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Assessing Atmospheric Levels of PCBs and PBDEs in Tampa Bay and Studies on Remediation of these compounds

Lukasz Talalaj

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Assessing Atmospheric Levels of PCBs and PBDEs in Tampa Bay and Studies on Remediation of these compounds.

by

Lukasz Talalaj

A thesis submitted in partial fulfillment of the requirement for the degree of Masters of Science Department of Environmental Science and Policy College of Arts & Science University of South Florida Saint Petersburg

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Abstract

Atmospheric levels of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) were measured around the Tampa Bay area. Total PCBs, $\sum_{56}$PCBs, ranged from 41.96-1250.96 pg/m$^3$ and total PBDEs, $\sum_{14}$PBDEs, ranged from 0.78-9.54 pg/m$^3$ at 5 sites with unique land-use classifications. PCB congener profiles indicated significant differences between most sites while PBDE congener profiles were more uniform. The use of Zero Valent Metals (ZVM) to remediate PBDEs was also explored. In a five hour study 0.8% Mg/Pd bimetallic system showed a 99% degradation of BDE-47 (2,2',4,4'-tetrabromodiphenyl ether), following a step-wise debromination path with pseudo 1$^{st}$ order kinetics.
Chapter One: Background and Overall Research Project

Introduction

Persistent Organic Pollutants (POPs) are a class of chemical substances that are resistant to environmental degradation processes. Due to their stability and hydrophobic properties, POPs tend to bioaccumulate in some organisms and biomagnify up the food chain, adversely affecting health. The transport mechanisms governing the movement of POPs are dependent on their physico-chemical properties and application methods. Open-ended applications such as surface additives or paints tend to enter with greater ease than completely or nominally closed systems like electrical equipment or heat transfer systems (WHO, 1993). In either case of use, POPs inevitably find their way into the environment through product wear and bleed, spills, and improper handling and disposal. Further intensifying the issue, these POPs undergo photolytic, microbial, and thermal degradation processes that can end up yielding more toxic compounds. For example, in the case of halogenated POPs impartial degradation alters the parent POP’s chemical characteristics, producing lighter, more mobile and toxic byproducts.

Once released into the environment, POPs become partitioned between air, water, soil and biota and undergo constant flux between phases. This exchange is dependent on the pollutant’s physical and chemical properties, weather, matrix properties, and environmental disturbances. Once in the environment, POPs tend to undergo multiple reactions that allow them to migrate away from their original application sources and
have shown migration at local, regional, and global scales (Eckhardt et al., 2007; Alegria et al., 2008). Soil and groundwater movement of POPs are the primary transport mechanisms for local and regional scales, while long-range atmospheric transport (LRAT) is widely recognized as the dominant way of global distribution. This study focuses on polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs).

**Polychlorinated Biphenyls**

PCBs are a group of synthetic chlorinated organic aromatic compounds. A PCB consists of a biphenyl acting as the backbone with the possibility of up to 10 chlorines around each ring. The various combinations allow for 209 unique compounds called congeners (Figure 1).

![PCB structure](image)

**Figure 1:** PCB structure

To improve description of each congener and simplify current IUPAC and CAS systems, a BZ numbering system was proposed by Ballshmiter and Zell. In this system congeners are arranged in an ascending order based on orientation and degree of chlorination around
the biphenyl structure. Thus, 2,2',4,4'-tetrachlorobiphenyl would be labeled as PCB-47 under the BZ system, with chlorines on the 2(ortho) and 4(para) positions of both rings. The congeners are also broken down even further by the degree of chlorination into homolog classes (e.g. dichloro and trichloro homologues) to help ease analysis efforts (Erickson, 1992; Wiegel and Wu, 2000).

The first "PCB-like" chemical was discovered in 1865 as byproduct of coal tar. In 1929, PCBs were commercially manufactured for uses ranging from electrical equipment to plastics, with 75% of US sales coming from capacitor and transformer fluids (Erickson, 2001). In 1977 PCBs began to be regulated by the Toxic Substance Control Act (TSCA) and ultimately were banned by the Environmental Protection Agency (Erickson, 1992).

