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Fate of polybrominated diphenyl ethers during wastewater treatment process producing reclaimed water

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Fate of Polybrominated Diphenyl Ethers during Wastewater Treatment Process

Producing Reclaimed Water

by

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A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Environmental and Occupational Health
College of Public Health
University of South Florida

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Date of Approval:
November 20, 2013

Keywords: persistent organic pollutants, brominated flame retardants, mass loading,
point source, endocrine disrupting compounds

Dedication

Without the support and understanding from my husband, son, and parents, this

dissertation would not have been possible. It's been a long road, but there is always

light at the end.

"Two roads diverged in a wood, and I— I took the one less traveled by, And that has

made all the difference." – Robert Frost

Acknowledgments

I am grateful to the Department of Environmental and Occupational Health in the College of Public Health for their continued support and financial assistance during my research. As well, I am appreciative of the guidance I received from my advisor and major professor, Dr. Foday Jaward, and committee members: Dr. Robert McDermott, Dr. Steve Mlynarek, and Dr. Ira Richards.

I have to extend a special thanks to the countless undergraduate and graduate students who assisted me during my project. I would not have been able to complete my sampling, extraction, and analysis without you guys. You have been the best group of volunteers I could have asked for! I hope you gained as much from your experience in the lab as I gained from you being there to help out. There are a few students that I must especially thank for their continued assistance: Nicole Lavick and Jessica Rubano.

I would also like to thank Howard F. Curren Advanced Wastewater Treatment Plant for the unrestricted access to poop, poop, and more poop. And to the guys that work there, thanks for helping me collect some of the more "lovely" samples. I must especially thank Tim Ware, Dan Vanderschuur, and Rob Decker for their assistance throughout my sampling and then even after - with the calculations.

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List of Abbreviations

AS	activated sludge
ATSDR	Agency for Toxic Substances and Disease Registry
AWTP	Advanced Wastewater Treatment Plant
BDE	brominated diphenyl ether
BOD	biological oxygen demand
C	Celsius
CPSC	Consumer Product Safety Commission
DCM	methylene chloride
DO	dissolved oxygen
dscfm	dry standard cubic feet per minute
ECNI	electron capture negative ionization
EDC	endocrine disrupting compound
EPA	Environmental Protection Agency
FS	final sludge
GC/MS	gas chromatography/mass spectrometry
IARC	International Agency for Research on Cancer
INF	influent

kg	kilogram
L	liter
lb	pound
m	meter
µg	microgram
µL	microliter
mg	milligram
mL	milliliter
MGD	million gallons per day
ng	nanogram
nL	nanoliter
NCASI	National Council for Air and Stream Improvement, Inc.
NOCEPM	NCASI Organic Compound Elimination Pathway Model
NTP	National Toxicology Program
PBB	polybrominated biphenyl ether
PBDE	polybrominated diphenyl ether
PCB	polychlorinated biphenyl
pg	picogram
pL	picoliter
PS	primary sludge

PSE   primary sedimentation effluent

PUF   polyurethane foam

QA/QC   quality assurance/quality control

RAS   return activated sludge

S/N   signal to noise ratio

SS   suspended solids

SSE   secondary sedimentation effluent

TSS   total suspended solids

UNEP   United Nations Environment Programme

UV   ultraviolet

WAS   waste activated sludge

WWTP   wastewater treatment plant

Abstract

Polybrominated diphenyl ethers (PBDEs), flame retardants, have been applied to
consumer goods, such as furniture, electrical devices, textiles, and appliances for
decades. Due to their physico-chemical properties, PBDEs are semi-volatile and easily
leach off the consumer good during aging, stress, or normal wear and tear of the good.
Once airborne, they pose an environmental health threat because they can adsorb onto
dust particles, soil, or other particulates that can be inhaled, ingested, or come into
contact with the dermal layer. Additionally, PBDEs have a molecular structure similar to
other persistent organic pollutants, such as polychlorinated biphenyls and
polychlorinated dibenzo-p-dioxins and furans. They are a health threat due to their
endocrine-disrupting nature by affecting thyroid functioning, fertility, and child
development. The purpose of the study is to measure selected PBDEs in a wastewater
treatment plant (WWTP) that produces reclaimed water, such that a mass balance can
be completed, and to compare this mass balance with theoretically expected
concentrations. The mass balance includes the collection of samples from wastewater,
sewage sludge, and air at points within the WWTP. The PBDEs examined are BDE-28,
47, 99, 100, 153, 154, and 183. The second part of the study will compare effluent
concentrations to reclaimed water concentrations in order to examine the potential
exposure (if any) of using reclaimed water. Influent concentration of mean Σ_7PBDE was
found to be 49,117 pg/L and effluent concentration was 4,603 pg/L, illustrating a 91%

removal rate of PBDEs during the wastewater treatment plant. Sludge samples contained the highest total concentrations of PBDEs with mean Σ_7PBDE ranging from 14.0 to 41.3 µg/kg dry weight. Air samples were highest at the post-aeration (248 pg/m^3 mean Σ_7PBDE) step due to the use of highly oxygenated air assisting in the release and volatilization of the PBDEs. Sludge was found to carry the largest mass loading at 14.2 lb/day Σ_7PBDE. Of the total mass loading of PBDEs from the WWTP, sludge is responsible for 86.7%, followed by reclaimed water and effluent (11.7% and 1.6%, respectively). The mass loading from air was negligible with less than 0.01% contribution to the total mass loading. Whereas reclaimed water overall had higher PBDE congener mean concentrations than the effluent, the independent samples t-test found no statistically significant differences between the two groups. The results of this study can be used to improve the wastewater treatment process to reduce the impact of PBDEs being released into the environment by WWTPs, and to educate the public on utilizing reclaimed water in a safe and healthy manner.

Chapter One

Introduction and Problem Statement

Polybrominated diphenyl ether (PBDE), a flame retardant that is a

microconstituent of concern, is ubiquitous in the environment, animals, and humans

(Agency for Toxic Substances and Disease Registry (ATSDR), 2004). The scientific

evidence on human health effects of PBDEs is scant, but it has been shown to affect the

thyroid gland and liver in rats and mice (ATSDR, 2004). Because of PBDEs' endocrine-

disrupting properties, there is a cause for alarm and concern about the potential health

consequences to exposure to PBDEs in developing infants and children. Although

several formulations of PBDEs have been banned from production throughout the world

(Lober, 2008), environmental concentrations are steadily rising (Betts, 2002). In order

to understand the release of PBDEs into the environment, exposure sources must be

investigated. The purpose of this study is to characterize the fate and transport of

PBDEs in a wastewater treatment plant that produces reclaimed water.

One such potential source for environmental release is wastewater treatment

plants (WWTPs). Along with the discharge of effluent that may contain PBDEs into local

receiving waters, many WWTPs prepare their sludge for agricultural uses such as

fertilizer (Tan et al., 2007). Because of PBDEs' physico-chemical properties, they can

adsorb or accumulate onto the sludge, and increase the risk of exposure to humans and

animals. Additionally, some WWTPs dispense reclaimed water for public non-potable use, such as irrigation, which is another possible avenue into the environment and a potential source for human exposure. Despite this, research examining the fate and transport of PBDEs in wastewater remains understudied, and virtually no research has looked at PBDEs in reclaimed water. As such, this study will be among the first to examine this microconstituent in reclaimed water. As well, it will be one of the few studies to investigate the WWTP as an all-inclusive point source by examining the wastewater, sewage sludge, and air released by the WWTP.

People are becoming increasingly aware of microconstituents of possible concern in the public water supply; for example, the potential public and environmental health threats posed by personal care products and pharmaceuticals, such as birth control pills (e.g., estradiol and endocrine disruption) and antibiotics (contributing to antibiotic resistance), in the water supply have received growing media attention over the last few years (Carballa, Omil, & Lema, 2007). As such, there is a greater need for public health professionals to educate residents and to address their concerns about the water supply, particularly as alternative water sources such as reclaimed water become increasingly common. Yet without some baseline understanding of potential exposure routes of PBDEs from the wastewater treatment plant, public health professionals cannot respond to residents' concerns and perceptions of reclaimed water. Although PBDEs are but one example of microconstituents of possible concern in the public water supply, this research could be a model for future studies that aim to obtain better data related to microconstituents in the public water supply.

The purpose of the study is to measure selected PBDEs in a WWTP, such that a mass balance can be completed, and to compare this mass balance with theoretically expected concentrations. The mass balance will include the collection of samples from the wastewater, sewage sludge, and air at points within the WWTP. The PBDEs to be examined are BDE-28, 47, 99, 100, 153, 154, and 183; these are seven of the major congeners detected in the environment. The second part of the study will include the examination of effluent concentrations versus reclaimed water concentrations in order to address concerns of reclaimed water use. The specific objectives of this study are to:

1. Characterize the fate and transport of PBDE concentrations within the wastewater treatment plant.

2. Compare the observed mass balance of PBDE concentrations to the predicted values in the theoretical model.

3. Examine PBDE concentrations in reclaimed water and effluent.

Chapter Two

Literature Review

Flame Retardants

Flame retardants pose a classic public health problem. In order to provide fire safety, are flame retardants creating undue health and environmental risks through their use and application? According to the U.S. Consumer Product Safety Commission (CPSC), there was an estimated annual average of 362,300 fires, 2,260 deaths, 12,820 injuries, and $6.68 billion in property damage from 2009 to 2011 from residential fires (CPSC, 2013). Approximately 4% of those fires were started with either the upholstered furniture or a mattress being the first item ignited (CPSC, 2013). Additionally, those items were responsible for 33% of the fire deaths (CPSC, 2013). Some have suggested the risk of exposure to flame retardants outweighs the benefit (Shaw et al., 2011). However, there first needs to be a clearer understanding of flame retardants' risks before calling for the elimination of their use.

Polybrominated Diphenyl Ethers

Polybrominated diphenyl ether (PBDE) is a flame retardant compound that is added to plastics and foam products to reduce the ability to burn (ATSDR, 2004). The United States has some of the world's most stringent fire-safety regulations, and

therefore most consumer goods have some form of PBDEs in them (Betts, 2002).

However, because of the chemical's properties (i.e., semi-volatile nature and

hydrophobicity) and the structure of consumer goods, such as the open-cell structure in

foam used in couches, PBDE readily escapes consumer goods to become airborne or

sorbed onto dust and particulates (Betts, 2002). Additionally, PBDEs are not covalently

bonded to the polymers of consumer goods, and therefore increase their potential for

leaching out of the good (Alaee, Arias, Sjodin, & Bergman, 2003). Due to their

widespread use and resistance to degradation, PBDEs have been detected in urban and

rural soils, surface waters, sediment, air, sewage sludge, treated wastewater effluent,

and most biota including shellfish, fish, birds, and mammals, as well as in humans

(Oram & Hunt, 2008). PBDEs have even been found in the Arctic, where their levels

have increased exponentially over the last two decades; conversely, levels of dioxins,

furans, and polychlorinated biphenyls (PCBs) in the Arctic have stabilized or decreased

(Betts, 2002).

The chemical structure of PBDE is shown below (Figure 1). The double

halogenated aromatic ring structure is similar to PCBs. One to ten bromine atoms attach

to the diphenyl ether molecule to form the various homologous groups of PBDEs:

mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and decabrominated

diphenyl ethers (ATSDR, 2004). Lower brominated PBDEs are defined as having one to

five bromine atoms per molecule; whereas higher brominated PBDEs have over five

bromine atoms (ATSDR, 2004). Research indicates that the lower brominated PBDEs

are more toxic than the higher ones (Birnbaum & Staskal, 2004). There are 209

possible compounds, called congeners, from the attachment of the bromine atoms to the rings (ATSDR, 2004). However, only seven congeners comprise 95% of all detected PBDEs: BDE-28, 47, 99, 100, 153, 154, and 209 (Kuhn, Ellis, & Wilbur, 2003).

$(x + y = 1\text{-}10)$
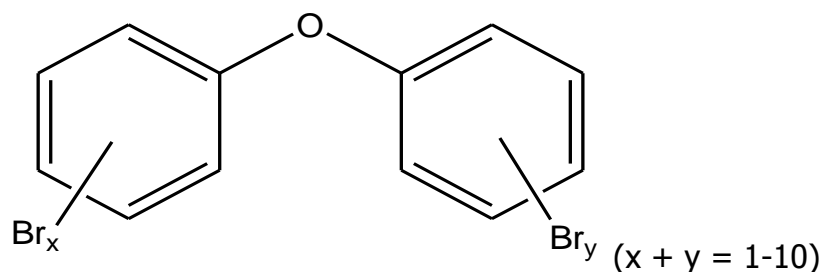
Figure 1. Chemical structure of PBDE.

PBDEs consist of three commercial formulations, Penta-BDE, Octa-BDE, and Deca-BDE, with numerous congeners within those three formulations (Lorber, 2008) (see Appendix A). In 2004, manufacturers voluntarily withdrew the Penta-BDE and Octa-BDE formulations from the marketplace, leaving the Deca-BDE formulation as the only PBDE being manufactured in the U.S. (Lorber, 2008). Deca-BDE formulation will be phased out by end of 2013, as well (Hess, 2009). An important note is that although there has been a ban in place on the manufacturing of the Penta-BDE and Octa-BDE formulations, the stockpile of those formulations is such that the ban has not actually resulted in the non-use of those formulations in consumer goods (Lorber, 2008). Additionally, consumer goods still require flame retardants; therefore, there was not a total elimination of retardants, but rather a substitution with a different compound. Europe primarily uses melamine as a flame retardant for polyurethane foam products,

whereas the U.S. uses tris (1,3-dichloro-2-propyl) phosphate (Environmental Protection Agency [EPA], 2005). Hexabromocyclododecane is now the most widely used flame retardant for construction materials and textiles (Guerra, Alaee, Eljarrat, & Barceló, 2011). However, these substitutions were done without prior understanding of these compounds' persistence and toxicity (Guerra et al., 2011).

Concern has been raised that the Deca-BDE formulation may actually break down into the Penta formulation when exposed to ultraviolet light, a process called photolytic debromination (Bezares-Cruz, Jafvert, & Hua, 2004; Erikkson, Green, Marsh, & Bergman, 2004; Söderstöm, Sellström, De Wit, and Tysklind, 2004). According to modeling estimates, approximately 13% of the Penta-BDE formulation found in the environment is a result of the debromination of Deca-BDE (Schenker, Soltermann, Scheringer, & Hungerbuhler, 2008). Additionally, research suggests that the Penta-BDE formulation and its congeners tend to persist and bioaccumulate more readily in the environment, as compared to the other two formulations (Betts, 2002). As such, it is the most detected formula in wildlife and the environment, and one congener in particular, BDE-47, is detected more often (Betts, 2002). It should be noted, however, that BDE-47 is not the major congener in any commercial product; but it usually makes up about 70% of the total PBDEs found in samples from wildlife (Betts, 2002). This may be due to the toxicokinetics of BDE-47. Research shows that it is excreted very slowly from the body, allowing for the levels to remain high in wildlife (Betts, 2002). Additionally, BDE-47 is lightweight, as compared to other congeners, which allows for it to hop to distant regions, such as the Arctic (Betts, 2002).

Some classes of chemicals, such as PBDEs, have the ability to hop from one region to the next through an efficient and rapid form of transport known as the "grasshopper" effect (Gouin et al., 2002). These chemicals transfer from being airborne to adhering to surfaces, such as vegetation and top soils (Gouin et al., 2002). Some outside force creates the catalyst to transfer the chemical from one state (gas-phase) to the other (partitioned to solids/aerosols), which allows it to move with the meteorological cycles in the area (Harner & Shoeib, 2002). Researchers have found that temperature plays a role in this phase-transfer. In warm temperatures, the chemical prefers the gas-phase allowing for transport, and in cold temperatures, the chemical favors partitioning onto aerosols for deposition (Harner & Shoeib, 2002). This can explain the abundance and increase in levels of PBDEs in the Arctic region. PBDEs released from the warmer United States are transported in the gas-phase northward until they reach the colder Arctic, where they partition onto the surface area. As such, there is growing concern over the release of PBDEs into the environment because of their global transport capabilities.

Health Effects of Polybrominated Diphenyl Ethers

The scientific evidence on human health effects of PBDEs is scant, but it has been shown to affect the thyroid gland and liver in rats and mice (ATSDR, 2004). High concentrations of PBDEs may cause neurobehavioral alterations and affect the immune system in animals (ATSDR, 2004). An additional concern of PBDEs is that the chemical structure is similar to polychlorinated biphenyls and dioxins, which are known

carcinogens that bioaccumulate in the body (ATSDR, 2004) (see Table 1). Toxicological

studies have found that exposure to this class of chemical is linked with endocrine

disruption, neurological defect, and certain types of cancers (Birnbaum & Staskal, 2004;

Darnerud, Eriksen, Johannesson, Larsen, & Viluksela, 2001; Meerts, van Zanden, Luijks,

van Leeuwen-Bol, Marsh, Jakobsson, et al, 2000).

Table 1. Cancer Classification by Agency of PBDEs, PCBs, and PBBs.

Chemical	Group	Agency
Polychlorinated biphenyls (PCBs)	1	IARC[1]
Polybrominated biphenyls (PBBs)	2A	IARC[1]
Polybrominated biphenyls (PBBs)	Reasonably anticipated	NTP[2]
Decabromodiphenyl oxide (Deca-BDE)	3	IARC[1]
Decabromodiphenyl oxide (Deca-BDE)	C	EPA[3]

1. International Agency for Research on Cancer (IARC) places chemicals into 5 cancer-causing potential categories - Group 1: Carcinogenic to humans; Group 2A: Probably carcinogenic to humans; Group 2B: Possibly carcinogenic to humans; Group 3: Unclassifiable as to carcinogenicity in humans; and Group 4: Probably not carcinogenic to humans (IARC, 2013).
2. National Toxicology Program (NTP) identifies 2 groups: "known to be human carcinogens" and "reasonably anticipated to be human carcinogens" (NTP, 2011).
3. Environmental Protection Agency (EPA) uses a 5-level rating system - Group A: Carcinogenic to humans; Group B: Likely to be carcinogenic to humans; Group C: Suggestive evidence of carcinogenic potential; Group D: Inadequate information to assess carcinogenic potential; and Group E: Not likely to be carcinogenic to humans.

Environmental toxicology has shown that there may be long-term health risks

associated with chronic exposure to low-level concentrations of some microconstituents,

in particular those endocrine-disrupting compounds (EDCs) (Daughton & Ternes, 1999),

which PBDEs are a type of EDC. Endocrine-disrupting compounds interfere with the

natural hormones in the body to produce serious health effects (Levine & Asano, 2004).

Negative health effects have been documented in growth rates of amphibians, fish, and

other wildlife at trace levels – as low as parts per trillion (Daughton & Ternes, 1999).

Therefore, concern exists as to PBDEs' impact at trace levels for long-term exposures.

A study found that infants and children under the age of four in Norway have levels of PBDEs in their blood that were 1.6-3.5 times higher than their adult counterparts (Thomsen et al, 2002). Indoor environment, diet, and breast milk have been determined to be the sources of exposure for humans (Lorber, 2008). Because of PBDEs' endocrine-disrupting properties, there is a cause for alarm and concern about the potential health consequences to exposure to PBDEs in developing infants and children.

Wastewater Treatment Plants

Historically, the wastewater treatment process has predominately dealt with the immediate impact of receiving waters to the environment, such as oxygen depletion and eutrophication (Kreuzinger, Clara, Strenn, & Kroiss, 2004). Appropriate technologies have been developed to control these regulated parameters to ensure the health of the environment and the public (Kreuzinger et al., 2004). However, recent scientific advances (Oppenheimer, Stephenson, Burbano, & Liu, 2007), as well as public knowledge, have shifted the focus to include emerging micropollutants like endocrine-disrupting compounds (EDC) (Kreuzinger et al., 2004). Studies have shown that wastewater effluent is a major source of EDC contamination of receiving waters (Kreuzinger et al., 2004; Oppenheimer et al., 2007; Richardson, 2007; Tan et al., 2007), which may ultimately become drinking water (Richardson, 2007). This

contamination occurs as a result of incomplete removal of EDCs during the wastewater treatment process (Richardson, 2007; Tan et al., 2007). Although the human health effects of EDCs are still unknown, but clearly demonstrated in animal and field studies (Richardson, 2007), it is imperative that adequate control measures occur within the wastewater treatment plant to ensure only healthy effluent water is discharged into the environment.

Endocrine disrupting compounds (EDC) are natural and synthetic chemicals that are known or predicted effects to the endocrine system (Richardson, 2007). The U.S. Environmental Protection Agency defines an EDC as "an exogenous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body which are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior" (Kavlock et al., 1996, p. 715). These agents include natural estrogens, natural androgens, phytosteroids, isoflavenoids, synthetic estrogens, pesticides, phthalates, nonionic surfactants (alkylphenol ethoxylate), dioxins, polychlorinated biphenyls, parabenes, bisphenol A, and organic tins (Richardson, 2007). Wildlife can be exposed to EDCs via the aquatic environment contaminated with effluent discharge, whereas humans are exposed through drinking water produced with these receiving waters (Richardson, 2007).

