE-183 was present in only one sample, therefore this analysis was not performed for this congener. Other congeners presented no significant correlation between temperature and concentrations (Figure 3.3). Since wastewater and biosolids are rich in organic matter, PBDEs will strongly adhere to the particle-phase independent of temperature during the wastewater treatment due to their hydrophobicity (estimated  $\log K_{ow}=10.33$  (Braekevelt et al., 2003)).

Figure 3.3 – Temperature effect on the concentration of BDE-47 and BDE-99 in biosolids.



Another factor which may influence PBDE concentration is rainfall. Rainfall may influence the solids load to the WWTP and therefore the source strength of PBDEs. Total precipitation received during the week prior to sample collection was compared with PBDE congener concentration (NOAA). However, PBDE congeners were present at similar levels under both dry and wet conditions (Figure 3.4). Concentration measurements do not provide any information on total loads to the WWTP. A careful examination of flows through the plant before, during, and after large storms would be required to determine the effect of precipitation events on PBDE loads. Higher levels of precipitation could bring more PBDEs to the WWTP or just dilute the PBDEs present in the wastewater, but the results do not indicate any relationship between concentration in biosolids and precipitation. Usage patterns of commercial BDE formulations and the hydrophobicity of the PBDE congeners appear to be the most important factors governing observed concentrations in biosolids. Additional analysis of meteorological conditions, storm flows, and process management factors is required to establish any other important governing factors.

Figure 3.4 – Precipitation effect on the concentration of PBDEs in biosolids. Levels of precipitation do not influence the variability of concentration considerably.



## 3.2 Soil

Concentrations observed in soil samples ( $\Sigma$  of all congeners analyzed in this study) ranged from below quantization limit (BQL) to 386  $\mu\text{g/kg d.w.}$  Average concentration in surface soil collected from fields that had not received biosolids was 6.8  $\mu\text{g/kg d.w.}$  and the range varied from BQL (in 75% of the samples all congeners were BQL) to 37  $\mu\text{g/kg d.w.}$  (Appendix F). Fields with a single application had an average concentration of 18  $\mu\text{g/kg d.w.}$  and levels that ranged between BQL (in 19% of the samples all congeners were BQL) and 69  $\mu\text{g/kg d.w.}$  (Appendix G), and fields with multiple applications had an average of 52  $\mu\text{g/kg d.w.}$  and a range of BQL - 386  $\mu\text{g/kg d.w.}$  (in one sample all congeners were BQL) (Appendix H). The dominant congeners found in agricultural soils were BDE-47, BDE-99, and BDE-209, as was found in the biosolids. In calculating mean concentration values, results identified as BQL, were substituted with a value of 0.5 MDL for each congener. Therefore, the mean

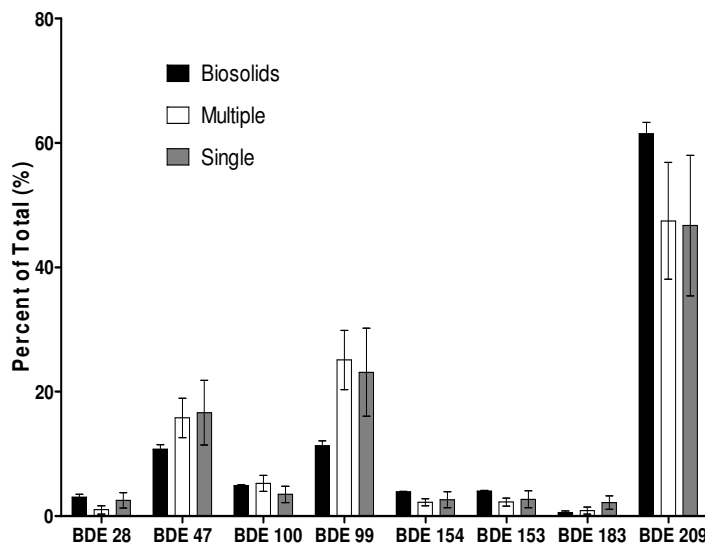
concentration value for the zero application fields may be higher than the actual mean due to the substitution of the 0.5 MDL values for congeners which were BQL.

A recent study analyzed soil samples from fields that have received biosolids application (Eljarrat et al., 2008). The samples were collected in Spain and the levels of PBDEs varied from 21 to 690  $\mu\text{g/kg d.w.}$  Eljarrat et al. (2008) concluded that soil amended by sewage sludge will contain higher PBDE concentrations, which is similar to what we found in this study. Their study presented concentrations in the same order of magnitude as ours. A study (Hassanin et al. 2004) completed in United Kingdom and Norway analyzed soil samples and found maximum concentrations of 12  $\mu\text{g/kg d.w.}$  ( $\Sigma$  all PBDEs congeners analyzed: 17, 28, 32, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 166, 181, 183, and 190). It is important to notice that these samples were collected in remote areas representing background soil concentrations (BDE-209 was not analyzed for and therefore total concentrations could be higher given that BDE-209 is usually present at higher concentrations). The same study also concluded that the congener distribution found matched that of the penta-BDE commercial mixture and that the higher brominated congeners were retained by the soil more easily and more efficiently than the lower brominated compounds, which could be due to their hydrophobicity. Hale et al. (2002) reported a concentration of (sum of BDE-47, BDE-99, and BDE-100) 76  $\mu\text{g/kg d.w.}$  from a soil near a foam production facility in the U.S. Mid-Atlantic region. This value is comparable to the mean value found by our study in soils that receive multiple biosolids application. The same group also analyzed two other soil samples downwind from the same facility and they found BDE-47, BDE-99, and BDE-100 in one of the samples in the amount of 13.6  $\mu\text{g/kg d.w.}$  (Hale et al. 2002), which

indicates the possibility of short range transport. Wang et al. (2005) analyzed soil and sediment samples collected in the surrounding area of an electronic waste disposal and recycling facility in China. The highest concentration found was 824  $\mu\text{g/kg d.w.}$  for hepta-BDE in one type of soil, but penta-BDE was responsible for the highest consistent concentration in the two types of soil and sediment. Wang's study represents a worst case scenario, where the soils received daily PBDE loads.

The congener distribution was plotted for biosolids, fields with multiple application and fields with single application (Figure 3.5). Zero application fields had mostly concentrations BQL; therefore they were left out of this analysis. The congener pattern observed in the soils which received biosolids is very similar to that of the biosolids. BDE-209 constituted the major component of all the fields and the biosolids analyzed. Biosolids and fields receiving biosolids generally contained approximately equal amounts of BDE-47 and -99, and these two congeners made up approximately 40 to 50% of the total concentration.

Figure 3.5 – The congener pattern in biosolids, fields with multiple biosolids application and fields with a single biosolids application. Error bars are standard error for biosolids (n=30), multiple application fields (n=69), and single application fields(n=68).



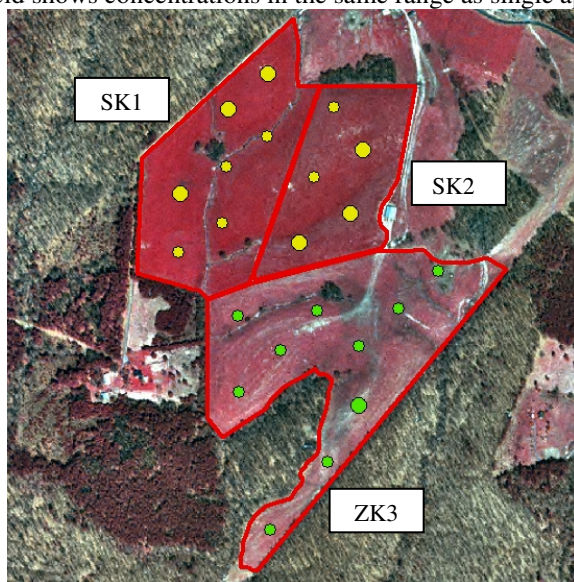
The prevalence of BDE-209 in all the samples may be because deca-BDE is the only commercial formula being used in the U.S. However, biosolids applications for some of these fields occurred well before the removal of penta-BDE from the market, and the penta-BDE congeners (47 and 99) are also prevalent in the soils receiving biosolids. Although BDE-209 undergoes photo- and bio-degradation under laboratory conditions (Ahn et al, 2006; Bezares-Cruz et al, 2004; Fang et al, 2008; Gerecke et al, 2005), the extreme hydrophobicity of this compound is likely to keep this chemical immobilized in organic matter for years. The presence of BDE-209 in soils with no biosolids applications (three of the zero application fields had quantifiable concentrations of BDE-209) indicates another source of this very non-volatile chemical (estimated vapor pressure –  $\log P = -8.4$  – (Hui-Ying et al., 2007)).

Sample collection locations were recorded with a GPS unit and observed concentrations were plotted on satellite images of the fields using ArcMap (ESRI GIS

and Mapping Software, Vienna, VA). Mapping of concentration values was used to assist in interpreting results from a spatial perspective. In the maps showed in this paper, the zero application fields are represented with green dots, the single application fields are represented with yellow dots, and the multiple application fields are represented with red dots. Each dot on the map represents a single sample (duplicates were collected in 13 of the 30 fields sampled) and the sizes of the dots are proportional to the concentration observed in that soil sample.

In zero application fields, concentration results were typically BQL with only three of the 10 fields sampled with any congeners above BQL. Examination of concentration and congener pattern data suggests that field ZK3 did receive a biosolids application despite official records (the congener pattern for field ZK3 matches the observed pattern in biosolids). Field ZK3 borders two fields that received a single biosolids application: SK1 and SK2 (Figure 3.6). The total concentration of PBDEs in field ZK3 was 12 µg/kg d.w., matching the concentration found in field SK1 (12.6 µg/kg d.w.), while the mean concentration in field SK2 was slightly higher at 20.1 µg/kg d.w. This proximity of pattern and total concentration indicates either a recording error where the field did receive biosolids, or there are other means of transport influencing the concentration on this field.

Figure 3.6 – A zero application field that does not show same concentrations as the same type fields. Instead, this field shows concentrations in the same range as single application fields.



### 3.2.1 Effect of Required Biosolids Application Buffer Zones

The multiple application fields MH6C and MH5C have much larger PBDE concentrations than the zero application fields in the same area (Figure 3.7). However, lower concentrations were found at two locations in field MH5C. These two sampling points were near low lying areas or waterways and were probably inside a required buffer zone. The spatial visualization of concentrations for single and zero application fields is clear in Figure 3.8. Fields SI2 and SI4 exhibit concentrations typical for a single biosolids application, and field ZI6 is typical for fields with zero applications. However, concentrations observed in the single application Field SI5 appear to be much lower than expected.



Figure 3.7 – Multiple application fields and zero application fields.