The primary manufacturer of polychlorinated biphenyl products in the U.S. was Monsanto Company based in Missouri. The company marketed PCBs under the trademark name Aroclor®, which consisted of a mixture of various PCBs as well as other halogenated compounds. Aroclor series trademark is followed by a four digit number that indicates the type of product as well as the average percent of chlorine by weight (Erickson, 2001). For example, one of the most utilized mixtures, Aroclor 1254, signified that the PCB was defined by the “12” and that it was 54% chlorine by weight.

PCBs are clear, odorless and are either liquids or resinous. Increasing chlorination makes them more resinous (Erickson, 2001). Due to low flammability, high dielectric constant, high thermal conductivity, high flash point (170-380°C) and chemical stability characteristics, PCBs were ideal industry chemicals. PCBs were primarily used as flame retardants in heat capacitors and transformers (WHO, 2003). PCBs served as flame retardants in two ways, first by their flame retardant characteristics, and second by
hydrochloric acid, which is PCBs combustion product that acts as a fire quencher (Erickson, 2001; WHO, 2003). Additional applications of PCBs were as plasticizers, joint sealants, wax extenders, and pesticide extenders.

Once released into the environment PCBs partition between air, water and soil. Atmospheric transport is recognized as the primary way of global distribution. Although PCBs are heavy compounds with relatively low volatility they are still susceptible to volatilization and atmospheric deposition (Leister & Baker, 1994; Erickson, 1992). Ambient air is normally dominated by lighter congeners of low degree of chlorination while aerosols contain congeners with high degree of chlorination (WHO, 1993).

Partitioning of PCBs into the atmosphere is initialized by direct vaporization of the contaminant from point source locations, evaporation from water ways, and soil-air exchange (Wong et al., 2010). Although higher concentrations are typically found in industrialized regions, significant levels of PCBs have been identified in remote and rural areas (Vorhees et al., 1997). A 2004 study in southern Mexico showed a range from 34 pg m$^{-3}$ in suburban areas to 213 pg m$^{-3}$ in rural areas supporting the theory that PCBs can undergo large scale atmospheric movement from distant sources (Alegria et al., 2008). The same study profiled PCBs redistribution based on congener specificity, showing that air was dominated by tri- congeners, which are relatively more volatile with higher partial pressure and increased Henry’s law constants in comparison to more chlorinated PCBs (Alegria et al., 2008; WHO, 2003).

Air-water exchange by wet/dry deposition, runoff, direct spills/leaching, and sediment-water exchange introduces PCBs into waterway systems. Once in the water column,
PCBs partition into three phases, colloidal, particulate, and dissolved. PCBs solubility increases with lower chlorination (e.g., MonoCB 4.0 g/m³ at 25°C, DecaCB 7.6×10⁻⁴ g/m³ at 25°C). Thus, the dissolved water phase concentrations are dominated by PCB congeners with lower chlorination (Erickson, 1992). The colloidal and particulate phases contain more highly chlorinated congeners as they tend to adsorb to dissolved organic carbon as well as black carbon (Persson et al., 2002; Zhou et al., 1996; Orecchio, 2010). A water column distribution study done on Pearl River Estuary in South China found ΣPCB concentrations in dissolved phase (18.0-7180 pg/L) were much lower than those in the particle phase (21.3-14700 pg/L), and also showed a seasonal dependence, with particle phase concentration exceeding dissolved phase concentration in flood season while in dry season dissolved phase contained the majority of PCBs (Chen et al., 2011). The authors attributed seasonal dependency to dilution from rainfall as well as the high suspended particular matter from freshwater flow during wet season.

A study by Chen et al. (2011) showed that PCBs with lower solubility and higher chlorination have the tendency to adsorb to suspended particles at a much higher ratio. This process of adsorption and sedimentations serves as a way for PCBs to be stored in marine systems for extended periods of time, where it is slowly redistributed back into the water column. Soil contamination also follows similar mechanisms, with organic carbon rich areas providing greatest adsorption potential and therefore lower vaporization and lower soil-air exchange rates.
Polybrominated Diphenyl Ethers

PBDEs are a group of synthetic brominated organic compounds. A PBDE consists of a diphenyl ether acting as the backbone with the possibility of up to 10 bromines around each ring. PBDEs can exist in 209 different variances called congeners that have adapted the same naming system as PCBs due to their structural similarities.