Conventional wastewater treatment plants are a major source of EDC pollution because these compounds may not be totally removed or degraded by chemical, physical, and biological treatment processes within the plants (Tan et al., 2007). Adequate removal of EDCs is dependent on two aspects: the physiochemical properties

of the compounds and the nature of the treatment processes involved (Tan et al., 2007). During conventional wastewater treatment, the major pathways for removal of compounds are: 1) volatilization, 2) adsorption onto solids, 3) biodegradation, and 4) chemical degradation (Tan et al., 2007). The volatilization of compounds is determined by Henry's Law (Khanal et al., 2006). Because EDCs have low vapor pressures, they are likely to have small Henry's Law constants (Khanal et al., 2006). Therefore, removal of EDCs due to volatilization is likely to be limited (Khanal et al., 2006). EDCs are generally hydrophobic causing them to sorb onto particles (Ivashechkin, Corvini, & Dohmann, 2004), suggesting the best removal process would be to concentrate them into the wastewater sludge (Tan et al., 2007). K_{ow}, the octanol-water partition coefficient, is the measure of a chemical's hydrophobicity (Mackay, 2001). This dimensional coefficient is defined as the ratio of solubilities of the chemical in octanol and water (Mackay, 2001). It can also be expressed as log K_{ow} because of the large range of values possible. Due to EDCs' hydrophobicity, they generally have large log K_{ow}s (Mackay, 2001) (see Appendix A for PBDEs physico-chemical properties, including log K_{ow} values). It is believed that subsequent mechanical techniques of solids removal from conventional wastewater treatment should then result in significant removal of EDCs (Tan et al., 2007).

Chemical and environmental factors (e.g., structure and pH, respectively) together determine a compound's ability to be biodegraded (Ivashechkin et al., 2004), which makes it difficult to predict biodegradation (Tan et al., 2007). An additional concern is synthetic compounds have not been present in the environment long enough

for microorganisms to develop the abilities to biodegrade these compounds (Tan et al., 2007). It has been found that less than 10% of synthetic compounds are removed by biodegradation, with the majority of the compounds remaining in the aqueous phase and the remaining amount adsorbing to the sludge (Filali-Meknassi et al., 2004). However, for wastewater treatment plants utilizing anaerobic digestion, there is no considerable degradation of EDCs (Ivashechkin et al., 2004). Subsequently, conventional wastewater and drinking water plants do not completely remove EDCs (Richardson, 2007). Therefore, advanced tertiary treatments, such as ozonation, ultrafiltration, ultraviolet (UV) disinfection, and reverse osmosis, are being investigated for their abilities to complement the conventional processes (Filali-Meknassi et al., 2004; Tan et al., 2007).

NOCEP Model

The National Council for Air and Stream Improvement, Inc. (NCASI) Organic Compound Elimination Pathway (NOCEP) Model can be used to predict the fate of organic compounds within the wastewater treatment plant (NCASI, 2005). By examining the wastewater just at the aeration basin and secondary clarifier, the elimination of organic compounds can be quantified (Barton, 1987). Three elimination pathways are considered in the model: 1) air stripping, 2) adsorption onto solids, and 3) biodegradation (Barton, 1987). The model also calculates the fraction remaining in the plant effluent. This percent remaining in the effluent, when released into local receiving waters, can pose a threat to the environment and humans. The model uses the

physico-chemical properties of the organic compound and the operational parameters of the WWTP to determine the fate of the compound (Barton, 1987). Three assumptions underlie use of this model: 1) aeration basins are completely mixed, 2) first-order biodegradation kinetics are in place, and 3) all phase transfers are in a steady-state (NCASI, 2000). Utilizing a modified version of the NOCEP Model created for academic purposes (Luthy & Cunningham, 2001), the study will compare theoretical removal rates to calculated removal rates found for PBDEs in a WWTP. This study will be among the first to examine use of the NOCEP Model with PBDEs.

As an example, using operational parameters for the WWTP to be used in this project and physico-chemical properties for BDE-47, the model created by Luthy and Cunningham predicted the fate of BDE-47 to be as follows: 0.61% removed by stripping, 98.17% removed by solids partitioning, 0.01% removed by biodegradation, and 1.22% remaining in the plant effluent. Each BDE to be examined will be run in the model separately. However, it is assumed that other BDEs will not differ significantly for the purposes of hypothesis formulation. Based on this, **the first null hypothesis is that PBDE concentrations will follow the predicted values [H_0: $PBDE_{theoretical}$ = $PBDE_{observed}$].**

One concern with the model however is that it does not consider reclaimed water as an additional sink. In a pilot study conducted in 2009 (see Appendix B), results indicated that PBDEs remained in the reclaimed water. For example, the concentration of BDE-47 in the reclaimed water was found to be 8.23×10^{-4} pg/μL, whereas the effluent concentration was 1.05 pg/μL. Because the reclaimed water at the WWTP is

drawn prior to the effluent channel, the reason for this lower concentration in the reclaimed water is unclear. The only observable difference is the wastewater is chlorinated prior to the removal of the reclaimed water channel, and then following the reclaimed water channel, it is dechlorinated for the effluent. Therefore, chlorine is still present in the reclaimed water. However, my understanding is that chlorine plays no role in the degradation of PBDEs and therefore should not affect the concentration levels. As such, **the second related null hypothesis is that there is no difference in concentration levels between reclaimed water and effluent [H_0: PBDE$_{reclaimed}$ = PBDE$_{effluent}$].** This study will also be among the first to examine concentration levels of a microconstituent in reclaimed water.

Reclaimed Water

As the water shortage crisis worldwide worsens, alternative water supplies are being sought (Sorgini, 2007). One of the most discussed alternative water sources is water reuse, also known as reclaimed water (Sorgini, 2007). Reclaimed water is a viable alternative source because it conserves water by reusing treated wastewater that is then used predominantly for non-potable purposes, such as irrigation and industrial systems (closed-system cooling) (Huertas et al., 2008; Sorgini, 2007). However, reclaimed water has uses beyond non-potable consumption, and can be utilized for both direct and indirect potable use, such as human consumption and aquifer storage and recovery (Sorgini, 2007). Reclaimed water also serves as an environmental safety

measure because it limits the wastewater discharge into receiving waters (Huertas et al., 2008).

Producing potable water is an expensive enterprise (Sorgini, 2007). However, when one considers that only 21% of withdrawn groundwater in the United States is actually for household use, including direct human consumption (Sorgini, 2007), it is not economical to produce consumption grade water that will not reach the public directly. About 74% of groundwater withdrawals that have been treated for direct consumption is used for irrigation – putting the water shortage at an additional hardship in many areas throughout the U.S. (Sorgini, 2007). In these areas, non-potable reclaimed water can be utilized instead of consumption grade water for irrigation by both the public (lawns) and agricultural purposes (crops). One of the benefits of reclaimed water that has been proven to be environmentally and economically beneficial is its use for non-potable purposes (Sorgini, 2007). Furthermore, recent advances in reclaimed water technology have reduced the operating costs, improved efficiencies, and enhanced the quality of the end product, making reclaimed water a more likely alternative water source for many communities (Gunderson, 2007). Consequently, it is currently part of many cities' water resource planning in California, Florida, and throughout the arid Southwest (Gunderson, 2007), as well as in areas that are seeking sustainable sources such as the Pacific Northwest (Cleveland, Fowler, McCarthy, & Topolski, 2007).

Concerns and Perception of Reclaimed Water

Before any reclaimed water project can become a reality, the public must accept it (Bridgeman, 2004; Friedler, Lahav, Jizhaki, & Lahav, 2006). Prior to examining the public acceptance, it is beneficial to understand the public's perception of reclaimed water and its various uses (Bridgeman, 2004). If the public thinks negatively of the project, then understanding their perception will assist in modifying these negative perceptions that could jeopardize future reclaimed water projects. An example of public interference with a project is in Los Angeles, where a water reuse project had to be placed on hold because of negative public reaction (Greene, 2000).

Because of the water shortage in California, Los Angeles' utilities officials initiated a "toilet-to-tap" program that would have utilized reclaimed wastewater for indirect potable purposes (Greene, 2000). Although 40 California cities currently use reclaimed wastewater for non-potable purposes, the proposed project would have been the first one to utilize it for indirect consumption (Greene, 2000). For three years, reclaimed water would have been pumped into an aquifer (Greene, 2000) to allow for continual and natural remediation of the water. Then, for five years, the aquifer water would be withdrawn and combined with well water to create a 20-80 mix that would then be treated in a drinking water plant before being distributed to the public (Greene, 2000). While in the development stage, officials found the public was already divided (Greene, 2000). Supporters believed that the filtration process, as well as the chemical disinfection used, would make the reclaimed water cleaner than tap water (Greene, 2000). Conversely, the opponents claimed that there was not sufficient epidemiological

evidence to support that there are no health risks to direct consumption of reclaimed water (Greene, 2000). Additionally, the opponents were concerned about the lack of specific treatment processes that would be directed at removing trace microconstituents (Greene, 2000). Therefore, the project was suspended until sufficient public support and epidemiological evidence could be gathered (Greene, 2000).

Friedler and colleagues (2006) found that health consequences were the public's primary concern when they examined attitudes towards various reclaimed wastewater uses in Israel. When considering medium contact reuse (defined as landscaping, domestic toilet flushing, and firefighting), respondents favored reclaimed water usage because of potential financial gain, although perceived health effects negatively affected the support (Friedler et al., 2006). Thus, a major goal of any public campaign should be to clarify any misinformation concerning health risks associated with reclaimed water (Friedler et al., 2006).

However, research is needed to demonstrate the safety of reclaimed water (Crook, 2000). The definitive data on the safety of reclaimed water are lacking (Crook, 2000). One of the reasons for the lack of data is that most reclaimed water research was performed by individual utilities with specific issues that could not be generalizable to other utilities or states (Crook, 2000). Additionally, when regulators developed reclaimed water criteria for the protection of public health, there was no money to research any data gaps, and therefore, they used antiquated "best practices" (Crook, 2000). Since then, new technologies and better detection measures have been developed that could ascertain the effect of reclaimed water on public health (Crook,

2000). However, these new technologies and detection measures have not been validated or are not commonly used. This study will be among the first to investigate reclaimed water for a microconstituent of concern.

Communicating Scientific Results

Upon discovering an environmental health issue which might raise concerns, it is imperative to inform and educate the public and the scientific community on those findings. The message created to raise awareness of the issue must be prepared without raising panic or leading to confusion. Several messages must be written to correspond to the intended audience, as well as the mode of communication. It is also important to remember that disseminating messages differs from communicating messages; the former is a one-way tool to get the message out, whereas the latter is a two-way discourse to allow for further discussion. Lastly, any communication campaign must be evaluated for effectiveness and efficiency. It should be determined whether the message was received by the intended audiences, and whether the audiences understood the message, i.e., did the message educate/inform the public on the presence of the environmental health issue (Schiavo, 2007; Thomas, 2006).

One of the first audiences that findings should be reported to is the scientific community. The importance of communicating with the scientific community is that the findings can be reviewed, and debates can ensue that can accept or reject the data and the interpretations (Dolphin, 1997). Communication to the scientific community can be formal or informal (Ray & Donohew, 1990), including journal articles, manuscripts,

reports, oral/poster presentations, and round table discussions. Depending on the seriousness of the issue, the first communication phase could be an oral/poster presentation or round table discussion to allow for a more intimate discussion with fellow researchers. Based on comments and discussion, the next route would be to prepare a report or manuscript. This would then be sent to colleagues and researchers in the same field to gain their input on the findings. And finally, a journal article would be written for a specific publication to reach the appropriate audience.

Once the findings have been discussed in the scientific community and are not rejected, key messages should be defined for politicians and decision makers in order to impact policy decisions (Thomas, 2006). If the issue is a result of industrial release, then it is important to tailor the message to the need for creating guidelines and recommendations for monitoring, as well as ensuring industries are required to mitigate the release. The key messages would be brief and concise, but allow the politicians and decision makers the opportunity to seek additional information (Thomas, 2006; United Nations Environment Programme [UNEP], 2010). And they should have access to the scientific findings in both scientific language and layman's terms (UNEP, 2010). Although industries under scrutiny may try to discount the findings, a well-prepared researcher can show that the findings have undergone a complete review by the appropriate scientific community first.

Chapter Three

Sampling Site

Howard F. Curren Advanced Wastewater Treatment Plant (AWTP), located at the

Port of Tampa, FL, provides tertiary treatment to wastewater from approximately

350,000 residents of the City of Tampa before discharging it to the Hillsborough Bay. In

2011, its average annual flow was 58 million gallons per day (MGD) with average total

suspended solids (TSS) and biological oxygen demand (BOD) of 136 mg/L and 151

mg/L, respectively. The Curren AWTP produces reclaimed water for industrial and

residential use at a rate of 2.79 MGD in 2011 (Howard F. Curren AWTP, 2011).

The Curren AWTP provides preliminary, primary, secondary, and tertiary

treatment with disinfection. The basic unit processes include the following:

- Preliminary treatment: Pre-aeration, screening, grit removal, influent pumping

- Primary treatment: Primary sedimentation

- Secondary treatment: Air activated sludge, final sedimentation

- Tertiary treatment: Nitrification, denitrification, final sedimentation, disinfection,

  dechlorination

Figure 2 shows the site plan. Figure 3 shows the process flow diagram. Detailed

discussion of the unit process capacities follows.
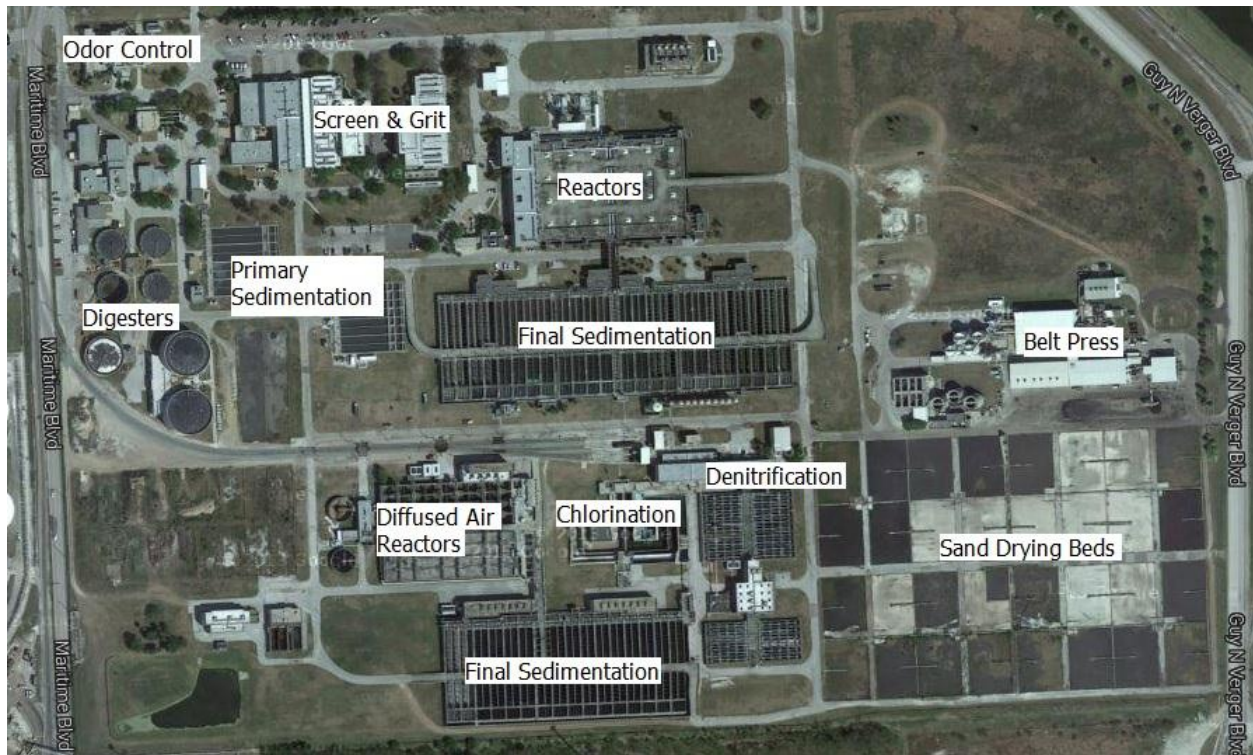
Figure 2. Site plan of Howard F. Curren AWTP.

Preliminary treatment removes materials that may clog and damage equipment, cause excessive wear to equipment and structures, or reduce the efficiency of the treatment process. The first step in the process is pre-aeration of the influent to remove hydrogen sulfide (the cause of the odor) from the waste stream and then treatment of the hydrogen sulfide with sodium hydroxide in mist odor control towers. The sewage is then screened and grit removed. In screening, sewage passes through bar screens with 3/8" spacing to remove large solid materials. The flow is then reduced to one foot per second to allow sand and other abrasive materials to settle out. Pre-treated sewage is now pumped to primary sedimentation (Howard F. Curren AWTP, 2009).
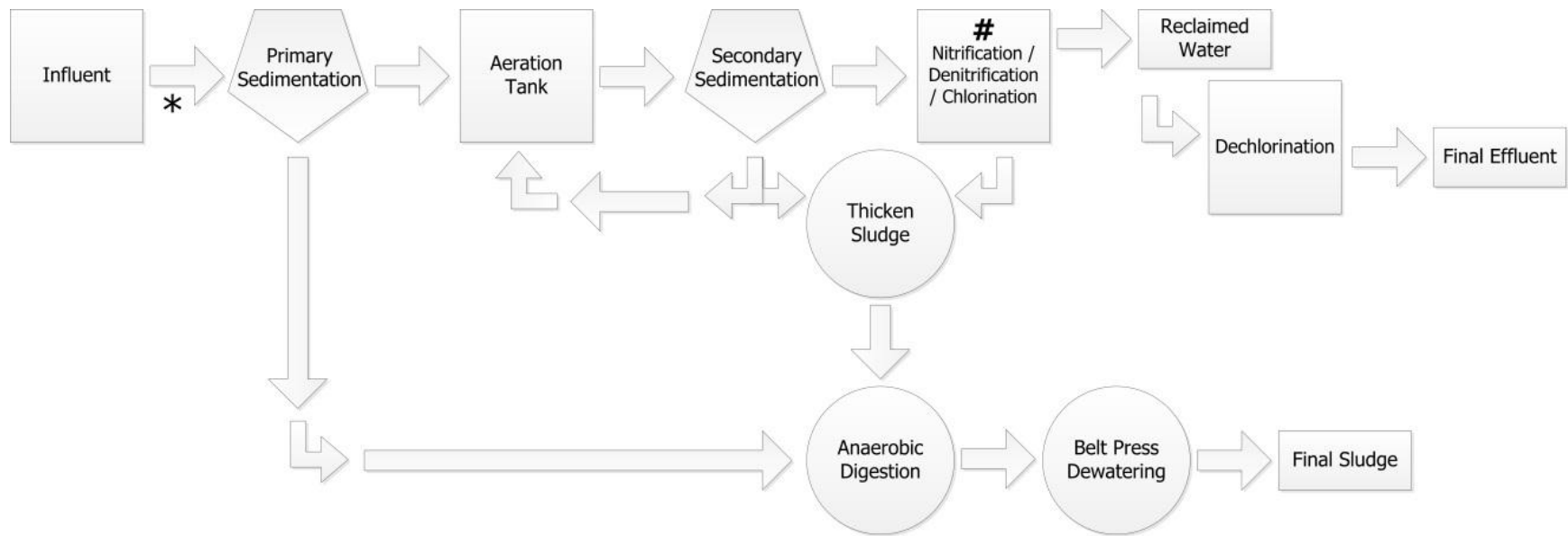
Figure 3. Process flow diagram of Howard F. Curren AWTP.

* Prior to primary sedimentation, there is Screen & Grit Removal step.
# The Nitrification/Dentrification process includes a waste/recycle of the sludge.

The primary treatment process removes approximately 50% of the settleable solids and 30% of BOD through primary sedimentation using eight tanks (see Table 2 for tank volumes and number of tanks for each process) and a 1.2 hour residence time. The primary sludge, the solids at the bottom of the tank, is pumped to anaerobic digestion; sludge processing will be discussed later (Howard F. Curren AWTP, 2009).

Table 2. Number of tanks and respective volumes at Howard F. Curren AWTP.

Process	Volume (MG)	Number
Primary sedimentation	0.5	8
Aeration	1.3	2
Secondary sedimentation	1.5	6
Nitrification	2.1	3
Nitrification sedimentation	1.5	8

In the secondary treatment, the remaining organic and inorganic solids from the primary sedimentation effluent are removed. Air activated sludge removes carbonaceous BOD_5 in two enclosed tanks by entering in a plug flow pattern. Return activated sludge (RAS) is combined in the carbonaceous reactors to form mixed liquor. Next sewage enters the carbonaceous sedimentation tanks (final sedimentation) where the activated sludge is removed from the mixed liquor through gravity settling. The activated sludge is either returned (RAS) to the reactors or wasted (waste activated sludge [WAS]) from the process. Approximately 93% is returned and 7% is wasted to be combined with the waste from the subsequent nitrification sedimentation process. Following secondary treatment, the overall removal of carbonaceous BOD_5 and TSS is approximately 90%. Only 20-25% of the total nitrogen has been removed at this point;

therefore, the next step in the process is removal of total nitrogen through nitrification/denitrification (Howard F. Curren AWTP, 2009).