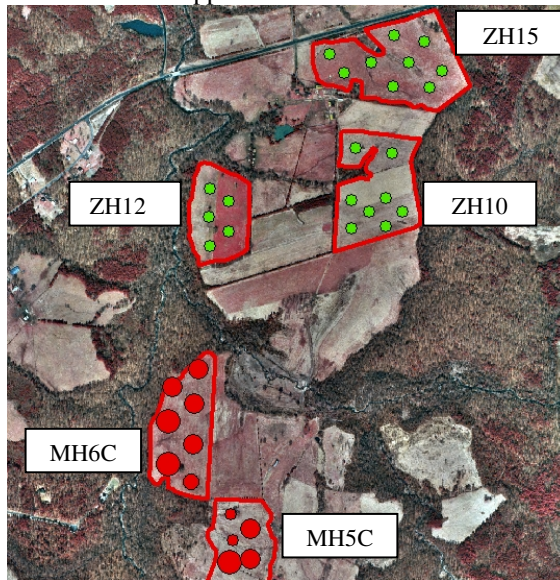
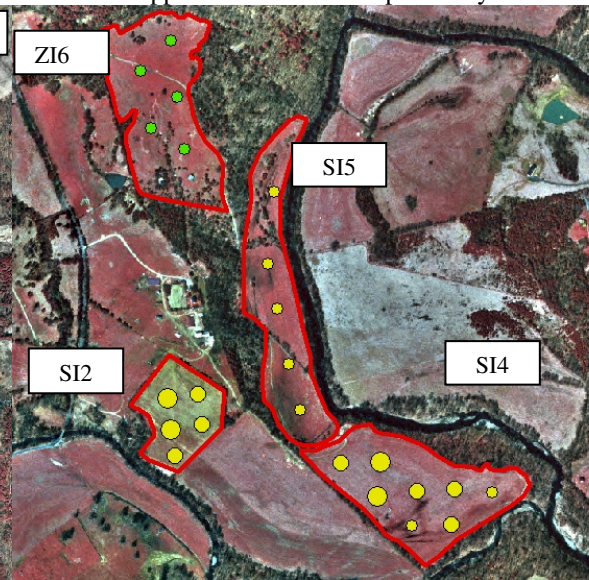


Figure 3.8 – Single application fields compared to a zero application field in the proximity.



In Virginia, buffer zones for biosolids application are well defined (HJR 118/SJR 117: Commission on the Future of Virginia's Environment). For occupied dwellings, a minimum distance of 61 m to the application area must be respected. For surface application, with no form of incorporation, the application area should be 30.5 m away from any water supply wells and springs, 15 m away from perennial streams and other surface waters except intermittent streams, 7.6 m away from intermittent streams/drainage ditches, and 3 m away from agricultural drainage ditches with slopes equal to or less than 2.0%. The information received from the applicator on Field SI5 (Figure 3.8) was that this field received a single application of biosolids. It is questionable if this information is reliable since the field is very narrow and even had ditches running through the middle of the field. The concentrations found in this field were equivalent to the zero application fields (all BQL). More examples of lower concentrations found near waterways were found in field MD2 (Figure 3.9) where 86%

lower concentrations were found at one point (top right of the field) near a waterway and also 94% lower concentration than the bordering field. Field MG1E (Figure 3.10) has a stream running along the border of the field. This could be one of the reasons why field MG1E has 84% lower concentrations than the adjacent field MG1B.

Figure 3.9 – Field MD2 has a similar concentration profile as field MD1 but one point near a tree buffer has much lower concentration than the other points in the field.

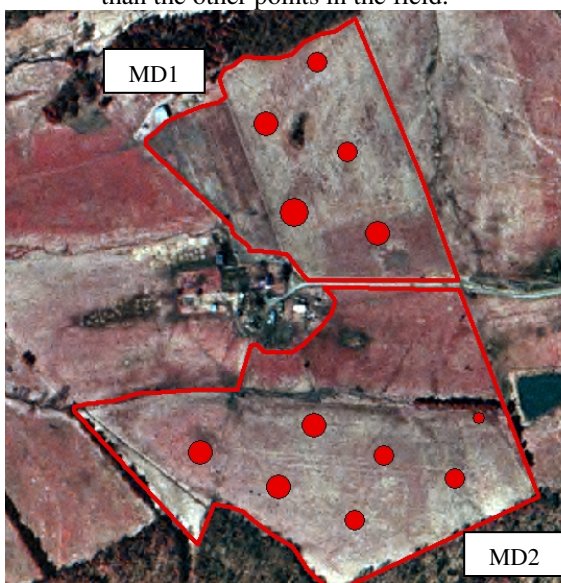
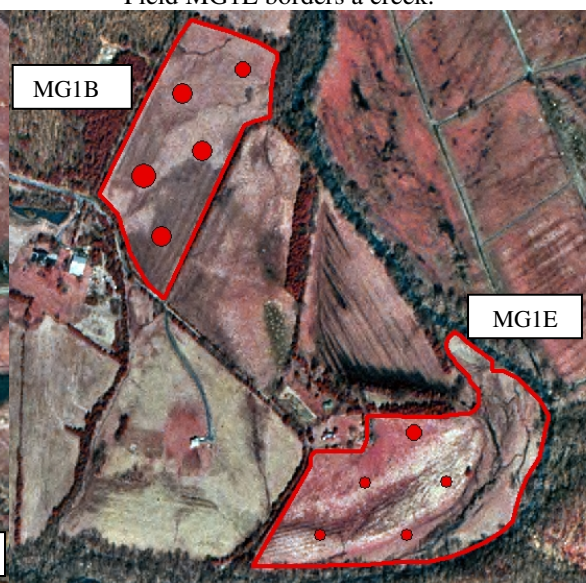


Figure 3.10 – Two multiple application fields. Field MG1E borders a creek.



### 3.2.2 Effect of Application Rate

The hydrophobic nature ((estimated log Kow range: 4-10 (Braekevelt et al., 2003)) of PBDEs indicates they will have a strong affinity for soil organic carbon, and from this it can be inferred that PBDEs will be persistent in soils with moderate or high organic carbon content. If PBDEs are relatively persistent, then fields receiving multiple biosolids applications will have higher soil concentrations overall than those with a single application. Mean total PBDE concentrations for single and multiple application field

groups were compared using an unpaired t test with 95% of confidence level. This analysis revealed that concentrations in the multiple application group were significantly higher than those in the single application group ( $p=0.012$ ) (Figure 3.11). The zero application group results were not considered in comparison with the other groups since so many of the concentrations were BQL. If BDE-209 is excluded from the total concentration value, the unpaired t test performed also shows that the averages are different for fields with multiple applications and fields with a single application ( $p=0.017$ ).

A weak relationship ( $r^2=0.23$ ) between application rate and concentrations was observed for fields with a single biosolids application (Figure 3.12), while a slightly stronger relationship was observed ( $r^2=0.38$ ) for fields that received multiple biosolids application (Figure 3.13).

Figure 3.11 – Mean and standard deviation of concentrations for fields that have received different numbers of biosolids treatments (n=68 for single and n=69 for multiple). Average value for the multiple applications fields is significantly different from the single application fields ( $p=0.012$ ).

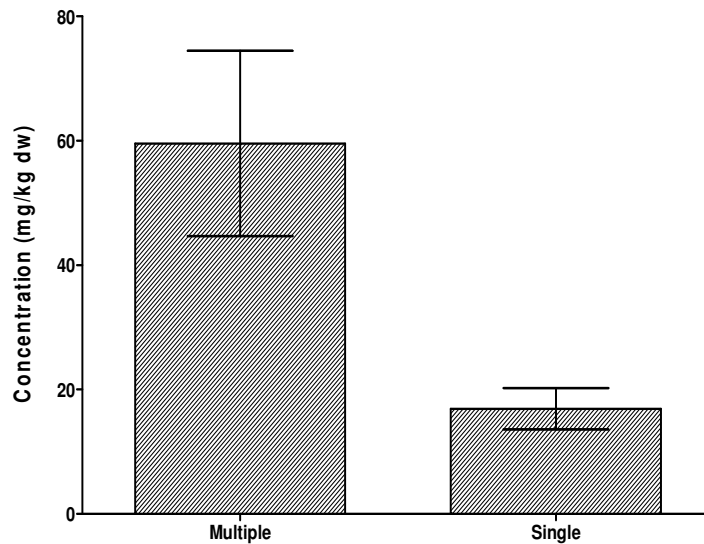


Figure 3.12 – Relationship between observed concentrations and application rate for fields that received a single biosolids application ( $r^2=0.23$ ). A statistical Spearman correlation test was performed and the results indicate that this correlation is significant ( $p=0.049$ ).

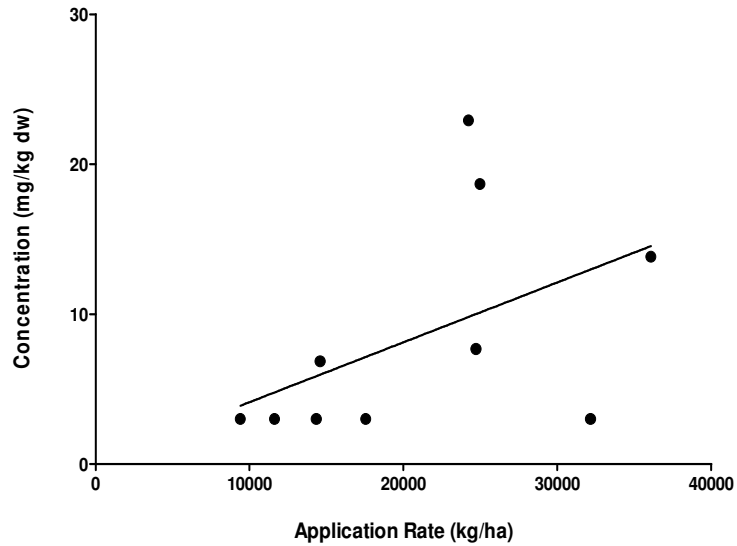
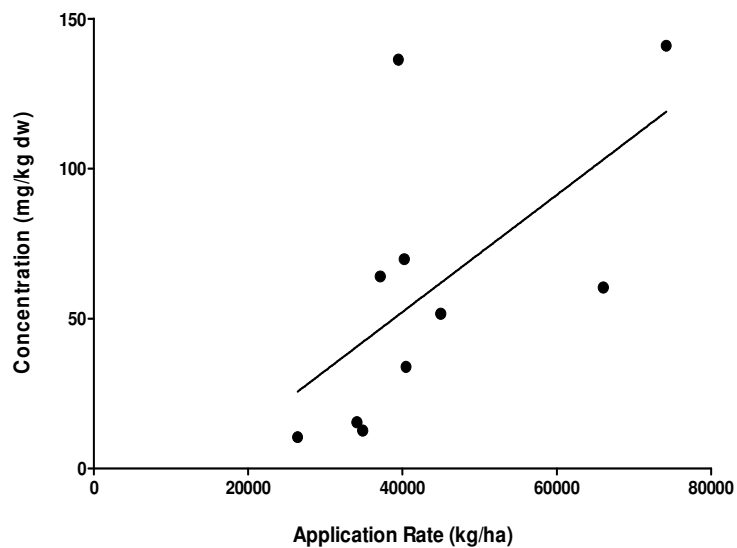


Figure 3.13 – Relationship between observed concentrations and application rate for fields with multiple application of biosolids ( $r^2=0.38$ ). A statistical Spearman correlation test was performed and the results indicate that this correlation is not significant ( $p=0.105$ ).