![PBDE structure](image)

**Figure 2: PBDE structure**

Polybrominated diphenyl ethers are used as flame retardants to reduce property loss, injuries, and death from fires. By slowing down the ignition, PBDEs allow for more escape time in the case of a fire. During high heat scenarios and ignitions, PBDEs start to breakdown 50 degrees Celsius prior to its associated polymer, and allows for the bromines to take out the high energy radicals that are formed as a result of combustion (Price, 1998; Rahman, 2001). Since their initial production in the 1970s they have accounted for 25% of global flame retardants (Hardy, 2000). Out of 175 various flame retardants PBDEs dominate the marked due to their low cost and high performance efficiency (Birnbaum, 2004). PBDEs are produced by brominating diphenyl ether in the presence of a catalyst. The three major products of this process are the main commercial products that have been produced for the last 40 years. Brominated flame retardants (BFRs) are introduced into associated polymers of the goods through either reactive or
additive nature. Dissolving the flame retardants into the polymer rather than chemically bonding them into the material becomes problematic as it tends to leach easier (de Wit, 2002; Renner, 2000).

BFRs have been in production by 12 companies all over the world since the 1970s. The major producers in the U.S. are Albemarle Corporation and Chemtura (previously Great Lakes Chemical Corporation) (de Wit, 2002). The major commercial products that have been synthesized are categorized in Table 1 as pentaBDEs, octaBDEs, and decaBDEs (WHO/ICPS, 1994b).

**Table 1:** Composition of PBDE commercial products in percent BDE congeners present

<table>
<thead>
<tr>
<th>Product</th>
<th>tetraBDEs</th>
<th>pentaBDEs</th>
<th>hexaBDEs</th>
<th>heptaBDEs</th>
<th>octaBDEs</th>
<th>nonaBDEs</th>
<th>decaBDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PeBDE</td>
<td>24-38</td>
<td>50-60</td>
<td>4-8</td>
<td>10-12</td>
<td>44</td>
<td>31-35</td>
<td>&lt;1</td>
</tr>
<tr>
<td>OcBDE</td>
<td>10-12</td>
<td>44</td>
<td>31-35</td>
<td>10-11</td>
<td>&lt;3</td>
<td>97-98</td>
<td></td>
</tr>
<tr>
<td>DeBDE</td>
<td>&lt;3</td>
<td>97-98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PentaBDE commercial standard consists mainly of BDE- 47 (2,2’,4,4’-tetraBDE) and BDE-99 (2,2’,4,4’,5-pentaBDE). They were introduced into flexible polyurethane foam such as furniture and made up 10% of the products’ weight. OctaBDE was primarily utilized in high impact plastic products such as casings for computers, kitchen appliances, fax machines, phones, and car trimmings (Turnbull, 2008). DecaBDE, consisting mainly of BDE-209 and NonaBDEs, is used in plastics that act as adhesives and coatings for products that include television casings, wire coating, and other electronics (Turnbull, 2008). The world demand in 2001 for the 3 commercial PBDEs exceeded 67,390 tonnes, 49% of it being utilized in the United States (Brominated Sci. and Env. Forum, 2003).
Table 2: PBDE compositions and 2001 demand (US EPA PBDE Project Plan, 2006).