Nitrification is the process of removing nitrogen through the conversion of organic nitrogen and ammonia to nitrate. Carbonaceous effluent enters the nitrification tanks in a plug flow pattern along with nitrification return sludge and raw sewage, both of which act as a food source for the nitrifying bacteria, forming the nitrification mixed liquor. In the nitrification sedimentation tanks, the activated sludge is removed from the nitrification mixed liquor by gravity settling. 99.8% of the activated sludge is returned to the nitrification tanks, whereas the remaining 0.2% is wasted activated sludge. Approximately 95% of carbonaceous BOD_5 and suspended solids have been removed at this point (Howard F. Curren AWTP, 2009).

Denitrification is the conversion of nitrate into nitrogen gas, which is ultimately released into the atmosphere. The anaerobic process is completed across 32 denitrification filters. Methanol is used as the food source. From the raw sewage to denitrification, more than 90% of the nitrogen present is removed from the wastewater stream in the form of nitrogen gas (Howard F. Curren AWTP, 2009).

Because of the lack of oxygen, there is little or no dissolved oxygen (DO), and therefore, DO levels must be 5.0 mg/L before discharge into the Bay by providing diffused air in the post-aeration chlorination tanks. Disinfection occurs in the post-aeration chlorination tanks to create a chlorine residual of over 1.0 mg/L. If the effluent will be reused as reclaimed water, the chlorine is not removed. For effluent that will be

discharged to the Bay, the chlorine is removed through the addition of sulfur dioxide (Howard F. Curren AWTP, 2009).

As stated earlier, the sludge is processed first from the removal of solids during the primary sedimentation. The primary sludge is stabilized by anaerobic digestion. The WAS from the secondary sedimentation and nitrification sedimentation processes are first thickened and then also stabilized in the anaerobic digestion tanks. The ratio of primary sludge to thicken sludge in the anaerobic digestion tanks is 60% to 40%. Digested sludge from the anaerobic digestion tanks is dewatered by the belt filter presses or dried on sand drying beds, at a ratio of 95% to 5%. The biosolids that are produced through the belt filter press can be used as a soil amendment or land application (Howard F. Curren AWTP, 2009).

Chapter Four

Phase One: Fate of Polybrominated Diphenyl Ethers

Introduction

Polybrominated diphenyl ether (PBDE), a flame retardant that is a

microconstituent of concern, is ubiquitous in the environment, animals, and humans

(ATSDR, 2004). The scientific evidence on human health effects of PBDEs is scant, but

it has been shown to affect the thyroid gland and liver in rats and mice (ATSDR, 2004).

High concentrations of PBDEs may also cause neurobehavioral alterations and affect the

immune system in animals (ATSDR, 2004).

PBDEs consist of three commercial formulations, Penta-BDE, Octa-BDE, and

Deca-BDE, with numerous congeners within those three formulations (Lorber, 2008).

Research suggests that the Penta-BDE formulation and its congeners tend to persist

and bioaccumulate more readily in the environment, as compared to the other two

formulations (Betts, 2002). As such, it is the most detected formula in wildlife and the

environment, and one congener in particular, BDE-47, is detected more often (Betts,

2002).

Although several formulations of PBDEs have been banned from production

throughout the world (Lober, 2008), environmental concentrations are steadily rising

(Betts, 2002). In order to understand the release of PBDEs into the environment,

exposure sources must be investigated. One such source is the wastewater treatment plant. The purpose of this study is to characterize the fate and transport of PBDEs in a wastewater treatment plant that produces reclaimed water.

Materials and Methods

<u>Sampling Plan</u>

Sampling occurred over a three month period in the summer, with sampling occurring one day each month for wastewater and sludge samples, and air sampling occurring over three 48-hour periods once each month. This sampling plan allowed for minimal fluctuations in PBDE concentrations from month to month, as well as limited the effect of seasonal variations on concentration levels. The wastewater and sludge samples were collected during a 48-hour operation of the high volume air sampler. It is assumed that the PBDE concentrations within the WWTP are at steady state within the 48-hour period of collection, meaning although the sampler is running for 48-hours, the concentration found in the air can be directly linked to the wastewater collected at one point in time during that timeframe. In order to ensure the integrity of the study, proper quality assurance/quality control (QA/QC) was utilized, including but not limited to the collection of field, lab, and transportation blanks (to illustrate freedom from contamination) and spiking of samples prior to analysis (to illustrate precision and recovery).

<u>Wastewater Sampling</u>

Wastewater was collected through grab sampling at various points throughout the WWTP using prebaked (450 °C for 4.5 hours), cleaned amber jars. Because there may be concern that a grab sample is not a representative sample, the sampling period was over a three month period, with collecting occurring on one day each month coinciding with the air sampling. The sample locations were at eight designated points within the treatment process, with many points utilizing the sampling location that the WWTP uses for their own sampling and testing points. The sample locations were: 1) influent, 2) primary sedimentation, 3) carbonaceous / sedimentation, 4) diffused air reactors (nitrification), 5) nitrification sedimentation, 6) denitrification, 7) reclaimed water, and 8) effluent. (See Appendix C).

Two-liters of wastewater were collected in amber jars at each sample location. The reported concentrations took the one-liter per sample into consideration while calculating final concentrations. All samples were kept in ice coolers with dry ice (<4 °C) during collection and transport. Once at the lab, all samples were kept in a walk-in refrigerator (<4 °C) until extraction.

<u>Sludge Sampling</u>

Sludge was collected through grab sampling at various points throughout the WWTP using prebaked, cleaned amber jars (450 °C for 4.5 hours). Similar to the wastewater sampling, the sludge was collected at the same time as the wastewater samples over a three month period, with collection occurring one day each month. The

sampling locations were at four designated points within the treatment process. The

sample locations were: 1) primary sludge from clarifier, 2) thickened sludge from

clarifiers' waste stream, 3) predigested / digested sludge, and 4) belt filter dewatering.

(See Appendix D). One amber jar per sample location was used to collect the necessary

amount of sludge for extraction and analysis. All samples were kept in ice coolers with

dry ice (<4 °C) during collection and transport. Once at the lab, all samples were kept

in a walk-in refrigerator (<4 °C) until extraction.

Air Sampling

A high volume air sampler (model TE-1000 PUF, Tisch Environmental, Inc.) was

used for collection of air samples at points within the WWTP. The high volume air

sampler was calibrated according to manufacturer's specifications prior to each use.

Field blanks were also drawn to verify the precision of the instrument. The air sampling

occurred over a two month period with two-machines running concurrently side-by-side

for a 48-hour period once per month. In order to ensure detectable levels of PBDEs in

the air, it is believed that 48-hour sampling is more conducive than the 24-hour

standard of the Environmental Protection Agency sampling plan (TO-13A). The reported

concentrations took the extended sampling time and dual machines into consideration

while calculating final concentrations. The sampling locations within the plant were: 1)

pre-treatment (odor removal), 2) grit and screen removal, and 3)

carbonaceous/sedimentation. (See Appendix E).

The air sampler used a prebaked (400 °C for 4 hours) quartz microfiber filter (10.16 cm circle, Tisch Environmental, Inc.) for particulate collection and a hexane rinsed glass cartridge containing a pre-extracted polyurethane substrate (PUF) (2" long, Tisch Environmental, Inc.) for vapor collection and a cleaned Amberlite[TM] XAD[TM]-2 adsorbent (30g, Supelco, Inc.) for vapor collection and break through. All PUFs were washed through Soxhlet extraction using methylene chloride for 16 hours, dried in a desiccator for 24 hours, and stored in prebaked, cleaned amber jars until ready for use. The Amberlite[TM] XAD[TM]-2 adsorbent was cleaned through Soxhlet extraction in a prebaked (100 °C for 2 hours) cellulose extraction thimble (35 mm x 94 mm, Whatman International Ltd.) using methylene chloride for 16 hours, changed to fresh methylene chloride for an additional 16 hours, dried under a hood for 4 hours, and stored in prebaked, cleaned amber jars in the refrigerator (<4 °C) until ready for use.

Each glass cartridge containing the PUF/XAD[TM]-2 were prepared 24 hours prior to deployment, wrapped in aluminum foil, and stored in opaque container in the refrigerator until ready for use. The glass cartridges were transported to field site in ice coolers with dry ice (<4 °C). One prepared glass cartridge was placed in each high volume air sampler that was scheduled to start sampling at midnight that day and to run for 48 hours. The day following the 48 hour period, each glass cartridge was collected and stored in container in ice cooler with dry ice (<4 °C) for transportation back to the lab. The glass cartridges were stored in a walk-in refrigerator (<4 °C) until extraction.

Of note, there was access to only two high volume air samplers. Therefore, they were placed at one location side-by-side and run for three 48 hour periods. Then they were moved to the next location to run for three 48 hour periods. Then they were moved to final location for three 48 hour sampling periods. The sampling frame for air was therefore over a longer stretch of time because of the inability to sample all three locations at the same time. It is assumed that this had no impact on the sampling, collecting, and analyzing of air samples.

Sample Extraction

Prior to extraction, all samples, regardless of the sampling matrix, were spiked with a recovery standard or surrogate of BDE-35 and BDE-181 (Cambridge, Inc). This spiking was used to determine recovery rates during the extraction and clean-up processes. Wastewater and sludge samples were extracted following the Environmental Protection Agency (EPA) method for *PBDEs in water, soil, sediment, and tissue* (Method 1614) with slight modifications (see Appendix G). Briefly, wastewater samples were extracted using liquid-liquid extraction with methylene chloride followed by concentration by rotavaporation, run through a sodium sulfate channel for removal of water, clean-up on a multilayer silica gel column, and nitrogen evaporation to the final sample volume. Residual sulfur in the samples was removed using dilute nitric acid cleaned-copper powder (EPA Method 3660B) prior to clean-up stage. Wastewater samples containing visible solids were handled similarly to a published method (Rayne & Ikonomou, 2005). Briefly, spiked samples were transferred into a porcelain Buchner

funnel (126-mm diameter), and filtered under vacuum over pre-baked Whatman No.7 GF/C filters (11-cm diameter, nominal pore size 1.2 μm) into a 1-L vacuum solvent-rinsed filter flask. The amber jars containing the samples were rinsed three times with deionized Milli-Q grade water to remove all deposits, and the rinses were passed through the filter as well. The solids with the respective filters were Soxhlet extracted in pre-baked extraction thimbles (Whatman) for 18 hours with methylene chloride followed by concentration by rotavaporization. After which time, the Soxhlet extractions were combined with the liquid-liquid extractions.

Following the transferring of sludge samples into a solvent-rinsed Teflon tube and centrifuging at 1000 rpm for 10 min, ~10 g of sludge solids were Soxhlet extracted in pre-baked extraction thimbles (Whatman) for 18 hours with methylene chloride followed by concentration by rotavaporation, run through a sodium sulfate channel for removal of water, treated with cleaned-copper powder, clean-up on a multilayer silica gel column, and nitrogen evaporation to the final sample volume. Approximately 5 g of sodium sulfate was added to each thimble with the sludge sample prior to Soxhlet extraction for preliminary removal of excess water. Due to the Belt Press samples containing very little water, instead of centrifuging them, ~10 g of sample was added to a solvent-rinsed glass mortar and pestle and ground with ~5 g of sodium sulfate, and then added to the thimble for extraction.

Air samples were extracted following the EPA method for *Compendium of methods for the determination of toxic organic compounds in ambient air* (Method TO-13A). The sample substrate (filter, PUF, or XAD[TM]-2) was Soxhlet extracted for 16 hours

with methylene chloride followed by concentration by rotavaporation, clean-up on a silica gel column, and nitrogen evaporation to the final sample volume.

All glassware and apparatus used to handle samples were washed, dried, and solvent-rinsed following EPA Method 1614: methanol, hot tap water, another methanol rinse, acetone, and then methylene chloride. Baking of glassware was minimized, however, after particularly dirty samples, baking some glassware at 450 °C for 4.5 hours was warranted. Immediately prior to extraction, the Soxhlet apparatus were pre-extracted for 4 hours with methylene chloride. The extracted methylene chloride was replaced with fresh solvent and the thimble samples were added and then extracted. All solvents used were pesticide-quality, lot-certified to be free from interferences (Fisher Scientific).

Sample Analysis

PBDE determination of the wastewater and sludge was performed using a HP-7890A gas chromatography (GC) (Agilent Technologies) coupled to a HP-5975C quadrupole mass spectrometer (MS) detector (Agilent Technologies). The GC-MS was calibrated to manufacturer's specifications, as well as operated according to the EPA's specifications for analysis of samples of mixed matrices. The GC column was a 20 m x 0.18 mm i.d. x 0.36 μm film thickness DB-5MSUI capillary column (Agilent Technologies). Helium was used as the carrier gas. 0.5 μL of sample solution was injected in pulsed splitless mode. The injector temperature was 250 °C and the purge time was 0.5 min after injection. The oven temperature was programmed as follows:

100 °C for 0.5 min, then increased at 40 °C/min to 260 °C and held for 4.5 min, then increased at 20 °C/min to 320 °C and held for 8 min. Ionization was performed in electron capture negative ionization (ECNI) mode, using methane as reagent gas at a rate of 1.2 mL/min. The transfer line, source, and quadrupole temperatures were 300, 250, and 150 °C, respectively. PBDEs were analyzed in the selected ion-monitoring (SIM) mode, and isotopic bromine anions were monitored (m/z 79 and 81).

Because the air samples were extracted and analyzed first, the use of the GC/MS equipment differed. PBDE determination of the air was performed using a HP-6890 GC (Agilent Technologies) coupled to a HP-5973 quadrupole MS detector (Agilent Technologies). The GC column was a 15 m x 0.25 mm i.d. x 0.25 μm film thickness DB-5MS capillary column (Agilent Technologies). Helium was used as the carrier gas. 1 μL of sample solution was injected in splitless mode. The injector temperature was 250 °C and the purge time was 1.0 min after injection. The oven temperature was programmed as follows: 60 °C for 1.0 min, then increased at 10 °C/min to 150 °C, then increased at 5 °C/min to 300 °C and held for 5 min. Ionization was performed in electron capture negative ionization (ECNI) mode, using methane as reagent gas at a rate of 1.2 mL/min. The transfer line, source, and quadrupole temperatures were 250, 150, and 106 °C, respectively. PBDEs were analyzed in the selected ion-monitoring (SIM) mode, and isotopic bromine anions were monitored (m/z 79 and 81).

The identification of seven PBDE congeners (BDE-28, 47, 99, 100, 153, 154, and 183) was based on their retention times and the ratios of monitored ions relative to prepared congener standards (Table 3). Quantitative determination incorporated an

external standard method, using a 5 concentration level calibration (linear) curve (Table 4).

Table 3. Retention times and ions monitored per PBDE congener.

Congener	Retention Time	Ions (m/z)
BDE 28	6.332	79, 81
BDE 47	8.237	79, 81, 404.8
BDE 99	10.667	79, 81, 402.8
BDE 100	10.183	79, 81, 402.8
BDE 153	12.196	79, 81, 401.8
BDE 154	11.701	79, 81, 401.8
BDE 183	13.805	79, 81, 481.7

Table 4. Coefficient of determination (R^2) per PBDE congener.

Congener	R^2
BDE 28	1.000
BDE 47	1.000
BDE 99	1.000
BDE 100	1.000
BDE 153	1.000
BDE 154	1.000
BDE 183	0.999

Quality Assurance and Quality Control

Any concentration results found during an analysis of environmental samples are limited in quality by the sensitivity and selectivity of the analytical equipment used. In order to reduce the effects of limit of detection, this study followed analytical protocols prepared and validated by the EPA for sampling and analysis of PBDEs (e.g., EPA Method 1614). The GC/MS was inspected for precision by spiking a test sample with a

known concentration of PBDE standards to measure the recovery and sensitivity of the machine. The samples were also spiked with mirex prior to analysis (to serve as the internal standard). Additionally, the instrument detection limit was considered by using the standard signal to noise ratio of ≥ 3 on the GC/MS, in order to differentiate the peaks generated by the PBDEs of interest and those from background artifacts. Any sample that did not have peaks ≥ 3 was recorded as non-detectable or ND. BDE-35 and BDE-181 surrogate recoveries ranged between 60.4 and 104.5% (mean % recovery $\pm$ SD = 75.5% $\pm$ 18.6) and 42.1 and 99.9% (77.3% $\pm$ 21.6), respectively. Because the average recovery rates were relatively high, none of the data presented here was corrected for recovery. A blank instrumentation sample (hexane) was analyzed together with every batch of five samples to monitor instrument performance and detect any sample carry-over.

For method validation, deionized Milli-Q grade water samples were spiked with a PBDE standard solution containing all PBDE congeners of interest (50 pg/mL) and analyzed together with the field, laboratory, and transportation blanks. The recoveries of individual PBDE congeners ranged from 70 to 95%.

Data Analysis

Data analysis included descriptive statistics. The descriptive statistics used were measures of central tendency (mean), measures of variability (standard deviation), and 95% confidence intervals. All detected levels of PBDEs were calculated and recorded in

concentrations of picogram/liter (pg/L) for liquid samples, microgram/kilogram (μg/kg dry weight) for solid samples, and picogram/cubic meter (pg/m^3) for air samples.

Mass balances of PBDEs at the various treatment steps and the overall process were calculated according to the formulae presented below (based on research completed by Katsoyiannis and Samara (2005)) (flow rates correspond to Figure 4).

Primary treatment
BDE_{in} (g/d) = BDE_{INF} (g/m^3) x Q_{INF} (m^3/d)
BDE_{out} (g/d) = BDE_{PSE} (g/m^3) x (Q_{INF} - Q_{PS}) (m^3/d) + BDE_{PS} (g/g) x Q_{PS} (m^3/d) x SS_{PS} (g/m^3)

Secondary treatment
BDE_{in} (g/d) = BDE_{PSE} (g/m^3) x (Q_{INF} - Q_{PS}) (m^3/d)
BDE_{out} (g/d) = BDE_{SSE} (g/m^3) x (Q_{INF} - Q_{PS}) (m^3/d) + BDE_{AS} (g/g) x (Q_{AS} - Q_{AS-2}) (m^3/d) x SS_{AS} (g/m^3)

Total treatment
BDE_{in} (g/d) = BDE_{INF} (g/m^3) x Q_{INF} (m^3/d)
BDE_{out} (g/d) = BDE_{SSE} (g/m^3) x (Q_{INF} - Q_{PS}) (m^3/d) + BDE_{PS} (g/g) x Q_{PS} (m^3/d) x SS_{PS} (g/m^3) + BDE_{AS} (g/g) x (Q_{AS-2}) (m^3/d) x SS_{AS} (g/m^3)

Sludge stream
BDE_{in} (g/d) = BDE_{PS} (g/m^3) x Q_{PS} (m^3/d) + BDE_{AS} (g/m^3) x Q_{AS} (m^3/d)
BDE_{out} (g/d) = BDE_{FS} (g/m^3) x Q_{FS} (m^3/d)

Mass loading of effluent was calculated directly as the mass concentration of PBDEs multiplied by the volumetric flow rate and the corresponding unit conversions (shown). Sludge loading was calculated using a solids balance across the belt press filter. Using the density of water (62.4 lb/ft^3) and the specific gravity of the sampled sludge (1.3) (North, 2004), sludge calculations were converted from volume to mass. Solids through the belt press were assumed to be 96% based on internal testing at the WWTP on normal performance of the belt press. Air loading was calculated as the dry
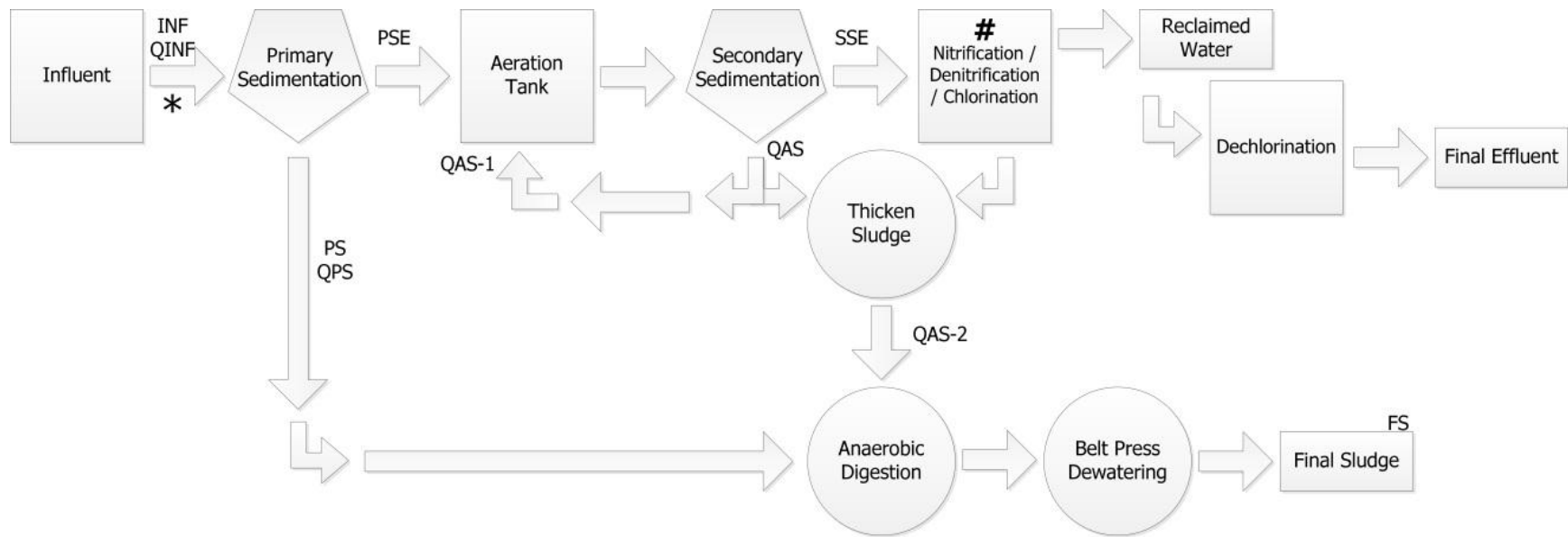
Figure 4. Process flow diagram of Howard F. Curren AWTP with flow rates.