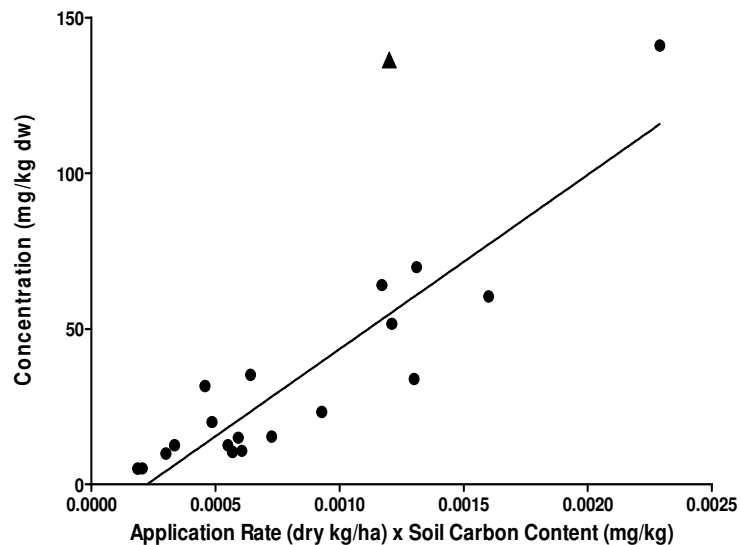
### 3.2.3 Effect of Soil Carbon Content

After initial examination of the soil concentration data and considering the chemical and physical properties of PBDEs, a second hypothesis was developed: the concentration of PBDEs in soils receiving biosolids applications can be predicted from the application rate and the carbon content of the soils (ranging from 1.58% to 3.33% carbon). The sum of all application rates received by each field was multiplied by the soil percent carbon and the relationship with the concentration was characterized (Figure 3.14). The relationship exists with application rates and carbon content if analyzed separately but the relationship is stronger when the two variables are multiplied ( $r^2=0.84$ ). The relationship with the application rate (considering all fields) yielded an  $r^2=0.51$ , and the relationship with soil percent carbon yielded an  $r^2=0.43$ . A linear relationship can be distinguished for all of the fields that received biosolids application (whether it was more than one or just a single application) with the exception of one outlier (field MA3) that was removed from the calculations but is shown on Figure 3.14. MA3 may have received a greater application rate of biosolids than was recorded, or the biosolids material applied may have been especially high in PBDE content.

The strong correlation observed indicates that the amount of biosolids applied will have a direct influence on the soils PBDEs concentration, and that the higher the organic content of the soil, the more stable these compounds are going to be in soil. Using this relationship as a tool to further investigate field ZK3, we calculated an application rate value from the observed concentration and soil carbon content. The calculated application rate for field ZK3 was 63% lower than the recorded application rate for the two neighboring fields. Another possibility for abnormal concentrations observed in field

ZK3 could be short-range transport from the fields nearby. It is possible that these fields were fully tilled in the past, and during tillage, a considerable amount of dust ascends in the air. Windblown dust could have carried PBDEs to this specific field, considering its closeness to the other two fields. However, atmospheric processes would likely only transport a fraction of that applied on the other fields.

Figure 3.14 – Relationship between the concentrations of the fields that have received biosolids application with their total application rate multiplied by their carbon content. Point represented by a triangle is the outlier that was removed from the calculations.



Differences in observed PBDE concentrations between fields that one would expect to be similar can illustrate the effect differing soil conditions on the fate of PBDEs. Field SE3 (Figure 3.15) and field SE1 received application of biosolids on the same dates (these fields had both one biosolids application and for an unknown reason received the calculated application rate split between two years). The biosolids application rate multiplied by the soil carbon content gives us an idea of the amount of PBDEs applied and the retention of PBDEs after application. Field SE3 ( $9.3 \times 10^{-4}$



(kg/ha)\*(mg/kg)) had an application rate\*soil carbon value around 50% higher than that for field SE1 ( $6.1 \times 10^{-4}$  (kg/ha)\*(mg/kg)). Field SE3 received a 12% larger application rate and it has a 36% higher carbon content, which partly explains the higher observed concentration for this field. Along the same line of thought, field MA3 (Figure 3.16) received a similar application rate as field MA2. However, MA3 received its last application in the year 2005 while MA2 received its last application in 2002. Also, the carbon content of field MA3 ( $3.0 \times 10^{-8}$  mg/kg) is about twice the value for field MA2 ( $1.6 \times 10^{-8}$  mg/kg). The higher organic matter of field MA3 could increase the persistence of PBDEs in this field. The soil samples from all fields were collected in 2006, only one year after the last application in MA3; thereby limiting the time for PBDE degradation to occur.

Figure 3.15 – Two single application fields with similar application year but with different soil percent carbon (SE3 had the higher value of soil percent carbon) and application rate.

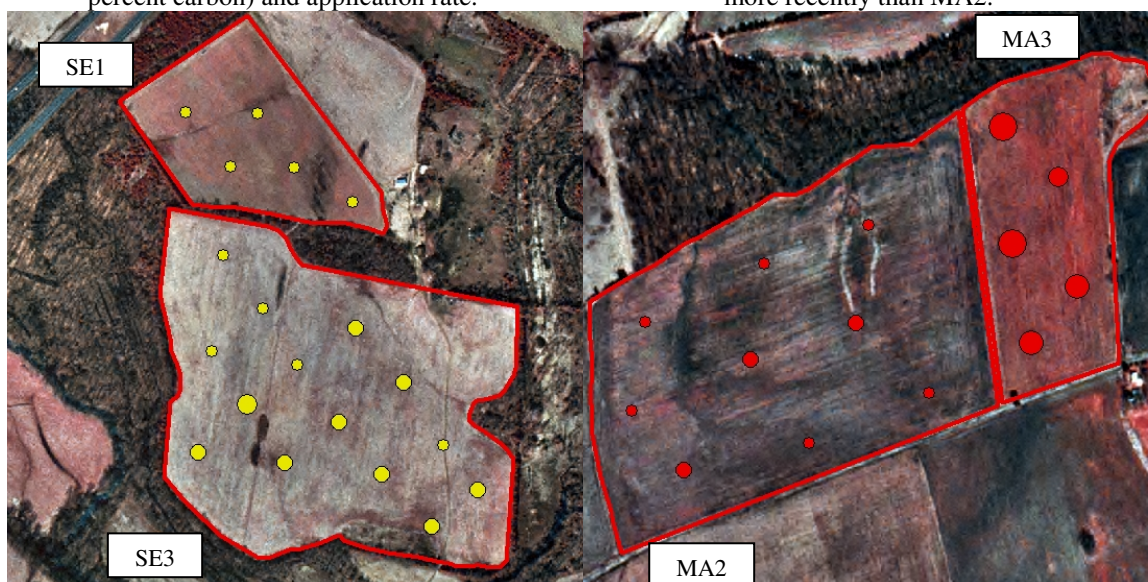
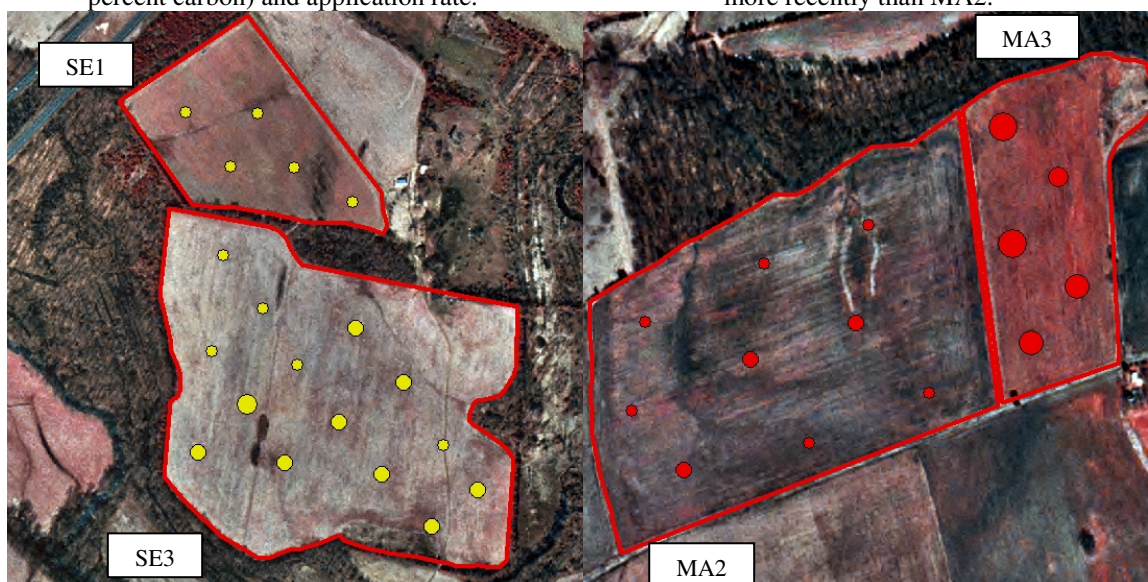


Figure 3.16 – Two multiple application fields with similar application rate. MA3 had a higher soil percent carbon and received the last application more recently than MA2.



### 3.2.4 Estimation Exercise

Our analysis so far indicates that the main factor controlling the concentrations of BDEs in soils is the load of biosolids received. While the concentrations of PBDEs measured in biosolids in this study cannot be assumed identical to those applied to the agricultural fields sampled, these results are useful in establishing an estimated PBDE load in order to examine the persistence of PBDEs in soils. To develop a prediction tool for PBDE concentration in soils, we developed a simple equation that will give a rough estimate of concentration if some aspects of the soil are known. This equation assumes no degradation after application.

$$\text{Predicted Concentration} \left( \frac{\text{mg}}{\text{kg}} \text{ d.w.} \right) = \frac{[\text{PBDE}] \times \text{Application Rate} \times \text{Area}}{\text{Soil Volume} \times \rho}$$

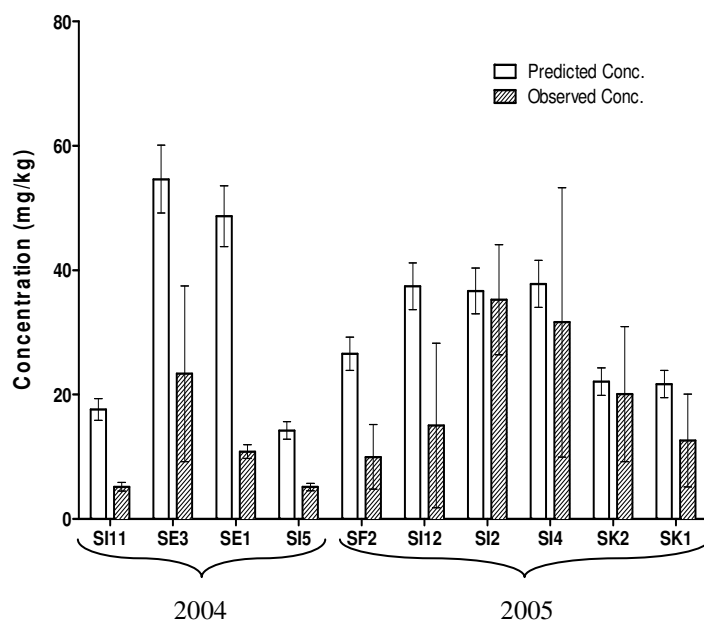
Equation 6

We have made some assumptions in order to perform calculations: 1) mean concentration of PBDEs in biosolids was  $1500 \pm 150 \mu\text{g/kg d.w.}$ , 2) average soil density of  $\rho = 1.3 \text{ g/cm}^3$ , and 3) incorporation depth of 7.6 cm for each field. The incorporation depth of 7.6 cm was chosen to mimic the no till practice (disking of the field occurs even with a no till method) that we observed in all of the single application fields where samples were collected. With these assumptions and the data we collected from the fields that have received a single biosolids application, we calculated what the predicted concentration of PBDEs if the biosolids was the only source.



The general trend observed is that the predicted concentration was larger than the observed concentration (Figure 3.17). Each bar of the plot represents the mean concentration (predicted or observed) with lower and upper limits (error bars). Lower and upper limits for the observed concentrations were calculated using the standard deviation obtained when calculating the mean PBDE concentration in each field. For predicted concentrations, the lower and upper limits were calculated using the standard deviation obtained when calculating the mean PBDE concentration in biosolids. The results of this exercise suggest that there is some disappearance of PBDEs. This disappearance could be due to degradation or volatilization, but also due to variations in application rate and/or source of PBDEs, and management of the field after biosolids application. In Figure 3.17, the fields are ordered by date of application, from the oldest to the more recent ones. The range of application dates for these fields was relatively narrow; fields SI11, SE3, SE1, and SI5 received application in 2004 and the rest of the fields received biosolids in 2005. Two of the fields (SE3 and SE1) received a high application rate that was spread out between 2003 and 2004. The large difference between the predicted and observed concentrations in fields receiving biosolids in 2004 suggests PBDE concentrations are being reduced over time by biotic or abiotic processes.