<table>
<thead>
<tr>
<th>Commercial PBDE Products</th>
<th>% Composition of Commercial Mixtures</th>
<th>2001 Demand in America (Metric Tonns)</th>
<th>% of World Demand in Americas</th>
</tr>
</thead>
<tbody>
<tr>
<td>PentaBDE (BDE-71)</td>
<td>TetraBDEs 24-38</td>
<td>7100</td>
<td>95%</td>
</tr>
<tr>
<td></td>
<td>PentaBDEs 50-60</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HexaBDEs 4-8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OctaBDE (BDE-79)</td>
<td>HexaBDEs 10-12</td>
<td>1500</td>
<td>40%</td>
</tr>
<tr>
<td></td>
<td>HeptaBDEs 44</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OctaBDEs 31-35</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NonaBDEs 10-11</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DecaBDEs &lt;1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DecaBDE (BDE-83r)</td>
<td>NonaBDEs &lt;3</td>
<td>24500</td>
<td>44%</td>
</tr>
<tr>
<td>Saytex 102E</td>
<td>DecaBDEs 97-98</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PBDEs are outstanding flame retardant chemicals. However, their negative effects on the environment, animals and humans are areas of past and ongoing investigation. Since their production in the 1970s increased, the levels in the environment have been exponentially increasing, with doubling times of 4 to 6 years (Hites, 2004). PBDEs have been found to persist and accumulate in the environment and are taking on a similar path as the PCBs. The exact pathways by which PBDEs enter the environment are still not completely known and need further research, although leaching after disposal seems to be the primary pathway, especially considering the mechanism used to introduce PBDEs into polymers. PBDEs were first discovered in Swedish fish samples in 1981, and since then have been globally detected in the environment and humans (Anderson and Blomkvist, 1981; Hites, 2004).
PBDEs are structurally similar to PCBs and therefore exhibit similar physical and chemical properties. Both are very lipophilic and have lower water solubility and vapor pressure with increasing halogenation, high binding affinity to particles, and strong resistance to acids, bases, light, heat, and oxidizing and reducing agents (Wong et al., 2001; Pijnenburg et al., 1995; Allchin et al., 1999). Due to these similarities, similar partitioning and exchange of PBDEs in the environment have been proposed (Watanabe & Sakai, 2003).

Due to the extensive bioaccumulation of PBDEs various regulatory schemes have been enacted. Europe has lead the way by banning pentaBDE and octaBDE in 2004 and decaBDE in 2008. In the U.S., the main producers of PBDEs voluntarily phased out pentaBDEs and octaBDEs technical mixtures in 2004 after the European ban, as the lower chlorinated mixtures were deemed more toxic and prevalent in the environment. DecaBDEs mixtures remain in production, although in December of 2009 Albemarle and Chemtura Corporation, the biggest producers in U.S., as well as the leading importer ICL Industrial Products, announced voluntary phase out of decaBDE by the end of 2012 (US EPA, 2009). Despite the phase out of penta and octa mixtures, and the highest consumption coming from decaBDEs, the majority of PBDEs detected are of less chlorinated nature (Rahman, 2001).

**Degradation of PCBs and PBDEs**

PCBs and PBDEs exhibit subtle differences despite structural similarities. Both species are susceptible to biodegradation, but PBDEs seem to be more susceptible, as seen in numerous studies citing BDE-47 (2,2’,4,4’-tetrabromo diphenyl ether) and other lower
brominated congeners as the dominant congeners in samples, except in sediment (Hites, 2004). Additionally, the C-Br bond is weaker than C-Cl bond, predicting greater susceptibility to environmental degradation. Even though regulations and phase outs ended the production and use of some of the congeners of greatest concern, decaBDEs are still being utilized, resulting in continued pollution of the environment. This is of special concern because, although decaBDEs are deemed the safest of PBDEs, they undergo continuous environmental degradation that yields byproducts that are more toxic than the parent compounds.

Laboratory studies have shown that aerobic and anaerobic degradation and photolysis are possible ways of degradation. However, it’s questionable whether these results can be extrapolated to environmental conditions and scenarios (Robrock et al., 2008; Sanchez-Prado et al., 2005). PBDEs are degraded into lighter, more stable, more toxic, and more mobile congeners with greater half-lives (Eriksson et al., 2004). Similar to PCBs, PBDEs thermally degrade and form very toxic byproducts such as PBDDs (polybrominated dibenzo dioxins) and PBDFs (polybrominated dibenzo furans). Thermal degradation of PBDEs can occur during synthesis of BFRs, formulation of polymers, use of consumer goods at high temperatures, accidental fires, and incomplete incineration (Dumler et al., 1989; Rahman et al., 2001; Sakai et al., 2001).