* Prior to primary sedimentation, there is Screen & Grit Removal step.
# The Nitrification/Dentrification process includes a waste/recycle of the sludge.

Q_{INF}, flow rate of influent (223,301 m^3/d), Q_{PS}, flow rate of primary sludge (18,031 m^3/d), Q_{AS}, flow rate of activated sludge (161,435 m^3/d), Q_{AS-1}, flow rate of recirculated activated sludge (66,812 m^3/d), Q_{AS-2}, flow rate of waste activated sludge (20,921 m^3/d).

weight, volumetric air transfer rate (dry standard cubic feet per minute [dscfm])

multiplied by the dry weight concentration. Mass loading of PBDEs were calculated

according to the formulae presented below (based on research completed by North

(2004)).

Liquid phase (effluent)
Flow rate 10^6 gallon/day x concentration (mg/L of PBDE) x 3.78E6 L/10^6
gallon x lb/0.45E6 mg = loading (lb/day)

Solid phase (final sludge)
Sludge flow rate (gallon/minute) x 1440 min/day x ft^3/7.48 gallon x 62.4
lb/ft^3 x 1.3 x % solids x 0.96 lb solids out of belt press/1 lb solids into belt
press x dry weight PBDE concentration (mg/kg of PBDE) x kg/10^6 mg =
loading (lb/day)

Air phase
Flow rate (dscfm) x concentration ($\mu g/m^3$ of PBDE) x m^3/35.31 ft^3 x 1440
min/day x lb/4.54E8 μg = loading (lb/day)

Data quantification were performed using ChemStation G2070BA software

(Agilent Technologies). All peaks were verified and then if needed, manually integrated.

Data management and graphing were performed using Microsoft Excel 2010.

Results and Discussion

Measurement of PBDE congeners was performed for wastewater, sludge, and air

samples (Tables 5, 6, and 7). Influent concentration of mean Σ_7PBDE was found to be

49,117 pg/L and effluent concentration was 4,603 pg/L, illustrating a 91% removal rate

of PBDEs during the wastewater treatment plant. There was a considerable spike in

PBDE concentrations during the nitrification process due to the use of diverted raw sewage being added at the headstream to supplement the food required for the nitrifying bacteria. As expected, sludge samples contained the highest total concentrations of PBDEs with mean Σ_7PBDE ranging from 14.0 to 41.3 µg/kg dry weight. Air samples were highest at the post-aeration (248 pg/m^3 mean Σ_7PBDE) step due to the use of highly oxygenated air assisting in the release and volatilization of the PBDEs.

Overall, PBDE congener contribution differed by sample matrix (Figure 5). Wastewater and air consisted mainly of BDE-47 (52% and 62%, respectively), whereas sludge was made up of BDE-99 (48%). This is not unexpected due to the higher log K_{ow} of BDE-99 than the log K_{ow} of BDE-47, illustrating the higher likelihood to find the larger PBDEs in the suspended solids. The high concentration of BDE-47 in the air gives further support to the ability of BDE-47's long range transport capabilities (Betts, 2002).
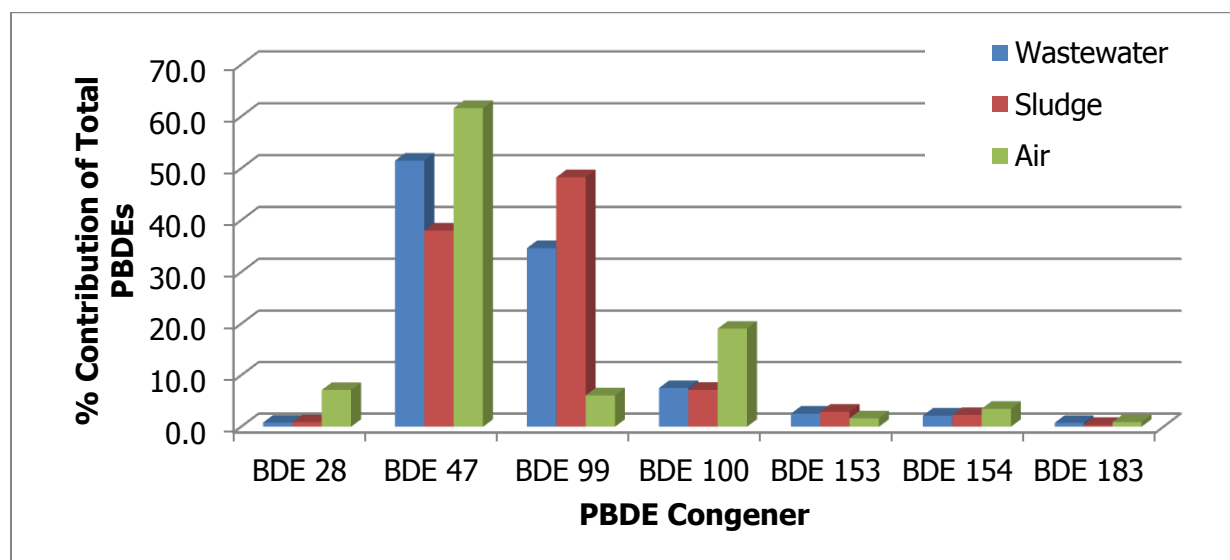
Figure 5. PBDE congener percent contribution relative to total PBDEs in wastewater, sludge, and air.

Table 5. Congener-specific BDE mean concentrations (pg/L) in wastewater.

Sample	PBDE Congeners (pg/L)						
	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Influent	462	23832	18186	3392	1502	1107	636
Primary sedimentation	701	16787	15096	2788	1221	966	532
Secondary sedimentation	ND	ND	2460	1154	310	259	363
Nitrification	1900	115010	75779	16381	5181	4470	941
Nitrification sedimentation	ND	ND	ND	ND	141	140	ND
Denitrification	ND	ND	ND	ND	ND	ND	ND
Reclaimed	ND	10821	2270	705	ND	130	ND
Effluent	ND	4603	ND	ND	ND	ND	ND

See Appendix I for raw data.

Table 6. Congener-specific BDE mean concentrations (µg/kg dry weight) in sludge.

Sample	PBDE Congeners (µg/kg dry weight)						
	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Primary sludge	0.4	15.5	20.3	2.9	1.2	0.9	0.1
Thicken sludge	0.2	8.9	10.7	1.6	0.7	0.5	0.1
Digested sludge	0.1	5.3	6.7	1.0	0.4	0.3	0.1
Belt press sludge	0.2	5.8	6.8	1.1	0.4	0.4	0.1

See Appendix I for raw data.

Table 7. Congener-specific BDE mean concentrations (pg/m^3) in air.

Sample	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Odor Control	ND	ND	ND	ND	ND	0.5	0.6
Screen & Grit	16.5	ND	2.1	ND	ND	1.1	0.4
Post-Aeration	13.0	157.0	14.7	48.6	5.9	6.8	2.2

PBDE Congeners (pg/m^3)

See Appendix I for raw data.

Due to the nature of the WWTP, a synthetic compound may not be completely removed or degraded within the biological reactor, and therefore it may be that a portion of it will be released into the environment. It may be discharged with the effluent, distributed with the sludge, or volatilized into the air. Persistent organic pollutants, such as PBDEs, are more likely to remain stable once in the environment because they have little biodegradation (Katsoyiannis & Samara, 2005).

The mass balances of PBDEs in the Howard F. Curren WWTP were calculated from the concentrations in the wastewater and sludge samples, the concentration in the suspended solids in the sludge, and corresponding flow data (Figure 4) – only considering the primary and secondary treatment processes because these are the sites of the handling of the majority of the solids present in the wastewater stream. Flow rates were based on 3-month averages over the sampling period. If there were any degradation or physical loss of PBDEs, there would be a theoretical balance of 100%, illustrating the partitioning of PBDEs from the solids to the settled effluent (Katsoyiannis & Samara, 2005). However, incomplete agreements in balances may be a result of sampling errors, methodology inconsistencies, and of course, the complex nature of analyzing wastewater streams. Table 8 shows the mass balances of the primary, secondary, and total treatment, and sludge stream.

Figures 6, 7, and 8 show the mean "gain" (negative graph bars) and "loss" (positive graph bars) of individual PBDEs in primary, secondary, and total treatment, and sludge stream. In primary treatment, the overall loss of PBDEs is low (ranging from 19% to 35%), with a gain in BDE-28. Because primary treatment is tasked with removal

Table 8. Mass balances of primary, secondary, and total treatment, and sludge stream.

Mass Balance	PBDE Congeners (g/d)							
	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	Σ PBDEs
Primary Treatment In	0.10	5.32	4.06	0.76	0.34	0.25	0.14	65.43
Primary Treatment Out	0.14	3.46	3.12	0.58	0.25	0.20	0.11	47.18
% loss	**-40**	**35**	**23**	**24**	**25**	**19**	**23**	**28**

Mass Balance	PBDE Congeners (g/d)							
	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	Σ PBDEs
Secondary Treatment In	0.14	3.45	3.10	0.57	0.25	0.20	0.11	46.77
Secondary Treatment Out	3.55E-04	0.01	0.52	0.24	0.06	0.05	0.07	3.89
% loss	**99.8**	**99.6**	**83**	**58**	**74**	**73**	**32**	**92**

Mass Balance	PBDE Congeners (g/d)							
	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	Σ PBDEs
Total Treatment In	0.10	5.32	4.06	0.76	0.34	0.25	0.14	65.43
Total Treatment Out	4.31E-04	0.02	0.53	0.24	0.07	0.05	0.07	3.99
% loss	**99.6**	**99.7**	**87**	**68**	**81**	**78**	**47**	**94**

Mass Balance	PBDE Congeners (g/d)							
	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	Σ PBDEs
Sludge Stream In	45	1722	2086	313	134	102	18	39749
Sludge Stream Out	6	198	232	38	14	12	2	4302
% loss	**87**	**89**	**89**	**88**	**90**	**88**	**87**	**89**

of large materials, not with the removal of solids, this is not unreasonable. However, the gain in BDE-28 is likely an anomaly of the small sample size. Expectedly, the mass balances were much higher for the secondary treatment, where the principal task is solids management. Because of the large log K_{ow} of PBDEs, one would expect to see PBDE removal from the wastewater stream during the process of solids removal, such as demonstrated during the secondary treatment.
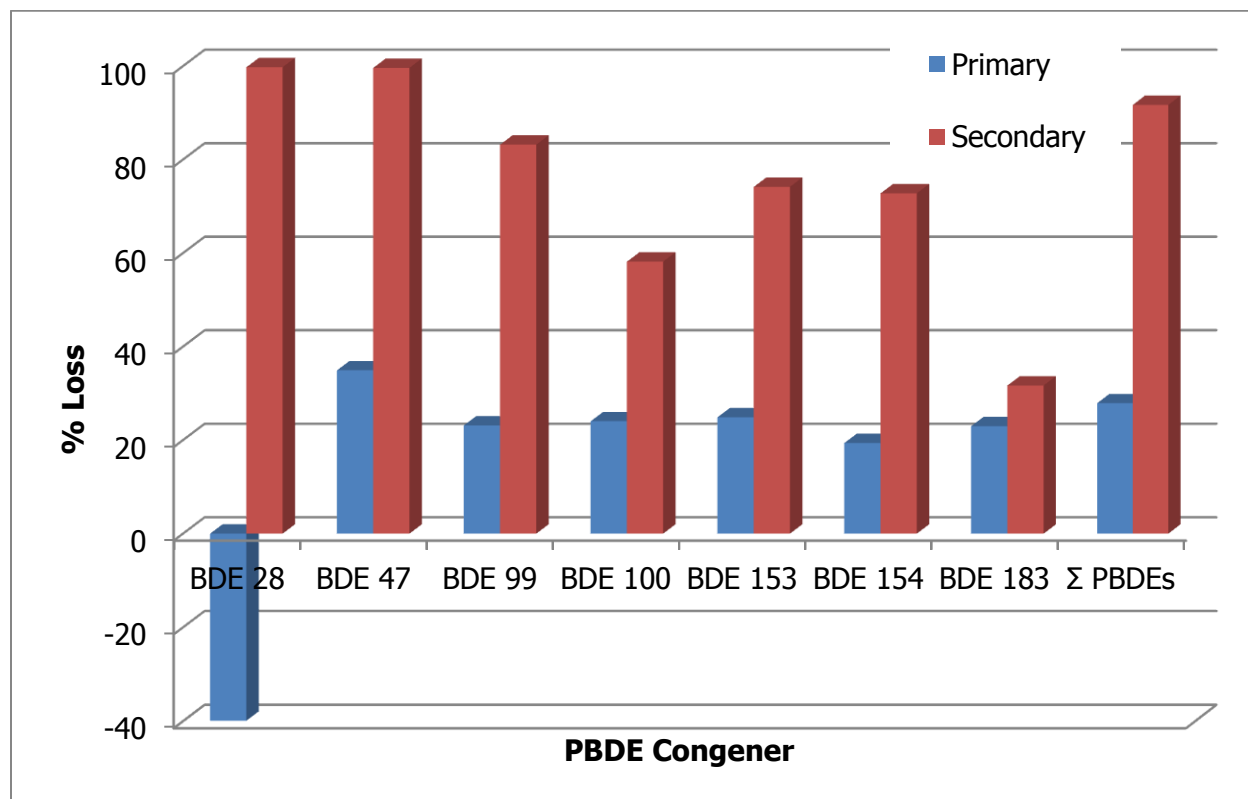
Figure 6. Mass balance of PBDEs through primary and secondary treatment processes (negative graph bars indicate percentage gain).

The total treatment considers primary and secondary treatment combined. The overall mass balances were high for the total treatment (Figure 7). Total loss for Σ_7PBDE was

found to be 94%. Again, this illustrates the partitioning of PBDEs to the solids for removal from the wastewater stream. As such, it is imperative for examination of the sludge stream for mass loading of PBDEs into the environment.
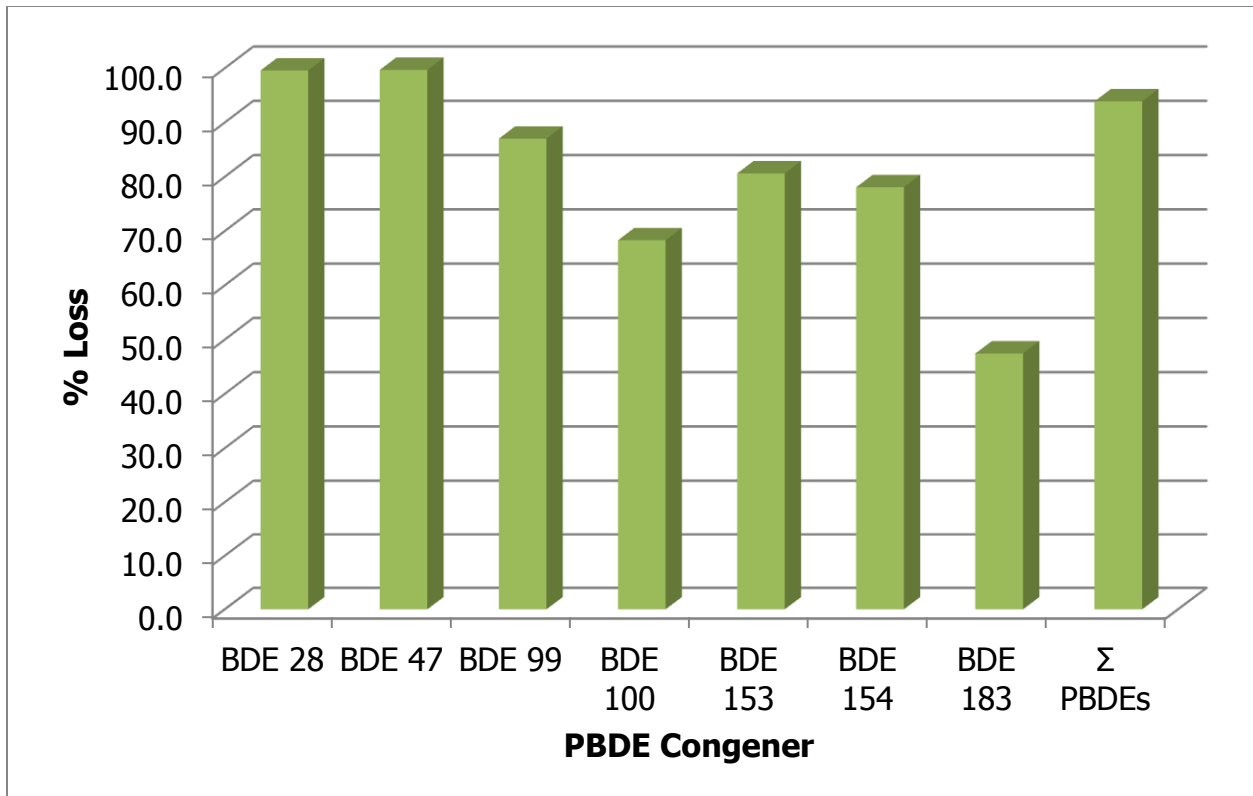
Figure 7. Mass balance of PBDEs through total treatment process.

Anaerobic digestion of sludge, as used in Curren AWTP, has not been studied thoroughly, in particular for fate of PBDEs during the treatment stages (Katsoyiannis & Samara, 2005). Figure 8 shows the mass balance of PBDEs during the sludge treatment (anaerobic digestion, thickening, and dewatering). Examination of these $PBDE_{in}$ versus $PBDE_{out}$ of the sludge stream can identify the effect of degradation of PBDEs during digestion, if any.
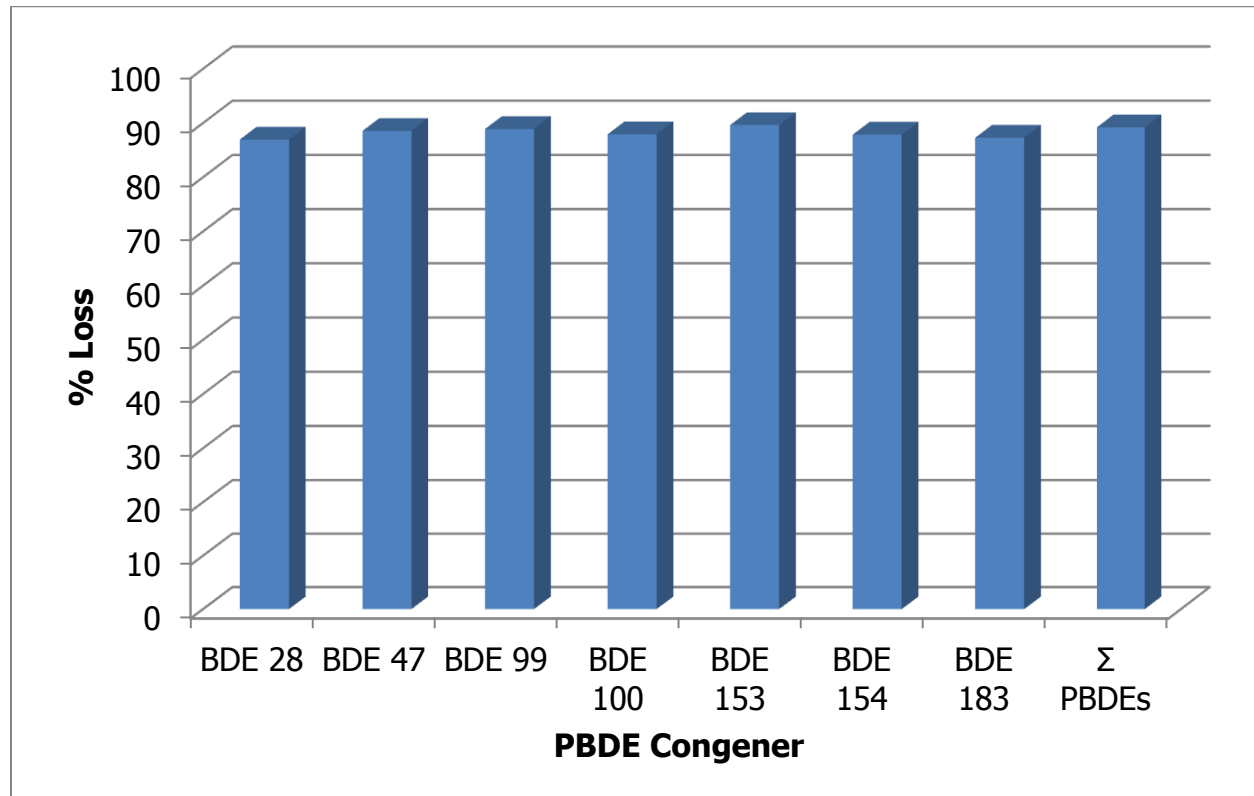
Figure 8. $PBDE_{in}/PBDE_{out}$ through the sludge treatment stream.