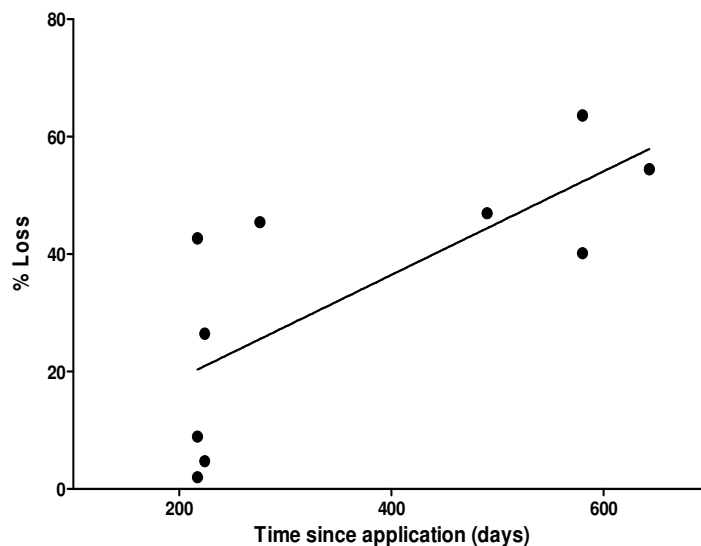
Figure 3.17 – Predicted concentration of PBDEs for fields that have received a single biosolids application compared to the observed concentrations. Lower and upper limit concentrations were plotted on each bar. For predicted concentrations, the lower and upper limits vary according the standard deviation of the average concentration of biosolids used. For observed concentrations, the lower and upper limits were calculated using the standard deviation for soil concentration for each of the fields. First four fields on the x-axis received application in 2004 and all other fields received application in 2005.



As our results suggest that some dissipation/degradation may be taking place, we evaluated the percent loss observed from the predicted concentration to the observed concentration as a function of time (number of days from the application date to collection date) (Figure 3.18). This analysis was performed only for the single application field, since they received biosolids from the same WWTP. The estimated half life for total PBDEs is 553 days, which indicates that PBDEs have a high level of persistence. More controlled experiments, which would include repeated soil sampling of a field, repeated sampling of fields with different types of soil, and incorporation of biodegradation and photodegradation studies, is needed to better

estimate the half life of these chemicals and to better understand their disappearance in the soil environment.

Figure 3.18 – Estimation of degradation rate for fields with a single application of biosolids ( $r^2=0.54$ ).



### 3.3 Conclusions

PBDEs were found in both biosolids and soils from the Mid-Atlantic region of the U.S. The mean value for the total PBDE concentration in biosolids samples was  $1496 \pm 158 \mu\text{g/kg d.w.}$ , which is similar to that found in other parts of the U.S. as well as Europe, even though Europe shows some concentrations that are one order of magnitude lower. Our results also suggest that PBDE concentrations in biosolids from the sampled WWTP did not vary a great deal although a trend was detected for BDE-209 (concentration decreasing with time). This work suggests that PBDEs are relatively persistent in agricultural soils and that one can observe a cumulative effect with multiple applications of biosolids. Our analysis also suggests that while biosolids

should be considered an important source for PBDE in agricultural soils, they are not the only source. This work also generates many questions with respect to the bioavailability of soil PBDEs. For example, PBDE exposure to soil-dwelling organisms such as earthworms could lead to bioaccumulation by species higher in the food chain such as birds. Also, many farms are used to grow pasture, hay, corn, soy beans, etc, and questions remain whether soil PBDEs are available for plant uptake. Evidence of disappearance was also found in this study and will be investigated in more depth. Further controlled experiments examining PBDE fate in soils are needed to more accurately predict the half-lives of specific PBDE congeners.

## Appendices

APPENDIX A – Moisture content, standard calcium content and total percentage of solids in biosolids samples from Mid-Atlantic WWTP.

<b>Sample Name</b>	<b>Moisture (%)</b>	<b>% Solids</b>
Limed A 7/20/2005	64.0	NA
Limed B 7/20/2005	64.0	NA
Limed A 9/19/2005	69.6	18.6
Limed B 9/19/2005	69.6	18.6
Limed A 1/5/2006	68.2	28.0
Limed B 1/5/2006	68.2	28.0
Limed A 03/06/2006	68.5	26.7
Limed B 03/06/2006	68.5	26.7
Limed A 05/25/2006	68.8	27.0
Limed B 05/25/2006	68.8	27.0
Limed A 07/25/2006	65.7	32.4
Limed B 07/25/2006	65.7	32.4
Limed A 09/28/2006	66.2	31.4
Limed B 09/28/2006	66.2	31.4
Limed A 11/28/2006	66.6	29.9
Limed B 11/28/2006	66.6	29.9
Limed A 01/29/2007	66.5	28.9
Limed B 01/29/2007	66.5	28.9
Limed A 03/30/2007	67.2	29.7
Limed B 03/30/2007	67.2	29.7
Limed A 05/30/2007	71.2	30.0
Limed B 05/30/2007	71.2	30.0
Limed A 08/10/2007	63.9	34.5
Limed B 08/10/2007	63.9	34.5
Limed A 10/02/2007	65.9	39.0
Limed B 10/02/2007	65.9	39.0
Limed A 12/03/2007	64.9	31.2
Limed B 12/03/2007	64.9	31.2
Limed A 03/13/2008	74.2	26.8
Limed B 03/13/2008	74.2	26.8

APPENDIX B – Fields, soil characteristics, samples collected, application of biosolids.

<b>Field Code</b>	<b>Area (acre)</b>	<b>Soil type</b>	<b>Carbon %</b>	<b># of samples</b>	<b>Collection Date</b>
MA2	27.7	loam	1.58	9	3/20/2006
MA3	9.6	loam	3.04	5	3/20/2006
MA10	30.1	loam	2.13	10	3/20/2006
MD1	27.7	loam	3.09	5	3/22/2006
MD2	15.5	loam	2.42	7	3/22/2006
MG2	22.3	silt loam	3.21	7	3/24/2006
MG1E	16.7	silt loam	2.15	5	3/24/2006
MG1B	12.1	silt loam	3.16	5	3/24/2006
MH6C	21.4	loam	3.26	7	3/24/2006
MH5C	34.7	loam	2.7	5	3/24/2006
SE3	46.5	loam	2.57	14	3/23/2006
SE1	14.9	loam	1.89	5	3/23/2006
SF2	17.5	loam	1.71	6	3/23/2006
SI2	9.2	loam	2.65	5	3/25/2006
SI4	24.6	loam	1.83	8	3/25/2006
SI5	16.7	loam	1.99	5	3/25/2006
SI11	16.2	loam	1.77	5	3/25/2006
SI12	14.6	loam	2.4	5	3/25/2006
SK2	14.5	loam	3.33	5	4/1/2006
SK1	18.1	loam	2.33	7	4/1/2006
ZB5	11.6	silt loam	3.27	6	3/22/2006
ZC8	27.7	loam	2.58	9	3/22/2006
ZC11	31.2	loam	1.82	9	3/22/2006
ZC14	16.4	loam	2.08	5	3/22/2006
ZH10	24.2	loam	2.12	8	3/24/2006
ZH12	15.7	loam	1.83	5	3/24/2006
ZH15	26.1	loam	1.82	9	3/24/2006
ZI6	15.6	loam	3.13	6	3/25/2006
ZJ4	24.2	loam	3.04	9	4/1/2006
ZK3	31.7	loam	2.89	10	4/1/2006

<b>Field Code</b>	<b>Year of Application</b>	<b>App. Rate (dry ton/acre)</b>	<b>Biosolids Source</b>
	05/95, 05/98,		
MA2	10/02	14.09	Limed, Digested liquid
	10/94, 04/99,		Limed, Digested, Limed
MA3	10/05	15.97	liquid
MA10	10/94, 08/99	13.79	Limed, Digested liquid
	08/93, 08/97,		Limed, Two types of
MD1	09/01, 11/05	30.02	digested
	08/93, 08/97,		
MD2	09/01	26.72	Limed, Digested
MG2	08/94, 11/98	16.37	Limed
	10/95, 08/99,		
MG1E	06/02	10.68	Limed, Digested
	10/95, 08/99,		Limed, Two types of
MG1B	06/02, 07/05	15.02	digested
	09/92, 12/96,		Limed, Digested, Digested
MH6C	03/01*, 04/02*	16.282	liquid
	08/92, 12/96,		
MH5C	02/01*, 02/02*	18.194	Limed, Digested
SE3	10/03*, 08/04*	14.6	Limed
SE1	10/03*, 08/04*	13.01	Limed
SF2	06/05	7.1	Limed
SI2	08/05	9.8	Limed
SI4	08/05	10.1	Limed
SI5	11/04	3.8	Limed
SI11	06/04	4.7	Limed
SI12	08/05	10	Limed
SK2	08/05	5.9	Limed
SK1	08/05	5.8	Limed
ZB5	NA	NA	NA
ZC8	NA	NA	NA
ZC11	NA	NA	NA
ZC14	NA	NA	NA
ZH10	NA	NA	NA
ZH12	NA	NA	NA
ZH15	NA	NA	NA
ZI6	NA	NA	NA
ZJ4	NA	NA	NA
ZK3	NA	NA	NA

APPENDIX C – Recoveries of surrogate using the ASE extraction method.

<b>Sample</b>	<b>Recovery (%) with hexane</b>	<b>Recovery (%) with DCM:Hexane 4:1</b>
A	86.33	87.9
B	91.58	88.28
C	66.68	59.68
D	64.45	51.1
E	96.83	51
F	15.33	59.28
G	27.05	60.53
H	27.9	57.95
I	73.08	55.75
J	50.85	61.45

APPENDIX D – Ions monitored for chromatographic analysis.

<b>Compound</b>	<b>Ions</b>
BDE-28	79, 81, 161
BDE-47	79, 81, 161
BDE-100	79, 81, 161, 403
BDE-99	79, 81, 161, 405
BDE-154	79, 81, 161, 430
BDE-153	79, 81, 161, 430
BDE-183	161, 483, 561
BDE-209	484, 486
13C12 BDE-209	493, 495, 497
13C12 PCB-138	338, 372
PCB-209	464, 482



APPENDIX E – Congener concentration for each biosolids sample and its duplicate.