**Exposure and Health Effects**

Human exposure to PCBs/PBDEs occurs through dermal contact, inhalation, and low-level food contamination (Erickson, 1992). Consumption of contaminated meats, fish, and poultry is the primary source of exposure (ATSDR, 2000). Due to their lipophilicity,
these pollutants bioaccumulate and biomagnify up the food chain. Although dietary intake accounts for the greatest percent of exposure, inhalation of dust containing PCBs has gained attention due to elevated levels of PCBs in indoor air in relation to outdoor levels. A study of indoor dust samples in U.K. primary schools showed maximum ΣPCB levels to be at 560 ng g⁻¹, which is not nearly as alarming as the average levels of 2774 ng g⁻¹ in U.S. daycare centers (Harrad et al., 2010; Wilson et al., 2001 & 2003). A similar pattern is seen with PBDEs in house dust in US locations, with significantly higher concentrations averaging 600 to 41,000ng/g (Stapleton et al., 2005; Rudel et al., 2003; Sharp and Lunder, 2004). This correlation is reflective of US consumption, which accounts for 50% of the world’s production. Again, inhalation exposure accounts for approximately 1% of the dietary intake. However, it can be a lot more significant in areas with a higher PCB/PBDE burden.

PCB levels have been increasing throughout the mid-20th century, creating controversy with respect to range of contamination, toxicity and effects in the environment. All PCB toxicology data has been obtained from animal testing, with limited human occupational exposure studies. Animal testing in numerous studies showed carcinogenic, immunotoxic, behavioural, reproductive, and developmental effects (WHO, 2003). PCBs have shown similar effects in animals as well as humans (WHO, 2003). A case examining PCB and PCDF exposure in humans was conducted upon accidental consumption of rice oil in Japan (1968) and Taiwan (1979). The symptoms of the 2000 patients affected included chloracne, hyperpigmentation, hormonal effects, neuropathy, chronic bronchitis, liver effects, carcinogenic effects, and neurobehavioural effects (WHO, 2003). Infants of exposed mothers also showed endocrinological and
neurobehavioral effects and hearing deficit (WHO, 2003). PCBs that accumulate in tissue, milk, and serum of mothers are ultimately passed down onto newborns. However, these levels have been on a steady decline due to the ban of PCBs, strict regulation and monitoring (Jaraczewska et al., 2006). It is also important to note that there are no documented studies or reports on effects of PCBs on humans from low level of exposure over a long period of time, as seen in environmental contamination.

PBDEs and PCBs initiate similar genetic modification that result in carcinogenic effects. Although PBDE toxicity is not as well understood as that of PCBs, they are identified as endocrine disruptors and neurotoxins (WHO, 1994). Toxicity varies between congeners and is dependent on the substitution of the bromines on the rings. Ortho-positioned halogens on both PCB and especially PBDEs hinder the rotation of rings and greatly decrease the odds of the toxin binding to various protein receptors. It is generally concluded that toxicity of PBDEs increases with less bromination as a result of their ability to pass through membrane with greater ease (Rahman, 2001).

**POPs in Tampa Bay Area**

Tampa Bay, situated along the Gulf of Mexico, is a large natural harbor that also serves as Florida’s largest open-water estuary. The Tampa Bay harbor borders Pinellas, Hillsborough, and Manatee Counties. According to the U.S. 2010 Census data, the respective populations are 916,542 for Pinellas, 1,229,226 for Hillsborough, and 322,833 for Manatee. Land use is primarily urban, followed by agriculture, rangeland, forestland and wetland (Figure 3). For the purpose of this study the urbanized areas of the three counties surrounding Tampa Bay can be further classified into industrial, commercial, and residential ranging from high to low population density.
The Environmental Protection Commission of Hillsborough County previously conducted studies on PCB levels in Tampa Bay sediments, reporting alarming levels of PCBs in sediments near Port of Tampa, more specifically in Palm and Hillsborough Rivers. However, no studies have been done on PBDEs/PCBs in the atmosphere.
Remediation of PCB and PBDE compounds

Numerous thermal, biological and chemical remediation technologies have been studied to remediate POPs in the environment. However, these are restricted due to incomplete degradation, long remediation times, and slow dehalogenation. Traditional methods require large-scale dredging projects to clean up PCB/PBDE-contaminated soil by removal and exposure to high-temperature incinerators. During this process large volumes of soil are exposed to 400°C, at which point pollutants combust. This application method has the potential to form dioxin/furan-like byproducts from incomplete pyrolysis. Combustion technology, although effective, is costly and environmentally destructive.