Due to the high balances (87% to 90%), there is little degradation or biotransformation during the sludge treatment. Therefore, for reduction of PBDEs in the sludge, degradation or biotransformation is not an effective pathway for continued studies for these PBDE congeners (Clarke et al., 2010; Knoth, Mann, Meyer, & Nebhuth, 2007).

The relative distribution (mass loading) of PBDEs entering the environment from Curren AWTP is presented in Table 10. As seen with the mass balances above, sludge carries the largest mass loading at 14.2 lb/day Σ_7PBDE. Of the total mass loading of PBDEs from the WWTP, sludge is responsible for 86.7%, followed by reclaimed water

and effluent (11.7% and 1.6%, respectively). The mass loading from air was negligible with less than 0.01% contribution to the total mass loading.

A study completed by North (2004) tracking PBDE releases from a WWTP in Palo Alto, CA found that the mass loading of PBDEs was 2 lb/year from the effluent, 48 lb/year from sludge, and 6.1 x 10^{-7} lb/year from the stack emissions of the incinerated sludge (Table 9). The examined WWTP was a tertiary plant treating 25 MGD from residents (60%), industries (10%), and commercial businesses and institutions (30%). Whereas Curren AWTP is also a tertiary plant, but with a larger influent flow (58 MGD) and the make-up of the sewage is primarily residential. As such, the lower rates of mass loading from the Curren AWTP are understandable. An additional distinction between the North study and this study is the PBDEs under investigation. North analyzed 41 PBDE congeners, detecting 24 to 28 PBDE congeners. This study analyzed and detected only 7 PBDE congeners.

Table 9. Mass loading results for PBDEs in this study to other plant.

	lb/day			lb/year		
	Effluent	Sludge	Air	Effluent	Sludge	Air
This study	6.9E-04	3.9E-02	1.7E-09	0.3	14.2	6.2E-07
North (2004)	5.6E-03	0.1	1.7E-09	2.0	48.0	6.1E-07

Table 10. Mass loading for PBDEs in effluent, reclaimed water, sludge, and air.

Reclaimed	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	Σ PBDEs
Mass Loading (lb/day)	--	8.1E-04	1.7E-04	5.3E-05	--	9.8E-06	--	5.2E-03
Mass Loading (lb/year)	--	3.0E-01	6.2E-02	1.9E-02	--	3.6E-03	--	1.9

Effluent	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	Σ PBDEs
Mass Loading (lb/day)	--	3.5E-04	--	--	--	--	--	6.9E-04
Mass Loading (lb/year)	--	1.3E-01	--	--	--	--	--	0.3

Belt press sludge	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	Σ PBDEs
Mass Loading (lb/day)	5.3E-05	1.8E-03	2.1E-03	3.4E-04	1.3E-04	1.1E-04	2.1E-05	3.9E-02
Mass Loading (lb/year)	1.9E-02	6.5E-01	7.6E-01	1.2E-01	4.6E-02	4.1E-02	7.6E-03	14.2

Post-aeration	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	Σ PBDEs
Mass Loading (lb/day)	1.6E-11	2.0E-10	1.9E-11	6.2E-11	7.5E-12	8.6E-12	2.8E-12	1.7E-09
Mass Loading (lb/year)	6.0E-09	7.3E-08	6.8E-09	2.3E-08	2.7E-09	3.1E-09	1.0E-09	0.0

Chapter Five

Modeling of Polybrominated Diphenyl Ethers in Wastewater Treatment Plant

Introduction

Polybrominated diphenyl ether (PBDE), a flame retardant that is a

microconstituent of concern, is ubiquitous in the environment, animals, and humans

(ATSDR, 2004). The scientific evidence on human health effects of PBDEs is scant, but

it has been shown to affect the thyroid gland and liver in rats and mice (ATSDR, 2004).

High concentrations of PBDEs may also cause neurobehavioral alterations and affect the

immune system in animals (ATSDR, 2004). In order to understand the release of PBDEs

into the environment, exposure sources must be investigated. One such source is the

wastewater treatment plant.

The National Council for Air and Stream Improvement, Inc. (NCASI) Organic

Compound Elimination Pathway (NOCEP) Model can be used to predict the fate of

organic compounds within the wastewater treatment plant (NCASI, 2005). By

examining the wastewater just at the aeration basin and secondary clarifier, the

elimination of organic compounds can be quantified (Barton, 1987). The model

calculates the fraction remaining in the plant effluent. This percent remaining in the

effluent, when released into local receiving waters, can pose a threat to the

environment and humans. Utilizing a modified version of the NOCEP Model created for

academic purposes (Luthy & Cunningham, 2001), the study will compare theoretical

removal rates to calculated removal rates found for PBDEs in a WWTP. This study will

be among the first to examine use of the NOCEP Model with PBDEs.

Methods

In order to test the first hypothesis that observed concentrations of PBDEs

match those predicted in the model, mass balances were calculated for each PBDE

congener (Chapter 4, Table 8). Based on the total treatment removal, it will be possible

to determine whether or not actual concentrations conform to the NOCEP Model.

Results and Discussion

As discussed in Chapter 4, the total treatment's PBDE removal ranged from 47%

to 99.7%. Using the NOCEP Model, the theoretical removal of PBDEs ranged from

96.7% to 99.9%. Table 11 shows the theoretical pathway final calculations from the

NOCEP Model (see Appendix H for outputs from model). Table 12 shows the

comparison of the observed and theoretical PBDE removal.

Table 11. Theoretical removal pathway final calculations from NOCEP Model.

	% Removed						
Removal Pathway	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Stripping	6.07	0.57	0.04	0.01	0.00	0.02	0.00
Solids Partitioning	70.19	90.15	95.49	94.98	98.03	97.74	98.86
Biodegradation	20.40	8.16	3.93	4.40	1.74	1.98	1.01
Total Removal	**96.66**	**98.88**	**99.46**	**99.39**	**99.77**	**99.74**	**99.87**
Fraction Remaining in Effluent	3.34	1.12	0.54	0.61	0.23	0.26	0.13

Table 12. Observed versus theoretical PBDE removal (%).

PBDE Removal	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Observed	99.6	99.7	87.0	68.3	80.6	78.1	47.4
Theoretical	96.7	98.9	99.5	99.4	99.8	99.7	99.9

BDE-28 and 47 had a higher removal rate than theorized, whereas the other congeners had lower removal rates than theorized. Reviewing the theoretical removal pathway final calculations shows that biodegradation plays a role in the removal pathway. However, as was determined in the previous chapter, biodegradation plays little or no role in removal of PBDEs from the wastewater stream. Therefore, additional consideration must be made on the biodegradation rate that is inputted in the model program. Due to the lack of published biodegradation rates for purposes of this study, biodegradation rates used in the model were from the Zhang et al. (2013) study of bioaccumulation kinetics of PBDEs. Although the researchers surmise that bioaccumulation rates are comparable to biodegradation rates for PBDEs, a better removal pathway to consider may be photolytic debromination (Söderström et al., 2004).

Söderström and associates found that PBDEs, as a group of UV-light absorbing organobromine compounds, photolytically degrade into lower brominated BDEs (2004). The largest compound, BDE-209, degraded into lower brominated BDEs from hexa-BDE to nona-BDE regardless of matrix tested. When tested in sediment, sand, and soil, the half-life of UV-light irradiated BDE-209 was 53 hours, 37 hours, and 150-200 hours, respectively (Söderström et al., 2004). Additional studies also found the other PBDE

congeners photolytically degraded at varying rates (Eriksson et al., 2004). As such, photolytic debromination is a removal pathway to be added to the model if examining PBDE removal in the wastewater stream.

The lowest removal was observed in BDE-183. This may be caused by the low concentrations detected in the samples, which could be because of the extraction method or analysis equipment (GC/MS). Larger brominated BDEs are better detected on thinner, shorter columns due to their likelihood to degrade as they travel down the column (Stapleton, 2006). However, as was found during this study, a column with a thin film thickness ($\leq$ 0.25 μm) degrades easily after only a few samples because of the abrasive nature of the keeper solvent used (dodecane). Therefore, any future studies desiring to investigate the larger brominated BDEs (octa-BDE to deca-BDE) would need to be targeted with anticipated detection of those PBDEs.

Chapter Six

Phase Two: Reclaimed Water Versus Effluent

Introduction

Polybrominated diphenyl ether (PBDE), a flame retardant that is a

microconstituent of concern, is ubiquitous in the environment, animals, and humans

(ATSDR, 2004). The scientific evidence on human health effects of PBDEs is scant, but

it has been shown to affect the thyroid gland and liver in rats and mice (ATSDR, 2004).

High concentrations of PBDEs may also cause neurobehavioral alterations and affect the

immune system in animals (ATSDR, 2004).

PBDEs consist of three commercial formulations, Penta-BDE, Octa-BDE, and

Deca-BDE, with numerous congeners within those three formulations (Lorber, 2008).

Research suggests that the Penta-BDE formulation and its congeners tend to persist

and bioaccumulate more readily in the environment, as compared to the other two

formulations (Betts, 2002). As such, it is the most detected formula in wildlife and the

environment, and one congener in particular, BDE-47, is detected more often (Betts,

2002).

Although several formulations of PBDEs have been banned from production

throughout the world (Lober, 2008), environmental concentrations are steadily rising

(Betts, 2002). In order to understand the release of PBDEs into the environment,

exposure sources must be investigated. One such source is the wastewater treatment plant. The purpose of this study is to examine concentration levels of PBDEs in reclaimed water and compare them to levels in effluent.

Materials and Methods

Sampling

Samples were collected over a six week period in the Spring, with sampling occurring every Monday, Wednesday, and Friday. Sampling every other weekday allowed for minimal fluctuations in PBDE concentrations from day to day. The reclaimed water and effluent samples were collected during the same visit. In order to ensure the integrity of the study, proper quality assurance/quality control were utilized, including but not limited to the collection of field, lab, and transportation blanks (to illustrate freedom from contamination) and spiking of samples prior to analysis (to illustrate precision and recovery).

Reclaimed water and effluent were collected through grab sampling at their respective points in the WWTP (see Appendix D) using prebaked (450 °C for 4.5 hours), cleaned amber jars. Because there may be concern that a grab sample is not a representative sample, the sampling period was over a six week period, with collecting occurring on three days each week. The sample locations were at two designated points within the treatment process, with both points utilizing the sampling location that the WWTP uses for their own sampling and testing points. The sample locations were: 1) reclaimed water, and 2) effluent.

In order to ensure detectable levels of PBDEs in the wastewater, two-liters of each sample location were collected. The reported concentrations took the two-liters into consideration while calculating the final concentrations. Due to the presence of residual chlorine in the reclaimed water, 80 mg of sodium thiosulfate per liter of water was added to the sample at time of collection. All samples were kept in ice coolers with dry ice (<4 °C) during collection and transport. Once at the lab, all samples were kept in a walk-in refrigerator (<4 °C) until extraction.

Sample Extraction

Prior to extraction, all samples were spiked with a recovery standard or surrogate of BDE-35 and BDE-181 (Cambridge, Inc). This spiking was used to determine recovery rates during the extraction and clean-up processes. Wastewater samples were extracted following the EPA method for *PBDEs in water, soil, sediment, and tissue* (Method 1614) with slight modifications (see Appendix G). Briefly, wastewater samples were extracted using liquid-liquid extraction with methylene chloride followed by concentration by rotavaporation, run through a sodium sulfate channel for removal of water, clean-up on a multilayer silica gel column, and nitrogen evaporation to the final sample volume. Residual sulfur in the samples was removed with dilute nitric acid cleaned-copper powder (EPA Method 3660B) prior to clean-up stage.

All glassware and apparatus used to handle samples were washed, dried, and solvent-rinsed following EPA Method 1614: methanol, hot tap water, another methanol rinse, acetone, and then methylene chloride. Baking of glassware was minimized,

however, after particularly dirty samples, baking some glassware at 450 °C for 4.5 hours was warranted. All solvents used were pesticide-quality, lot-certified to be free from interferences (Fisher Scientific).

<u>Sample Analysis</u>

PBDE determination was performed using a HP-7890A gas chromatography (GC) (Agilent Technologies) coupled to a HP-5975C triple quadrupole mass spectrometer (MS) detector (Agilent Technologies). The GC/MS was calibrated to manufacturer's specifications, as well as operated according to the EPA's specifications for analysis of samples of mixed matrices. The GC column was a 20 m x 0.18 mm i.d. x 0.36 μm film thickness DB-5MSUI capillary column (Agilent Technologies). Helium was used as the carrier gas. 0.5 μL of sample solution was injected in pulsed splitless mode. The injector temperature was 250 °C and the purge time was 0.5 min after injection. The oven temperature was programmed as follows: 100 °C for 0.5 min, then increased at 40 °C/min to 260 °C and held for 4.5 min, then increased at 20 °C/min to 320 °C and held for 8 min. Ionization was performed in electron capture negative ionization (ECNI) mode, using methane as reagent gas at flow rate of 1.2 mL/min. The transfer line, source, and quadrupole temperatures were 300, 250, and 150 °C, respectively. PBDEs were analyzed in the selected ion-monitoring (SIM) mode, and isotopic bromine anions were monitored (*m/z* 79 and 81).

The identification of seven PBDE congeners (BDE-28, 47, 99, 100, 153, 154, and 183) was based on their retention times and the ratios of monitored ions relative to

prepared congener standards (see Chapter 5, Table 3). Quantitative determination incorporated an external standard method, using a 5 concentration level calibration curve (see Chapter 5, Table 4).

Quality Assurance and Quality Control

Any concentration results found during an analysis of environmental samples are limited in quality by the sensitivity and selectivity of the analytical equipment used. In order to reduce the effects of limit of detection, this study followed analytical protocols prepared and validated by the EPA for sampling and analysis of PBDEs (e.g., EPA Method 1614). The GC/MS was examined for precision by spiking a test sample with a known concentration of PBDE standards to measure the recovery and sensitivity of the machine. The samples were also spiked with mirex prior to analysis (to serve as the internal standard). Additionally, the instrument detection limit was considered by using the standard signal to noise ratio of ≥ 3 on the GC/MS, in order to differentiate the peaks generated by the PBDEs of interest and those from background artifacts. Any sample that did not have peaks ≥ 3 was recorded as non-detectable or ND. BDE-35 and BDE-181 surrogate recoveries ranged between 60.4 and 104.5% (mean % recovery $\pm$ SD = 75.5% $\pm$ 18.6) and 42.1 and 99.9% (77.3% $\pm$ 21.6), respectively. Because the average recovery rates were relatively high, none of the data presented here was corrected for recovery. A blank instrumentation sample (hexane) was analyzed together with every batch of five samples to monitor instrument performance and detect any sample carry-over.

For method validation, deionized Milli-Q grade water samples were spiked with a PBDE standard solution containing all PBDE congeners of interest (50 pg/mL) and analyzed together with the field, laboratory, and transportation blanks. The recoveries of individual PBDE congeners ranged from 70 to 95%.

Data Analysis

Data quantification were performed using ChemStation G2070BA software (Agilent Technologies). All peaks were verified and then if needed, manually integrated. Data management and graphing were performed using Microsoft Excel 2010. Differences between sampling groups were performed using SPSS v.21.0 (IBM).

Data analysis included descriptive and inferential statistics. The descriptive statistics used were measures of central tendency (mean), measures of variability (standard deviation), and 95% confidence intervals. **In order to test the second hypothesis** that concentrations of PBDEs in effluent and reclaimed water do not differ, an independent samples t-test (5% level of significance [$\alpha = 0.05$]) was run to determine whether or not concentrations were statistically different. Analysis of variance (ANOVA) was also run to determine the differences between sampling weeks and sampling days to examine the effect of weekly and daily fluctuations within wastewater streams, if any. Post-hoc Tukey HSD was performed as well.

With 18 samples in each group (n=18, N=36), and alpha = 0.05 & beta = 0.20, a standard deviation of 1.0 can be detected (Hay, 1963). The practical application of 1.0 standard deviation in means is unknown at this time due to the lack of

epidemiological evidence of PBDEs exposure concentrations with respect to human health effects. However, this is a foundational study that is exploring the concentrations of PBDEs from a wastewater treatment plant, and therefore detecting 1.0 standard deviation in means is a fair beginning point. All detected levels of PBDEs were calculated and recorded in concentrations of picogram/liter (pg/L).

Results and Discussion

Reclaimed Water

Table 13 shows that greater than 90% of the total PBDE concentrations in reclaimed water were due to BDE-47, 99, 100, 153, and 154, the major congeners of the Penta-formulation (see Appendix I for raw data). Based on the percent contribution relative to the total PBDEs, BDE-47 and BDE-99 are the major congeners in reclaimed water (Figure 9) with average concentrations of 4,938 and 1,483 pg/L, respectively. Previous studies have found that BDE-47 and BDE-99 bioaccumulate and biomagnify within the food chain (McDonald, 2002). Because they pose an environmental threat, the levels of BDE-47 and BDE-99 should be monitored in environmental discharges.

The sum of the major congeners in the Penta-formulation comprises 93% of the total PBDEs in the reclaimed water, while BDE-183 is only 0.3%. Because BDE-183 is a large congener (part of the heptabromodiphenyl class), it would typically partition into the sludge (log K_{ow} = 8.3) (ATSDR, 2004). The small concentration of BDE-183 is likely because of the small volume (0.6 mg/L) of total suspended solids that remain in the reclaimed water.

Table 13. Congener-specific BDE concentrations (pg/L) in reclaimed water.

	N	Mean (pg/L)	Std. Deviation	Std. Error Mean	95% C.I. Lower	Upper
BDE 28	12	464	197	57	339	589
BDE 47	12	4938	2082	601	3615	6261
BDE 99	10	1483	629	199	1033	1933
BDE 100	9	330	103	34	251	409
BDE 153	6	92	21	8	70	113
BDE 154	5	74	14	6	57	92
BDE 183	14	19	10	3	13	25
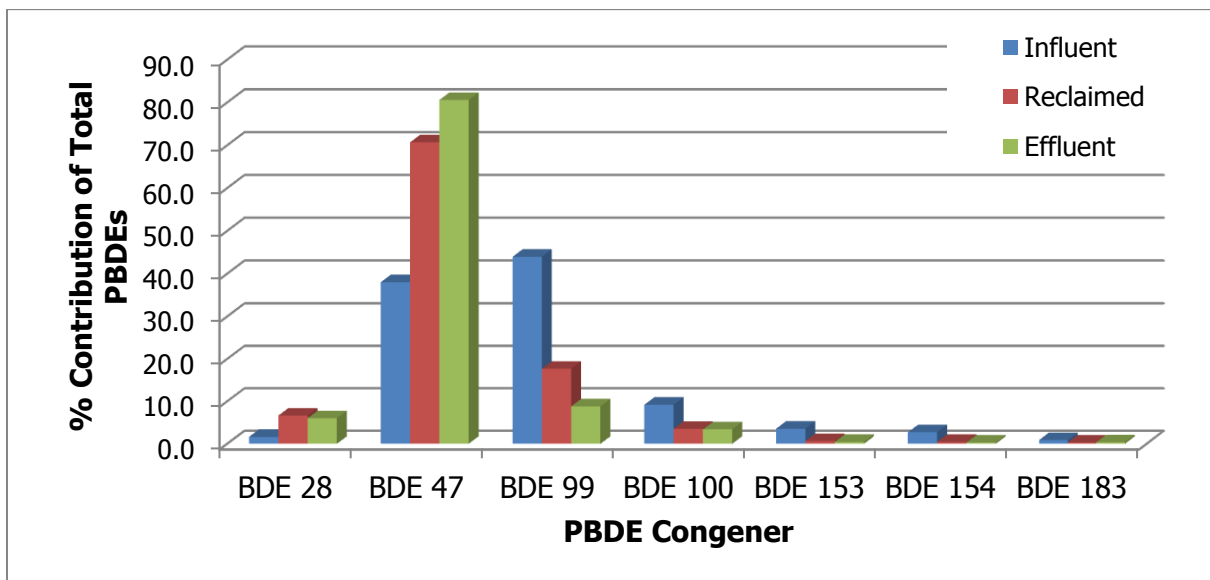
Figure 9. PBDE congener percent contribution relative to total PBDEs in influent, reclaimed water, and effluent.