<b>Concentrations (µg/kg d.w.)</b>	<b>BDE 28</b>	<b>BDE 47</b>	<b>BDE 100</b>	<b>BDE 99</b>	<b>BDE 154</b>	<b>BDE 153</b>	<b>BDE 183</b>	<b>BDE 209</b>	<b>Total</b>
Limed A									
7/20/05	49.2	169.8	72.7	176.6	56.6	58.8	6.6	827.3	1417.8
Limed B									
7/20/05	7.7	161.2	66.3	176.3	54.7	52.1	6.6	755.8	1280.7
Limed A									
9/19/05	55.6	244.3	93.3	253.4	68.2	71.5	6.6	934.1	1727.1
Limed B									
9/19/05	56.6	231.1	91.8	235.6	67.7	70.9	6.6	962.7	1723.1
Limed A									
1/05/06	51.7	192.8	80.5	200.8	61.7	64.4	6.6	926.3	1584.9
Limed B									
1/05/06	50.3	153.3	71.1	165.0	56.9	59.2	6.6	855.3	1417.7
Limed A									
3/06/06	53.0	145.3	72.2	152.7	58.5	60.3	6.6	859.1	1407.8
Limed B									
3/06/06	52.6	152.1	72.6	163.6	58.8	60.5	6.6	862.1	1429.0
Limed A									
5/25/06	55.4	176.4	79.6	185.5	63.2	65.4	6.6	904.8	1536.9
Limed B									
5/25/06	53.4	172.7	77.0	182.0	60.3	62.8	6.6	896.4	1511.2
Limed A									
7/25/06	46.7	158.2	70.1	173.1	54.4	56.5	6.6	786.5	1352.2
Limed B									
7/25/06	49.4	167.1	73.4	178.4	57.1	59.4	6.6	862.5	1454.0
Limed A									
9/28/06	46.8	148.8	67.5	153.4	53.9	55.1	6.6	834.3	1366.4
Limed B									
9/28/06	50.3	157.0	72.0	162.5	57.3	58.7	6.6	890.4	1454.8
Limed A									
11/28/06	51.9	151.5	72.1	163.4	57.7	59.4	6.6	841.9	1404.5
Limed B									
11/28/06	47.4	143.2	67.7	156.3	53.6	55.1	6.6	809.2	1339.1
Limed A									
1/29/07	48.7	137.3	66.1	144.8	54.1	55.4	57.0	853.0	1416.3
Limed B									
1/29/07	49.2	134.6	66.0	142.9	54.3	55.4	6.6	855.9	1364.9
Limed A									
3/30/07	50.0	145.1	68.2	145.9	55.5	57.2	6.6	933.4	1462.0
Limed B									
3/30/07	49.0	142.0	67.2	146.0	54.5	56.0	6.6	992.2	1513.6
Limed A									
	58.3	184.7	84.5	191.6	66.6	68.7	6.6	1058.9	1720.1

5/30/07									
Limed B									
5/30/07	58.8	190.7	83.0	199.9	66.0	68.5	6.6	1087.0	1760.5
Limed A									
8/10/07	7.7	136.3	64.4	148.9	51.2	52.8	6.6	872.7	1340.6
Limed B									
8/10/07	7.7	139.5	65.2	154.8	51.4	53.0	6.6	893.5	1371.7
Limed A									
10/02/07	48.3	170.1	72.8	173.2	56.1	57.7	6.6	1017.2	1602.1
Limed B									
10/02/07	47.6	169.2	71.1	172.0	55.7	57.1	6.6	1044.6	1623.9
Limed A									
12/03/07	7.7	128.0	61.5	129.2	50.3	51.5	6.6	862.2	1297.0
Limed B									
12/03/07	46.1	127.1	61.2	126.0	50.2	51.1	6.6	883.6	1352.1
Limed A									
03/13/08	64.8	150.1	79.1	161.5	69.5	70.7	6.6	1193.4	1795.8
Limed B									
03/13/08	64.5	154.6	81.0	157.8	69.3	70.1	6.6	1239.8	1843.9

APPENDIX F – No application soil congener concentration.

Concentration (ng/g)									
Sample									
Code	BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BDE 153	BDE 183	BDE 209	Sum
ZH10-1	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH10-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH10-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH10-4	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH10-5	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH10-6	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH10-7	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH10-8	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC14-1	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC14-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC14-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC14-4	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC14-5	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC11-1	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC11-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC11-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC11-4	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC11-	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880

4DP									
ZC11-5	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC11-6	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC11-7	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC11-8	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC11-9	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH15-1	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH15-1DP	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH15-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH15-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH15-4	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH15-5	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH15-6	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH15-7	0.287	0.281	0.191	3.428	0.299	0.309	0.249	3.012	8.056
ZH15-8	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH15-9	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZJ4-1	0.287	0.281	0.191	1.736	0.299	0.309	0.249	3.012	6.364
ZJ4-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZJ4-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	23.942	25.810
ZJ4-3DP	0.287	0.281	0.191	1.664	0.299	0.309	0.249	33.833	37.113
ZJ4-4	0.287	0.281	0.191	0.252	0.299	0.309	0.249	21.651	23.519
ZJ4-5	0.287	0.281	0.191	1.884	0.299	0.309	0.249	3.012	6.512
ZJ4-6	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZJ4-7	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZJ4-8	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZJ4-9	0.287	0.281	0.191	1.717	0.299	0.309	0.249	3.012	6.345
ZH12-1	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH12-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH12-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH12-4	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZH12-5	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZI6-1	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZI6-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZI6-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZI6-4	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZI6-5	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZI6-5DP	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZK3-1	0.287	0.281	0.191	1.508	0.299	0.309	0.249	3.012	6.136
ZK3-2	0.287	2.249	1.163	5.235	0.299	0.309	0.249	3.012	12.804
ZK3-3	0.287	1.975	0.191	4.627	0.299	0.309	0.249	3.012	10.949
ZK3-4	0.287	3.634	1.482	6.896	0.299	0.309	0.249	3.012	16.168
ZK3-5	0.287	2.061	0.191	4.792	0.299	0.309	0.249	3.012	11.199
ZK3-6	0.287	2.987	1.364	5.551	0.299	0.309	0.249	3.012	14.057
ZK3-6DP	0.287	3.244	1.513	6.758	0.299	0.309	0.249	18.914	31.574
ZK3-7	0.287	0.281	0.000	0.252	0.299	0.309	0.249	3.012	4.688

ZK3-8	0.287	1.773	0.191	3.979	0.299	0.309	0.249	3.012	10.099
ZK3-9	0.287	0.281	0.191	2.629	0.299	0.309	0.249	3.012	7.257
ZK3-10	0.287	0.281	0.191	2.278	0.299	0.309	0.249	3.012	6.906
ZB5-1	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZB5-1DP	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZB5-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZB5-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZB5-4	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZB5-5	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZB5-6	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC8-1	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC8-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC8-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC8-4	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC8-5	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC8-6	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC8-7	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC8-8	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
ZC8-9	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880

APPENDIX G – Single application soil congener concentration.

Sample Code	Concentration (ng/g)								Sum
	BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BDE 153	BDE 183	BDE 209	
SK2-1	0.287	2.688	0.191	4.476	0.299	0.309	0.249	3.012	11.510
SK2-2	0.287	6.256	1.771	8.908	0.299	0.309	0.249	3.012	21.090
SK2-3	0.287	4.968	1.534	7.258	0.299	0.309	0.249	3.012	17.916
SK2-4	0.287	5.689	1.704	7.287	0.299	0.309	0.249	22.263	38.086
SK2-5	0.287	2.886	0.191	4.609	0.299	0.309	0.249	3.012	11.841
SI4-1	0.287	5.451	1.338	6.512	0.299	0.309	0.249	23.479	37.924
SI4-2	0.287	9.328	2.203	11.245	0.299	0.309	0.249	32.850	56.770
SI4-3	0.287	10.957	2.578	12.838	0.299	0.309	0.249	41.403	68.920
SI4-4	0.287	4.143	0.191	5.076	0.299	0.309	0.249	19.594	30.149
SI4-4DP	0.287	3.216	0.191	3.785	0.299	0.309	0.249	3.012	11.348
SI4-5	0.287	2.981	0.191	3.693	0.299	0.309	0.249	18.526	26.536
SI4-6	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SI4-7	0.287	5.697	1.384	6.945	0.299	0.309	0.249	23.292	38.462
SI4-8	0.287	2.339	0.191	2.930	0.299	0.309	0.249	3.012	9.615
SI2-1	0.287	6.451	1.304	7.131	0.299	0.309	0.249	28.741	44.770
SI2-2	0.287	7.258	1.674	8.355	0.299	0.309	0.249	25.141	43.571
SI2-3	0.287	3.167	0.745	3.611	0.299	0.309	0.249	18.632	27.299

SI2-4	0.287	2.860	0.191	3.369	0.299	0.309	0.249	18.249	25.813
SI2-5	0.287	4.490	0.191	5.199	0.299	0.309	0.249	23.836	34.860
SI5-1	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SI5-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SI5-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SI5-4	0.287	0.281	0.191	1.524	0.299	0.309	0.249	3.012	6.152
SI5-5	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SE3-1	0.287	6.697	1.738	8.964	0.299	0.309	0.249	18.651	37.194
SE3-2	0.287	3.457	0.191	4.337	0.299	0.309	0.249	19.535	28.664
SE3-3	0.287	0.281	0.191	2.204	0.299	0.309	0.249	3.012	6.832
SE3-3DP	0.287	2.310	0.191	3.058	0.299	0.309	0.249	3.012	9.715
SE3-4	0.287	3.617	0.191	4.535	0.299	0.309	0.249	19.265	28.751
SE3-5	0.287	3.928	0.191	5.389	0.299	0.309	0.249	18.661	29.313
SE3-6	0.287	5.907	1.663	8.436	0.299	0.309	0.249	19.794	36.944
SE3-7	0.287	3.943	1.166	5.944	0.299	0.309	0.249	3.012	15.209
SE3-8	0.287	2.520	0.191	3.615	0.299	0.309	0.249	3.012	10.482
SE3-9	0.287	1.782	0.191	3.028	0.299	0.309	0.249	3.012	9.157
SE3-10	0.287	0.281	0.191	1.962	0.299	0.309	0.249	3.012	6.590
SE3-11	0.287	1.904	0.191	2.675	0.299	0.309	0.249	3.012	8.926
SE3-12	0.287	2.585	0.191	4.442	0.299	0.309	0.249	36.418	44.781
SE3-13	0.287	3.747	0.191	5.595	0.299	0.309	0.249	29.585	40.262
SE3-14	0.287	4.026	1.254	6.246	0.299	0.309	0.249	24.528	37.198
SK1-1	0.287	0.281	0.191	2.556	0.299	0.309	0.249	3.012	7.184
SK1-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SK1-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SK1-4	0.287	6.285	2.095	10.047	0.299	0.309	0.249	3.012	22.582
SK1-5	0.287	5.513	2.075	8.377	0.299	0.309	0.249	3.012	20.120
SK1-6	0.287	4.403	1.604	7.487	0.299	0.309	0.249	3.012	17.649
SK1-7	0.287	2.719	0.191	4.059	0.299	0.309	0.249	3.012	11.124
SI11-1	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SI11-2	0.287	0.281	0.191	1.784	0.299	0.309	0.249	3.012	6.412
SI11-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SI11-4	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SI11-5	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SE1-1	0.287	3.419	0.191	4.859	0.299	0.309	0.249	3.012	12.625
SE1-2	0.287	2.742	0.191	3.350	0.299	0.309	0.249	3.012	10.439
SE1-3	0.287	2.386	0.191	2.922	0.299	0.309	0.249	3.012	9.655
SE1-4	0.287	2.855	0.191	3.336	0.299	0.309	0.249	3.012	10.538
SE1-5	0.287	2.826	0.191	3.688	0.299	0.309	0.249	3.012	10.861
SF2-1	0.287	1.694	0.191	2.031	0.299	0.309	0.249	3.012	8.072
SF2-2	0.287	1.771	0.191	2.140	0.299	0.309	0.249	3.012	8.259
SF2-3	0.287	2.257	0.191	3.124	0.299	0.309	0.249	3.012	9.728
SF2-4	0.287	0.281	0.191	2.073	0.299	0.309	0.249	3.012	6.701
SF2-4DP	0.287	2.229	0.191	2.771	0.299	0.309	0.249	3.012	9.347
SF2-5	0.287	7.510	1.622	8.152	0.299	0.309	0.249	3.012	21.440
SF2-6	0.287	0.281	0.191	1.625	0.299	0.309	0.249	3.012	6.253
SI12-1	0.287	4.951	0.191	5.487	0.299	0.309	0.249	3.012	14.785
SI12-2	0.287	4.299	0.191	5.156	0.299	0.309	0.249	26.364	37.154