Biological methods have also been developed but have drawbacks. A study exploring three different biological cultures (ANAS195, D. hafniense, D. restrictus) for debromination of PBDEs showed similar mechanisms and had strong similarities to degradation of PCBs, although slower and less effective with PBDEs (He et al., 2006). The study found the anaerobic treatment to be impartial and slower for higher brominated congeners because of increased hydrophobicity.

Chemical techniques are the most widely used for remediation of POPs. Dechlorination of PCBs by zero-valent iron has been demonstrated at high temperatures (Chuang et al., 1995), but at 200°C or below little dechlorination of PCBs occurred. However, rates of dechlorination by iron have been increased by using palladium, a known hydrodechlorination catalyst (Wang and Zhang, 1997; Ravary and Lipczynska-Kochany, 1995; Neurath et al, 1997; Cheng et al, 1997; Li et al., 2000). Complete dechlorination of dissolved phase PCBs was observed when iron particles were coated with a small amount
of palladium (Grittini et al., 1995; Wang and Zhang, 1997; Korte et al, 2002; Liu et al, 2001). The preparation of the bimetal via mechanical alloying has been shown as an effective alternative to electrodeposition (DeVor et al, 2009a). In 2005, palladium-impregnated carbon ball-milled magnesium was utilized to dechlorinate 2, 4, 5-trichlorobiphenyl in two hours producing biphenyl, monochlorobiphenyl, and dichlorobiphenyl (Halle et al., 2005). In order to optimize the utilization of bimetallic metals in field-scale applications, the mechanisms of dehalogenation have been studied. DeVor et al (2009) concluded that the mechanism of dehalogenation is solvent-specific. Three possible solvent-specific mechanisms, all of which include the removal of the chlorine atom by hydrogen as the rate limiting step, were found, varying only in the exact nature of the hydrogen species (radical, hydride, or “hydride-like” radical) (DeVor et al, 2009b). Dechlorination of organic compounds by magnesium/palladium bimetals can take place in the presence of oxygen because of its self-limiting oxide layer (Engelmann et al., 2001). This approach trumps limitations of anaerobic conditions as well as the need for surface activations of zero valent metal (ZVM) iron (Muftikian et al., 1995; Fennelly and Roberts, 1998).

Photolytic degradation is another technique explored for POPs. Photolytic degradation plays a large role in the ability of POPs to break down in the environment into lower congeners, more so than anaerobic degradation. Numerous studies have proven that the degradation rate is based on solvent system, matrix ratios, and degree of halogenation (Raf et al., 2007; Wei et al., 2013). The path goes through debromination, having a higher rate with higher brominated congeners over the lower ones, and being faster in organic solvents compared with water (Mas et al., 2008). Whether in a solvent system or through
solid phase micro extraction, UV exposure produces highly toxic dibenzofurans (Sanchez-Prado et al., 2005). Incomplete debromination is another drawback, as it produces congeners with higher toxicity than the parent toxins.
Chapter Two: Determining ambient levels of PCBs and PBDEs in Tampa Bay

Introduction

Over the last several decades Tampa Bay has experienced heavy anthropogenic development and a population boom that has quadrupled since 1950. This trend has contributed to the release of POP into the local environment. There are several studies that have looked at levels of POPs in sediment and water. However, there is very limited data on atmospheric levels, especially PCBs and PBDEs.