Effluent

Table 14 shows that similar to the reclaimed water, greater than 93% of the total PBDE concentrations in the effluent were due to the major congeners of the penta-formulation, BDE-47, 99, 100, 153, and 154. Based on the percent contribution

relative to the total PBDEs, likewise BDE-47 and BDE-99 are the major congeners in effluent (Figure 9) with average concentrations of 3,979 and 1,526 pg/L, respectively.

The sum of the major congeners in the Penta-formulation comprises 94% of the total PBDEs in the effluent, while BDE-183 is only 0.4%. Additionally, the small concentration of BDE-183 is likely because of the 0.6 mg/L total suspended solids that remain in the effluent.

Table 14. Congener-specific BDE concentrations (pg/L) in effluent.

	N	Mean (pg/L)	Std. Deviation	Std. Error Mean	95% C.I. Lower	95% C.I. Upper
BDE 28	12	348	135	39	262	434
BDE 47	14	3979	2381	636	2605	5354
BDE 99	4	1526	374	187	930	2121
BDE 100	8	295	152	54	168	423
BDE 153	3	102	28	16	32	171
BDE 154	3	72	25	14	10	135
BDE 183	11	23	8	2	18	28

Reclaimed Water Versus Effluent

The total PBDE concentrations presented in Tables 13 and 14 illustrate all seven PBDEs were detected in the samples. As part of a different study, influent samples were also collected concurrently as the reclaimed water and effluent samples. Extraction and analysis of the influent samples followed the same method and were completed simultaneously as the reclaimed water and effluent samples. Data from the influent study is being used for a thesis, and therefore specifics of them will not be discussed here. However, the mean Σ_7PBDEs concentration in the influent was 17,857 pg/L; the reclaimed water and effluent's mean Σ_7PBDEs concentrations were 7,400 and 6,345

pg/L, respectively. This illustrates an overall removal rate of 59% of PBDEs in the reclaimed water and 64% in the effluent. Although WWTP's are not designed for removal of PBDEs, the moderate removal rate is a good indication that current practices do assist in the removal of PBDEs from the wastewater stream. However, advances in treatment processes may assist further in their removal.

Whereas reclaimed water overall had higher PBDE congener mean concentrations than in effluent, the independent samples t-test found no statistically significant differences between the two groups (Table 15). One can say as "safe" as effluent is with PBDE levels, reclaimed water is just as "safe". However, the caveat to the statement is that the effect of the mass loading of the reclaimed water to the affected areas is unknown. Additionally, studies should be completed in order to investigate the effects of reclaimed water use on plants and grasses, including uptake rates of PBDEs from a known source, in this case watering with reclaimed water. An additional concern is that these samples were taken at the source (the WWTP), because of the storage and then subsequent pumping of reclaimed water to residents, the end-user may have different concentrations of PBDEs in their reclaimed water than found at the source.

Due to the innovative nature of this research, there are no published studies to evaluate the results found in the comparison between the reclaimed water and effluent. However, results of contribution of total PBDEs are similar to a study published by Clarke and associates, with BDE-47 comprising the majority of reclaimed water and effluents load (71% and 81%, respectively). This indicates that this congener is not

Table 15. Independent samples *t*-test of reclaimed water and effluent per PBDE congener.

Independent Samples Test

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
BDE 28	Equal variances assumed	.476	.497	.996	26	.328	148	149	-158	454
	Equal variances not assumed			.996	24	.329	148	149	-159	455
BDE 47	Equal variances assumed	1.786	.193	1.874	26	.072	2446	1305	-236	5128
	Equal variances not assumed			1.874	20	.075	2446	1305	-273	5165
BDE 99	Equal variances assumed	2.445	.144	-.126	12	.902	-43	341	-786	700
	Equal variances not assumed			-.157	10	.879	-43	273	-655	570

Table 15. (Continued)

BDE 100	Equal variances assumed	.189	.670	1.324	17	.203	104	79	-62	270
	Equal variances not assumed			1.362	17	.192	104	77	-58	266
BDE 153	Equal variances assumed	.239	.640	-.616	7	.557	-10	16	-48	28
	Equal variances not assumed			-.550	3	.619	-10	18	-66	46
BDE 154	Equal variances assumed	1.590	.254	.156	6	.881	2	14	-31	35
	Equal variances not assumed			.134	3	.902	2	16	-50	55
BDE 183	Equal variances assumed	.743	.396	-.578	28	.568	-2	4	-10	6
	Equal variances not assumed			-.584	28	.564	-2	4	-10	6

only associated with the suspended solids, which are low in these samples, but is also dissolved in the aqueous phase (Clarke et al., 2010).

A one-way ANOVA was used to test the differences among the six sampling weeks across each individual PBDE congener. No statistically significant difference was found among the weeks (Table 16). Therefore, future studies can be assured that any fluctuations in wastewater streams across a similar sampling window can be minimal and will not affect the results.

Table 16. ANOVA of sampling weeks of reclaimed water and effluent per PBDE congener.

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
BDE 28	Between Groups	64409	5	12882	.360	.869
	Within Groups	643653	18	35759		
	Total	708063	23			
BDE 47	Between Groups	25870098	5	5174020	1.020	.432
	Within Groups	101415086	20	5070754		
	Total	127285183	25			
BDE 99	Between Groups	1382653	5	276531	.849	.552
	Within Groups	2606082	8	325760		
	Total	3988735	13			
BDE 100	Between Groups	52419	5	10484	.578	.717
	Within Groups	199543	11	18140		
	Total	251961	16			

Table 16. (Continued)

BDE 153	Between Groups	639	3	213	.328	.806
	Within Groups	3246	5	649		
	Total	3884	8			
BDE 154	Between Groups	773	3	258	.785	.561
	Within Groups	1313	4	328		
	Total	2086	7			
BDE 183	Between Groups	270	5	54	.554	.733
	Within Groups	1849	19	97		
	Total	2119	24			

Another one-way ANOVA was used to test the differences among the three sampling days (Mondays, Wednesdays, and Fridays) across each individual PBDE congener. Comparable to the weekly ANOVA test, no statistically significant difference was found among the days (Table 17). This is not without reason as fluctuations in volume may differ each day due to usage, but the respective concentration in the volume should not fluctuate. Consequently, future studies can also be assured that minimal fluctuations in wastewater streams will not affect results if sampling on different week days within the same sampling period.

Although the results indicate that sampling different days of the week and different weeks within the same sampling period does not affect measured concentrations, the next step in research would be to examine the impact of sampling different periods, such as dry versus wet periods or winter versus summer seasons, to investigate the effect of moisture and temperature on observed concentrations.

Table 17. ANOVA of sampling days of reclaimed water and effluent per PBDE
congener.

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
BDE 28	Between Groups	5886	2	2943	.088	.916
	Within Groups	702177	21	33437		
	Total	708063	23			
BDE 47	Between Groups	3016311	2	1508156	.279	.759
	Within Groups	124268872	23	5402994		
	Total	127285183	25			
BDE 99	Between Groups	190388	2	95194	.276	.764
	Within Groups	3798347	11	345304		
	Total	3988735	13			
BDE 100	Between Groups	20375	2	10187	.616	.554
	Within Groups	231586	14	16542		
	Total	251961	16			
BDE 153	Between Groups	10	2	5	.008	.992
	Within Groups	3874	6	646		
	Total	3884	8			
BDE 154	Between Groups	399	2	199	.591	.588
	Within Groups	1687	5	337		
	Total	2086	7			
BDE 183	Between Groups	197	2	98	1.125	.342
	Within Groups	1922	22	87		
	Total	2119	24			

Chapter Seven

Summary and Conclusions

A comprehensive PBDE sampling and analysis program for an advanced tertiary-level WWTP found that PBDEs do not appear to be substantially removed by the advanced treatment processes, but rather partition to other phases (from liquid to solid phase). Further, the high levels found in the resulting sludge may pose an environmental threat through use as a Class B biosolids land application. Additionally, the lower concentrations of PBDEs in the reclaimed water and effluent may result in a flux of PBDEs into receiving waters and areas, posing a potential public health threat to residents, local fisheries, and wildlife. Of the 7 congeners analyzed for, BDE-47 was found to have the largest abundance in the wastewater and air emissions, whereas BDE-99 was largest in the sludge.

The main conclusions found from this 3-part study can be summarized as follows:

- Overall removal rate of Σ_7PBDE from the wastewater treatment plant was found to be 91%.

- Comparing effluent, sludge, and air emissions from the WWTP, the sludge had the highest concentrations of PBDEs.

- Biodegradation plays little or no role in the removal of PBDEs from the WWTP.

- Primary treatment resulted in a 27% loss of Σ_7PBDE, as compared to the 92% loss following secondary treatment and 94% loss for the total treatment.

- Of the total mass loading of PBDEs from the WWTP, sludge is responsible for 87%.

- Due to the lack of biodegradation of PBDEs, the NOCEP Model is not an appropriate model for removal pathways for PBDEs – without applicable substitutions, such as the impact of photolysis on PBDEs.

- There is no statistically significant difference between PBDE levels in reclaimed water and effluent.

Whereas the study had some limitations, the results found are beneficial to the field of environmental health, and can serve as a starting point for further studies in the area. Some of the limitations included the small sample size, although the smaller standard deviations indicate some congruency with concentrations; limited sampling plan to only one season – cannot examine seasonal variations of PBDEs in the WWTP; and instrumental methodology limited the detection to predominately lower brominated PBDEs. However, the instrument analysis method was carefully and systematically developed and tested prior to sample analysis to ensure the seven PBDE congeners of interest to this study could be detected at trace levels.

Further studies should be focused on: (1) expansion of investigation of PBDE congeners, particularly BDE-209, and degradation products (polybrominated dibenzofurans and polybrominated dibenzo-p-dioxins) in the WWT process; (2) additional WWTPs to compare the effect of different processes on the effluent and the sludge produced, particularly plants that do not use nitrification/denitrification; and (3) examination of other microconstituents in reclaimed water versus effluent. Continuation of this study would include tracking the discharge of effluent into the Bay to examine PBDE concentrations in the environment, the PBDE concentration of reclaimed water at the consumer, and the PBDE concentrations of the biosolids in land application when used as a fertilizer, to include investigating the uptake of PBDEs in those impacted agriculture.

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Appendix A
Table of Select Physico-Chemical Properties of PBDEs

Table A1. Table of select physico-chemical properties of PBDEs.

Congener #	Compound / Substituents	Commercial Formulation	Fraction	Molecular weight	Log Kow[1]	Henry's Law constant (atm•m^3/mol)[1]	Bioconcentration Factor (BCF)[2]	Liquid Diffusivity (m^2/s)[3]
BDE 28	2,4,4'			406.9	5.94	5.03331×10^{-5}	6.76	3.85E-10
BDE 47	2,2',4,4'	Penta	38-42%	485.8	6.81	1.48038×10^{-5}	8.06	3.39E-10
BDE 99	2,2',4,4',5	Penta	45-49%	564.7	7.32	2.26992×10^{-6}	8.05	3.05E-10
BDE 100	2,2',4,4',6	Penta	7.8-13%	564.7	7.24	6.80977×10^{-7}	8.01	3.05E-10
BDE 153	2,2',4,4',5,5'	Penta	5.3-5.4%	643.6	7.90	6.61238×10^{-7}	8.48	2.78E-10
BDE 154	2,2',4,4',5,6'	Penta	2.7-4.5%	643.6	7.82	2.36862×10^{-6}	8.57	2.78E-10
BDE 183	2,2',3,4,4',5',6			722.5	8.27	7.30323×10^{-8}	8.65	2.56E-10

1. ATSDR, 2004.
2. Zhang et al., 2013.
3. Calculated using trichloroethylene's molecular weight and liquid diffusivity

Appendix B
Results of Pilot Study, 2009

Table A2. Results of pilot study, 2009.

Sample	Concentration (pg/μL)	Reduction (%)
Influent	247.04	-
Primary sedimentation	ND	-
Carbonaceous sedimentation	ND	-
Nitrification reactors	2.99	98.7897
Nitrification sedimentation	2.40	99.0285
Denitrification filters	1.15	99.5345
Reclaimed water	8.23E-04	99.9997
Effluent	1.05	99.5750
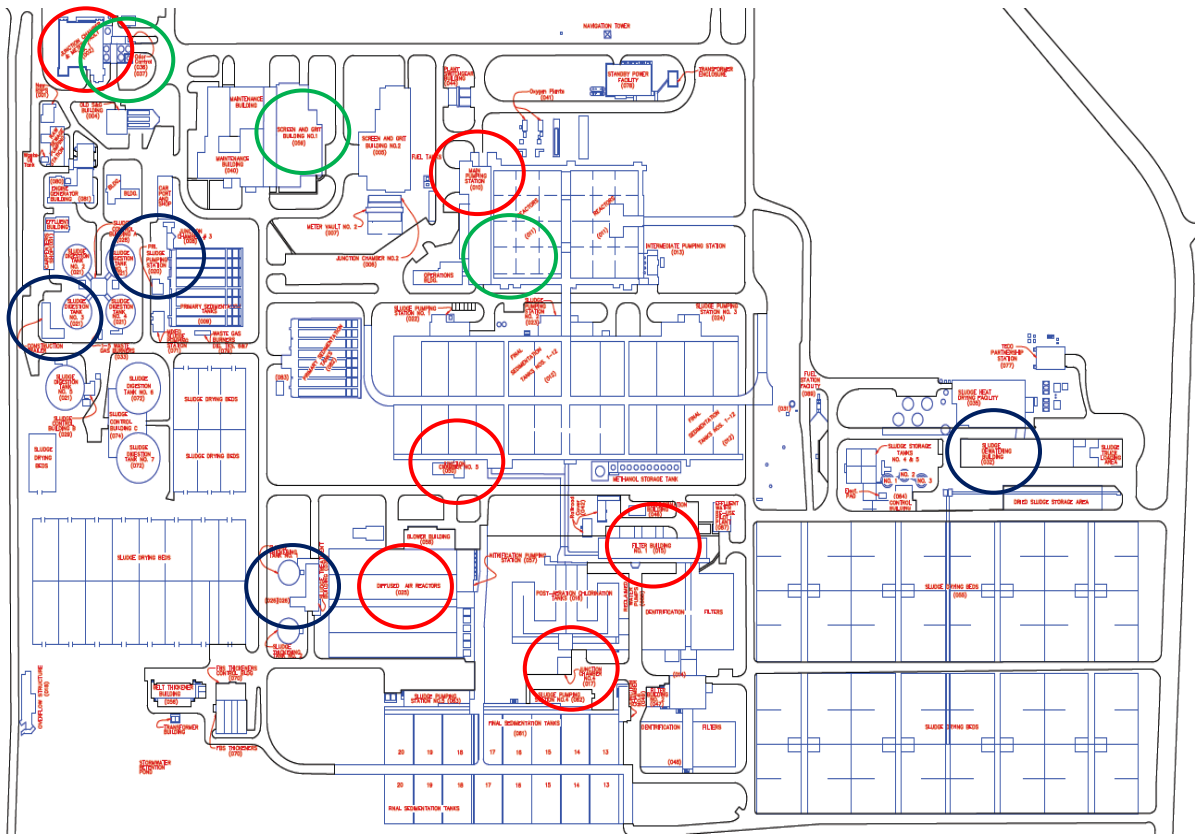
Figure A1. Map of wastewater treatment plant.

Appendix D
Chart of Wastewater Treatment Plant: Wastewater Sampling
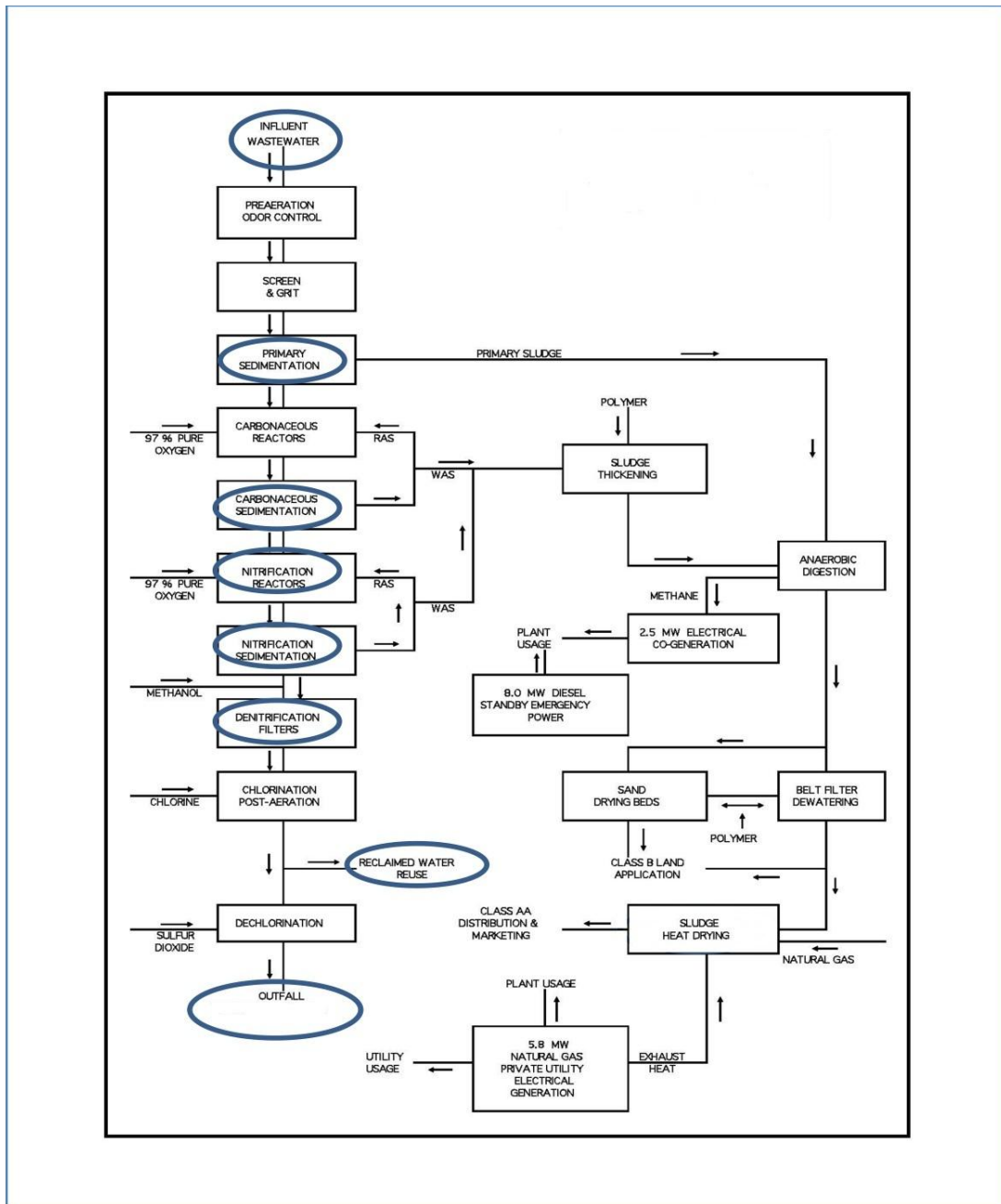
Figure A2. Chart of wastewater treatment plant: Wastewater sampling