SI12-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SI12-4	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
SI12-5	0.287	4.152	0.191	4.970	0.299	0.309	0.249	3.012	13.469

#### APPENDIX H – Multiple application soil congener concentration.

Sample Code	Concentration (ng/g)								Sum
	BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BDE 153	BDE 183	BDE 209	
MA3-1	0.287	21.456	6.503	28.992	3.591	3.900	0.249	32.941	97.919
MA3-2	0.287	16.873	6.914	30.970	3.719	4.440	0.249	34.757	98.208
MA3-3	0.287	45.632	12.485	61.739	6.442	7.375	0.249	59.887	194.097
MA3-4	0.287	13.302	5.141	22.617	2.853	3.370	0.249	34.126	81.945
MA3-5	0.287	40.245	12.295	57.866	6.410	7.248	0.249	85.174	209.775
MG1E-1	0.287	0.281	0.191	1.696	0.299	0.309	0.249	3.012	6.324
MG1E-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
MG1E-3	0.287	2.759	0.191	3.317	0.299	0.309	0.249	3.012	10.423
MG1E-4	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
MG1E-5	0.287	2.002	0.191	4.018	0.299	0.309	0.249	18.429	25.784
MG1B-1	0.287	11.140	3.746	15.781	2.375	2.225	0.249	33.519	69.323
MG1B-2	0.287	4.645	1.624	7.415	0.299	0.309	0.249	3.012	17.840
MG1B-3	0.287	9.246	2.656	11.465	0.299	0.309	0.249	20.846	45.356
MG1B-4	0.287	24.301	6.781	35.582	4.338	4.626	0.249	35.893	112.058
MG1B-5	0.287	13.802	4.266	19.026	2.583	2.282	0.249	33.387	75.884
MA2-1	0.287	3.359	1.426	5.770	0.299	0.309	0.249	3.012	14.711
MA2-2	0.287	1.733	0.191	2.775	0.299	0.309	0.249	3.012	8.854
MA2-3	0.287	2.706	1.181	4.814	0.299	0.309	0.249	3.012	12.857
MA2-4	0.287	3.369	1.362	6.278	0.299	0.309	0.249	3.012	15.165
MA2-5	0.287	2.420	0.191	4.551	0.299	0.309	0.249	3.012	11.318
MA2-6	0.287	3.693	1.360	6.622	0.299	0.309	0.249	3.012	15.831
MA2-7	0.287	1.780	0.191	3.254	0.299	0.309	0.249	3.012	9.381
MA2-8	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
MA2-9	0.287	3.229	1.283	5.630	0.299	0.309	0.249	3.012	14.297
MA2-9DP	0.287	4.770	1.777	8.299	0.299	0.309	0.249	3.012	19.001
MH5C-1	0.287	11.669	3.580	17.553	2.176	2.072	0.249	93.193	130.779
MH5C-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
MH5C-3	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
MH5C-4	0.287	11.985	3.642	18.158	2.081	1.966	0.249	30.559	68.928
MH5C-5	0.287	8.498	2.932	12.201	1.845	0.309	0.249	22.411	48.732
MD2-1	0.287	8.025	2.790	12.047	1.804	0.309	0.249	57.537	83.047
MD2-2	0.287	12.444	3.902	17.069	2.205	2.013	0.249	71.813	109.984
MD2-3	0.287	11.890	3.317	15.001	2.074	1.851	0.249	34.203	68.872
MD2-4	0.287	5.476	2.217	8.987	0.299	0.309	0.249	27.947	45.771

MD2-5	0.287	6.800	2.513	10.589	0.299	0.309	0.249	30.743	51.790
MD2-6	0.287	1.786	0.191	2.985	0.299	0.309	0.249	3.012	9.117
MD2-6DP	0.287	0.281	0.191	3.089	0.299	0.309	0.249	3.012	7.717
MD2-7	0.287	9.294	3.013	13.402	0.299	0.309	0.249	79.881	106.735
MH6C-1	0.287	5.061	1.652	7.861	0.299	0.309	0.249	21.885	37.603
MH6C-2	0.287	11.509	3.677	17.518	2.019	1.959	0.249	35.656	72.874
MH6C-3	0.287	6.390	2.332	10.001	0.299	0.309	0.249	38.688	58.555
MH6C-4	0.287	8.155	2.935	14.653	0.299	1.971	0.249	27.368	55.917
MH6C-5	0.287	7.305	2.801	12.675	0.299	0.309	0.249	29.088	53.014
MH6C-6	0.287	6.996	2.811	11.545	0.299	0.309	0.249	62.282	84.778
MH6C-7	0.287	15.935	5.692	28.181	3.407	3.416	0.249	68.829	125.995
								226.43	
MD1-1	0.287	38.739	17.342	86.112	7.583	9.673	0.249	2	386.418
MD1-2	0.287	15.071	6.165	29.534	3.281	3.145	0.249	41.038	98.771
MD1-3	0.287	6.481	2.827	13.348	0.299	0.309	0.249	19.588	43.388
MD1-4	0.287	8.973	4.245	20.020	2.250	2.270	0.249	69.846	108.139
MD1-5	0.287	7.585	3.562	16.069	2.018	1.886	0.249	36.800	68.456
MG2-1	0.287	5.260	2.345	9.617	0.299	0.309	0.249	3.012	21.377
MG2-2	0.287	8.925	2.950	13.112	0.299	0.309	0.249	30.735	56.865
MG2-3	0.287	4.331	1.721	6.965	0.299	0.309	0.249	3.012	17.173
MG2-4	0.287	6.455	2.354	8.767	0.299	0.309	0.249	3.012	21.731
MG2-5	0.287	6.197	2.347	10.256	0.299	0.309	0.249	18.453	38.397
MG2-6	0.287	7.201	2.562	11.617	0.299	0.309	0.249	20.110	42.634
MG2-6DP	0.287	5.053	1.740	7.936	0.299	0.309	0.249	3.012	18.884
MG2-7	0.287	9.015	2.877	12.778	0.299	0.309	0.249	28.251	54.065
MA10-1	0.287	2.094	1.164	3.214	0.299	0.309	0.249	3.012	10.627
MA10-2	0.287	0.281	0.191	0.252	0.299	0.309	0.249	3.012	4.880
MA10-3	0.287	3.724	1.410	4.594	0.299	0.309	0.249	3.012	13.884
MA10-3DP	0.287	3.821	1.549	5.005	0.299	0.309	0.249	3.012	14.530
MA10-4	0.287	3.039	1.426	3.879	0.299	0.309	0.249	3.012	12.499
MA10-5	0.287	4.784	1.873	6.934	0.299	0.309	0.249	20.293	35.027
MA10-6	0.287	3.352	1.620	5.806	0.299	0.309	0.249	3.012	14.933
MA10-7	0.287	2.487	1.076	3.580	0.299	0.309	0.249	3.012	11.299
MA10-8	0.287	2.158	0.191	3.081	0.299	0.309	0.249	3.012	9.586
MA10-9	0.287	2.315	0.191	3.637	0.299	0.309	0.249	3.012	10.299
MA10-10	0.287	3.603	1.597	5.503	0.299	0.309	0.249	20.053	31.900

## Bibliography

- Ackerman, L. K., Wilson, G. R., Simonich, S. L. 2005. Quantitative Analysis of 39 Polybrominated Diphenyl Ethers by Isotope Dilution GC/Low Resolution MS. *Anal. Chem.*, 77:1979-1987.
- Agency for Toxic Substances and Disease Registry (ATSDR). 2004. Toxicological profile for Polybrominated biphenyls and polybrominated diphenyl ethers – draft for public comment. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Ahn, M., Filley, T. R., Jafvert, C. T., Nies, L., Hua, I., Bezares-Cruz, J. 2006. Photodegradation of Decabromodiphenyl Ether Adsorbed onto Clay Minerals, Metal Oxides, and Sediment. *Environ. Sci. Technol.*, 40:215-220.
- Alaee, M., Arias, P., Sjödin, A., Bergman, Å. 2003. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environ. International*, 29:683-689.
- Alaee, M., Wenning, R. J. 2002. The significance of brominated flame retardants in the environment: current understanding, issues and challenges. *Chemosphere*, 46:579-582.
- Allen, J. G., McClean, M. D., Stapleton, H. M., Webster, T. F. 2008. Critical factors in assessing exposure to PBDEs via house dust. *Environment International*, 34:1085-1091.



- Antignac, J., Cariou, R., Zalko, D., Berrebi, A., Cravedi, J., Maumea, D., Marchand, P., Monteau, F., Riu, A., Andre, F., Bizec, B. L. 2008. Exposure assessment of French women and their newborn to brominated flame retardants: Determination of tri- to deca- polybromodiphenylethers (PBDE) in maternal adipose tissue, serum, breast milk and cord serum. *Environmental Pollution*, article in press.
- Bethune, C., Julshamn, K., Lundebye, A. 2005. A preliminary comparison of polybrominated diphenyl ether concentrations relative to lipid content and to levels of dioxins and dioxin-like polychlorinated biphenyls in Norwegian farmed Atlantic salmon (*Salmo salar*). *International Journal of Food Science and Technology*, 40:143-148.
- Bezares-Cruz, J., Jafvert, C. T., Hua, I. 2004. Solar Photodecomposition of Decabromodiphenyl Ether: Products and Quantum Yield. *Environ. Sci. Technol.*, 38:4149-4156.
- Birnbaum, L. S., Staskal, D. F. 2004. Brominated Flame Retardants: Cause for Concern? *Environmental Health Perspectives*, vol. 112, number 1.
- Braekvelt, E., Tittlemier, S. A., Tomy, G. T., 2003. Direct measurement of octanol–water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. *Chemosphere*, 51:563-567.
- Bromine Science and Environment Forum, <<http://www.bsef.com/>> Accessed August 2007.

- Brown, S. L., Henry, C. L., Chaney, R., Compton, H., DeVolder, P. S. 2003. Using municipal biosolids in combination with other residuals to restore metal-contaminated mining areas. *Plant and Soil*, 249:203-215.
- Butt, C. M., Diamond, M. L., Truong, J., Ikonomou, M. G., Schure, A. F. H. T. 2004. Spatial Distribution of Polybrominated Diphenyl Ethers in Southern Ontario As Measured in Indoor and Outdoor Window Organic Films. *Environ. Sci. Technol.*, 38:724-731.
- California Environmental Protection Agency. News Release, July 7, 2003. CAL/EPA Supports CHAN bill to ban two forms of chemical PBDE. (<http://www.calepa.ca.gov/PressRoom/Releases/2003/R2.htm>).
- Cetin, B. and Odabasi, M. 2005. Measurement of Henry's law constants of seven polybrominated diphenyl ether (PBDE) congeners as a function of temperature. *Atmospheric Environment*, 39:5273-5280.
- Chen, L., Mai, B., Xu, Z., Peng, X., Han, J., Ran, Y., Sheng, G., Fu, J. 2008. In- and outdoor sources of polybrominated diphenyl ethers and their human inhalation exposure in Guangzhou, China. *Atmospheric Environment*, 42:78-86.
- Clarke, B., Porter, N., Symons, R., Marriott, P., Ades, P., Stevenson, G., Blackbeard, J. 2008. Polybrominated diphenyl ethers and polybrominated biphenyls in Australian sewage sludge. *Chemosphere*, 73:980-989.
- Commonwealth of Virginia, Virginia Department of Health, Division of Wastewater Engineering <<http://www.biosolids.state.va.us/>> Accessed on February 2008.
- Council of the European Communities, < <http://www.consilium.europa.eu/>> Accessed on February 2008.