The only study looking at PCBs in Tampa Bay atmosphere was done by Poor (2002). Sampling at Gandy Bridge monitoring site over an 8 month period yielded no detectable PCBs in ambient air. However it is noteworthy to mention that method detection limits for the 17 PCB congeners analyzed ranged from 0.006-0.015 ng/m³. In a monitoring program between 1993-1998, sediment levels of PCBs ranged from no detectable levels to 1073 µg/kg (Grabe and Barron, 2002). For PBDEs, NOAAs National Mussel Watch Program determined levels in Tampa Bay (2004-2007) to range from 1.0 to 220 µg/kg in oysters, and from none detectable to 0.6 µg/kg in sediment (Kimbrough et al., 2009).

Other POPs detected in Tampa Bay environment include organochlorine pesticides (OCs) and polyaromatic hydrocarbons. OCs in ambient air averaged from not detectable to 0.083 ng/m³ and in sediment from 0.04 ng/m³ to 1.76 ng/m³. As for PAHs, ambient air
averaged from not detectable to 6.9 ng/m$^3$, and 0.009 ng/m$^3$ to 214 ng/m$^3$ for sediment (Poor, 2002; Grabe and Barron, 2002).

With atmospheric transport being recognized as the dominant path of global transport and primary human exposure pathway, it is imperative to assess atmospheric concentrations of PCBs and PBDEs. This study assessed ambient levels of PCBs and PBDEs in several locations around Tampa Bay that differ with regards to their land-use profiles.

**Methods**

**Sampling**

Air samples were taken at five locations around the Tampa Bay area (Table 3 and Figure 4) between May 25$^{th}$ and July 13$^{th}$ of 2010. The sampling locations represent five distinctive land use practice areas. Site 1 in downtown St. Petersburg represents an urbanized metropolitan area with a population density of 5693 inhabitants/square mile. It is associated with older historic buildings and newer residential high-rises. Site 2 in Safety Harbor is a suburban location primarily composed of residential homes and has a population density of 3,302 inhabitants/square mile. Site 3 in South Tampa has a density of 4,643 inhabitants/per square mile with a profile of high end suburban living. Site 4 in Port of Tampa is representative of an industrial site with the largest port in Florida, with a density of 2171 inhabitants/square mile. Site 5 in Palmetto has an agricultural/rural footprint with the least dense population of 624 inhabitants/square mile (2010 US Census). Eight to 10 samples were taken at each location using a high volume active air samplers that had an estimated volume draw of 0.3 m$^3$/min. Air was sampled for 24 hours at each site. Tables 4 – 8 show details of sampling at each site. Active air samplers were
constructed by placing an air vacuum pump (110V) in a large containers (3ft x 3ft x 4ft),
that connected to a Tisch Environmental head unit. The head unit consisted of 2
collection phases, a chamber holding a glass fiber filter and a canister directly below it
that housed polyurethane foam plugs (PUFs). The 8” by 10” glass fiber filters was
purchased from Staplex (TFAGF810) and PUFs free of flame retardants were obtained
from Tisch Environmental. PUFs were prepared by undergoing two 12 hour sequential
extractions with dichloromethane first and hexane second in a Soxhlet apparatus. Glass
fiber filters were baked at 450 °C for 6 hours prior to use. Air samplers were placed at a
minimal elevation of 2.5 meters above ground. Care was taken to place them away from
any obvious or potential direct source of POPs.

Table 3: Tampa Bay sampling location features

<table>
<thead>
<tr>
<th>Location</th>
<th>Site 1 (StP)</th>
<th>Site 2 (SH)</th>
<th>Site 3 (ST)</th>
<th>Site 4 (PoT)</th>
<th>Site 5 (Pal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location&lt;br&gt;Downtown&lt;br&gt;St.Petersburg</td>
<td>Safety Harbor</td>
<td>South Tampa</td>
<td>Downtown Tampa</td>
<td>Palmetto</td>
<td></td>
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<tr>
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<td>Sub-urban</td>
<td>Sub-urban</td>
<td>Industrial</td>
<td>Agricultural</td>
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<td>Population/sq. mi.</td>
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<td>3302.28</td>
<td>4643.14</td>
<td>2171.34</td>
<td>624.35</td>
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Figure 4: Sampling locations.
Table 4: Site 1 sampling parameters