Appendix E
Chart of Wastewater Treatment Plant: Sludge Sampling
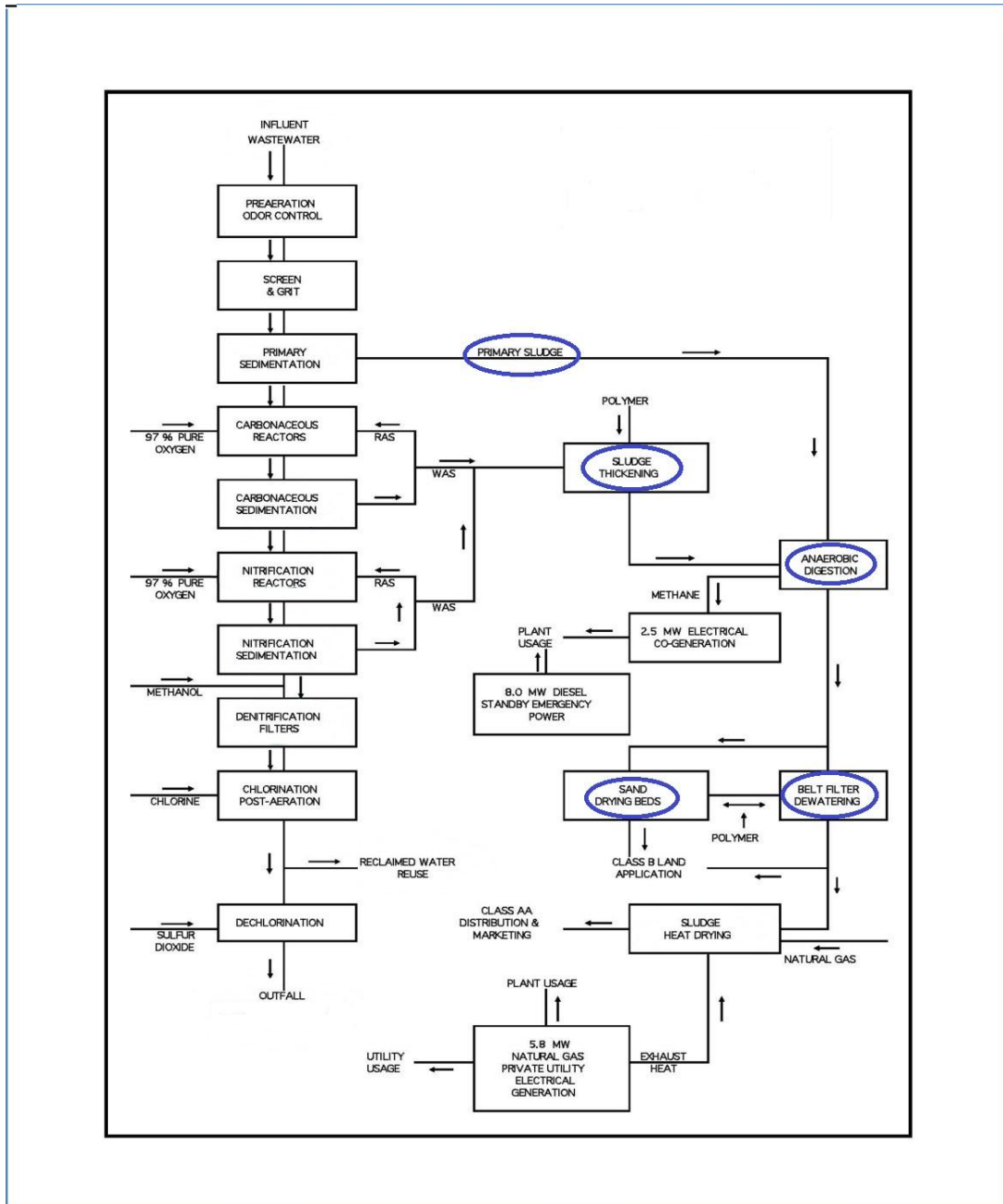
Figure A3. Chart of wastewater treatment plant: Sludge sampling

Appendix F
Chart Map of Wastewater Treatment Plant: Air Sampling
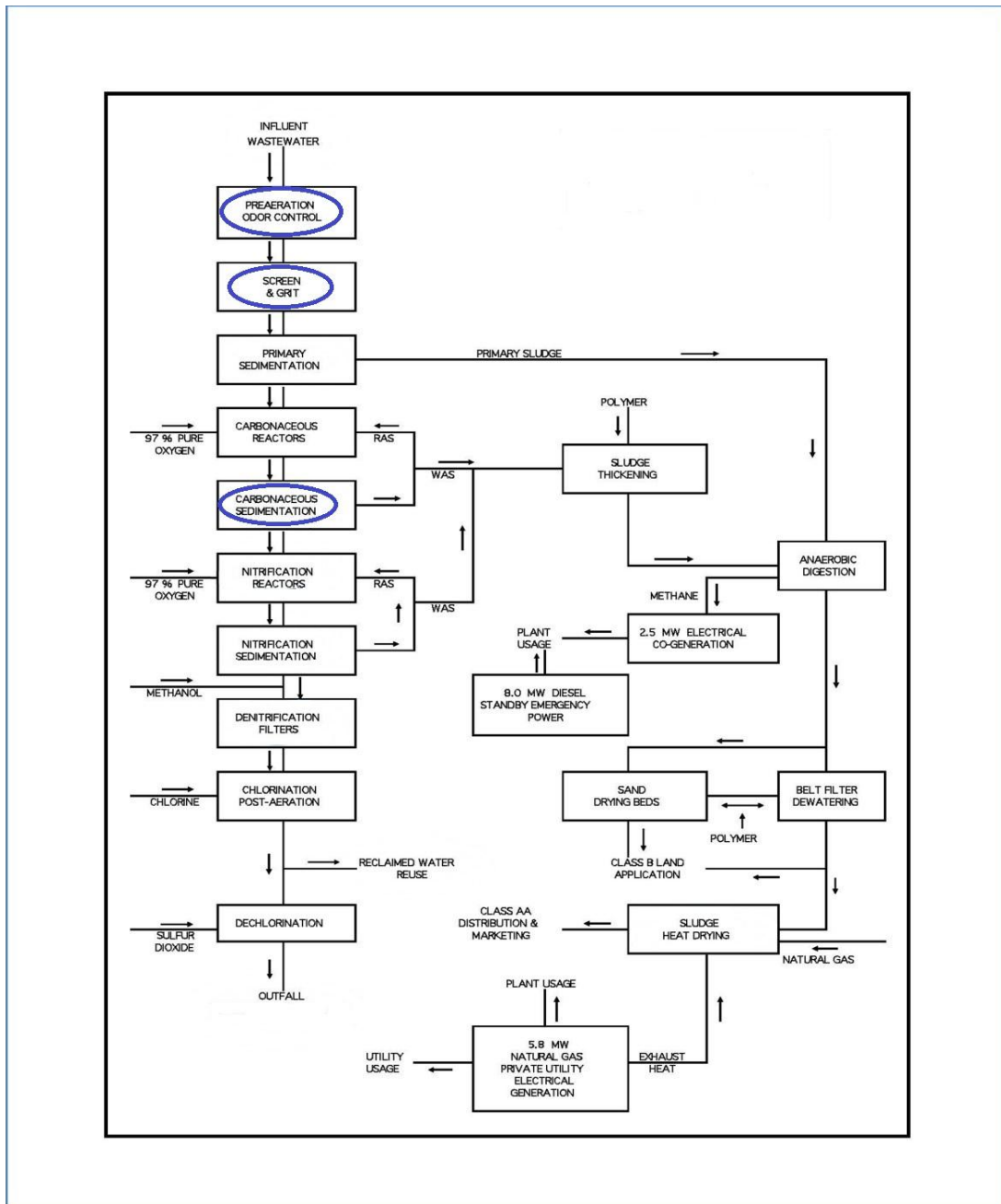
Figure A4. Chart of wastewater treatment plant: Air sampling

Appendix G
Flow Diagram of Extraction and Clean-up Process (EPA Method 1614)
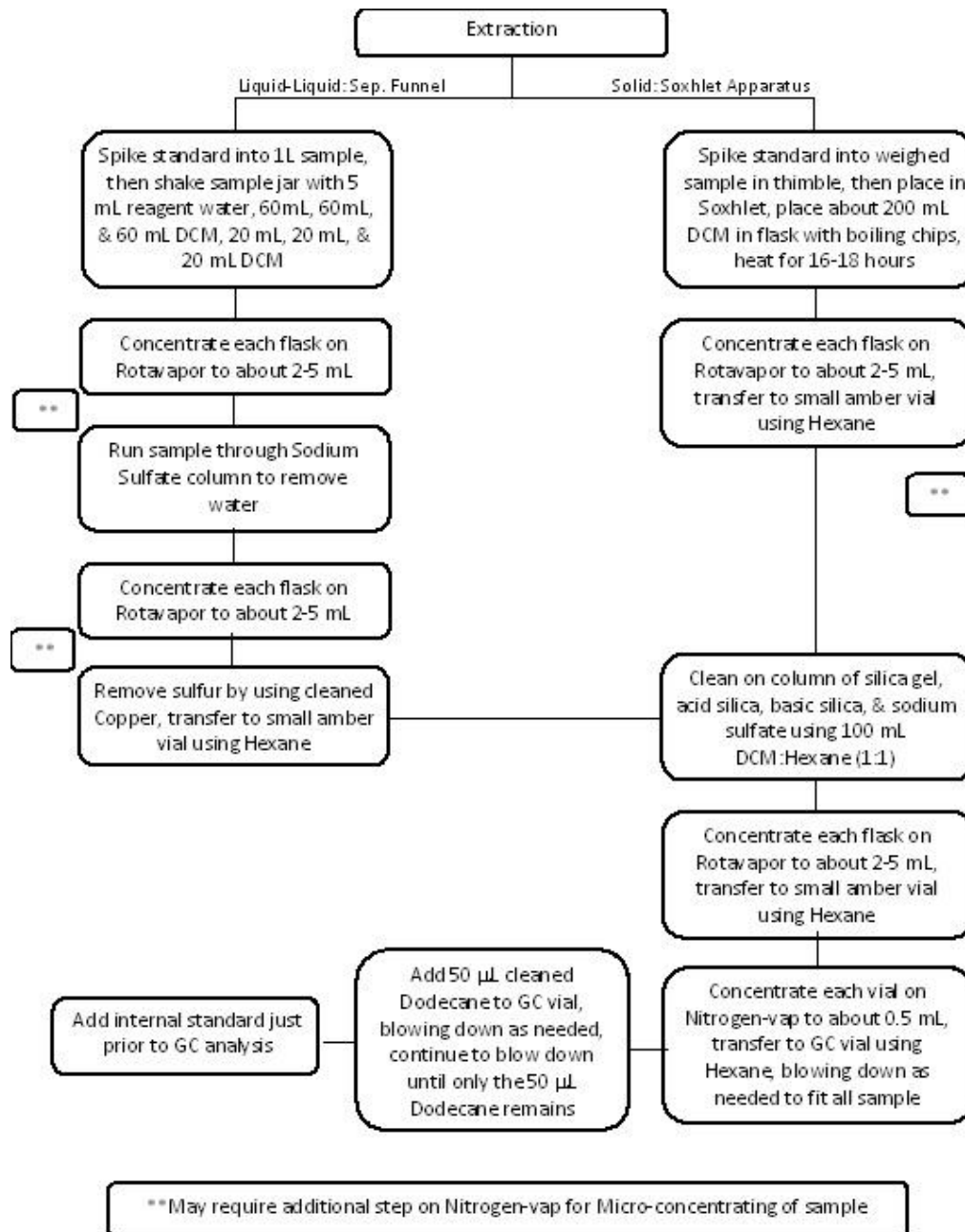
Figure A5. Flow diagram of extraction and clean-up process (EPA Method 1614)

Appendix H
Outputs of NOCEPM Per Each PBDE Congener

SUMMARY OF INPUTS

TREATMENT CONDITIONS	Value	Range	Units
Temperature	26	10-30	^{o}C
Aeration basin residence time	7	0.5-10.0	hr
Power input	0.09	0.01-0.1	kW/m^3
Dissolved O_2 saturation conc.	11.4	1.0-20.0	g/m^3
Aeration efficiency, No.	1.7	1.0-2.0	kg O_2/kWh
MLVSS	1.66	1.0-10.0	kg/m^3
Effluent Solids	0.0005	0.01-0.1	kg/m^3
Waste solids	0.9	0.01-1.0	kg/m^3
Aqueous Diff. O_2, 20 ^{o}C	2.10E-09	constant	m^2/s
MT Corr. Factor, a	0.7	0.1-1.0	--
T Corr for biodegradation, q_b	1.11	1.0-1.2	--
T Corr for mass transfer, q_{MT}	1.12	1.0-1.2	--
T Corr for H_{cc}, q_H	1.13	1.0-1.2	--

SUBSTANCE PROPERTIES			
Compound	**BDE-28**		
Liq. Diff., 20 ^{o}C	3.85E-10		m^2/s
Henry's Constant, 20 ^{o}C	2.09E-03		--
Octanol Water part. Coeff	8.71E+05		--
Biodeg rate @ 20 ^{o}C	6.76E+00		m^3/kg-d

SUMMARY OF OUTPUTS

INTERMEDIATE CALCULATIONS

Partition Coefficient, Kd (m^3/kg)	23.3865	m^3/kg
$k_l a$, oxygen	18.54	1/hr
$k_l a$, compound	6.48	1/hr
$k_g a$, compound	129.64	1/hr
$K_{tot} a$, compound	0.260	1/hr
Stripping rate constant (1/hr)	0.2601	1/hr
Partitioning to Solids and Removal Rate Constant (1/hr)	3.0085	1/hr
Biodegradation Removal Rate Constant (1/hr)	0.8745	1/hr

FINAL CALCULATIONS

Removal Pathway	% Removed
Stripping	6.07
Solids partitioning	70.19
Biodegradation	20.40
Total Removal	**96.67 %**
Fraction remaining in plant effluent	**3.33 %**

SUMMARY OF INPUTS

TREATMENT CONDITIONS	Value	Range	Units
Temperature	26	10-30	^{o}C
Aeration basin residence time	7	0.5-10.0	hr
Power input	0.09	0.01-0.1	kW/m^3
Dissolved O_2 saturation conc.	11.4	1.0-20.0	g/m^3
Aeration efficiency, No.	1.7	1.0-2.0	$kg\ O_2/kWh$
MLVSS	1.66	1.0-10.0	kg/m^3
Effluent Solids	0.0005	0.01-0.1	kg/m^3
Waste solids	0.9	0.01-1.0	kg/m^3
Aqueous Diff. O_2, 20 ^{o}C	2.10E-09	constant	m^2/s
MT Corr. Factor, α	0.7	0.1-1.0	--
T Corr for biodegradation, θ_b	1.11	1.0-1.2	--
T Corr for mass transfer, θ_{MT}	1.12	1.0-1.2	--
T Corr for H_{cc}, θ_H	1.13	1.0-1.2	--

SUBSTANCE PROPERTIES

Compound	BDE-47	
Liq. Diff., 20 ^{o}C	3.40E-10	m^2/s
Henry's Constant, 20 ^{o}C	6.15E-04	--
Octanol Water part. Coeff	6.46E+06	--
Biodeg rate @ 20 ^{o}C	8.06E+00	$m^3/kg\text{-}d$

SUMMARY OF OUTPUTS

INTERMEDIATE CALCULATIONS

Partition Coefficient, Kd (m^3/kg)	89.5089	m^3/kg
$k_l a$, oxygen	18.54	1/hr
$k_l a$, compound	6.00	1/hr
$k_g a$, compound	119.91	1/hr
$K_{tot} a$, compound	0.073	1/hr
Stripping rate constant (1/hr)	0.0728	1/hr
Partitioning to Solids and Removal Rate Constant (1/hr)	11.5147	1/hr
Biodegradation Removal Rate Constant (1/hr)	1.0427	1/hr

FINAL CALCULATIONS

Removal Pathway	% Removed
Stripping	0.57
Solids partitioning	90.15
Biodegradation	8.16
Total Removal	**98.88 %**
Fraction remaining in plant effluent	**1.12 %**

SUMMARY OF INPUTS

TREATMENT CONDITIONS	Value	Range	Units
Temperature	26	10-30	^oC
Aeration basin residence time	7	0.5-10.0	hr
Power input	0.09	0.01-0.1	kW/m^3
Dissolved O_2 saturation conc.	11.4	1.0-20.0	g/m^3
Aeration efficiency, No.	1.7	1.0-2.0	$kg\ O_2/kWh$
MLVSS	1.66	1.0-10.0	kg/m^3
Effluent Solids	0.0005	0.01-0.1	kg/m^3
Waste solids	0.9	0.01-1.0	kg/m^3
Aqueous Diff. O_2, 20 ^oC	2.10E-09	constant	m^2/s
MT Corr. Factor, α	0.7	0.1-1.0	--
T Corr for biodegradation, θ_b	1.11	1.0-1.2	--
T Corr for mass transfer, θ_{MT}	1.12	1.0-1.2	--
T Corr for H_{cc}, θ_H	1.13	1.0-1.2	--

SUBSTANCE PROPERTIES			
Compound	**BDE-99**		
Liq. Diff., 20 ^oC	3.05E-10		m^2/s
Henry's Constant, 20 ^oC	9.44E-05		--
Octanol Water part. Coeff	2.09E+07		--
Biodeg rate @ 20 ^oC	8.05E+00		$m^3/kg\text{-}d$

SUMMARY OF OUTPUTS

INTERMEDIATE CALCULATIONS

Partition Coefficient, Kd (m^3/kg)	196.5921	m^3/kg
k_la, oxygen	18.54	1/hr
k_la, compound	5.61	1/hr
k_ga, compound	112.23	1/hr
$K_{tot}a$, compound	0.011	1/hr
Stripping rate constant (1/hr)	0.0106	1/hr
Partitioning to Solids and Removal Rate Constant (1/hr)	25.2902	1/hr
Biodegradation Removal Rate Constant (1/hr)	1.0414	1/hr

FINAL CALCULATIONS

Removal Pathway	% Removed
Stripping	0.04
Solids partitioning	95.49
Biodegradation	3.93
Total Removal	**99.46 %**
Fraction remaining in plant effluent	**0.54 %**

SUMMARY OF INPUTS

TREATMENT CONDITIONS	Value	Range	Units
Temperature	26	10-30	^{o}C
Aeration basin residence time	7	0.5-10.0	hr
Power input	0.09	0.01-0.1	kW/m^3
Dissolved O_2 saturation conc.	11.4	1.0-20.0	g/m^3
Aeration efficiency, No.	1.7	1.0-2.0	$kg\ O_2/kWh$
MLVSS	1.66	1.0-10.0	kg/m^3
Effluent Solids	0.0005	0.01-0.1	kg/m^3
Waste solids	0.9	0.01-1.0	kg/m^3
Aqueous Diff. O_2, 20 ^{o}C	2.10E-09	constant	m^2/s
MT Corr. Factor, α	0.7	0.1-1.0	--
T Corr for biodegradation, θ_b	1.11	1.0-1.2	--
T Corr for mass transfer, θ_{MT}	1.12	1.0-1.2	--
T Corr for H_{cc}, θ_H	1.13	1.0-1.2	--

SUBSTANCE PROPERTIES

Compound	**BDE-100**	
Liq. Diff., 20 ^{o}C	3.05E-10	m^2/s
Henry's Constant, 20 ^{o}C	2.83E-05	--
Octanol Water part. Coeff	1.74E+07	--
Biodeg rate @ 20 ^{o}C	8.01E+00	$m^3/kg-d$

SUMMARY OF OUTPUTS

INTERMEDIATE CALCULATIONS

Partition Coefficient, Kd (m^3/kg)	173.7665	m^3/kg
$k_l a$, oxygen	18.54	1/hr
$k_l a$, compound	5.61	1/hr
$k_g a$, compound	112.23	1/hr
$K_{tot} a$, compound	0.003	1/hr
Stripping rate constant (1/hr)	0.0032	1/hr
Partitioning to Solids and Removal Rate Constant (1/hr)	22.3538	1/hr
Biodegradation Removal Rate Constant (1/hr)	1.0363	1/hr

FINAL CALCULATIONS

Removal Pathway	% Removed
Stripping	0.01
Solids partitioning	94.98
Biodegradation	4.40
Total Removal	**99.39 %**
Fraction remaining in plant effluent	**0.61 %**

SUMMARY OF INPUTS

TREATMENT CONDITIONS	Value	Range	Units
Temperature	26	10-30	^oC
Aeration basin residence time	7	0.5-10.0	hr
Power input	0.09	0.01-0.1	kW/m^3
Dissolved O_2 saturation conc.	11.4	1.0-20.0	g/m^3
Aeration efficiency, No.	1.7	1.0-2.0	$kg\ O_2/kWh$
MLVSS	1.66	1.0-10.0	kg/m^3
Effluent Solids	0.0005	0.01-0.1	kg/m^3
Waste solids	0.9	0.01-1.0	kg/m^3
Aqueous Diff. O_2, 20 ^oC	2.10E-09	constant	m^2/s
MT Corr. Factor, α	0.7	0.1-1.0	--
T Corr for biodegradation, θ_b	1.11	1.0-1.2	--
T Corr for mass transfer, θ_{MT}	1.12	1.0-1.2	--
T Corr for H_{cc}, θ_H	1.13	1.0-1.2	--

SUBSTANCE PROPERTIES

Compound	**BDE-153**	
Liq. Diff., 20 ^oC	2.78E-10	m^2/s
Henry's Constant, 20 ^oC	2.75E-05	--
Octanol Water part. Coeff	7.94E+07	--
Biodeg rate @ 20 ^oC	8.48E+00	$m^3/kg-d$

SUMMARY OF OUTPUTS

INTERMEDIATE CALCULATIONS

Partition Coefficient, Kd (m^3/kg)	481.0233	m^3/kg
k_la, oxygen	18.54	1/hr
k_la, compound	5.30	1/hr
k_ga, compound	105.95	1/hr
$K_{tot}a$, compound	0.003	1/hr
Stripping rate constant (1/hr)	0.0029	1/hr
Partitioning to Solids and Removal Rate Constant (1/hr)	61.8802	1/hr
Biodegradation Removal Rate Constant (1/hr)	1.0971	1/hr