- Covaci, A., Gheorghe, A., Voorspoels, S., Maervoet, J., Redeker, E. S., Blust, R., Schepens, P. 2005. Polybrominated diphenyl ethers, polychlorinated biphenyls and organochlorine pesticides in sediment cores from the Western Scheldt river (Belgium): analytical aspects and depth profiles. *Environ. International*, 31:367-375.
- Covaci, A., Voorspoels, S., de Boer, J. 2003. Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers (PBDEs) in environmental and human samples-a review. *Environ. International*, 29:735-756.
- Darnerud, P. O., Eriksen, G. S., Jóhannesson, T., Larsen, P. B., Viluksela, M. 2001. Polybrominated Diphenyl Ethers: Occurrence, Dietary Exposure, and Toxicology. *Environmental Health Perspectives*, 109:49-68.
- David Suzuki Foundation website. <<http://www.davidsuzuki.org/>> Accessed on May 2008.
- de Boer, J., Cofino, W. P. 2002. First world-wide interlaboratory study on polybrominated diphenylethers (PBDEs). *Chemosphere*, 46:625-633.
- de Boer, J., de Boer, K., Boon, J. P. 2000. Polybrominated Biphenyls and Diphenylethers. *The Handbook of Environmental Chemistry*, vol. 3, chapter 4.
- de Boer, J., Wester, P. G., van der Horst, A., Leonards, E. G. 2003. Polybrominated diphenyl ethers in influents, suspended particulate matter, sediments, sewage treatment plants and effluents and biota from the Netherlands. *Environ. Pollut.*, 122:63-74.

- de Wit, C. A. 2002. An overview of brominated flame retardants in the environment. *Chemosphere*, 46:583-624.
- Dietz, R., Rige't, F. F., Sonne, C., Letcher, R. J., Backus, S., Born, E. W., Kirkegaard, M., Muir, D. C. G. 2007. Age and seasonal variability of polybrominated diphenyl ethers in free-ranging East Greenland polar bears (*Ursus maritimus*). *Environmental Pollution*, 146:166-173.
- Dodder, N. G., Strandberg, B. Hites, R. A. 2002. Concentrations and spatial variations of polybrominated diphenyl ethers and several organochlorine compounds in fishes from the Northeastern United States. *Environ. Sci. Technol.*, 36:146-151.
- Eljarrat, E., Marsh, G., Labandeira, A., Barcelo, D. 2008. Effect of sewage sludges contaminated with polybrominated diphenylethers on agricultural soils. *Chemosphere*, 71:1079-1086.
- Eriksson, J., Green, N., Marsh, G., Bergman, A. 2004. Photochemical Decomposition of 15 Polybrominated Diphenyl Ether Congeners in Methanol/Water. *Environ. Sci. Technol.*, 38:3119-3125.
- ES&T Science News. < <http://pubs.acs.org/action/showNews?type=onlineNewsroom&journalCode=esthag>> Accessed May 2008.
- Fang, L., Huang, J., Yu, G., Wang, L. 2008. Photochemical degradation of six polybrominated diphenyl ether congeners under ultraviolet irradiation in hexane. *Chemosphere*, 71:258-267.
- Gebbink, W. A., Sonne, C., Dietz, R., Kirkegaard, M., Rige't, F. F., Born, E. W., Muir, D. C. G., Letcher, R. J. 2008. Tissue-specific congener composition of

- organohalogen and metabolite contaminants in East Greenland polar bears (*Ursus maritimus*). *Environmental Pollution*, 152:621-629.
- Gerecke, A. C., Hartmann, P. C., Heeb, N. V., Kohler, H. E., Giger, W., Schmid, P., Zennegg, M., Kohler, M. 2005. Anaerobic degradation of decabromodiphenyl ether. *Environ. Sci. Technol.*, 39:1078-1083.
- Gevao, B., Muzaini, S., and Helaleh, M. 2008. Occurrence and concentrations of polybrominated diphenyl ethers in sewage sludge from three wastewater treatment plants in Kuwait. *Chemosphere*, 71:242-247.
- Gouin, T., Harner, T. 2003. Modeling the Environmental Fate of the Polybrominated Diphenyl Ethers. *Environ. International*, 29: 717-724.
- Hale, R.C., La Guardia, M. J., Harvey, E., Mainor, T. M. 2002. Potential role of fire retardant-treated polyurethane foam as a source of brominated diphenyl ethers to the US environment. *Chemosphere*, 46:729-735.
- Hale, R. C., La Guardia, M. J., Harvey, E. P., Gaylor, M. O., Matteson Mainor, T., Duff, W. H. 2001a. Persistent pollutants in land-applied sludges. *Nature*, 412:140-141.
- Hale, R. C., La Guardia, M. J., Harvey, E. P., Matteson Mainor, T., Duff, M. H., Gaylor, M. O. 2001b. Polybrominated diphenyl ether flame retardants in Virginia freshwater fishes (USA). *Environ. Sci. Technol.*, 35:4585-4591.
- Hardy, M. L. 2002. The toxicology of the three commercial polybrominated diphenyl oxide (ether) flame retardants. *Chemosphere*, 46:757-777.
- Harrad, S., Hazrati, S., Ibarra, C. 2006. Concentrations of Polychlorinated Biphenyls in Indoor Air and Polybrominated Diphenyl Ethers in Indoor Air and Dust in

- Birmingham, United Kingdom: Implications for Human Exposure. *Environ. Sci. Technol.*, 40:4633-4638.
- Harrad, S., Ibarra, C., Diamond, M., Melymuk, L., Robson, M., Douwes, J., Roosens, L., Dirtu, A. C., Covaci, A. 2008. Polybrominated diphenyl ethers in domestic indoor dust from Canada, New Zealand, United Kingdom and United States. *Environment International*, 34:232–238.
- Harrison, E. Z., McBride, M. B., Bouldin, D. R. 1999. Land application of sewage sludges: an appraisal of the US regulations. *International Journal of Environment and Pollution*, 11:1-36.
- Hassanin, A., Breivik, K., Meijer, S. N., Steinnes, E., Thomas, G. O., Jones, K. C. 2004. PBDEs in European Background Soils: Levels and Factors Controlling Their Distribution. *Environ. Sci. Technol.*, 38: 738-745.
- Hassanin, A., Johnston, A. E., Thomas, G. O., Jones, K. C. 2005. Time Trends of Atmospheric PBDEs Inferred from Archived U.K. Herbage. *Environ. Sci. Technol.*, 39:2436-2441.
- Hazrati, S. and Harrad, S. Causes of Variability in Concentrations of Polychlorinated Biphenyls and Polybrominated Diphenyl Ethers in Indoor air. *Environ. Sci. Technol.*, 40:7584-7589.
- He, J., Robrock, K. R., Alvarez-Cohen, L. 2006. Microbial Reductive Debromination of Polybrominated Diphenyl Ethers (PBDEs). *Environ. Sci. Technol.*, 40: 4429-4434.
- Hu, C., Zhang, T. C., Huang, Y. H., Dahab, M. F., Surampalli, R. 2005. Effects of Long-Term Wastewater Application on Chemical Properties and Phosphorous

- Adsorption Capacity in Soils of a Wastewater Land Treatment System. *Environ. Sci. Technol.*, 39:7240-7245.
- Hui-Ying, X., Jian-Wei, Z., Qing-Sen, Y., Yan-Hua, W., Jian-Ying, Z., Hai-Xiao, J. 2007. QSPR/QSAR models for prediction of the physicochemical properties and biological activity of polybrominated diphenyl ethers. *Chemosphere*, 66:1998-2010.
- Huwe, J. K., Lorentzsen, M., Thuresson, K., Bergman, A. 2002. Analysis of mono- to deca-brominated diphenyl ethers in chickens at the part per billion level. *Chemosphere*, 46:635-640.
- Ikonomou, M. G., Rayne, S., Fischer, M., Fernandez, M. P., Cretney, W. 2002. Occurrence and congener profiles of polybrominated diphenyl ethers (PBDEs) in environmental samples from coastal British Columbia, Canada. *Chemosphere*, 46:649-663.
- Iranpour, R., Cox, H. H. J., Kearney, R. J., Clark, J. H., Pincince, A. B., Daigger, G. T. 2004. Regulations for Biosolids Land Application in U.S. and European Union. *Journal of Residuals Science & Technology*, 1:209-222.
- Jacobs, M. N., Covaci, A., Schepens, P. 2002. Investigation of Selected Persistent Organic Pollutants in Farmed Atlantic Salmon (*Salmo salar*), Salmon Aquaculture Feed, and Fish Oil Components of the Feed. *Environ. Sci. Technol.*, 36:2797-2805.
- Johnson, A. C., Sumpter, J. P. 2001. Removal of Endocrine-Disrupting Chemicals in Activated Sludge Treatment Works. *Environ. Sci. Technol.*, 35: 4697-4703.

- Johnson-Restrepo, B., Kannan, K., Addink, R., Adams, D. H. 2005. Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in a Marine Foodweb of Coastal Florida. *Environ. Sci. Technol.*, 39:8243-8250.
- Jones-Otazo, H. A., Clarke, J. P., Diamond, M. L., Archbold, J. A., Ferguson, G., Harner, T., Richardson, G. M., Ryan, J. J., Wilford, B. 2005. Is House Dust the Missing Exposure Pathway for PBDEs? An Analysis of the Urban Fate and Human Exposure to PBDEs. *Environ. Sci. Technol.*, 39:5121-5130.
- Kim, Y., Osako, M., Sakai, S. 2006. Leaching characteristics of polybrominated diphenyl ethers (PBDEs) from flame-retardant plastics. *Chemosphere*, 65:506-513.
- Knoth, W., Mann, W., Meyer, R., Nebhuth, J. 2004. Occurrence and fate of PBDE in sewage sludge from municipal waste water treatment plants. *Organohalogen Compounds*, 66:3749-3754.
- Li, A., Rockne, K. J., Sturchio, N., Song, W., Ford, J. C., Buckley, D. R., Mills, W. J. 2006. Polybrominated Diphenyl Ethers in the Sediments of the Great Lakes. 4. Influencing Factors, Trends, and Implications. *Environ. Sci. Technol.*, 40:7528-7534.
- Li, L., Xie, S., Cai, H., Bai, X., Xue, Z. 2008. Quantitative structure–property relationships for octanol–water partition coefficients of polybrominated diphenyl ethers. *Chemosphere*, 72:1602-1606.
- Lilienthal, H., Hack, A., Roth-Härer, H., Grande, S. W., Talsness, C. E. 2006. Effects of Developmental Exposure to 2,2',4,4',5-Pentabromodiphenyl Ether (PBDE-



- 99) on Sex Steroids, Sexual Development, and Sexually Dimorphic Behavior in Rats *Environmental Health Perspectives*, 114:194-201.
- Loganathan, B. G., Kannan, K., Watanabe, I., Kawano, M., Irvine, K., Kumar, S., Sikka, H. C. 1995. Isomer-specific determination and toxic evaluation of polychlorinated biphenyls, polychlorinated/brominated dibenzo-p-dioxins and dibenzofurans, polybrominated biphenyl ethers, and extractable organic halogen in carp from the Buffalo River, New York. *Environ. Sci., Technol.*, 29:1832-1838.
- Lorber, M. 2008. Exposure of Americans to polybrominated diphenyl ethers. *Journal of Exposure Science and Environmental Epidemiology*, 18:2-19.
- Luo, Q., Cai, Z. W., Wong, M. H. 2007. Polybrominated diphenyl ethers in fish and sediment from river polluted by electronic waste. *Science of the Total Environment*, 383:115-127.
- Ma, H., Allen, H. E., Yin, Y. 2001. Characterization of isolated fractions of dissolved organic matter from natural waters and a wastewater effluent. *Water Res.*, 35:985-986.
- Mai, B., Chen, S., Luo, X., Chen, L., Yang, Q., Sheng, G., Peng, P., Fu, J., Zeng, E. 2005. Distribution of Polybrominated Diphenyl Ethers in Sediments of the Pearl River Delta and Adjacent South China Sea. *Environ. Sci. Technol.*, 39:3521-3527.
- Manchester-Neesvig, J. B., Valters, K., Sonzogni, W. C. 2001. Comparison of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in Lake Michigan salmonids. *Environ. Sci. Technol.*, 35:1072-1077.

- Mandalakis, M., Atsarou, V., Stephanou, E. G. 2008. Airborne PBDEs in specialized occupational settings, houses and outdoor urban areas in Greece. *Environmental Pollution*, 155:375-382.
- Mantovi, P., Baldoni, G., Toderi, G. 2005. Reuse of liquid, dewatered, and composted sewage sludge on agricultural land: effects of long-term application on soil and crop. *Water Research*, 39:289-296.
- Marsh, G., Hu, J., Jakobsson, E., Rahn, S., Bergman, A. 1999. Synthesis and Characterization of 32 Polybrominated Diphenyl Ethers. *Environ. Sci. Technol.*, 33: 3033-3037.
- McDonald, T. A. 2002. A perspective on the potential health risks of PBDEs. *Chemosphere*, 46:745-755.
- McGrath, S.P., Chang, A.C., Page, A.L., Witter, E. 1994. Application of sewage sludge: Scientific perspectives of heavy metal loading limits in Europe and the United States. *Environ. Rev.*, 2:108-118.
- Moss, L. H., Epstein, E., Logan, T. L. 2002. Evaluating risks and benefits of soil amendments used in agriculture. Rep. 99-PUM-1. Water Environ. Res. Foundation, Alexandria, VA.
- Muraro, R.P., F.M. Roka, and R.E. Rouse. 2001. Budgeting costs and returns for southwest Florida citrus production, 2000-01. Economic Information Report EI-01-06, Department of Food and Resource Economics, University of Florida, Gainesville, FL.
- National Biosolids Partnership Annual Report – 2006-2007. Alexandria, VA. <[www.biosolids.org](http://www.biosolids.org)> Accessed on January 2008.

- North, K. D. 2004. Tracking Polybrominated Diphenyl Ether Releases in a Wastewater Treatment Plant Effluent, Palo Alto, California. *Environ. Sci. Technol.*, 38: 4484-4488.
- Nylund, K., Asplund, L., Jansson, B., Jonsson, P., Litzen, K., Sellstrom, U. 1992. Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge. *Chemosphere*, 24:1721-1730.
- Oberg, K., Warman, K., Oberg, T. 2002. Distribution and levels of brominated flame retardants in sewage sludge. *Chemosphere*, 48:805-809.
- Obreza, T.A. and O'Connor, G. A. 2003. The Basics of Biosolids Application to Land in Florida. SL 205 – fact sheet of the Soil and Water Science Department, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida.
- O'Connor, G. A., Elliott, H. A., Basta, N. T., Bastian, R. K., Pierzynski, G. M., Sims, R. C., Smith, Jr. J. E. 2005. Sustainable Land Application: An Overview. *J. Environ. Qual.*, 34:7-17.
- Official California Legislative Information. < <http://www.leginfo.ca.gov/> > Accessed on May 2008.
- Oros, D. R., Hoover, D., Rodigari, F., Crane, D., Sericano, J. 2005. Levels and Distribution of Polybrominated Diphenyl Ethers in Water, Surface Sediments, and Bivalves from the San Francisco Estuary. *Environ. Sci. Technol.*, 39:33-41.
- PBDEs overtaking PCBs. <[http://pubs.acs.org/subscribe/journals/esthagw/2005/sep/science/kb\\_pbde.html](http://pubs.acs.org/subscribe/journals/esthagw/2005/sep/science/kb_pbde.html)> Accessed February 2006.

- Peele, C. 2004. Washington State PBDE Chemical Action Plan.  
<<http://www.ecy.wa.gov/biblio/0403045.html>>
- Rayne, S., Ikonou, M. G., Whale, M. D., 2003. Anaerobic microbial and photochemical degradation of 4,4'-dibromodiphenyl ether. *Water Research*, 37:551–560.
- Rayne, S., Wan, P., Ikonou, M. 2006. Photochemistry of a major commercial polybrominated diphenyl ether flame retardant congener: 2,2',4,4',5,5' - Hexabromodiphenyl ether (BDE153). *Environment International*, 32:575-585.
- Robrock K. R., Korytar, P., Alvarez-Cohen, L. 2008. Pathways for the Anaerobic Microbial Debromination of Polybrominated Diphenyl Ethers. *Environ. Sci. Technol.*, 42: 2845–2852.
- Sanchez-Prado, L., Gonzales-Barreiro, C., Lores, M., Llompart, M., Garcia-Jarez, C., Cela, R. 2005. Photochemical Studies of a Polybrominated Diphenyl Ethers (PBDES) Technical Mixture by Solid Phase Microextraction (SPME). *Chemosphere*, 60:922-928.
- Schechter, A., Papke, O., Tung, K., Staskal, D., Birnbaum, L. 2004. Polybrominated Diphenyl Ethers Contamination of United States Food. *Environ. Sci. Technol.*, 38: 5306-5311.
- Schechter, A., Pöpke, O., Joseph, J. E., Tung, K. 2005. Polybrominated Diphenyl Ethers (PBDEs) in U.S. Computers and Domestic Carpet Vacuuming: Possible Sources of Human Exposure. *Journal of Toxicology and Environmental Health, Part A*, 68:501-513.

- Schoof, R. A. and Houkal, D. 2005. The Evolving Science of Chemical Risk Assessment for Land-Applied Biosolids. *J. Environ. Qual.*, 34:114–121.
- Sellstrom, U. and Jansson, B. 1995. Analysis of tetrabromobisphenol A in a product and environmental samples. *Chemosphere*, 31:3085-3092.
- Sellstrom, U., De Wit, C. A., Lundgren, N., Tysklind, M. 2005. Effect of Sewage-Sludge Application on Concentration of Higher-Brominated Diphenyl Ethers in Soils and Earthworms. *Environ. Sci. Technol.*, 39:9064-9070.
- Singh, R. P. and Agrawal, M. 2008. Potential Benefits and risks of land application of sewage sludge. *Waste Management*, 28:347-358.
- Sjodin, A., Patterson, D. G., Bergman, Å. 2001. Brominated flame retardants in serum from U.S. blood donors. *Environ. Sci. Technol.*, 35:3830-3833.
- Song, W., Li, A., Ford, J. C., Sturchio, N. C., Rockne, K. J., Buckley, D. R., Mills, W. J. 2005. Polybrominated Diphenyl Ethers in the Sediments of the Great Lakes. 2. Lakes Michigan and Huron. *Environ. Sci. Technol.*, 39:3474-3479.
- Stapleton, H. M. 2003. Assimilation and metabolism of polybrominated diphenyl ethers by the common carp. *Ph. D. Thesis, University of Maryland*, 251 pp.
- Stapleton, H. M., Dodder, N. G., Offenberg, J. H., Schantz, M. M., Wise, S. A. 2005. Polybrominated Diphenyl Ethers in House Dust and Clothes Dryer Lint. *Environ. Sci. Technol.*, 39:925-931.
- Stapleton, H. M., Brazil, B., Holbrook, R. D., Mitchelmore, C. L., Benedict, R., Konstantinov, A., Potter, D. 2006. In Vivo and In Vitro Debromination of Decabromodiphenyl Ether (BDE 209) by Juvenile Rainbow Trout and Common Carp. *Environ. Sci. Technol.*, 40:4653-4658.

- Staskal, D. F., Diliberto, J. J., DeVito, M. J., Birnbaum, L. S. 2005. Toxicokinetics of BDE 47 in Female Mice: Effect of Dose, Route of Exposure, and Time. *Toxicological Sciences*, 83:215-223.
- Strandberg, B., Dodder, N. G., Basu, I., Hites, R. A. 2001. Concentrations and Spatial Variations of Polybrominated Diphenyl Ethers and Other Organohalogen Compounds in Great Lakes Air. *Environ. Sci. Technol.*, 35:1078-1083.
- The Canadian Environmental Law Association, < <http://www.cela.ca/>> Accessed on February 2008.
- The Southeast Regional Climate Center, <<http://www.sercc.com/index.php>> Accessed on September 2008.
- Thomas, G. O., Moss, S. E. W., Asplund, L., Hall, A J. 2005. Absorption of decabromodiphenyl ether and other organohalogen chemicals by grey seals (*Halichoerus grypus*). *Environmental Pollution*, 133:581-586.
- Thuresson, K., Bergman, A., Jakobsson, K. 2005. Occupational Exposure to Commercial Decabromodiphenyl Ether in Workers Manufacturing or Handling Flame-Retarded Rubber. *Environ. Sci. Technol.*, 39:1980-1986.
- Tokarz, J. A., Ahn, M., Leng, J., Filley, T. R., Nies, L. 2008. Reductive Debromination of Polybrominated Diphenyl Ethers in Anaerobic Sediment and a Biomimetic System. *Environ. Sci. Technol.*, 42: 1157–1164.
- Tuerk, K. J. S., Kucklick, J. R., Becker, P. R., Stapleton, H. M., Baker, J. E. 2005. Persistent Organic Pollutants in Two Dolphin Species with Focus on

- Toxaphene and Polybrominated Diphenyl Ethers. *Environ. Sci. Technol.*, 39:692-698.
- USEPA. 1990. National Sewage sludge survey: Availability of information and data, and anticipated impacts in proposed regulations. Proposed Rule 40 CFR 503. Fed. Regist. 55:47210-47283.
- USEPA. 1993. The standards for the use or disposal of sewage sludge. 40 CFR Part 503. Fed. Regist. 58:9248–9404.
- Vonderheide, A. P., Mueller-Spitz, S. R., Meija, J., Welsh, G. L., Mueller, K E., Kinkle, B. K., Shann, J. R., Caruso, J. A., 2006. Rapid breakdown of brominated flame retardants by soil microorganisms. *J. Anal. At. Spectrom.*, 21:1232-1239.
- Voorspoels, S, Covaci, A, Veerle, LBJ, Neels, H, Schepens, P. 2007. Biomagnification of PBDEs in three small terrestrial food chains. *Environ. Sci. Technol.*, 41:411-416.
- Wang, D., Cai, Z., Jiang, G., Leung, A., Wong, M. H., Wong, W. K. 2005. Determination of polybrominated diphenyl ethers in soil and sediment from an electronic waste recycling facility. *Chemosphere*, 60:810-816.
- Wania, F., Lei, Y.D., Harner, T. 2002. Estimating octanol-air partition coefficients of nonpolar semivolatile organic compounds from gas chromatographic retention times. *Analytical Chemistry*, 74:3476-3483.

Welsh, G. 2008. Polybrominated Diphenyl Ethers: Soil Sorption and Microbial Degradation. University of Cincinnati, Department of Biological Sciences.

Wong, A., Lei, Y.D., Alaei, M., Wania, F. 2001. Vapor pressures of the polybrominated diphenyl ethers. Journal of Chemical and Engineering Data, 46:239-242.