FINAL CALCULATIONS

Removal Pathway	% Removed
Stripping	0.00
Solids partitioning	98.03
Biodegradation	1.74
Total Removal	**99.77 %**
Fraction remaining in plant effluent	**0.23 %**

SUMMARY OF INPUTS

TREATMENT CONDITIONS	Value	Range	Units
Temperature	26	10-30	^oC
Aeration basin residence time	7	0.5-10.0	hr
Power input	0.09	0.01-0.1	kW/m^3
Dissolved O_2 saturation conc.	11.4	1.0-20.0	g/m^3
Aeration efficiency, No.	1.7	1.0-2.0	kg O_2/kWh
MLVSS	1.66	1.0-10.0	kg/m^3
Effluent Solids	0.0005	0.01-0.1	kg/m^3
Waste solids	0.9	0.01-1.0	kg/m^3
Aqueous Diff. O_2, 20 ^oC	2.10E-09	constant	m^2/s
MT Corr. Factor, α	0.7	0.1-1.0	--
T Corr for biodegradation, θ_b	1.11	1.0-1.2	--
T Corr for mass transfer, θ_{MT}	1.12	1.0-1.2	--
T Corr for H_{cc}, θ_H	1.13	1.0-1.2	--

SUBSTANCE PROPERTIES

Compound	**BDE-154**	
Liq. Diff., 20 ^oC	2.78E-10	m^2/s
Henry's Constant, 20 ^oC	9.85E-05	--
Octanol Water part. Coeff	6.61E+07	--
Biodeg rate @ 20 ^oC	8.57E+00	$m^3/kg-d$

SUMMARY OF OUTPUTS

INTERMEDIATE CALCULATIONS

Partition Coefficient, Kd (m^3/kg)	425.1734	m^3/kg
k_la, oxygen	18.54	1/hr
k_la, compound	5.30	1/hr
k_ga, compound	105.95	1/hr
$K_{tot}a$, compound	0.010	1/hr
Stripping rate constant (1/hr)	0.0104	1/hr
Partitioning to Solids and Removal Rate Constant (1/hr)	54.6955	1/hr
Biodegradation Removal Rate Constant (1/hr)	1.1087	1/hr

FINAL CALCULATIONS

Removal Pathway	% Removed
Stripping	0.02
Solids partitioning	97.74
Biodegradation	1.98
Total Removal	**99.74 %**
Fraction remaining in plant effluent	**0.26 %**

SUMMARY OF INPUTS

TREATMENT CONDITIONS	Value	Range	Units
Temperature	26	10-30	^{o}C
Aeration basin residence time	7	0.5-10.0	hr
Power input	0.09	0.01-0.1	kW/m^3
Dissolved O_2 saturation conc.	11.4	1.0-20.0	g/m^3
Aeration efficiency, No.	1.7	1.0-2.0	kg O_2/kWh
MLVSS	1.66	1.0-10.0	kg/m^3
Effluent Solids	0.0005	0.01-0.1	kg/m^3
Waste solids	0.9	0.01-1.0	kg/m^3
Aqueous Diff. O_2, 20 ^{o}C	2.10E-09	constant	m^2/s
MT Corr. Factor, a	0.7	0.1-1.0	--
T Corr for biodegradation, q_b	1.11	1.0-1.2	--
T Corr for mass transfer, q_{MT}	1.12	1.0-1.2	--
T Corr for H_{cc}, q_H	1.13	1.0-1.2	--

SUBSTANCE PROPERTIES

Compound	**BDE-183**	
Liq. Diff., 20 ^{o}C	2.56E-10	m^2/s
Henry's Constant, 20 ^{o}C	3.04E-06	--
Octanol Water part. Coeff	1.86E+08	--
Biodeg rate @ 20 ^{o}C	8.65E+00	m^3/kg-d

SUMMARY OF OUTPUTS

INTERMEDIATE CALCULATIONS

Partition Coefficient, Kd (m^3/kg)	851.2676	m^3/kg
$k_l a$, oxygen	18.54	1/hr
$k_l a$, compound	5.03	1/hr
$k_g a$, compound	100.69	1/hr
$K_{tot} a$, compound	0.000	1/hr
Stripping rate constant (1/hr)	0.0003	1/hr
Partitioning to Solids and Removal Rate Constant (1/hr)	109.5095	1/hr
Biodegradation Removal Rate Constant (1/hr)	1.1191	1/hr

FINAL CALCULATIONS

Removal Pathway	% Removed
Stripping	0.00
Solids partitioning	98.86
Biodegradation	1.01
Total Removal	**99.87 %**
Fraction remaining in plant effluent	**0.13 %**

Appendix I
Raw Data

Table A3. Raw data of wastewater stream.

Wastewater Sample	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Influent 1A	ND	52691.4	35328.0	6814.7	2952.2	1999.7	1096.8
Influent 1B	ND	43588.4	30205.3	5480.4	2170.1	1615.8	848.2
Influent 2A	ND	9658.3	10672.6	1918.0	998.6	765.5	457.7
Influent 2B	604.2	22542.1	21676.4	3807.3	1669.0	1289.1	549.0
Influent 3A	ND	6730.7	5403.6	1131.0	603.1	477.3	426.9
Influent 3B	319.3	7783.4	5827.6	1200.8	619.1	493.3	438.5
Primary sedimentation 1A	659.2	15881.0	14668.9	2683.1	1157.0	931.1	477.5
Primary sedimentation 1B	696.6	17910.5	15616.5	2827.7	1235.1	986.1	529.2
Primary sedimentation 2A	ND	7809.2	8659.6	1546.8	769.8	613.2	432.4
Primary sedimentation 2B	629.5	17424.3	14854.8	2897.0	1301.6	1013.0	549.0
Primary sedimentation 3A	696.1	18171.2	16604.3	2924.5	1281.8	1013.6	555.6
Primary sedimentation 3B	821.5	23523.8	20173.8	3846.9	1579.9	1238.5	649.7
Secondary Sedimentation 1A	ND	ND	2713.5	689.3	380.9	314.5	383.5
Secondary Sedimentation 1B	ND	ND	2206.4	521.0	354.0	295.3	363.7
Secondary Sedimentation 2A	ND	ND	ND	2612.1	310.5	253.5	363.1
Secondary Sedimentation 2B	ND	ND	ND	2565.9	293.5	248.5	379.6
Secondary Sedimentation 3A	ND	ND	ND	247.7	258.8	218.8	350.5
Secondary Sedimentation 3B	ND	ND	ND	290.6	264.9	223.8	337.3
Nitrification 1A	1672.9	156832.8	65206.7	22317.5	6316.5	5928.4	885.1
Nitrification 1B	1891.8	93741.2	64635.3	12866.9	3759.0	3291.1	644.7
Nitrification 2A	1539.8	86129.8	67989.7	13017.6	4575.8	3742.1	851.0
Nitrification 2B	905.6	66607.5	54897.5	10209.8	3751.3	3006.8	797.1
Nitrification 3A	2412.1	128500.1	95357.7	17953.3	6019.5	4974.1	1214.0
Nitrification 3B	2980.2	158250.7	106589.8	21920.4	6665.2	5876.7	1255.2
Nitrification sedimentation 1A	ND	ND	ND	ND	ND	119.8	ND
Nitrification sedimentation 1B	ND	ND	ND	ND	149.9	145.1	ND
Nitrification sedimentation 2A	ND	ND	ND	ND	131.8	131.9	ND
Nitrification sedimentation 2B	ND	ND	ND	ND	ND	101.7	ND
Nitrification sedimentation 3A	ND	ND	ND	ND	ND	ND	ND
Nitrification sedimentation 3B	ND	ND	ND	ND	ND	199.6	ND

Note: Header spans "PBDE Congeners (pg/L)" across all congener columns.

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Table A3. (Continued)

Denitrification 1A	ND	ND	ND	ND	ND	ND	ND
Denitrification 1B	ND	ND	ND	ND	ND	ND	ND
Denitrification 2A	ND	ND	ND	ND	ND	ND	ND
Denitrification 2B	ND	ND	ND	ND	ND	ND	ND
Denitrification 3A	ND	ND	ND	ND	ND	ND	ND
Denitrification 3B	ND	ND	ND	ND	ND	ND	ND
Effluent 1A	ND	ND	ND	ND	ND	ND	ND
Effluent 1B	ND	ND	ND	ND	ND	ND	ND
Effluent 2A	ND	ND	ND	ND	ND	ND	ND
Effluent 2B	ND	ND	ND	ND	ND	ND	ND
Effluent 3A	ND	4954.2	ND	ND	ND	ND	ND
Effluent 3B	ND	4251.3	ND	ND	ND	ND	ND
Reclaimed 1A	ND	10796.8	2631.0	724.5	ND	163.8	ND
Reclaimed 1B	ND	12536.5	2604.1	797.1	ND	146.8	ND
Reclaimed 2A	ND	ND	ND	ND	ND	120.9	ND
Reclaimed 2B	ND	7506.2	1881.9	600.2	ND	106.6	ND
Reclaimed 3A	ND	9977.3	1577.8	598.6	ND	ND	ND
Reclaimed 3B	ND	13288.3	2656.3	804.8	ND	109.9	ND

Table A4. Raw data of sludge stream.

Sludge Sample	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
			PBDE Congeners (ug/kg dry wt)				
Clarifier 1A	0.6	25.8	31.1	4.8	1.7	1.4	0.1
Clarifier 1B	0.2	8.3	12.5	1.6	0.7	0.5	0.1
Clarifier 1C	0.8	28.8	40.4	5.2	2.1	1.6	0.3
Clarifier 2A	0.3	14.7	18.8	2.8	1.2	0.9	0.2
Clarifier 2B	0.3	11.2	16.3	2.2	1.0	0.7	0.2
Clarifier 2C	0.4	11.4	14.6	2.0	0.8	0.6	0.1
Clarifier 3A	0.3	9.9	10.2	1.7	0.6	0.5	0.0
Clarifier 3B	0.3	9.5	13.3	1.8	0.8	0.6	0.1
Clarifier 3C	0.4	20.2	25.1	3.7	1.6	1.2	0.1
Thickening 1A	0.2	9.9	13.1	1.9	0.9	0.7	0.1
Thickening 1B	0.2	9.4	12.4	1.8	0.8	0.6	0.1
Thickening 1C	0.2	8.9	10.6	1.6	0.6	0.5	0.1
Thickening 2A	0.2	8.6	10.1	1.6	0.7	0.6	0.1
Thickening 2B	0.3	8.8	9.3	1.3	0.5	0.4	0.1
Thickening 2C	0.2	5.9	7.1	1.0	0.5	0.3	0.1
Thickening 3A	ND	3.4	4.5	0.7	0.3	0.2	0.0
Thickening 3B	0.3	11.7	13.7	2.2	1.0	0.7	0.1
Thickening 3C	0.4	13.7	15.2	2.4	0.9	0.7	0.1
Predigested 1A	0.1	5.7	8.6	1.1	0.6	0.4	0.1
Predigested 1B	0.1	4.4	5.0	0.8	0.2	0.2	ND
Predigested 1C	ND	2.7	3.4	0.5	0.2	0.1	ND
Predigested 2A	ND	4.3	5.8	0.9	0.4	0.3	0.0
Predigested 2B	0.1	5.7	6.4	1.0	0.4	0.3	0.1
Predigested 2C	0.1	5.4	5.9	0.9	0.3	0.3	0.0
Predigested 3A	0.2	9.8	12.1	1.9	0.7	0.6	0.1
Predigested 3B	ND	5.0	7.3	1.1	0.5	0.4	0.1
Predigested 3C	0.1	5.1	5.9	0.9	0.3	0.3	0.0
Belt press 1A	0.1	4.6	4.5	0.8	0.2	0.2	0.1
Belt press 1B	0.3	ND	10.8	1.4	0.1	0.7	0.1
Belt press 1C	ND	1.3	1.9	0.3	0.1	0.1	ND
Belt press 2A	0.1	7.8	8.8	1.5	0.7	0.5	0.1
Belt press 2B	ND	3.9	4.1	0.7	0.3	0.1	ND
Belt press 2C	0.1	4.6	5.2	0.9	0.4	0.2	0.0
Belt press 3A	0.2	7.7	8.2	1.4	0.6	0.5	0.1
Belt press 3B	0.2	9.2	9.7	1.7	0.7	0.6	0.1
Belt press 3C	0.1	7.5	8.3	1.4	0.6	0.5	0.0

Table A5. Raw data of air emissions.

Air Sample	PBDE Congeners (pg/m3)						
	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Odor Control Filter A1	ND	ND	ND	ND	ND	ND	ND
Odor Control Filter A2	ND	ND	ND	ND	ND	ND	ND
Odor Control Filter B1	ND	ND	ND	ND	ND	0.6	1.0
Odor Control Filter B2	ND	ND	ND	ND	ND	ND	0.2
Odor Control Filter C1	ND	ND	ND	ND	ND	0.5	ND
Odor Control Filter C2	ND	ND	ND	ND	ND	0.5	ND
Odor Control PUF A1	ND	ND	ND	ND	ND	ND	ND
Odor Control PUF A2	ND	ND	ND	ND	ND	ND	ND
Odor Control PUF B1	ND	ND	ND	ND	ND	ND	ND
Odor Control PUF B2	ND	ND	ND	ND	ND	ND	ND
Odor Control PUF C1	ND	ND	ND	ND	ND	ND	ND
Odor Control PUF C2	ND	ND	ND	ND	ND	ND	ND
Odor Control XAD A1	ND	ND	ND	ND	ND	ND	ND
Odor Control XAD A2	ND	ND	ND	ND	ND	ND	ND
Odor Control XAD B1	ND	ND	ND	ND	ND	ND	ND
Odor Control XAD B2	ND	ND	ND	ND	ND	ND	ND
Odor Control XAD C1	ND	ND	ND	ND	ND	ND	ND
Odor Control XAD C2	ND	ND	ND	ND	ND	ND	ND
Grit & Screen Filter A1	ND	ND	ND	ND	ND	1.0	0.6
Grit & Screen Filter A2	ND	ND	2.0	ND	ND	1.6	ND
Grit & Screen Filter B1	ND	ND	ND	ND	ND	1.1	0.5
Grit & Screen Filter B2	ND	ND	2.1	ND	ND	1.3	0.4
Grit & Screen Filter C1	ND	ND	2.1	ND	ND	0.5	0.1
Grit & Screen Filter C2	ND	ND	ND	ND	ND	1.0	0.3
Grit & Screen PUF A1	18.4	ND	ND	ND	ND	ND	ND
Grit & Screen PUF A2	18.4	ND	ND	ND	ND	ND	ND
Grit & Screen PUF B1	ND	ND	ND	ND	ND	ND	ND
Grit & Screen PUF B2	ND	ND	ND	ND	ND	ND	ND
Grit & Screen PUF C1	12.7	ND	ND	ND	ND	ND	ND
Grit & Screen PUF C2	ND	ND	ND	ND	ND	ND	ND
Grit & Screen XAD A1	ND	ND	ND	ND	ND	ND	ND
Grit & Screen XAD A2	ND	ND	ND	ND	ND	ND	ND
Grit & Screen XAD B1	ND	ND	ND	ND	ND	ND	ND
Grit & Screen XAD B2	ND	ND	ND	ND	ND	ND	ND
Grit & Screen XAD C1	ND	ND	ND	ND	ND	ND	ND
Grit & Screen XAD C2	ND	ND	ND	ND	ND	ND	ND

Table A5. (Continued)

Post-Aeration Filter A1	10.9	174.9	11.1	35.2	3.5	5.6	ND
Post-Aeration Filter A2	2.1	42.2	3.9	21.7	ND	3.4	ND
Post-Aeration Filter B1	ND	45.3	5.0	16.8	ND	3.9	2.9
Post-Aeration Filter B2	ND	ND	ND	ND	ND	9.3	2.6
Post-Aeration Filter C1	ND	ND	ND	ND	ND	ND	ND
Post-Aeration Filter C2	18.8	274.2	18.6	66.6	5.9	8.7	3.9
Post-Aeration PUF A1	13.1	175.3	19.3	63.9	7.2	8.1	1.1
Post-Aeration PUF A2	17.9	181.0	23.8	61.3	8.5	9.7	2.1
Post-Aeration PUF B1	15.1	206.4	20.9	74.6	4.4	5.6	0.7
Post-Aeration PUF B2	ND	ND	ND	ND	ND	ND	ND
Post-Aeration PUF C1	ND	ND	ND	ND	ND	ND	ND
Post-Aeration PUF C2	ND	ND	ND	ND	ND	ND	ND
Post-Aeration XAD A1	ND	ND	ND	ND	ND	ND	ND
Post-Aeration XAD A2	ND	ND	ND	ND	ND	ND	ND
Post-Aeration XAD B1	ND	ND	ND	ND	ND	ND	ND
Post-Aeration XAD B2	ND	ND	ND	ND	ND	ND	ND
Post-Aeration XAD C1	ND	ND	ND	ND	ND	ND	ND
Post-Aeration XAD C2	ND	ND	ND	ND	ND	ND	ND

Table A6. Raw data of reclaimed water and effluent.

Sample	PBDE Congeners (pg/L)						
	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183
Reclaimed 1M	299.9	2852.6	ND	ND	ND	ND	ND
Reclaimed 1W	576.2	4631.9	897.8	303.5	ND	ND	6.5
Reclaimed 1F	584.3	6407.5	1881.0	467.8	127.5	88.4	36.1
Reclaimed 2M	ND	ND	2382.3	ND	75.1	64.9	12.7
Reclaimed 2W	ND	ND	2578.2	ND	104.7	82.0	21.9
Reclaimed 2F	264.9	3563.9	1149.8	294.2	81.7	ND	16.2
Reclaimed 3M	549.9	5607.2	811.7	269.4	ND	ND	6.5
Reclaimed 3W	213.4	1811.2	ND	ND	ND	ND	32.4
Reclaimed 3F	336.8	3831.0	ND	162.4	ND	ND	6.1
Reclaimed 4M	497.3	5771.8	1223.8	344.5	ND	ND	24.1
Reclaimed 4W	ND	ND	ND	ND	ND	ND	ND
Reclaimed 4F	ND	ND	ND	ND	ND	ND	13.7
Reclaimed 5M	563.7	6877.7	1222.8	351.3	83.8	82.6	21.1
Reclaimed 5W	ND	ND	ND	ND	ND	ND	ND
Reclaimed 5F	ND	ND	ND	ND	ND	ND	10.4
Reclaimed 6M	262.7	2836.1	ND	ND	ND	ND	ND
Reclaimed 6W	903.5	9175.7	1737.0	498.2	76.2	54.2	35.3
Reclaimed 6F	517.8	5888.0	941.8	277.2	ND	ND	24.3
Effluent 1M	337.2	3480.6	ND	142.1	ND	ND	ND
Effluent 1W	ND	5739.7	1585.4	431.1	107.2	64.7	ND
Effluent 1F	469.7	5742.4	1290.2	337.8	71.2	51.9	28.0
Effluent 2M	622.1	7557.7	2029.2	555.2	126.1	100.3	ND
Effluent 2W	ND	9868.3	1197.2	364.7	ND	ND	ND
Effluent 2F	366.5	3124.0	ND	125.2	ND	ND	ND
Effluent 3M	226.3	2989.2	ND	187.5	ND	ND	14.5
Effluent 3W	491.3	2345.8	ND	ND	ND	ND	ND
Effluent 3F	270.6	1765.5	ND	ND	ND	ND	22.8
Effluent 4M	326.9	2599.2	ND	ND	ND	ND	25.8
Effluent 4W	195.5	2214.8	ND	ND	ND	ND	39.9
Effluent 4F	ND	ND	ND	ND	ND	ND	ND
Effluent 5M	ND	ND	ND	ND	ND	ND	19.7
Effluent 5W	437.9	3380.4	ND	219.1	ND	ND	27.7
Effluent 5F	ND	ND	ND	ND	ND	ND	23.9
Effluent 6M	241.3	2898.7	ND	ND	ND	ND	18.2
Effluent 6W	191.2	ND	ND	ND	ND	ND	11.1
Effluent 6F	ND	2003.5	ND	ND	ND	ND	20.1

About the Author

Prior to the doctoral program at University of South Florida, Kristy A. Siegel received her Master of Public Health in Environmental Health and Health Promotion from Florida International University. She has a Bachelor of Science in Biology, minor in English Literature, from Barry University. During her doctoral studies, Ms. Siegel worked as a Research Associate on several projects including communicating the science and risks of reclaimed water, analysis of indoor and outdoor PBDE concentrations, and exploratory health study of older adults in The Villages, FL. She also worked for the Florida Children's Environmental Health Alliance developing a comprehensive health education campaign and study on childhood lead poisoning, after graduating with her M.P.H. Ms. Siegel has been a presenter at national and local conferences, and has coauthored several publications.