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<th>Date</th>
<th>Start</th>
<th>End</th>
<th>Date</th>
</tr>
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<td>12:50pm</td>
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<td>12</td>
<td>3-Jun</td>
<td>12:42pm</td>
<td>2:18pm</td>
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</tr>
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<td>16</td>
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<td>12:17pm</td>
<td>2:11pm</td>
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</tr>
<tr>
<td>6</td>
<td>20</td>
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<td>11-Jun</td>
</tr>
<tr>
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<tr>
<td>8</td>
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Table 5: Site 2 sampling parameters

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<td>9:25am</td>
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</tr>
<tr>
<td>3</td>
<td>8</td>
<td>31-May</td>
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<tr>
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</tr>
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</tr>
<tr>
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<td>17</td>
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<td>18-Jun</td>
<td>11:05am</td>
<td>11:57am</td>
<td>19-Jun</td>
</tr>
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</table>

Extraction

After each sampling, the glass fiber filter and PUFs were combined together and placed in a Soxhlet apparatus and extracted overnight using 1:1 hexane/DCM. The extracts were concentrated to 1 mL using a rotary evaporator followed by a gentle stream of ultrapure nitrogen and solvent-exchanged into isooctane.

Extracts were cleaned via column chromatography using alumina/silica. Columns were prepared by slurry packing each Pyrex glass column (1 cm i.d.) with 1g of activated (baked at 450°C) alumina and 2g of activated silica (baked at 450°C) followed by 2 cm of anhydrous sodium sulfate. Two column lengths of 50/50 hexane/DCM were passed through prior to application of samples. Each extract was eluted with approximately 25mL of 1:1 hexane:DCM, concentrated to 1ml using a rotary evaporator followed by a
gentle stream of ultrapure nitrogen and then solvent-exchanged into isooctane and placed in amber gas chromatography autosampler vials.

**Analysis**

Samples were analyzed for PCBs and PBDEs using Agilent GC-MS. Samples were analyzed by capillary gas chromatography - mass spectrometry (GC-MS) in the electron impact (EI) mode using an Agilent 6890 GC – 5973 MSD. The analysis was done on a 60-m DB-5 column (0.25 mm i.d., 0.25 µm film, J&W Scientific) with He carrier gas at 30 cm s⁻¹. Sample volumes of 2 µL were injected splitless (split opened after 1.0 min). Inlet and transfer line temperatures were 265°C and 250°C. The GC oven for temperature program was: 90°C (1 min), ramped to 160°C at 15°C min⁻¹, then to 280°C at 3°C min⁻¹ and held for 15 min. Ion source and quadrupole temperatures were 150°C and 106°C. Fourteen PBDE and 56 PCB congeners were measured as indicated in Table 9 below (PCB congeners co-eluted and were quantified together).

Injection standards were prepared from stock standards of individual compounds, also from AccuStandard. Calibration plots were made from 5-7 dilutions, ranging from 0.0005 to 0.025 ng µL⁻¹ for PCB and PBDE congeners. Samples were quantified versus a [¹³C₁₂]-PCB-105 internal standard using the linear regression algorithm provided by MSD Chemstation software or by using average response factors derived from the standards. The difference using the two approaches was typically less than 10 to 15%.
Table 9: Specific PCB and PBDE congeners analyzed

<table>
<thead>
<tr>
<th>PCB &amp; PBDE Congeners Analyzed</th>
<th>PCB-8</th>
<th>PCB-70</th>
<th>PCB-126</th>
<th>PCB-171</th>
<th>PBDE-17</th>
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</thead>
<tbody>
<tr>
<td>PCB-15</td>
<td>PCB-66</td>
<td>PCB-151</td>
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</tr>
<tr>
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<td>PCB-56/60</td>
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<td>PBDE-209</td>
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</tr>
</tbody>
</table>

Quality Control

Three blanks were deployed to test any cross contamination. Blanks consisted of taking PUF plugs to the field site, taking them out of their glass jars for about one minute and then storing them again in their containers. These were then treated as samples. Ten samples were tested for breakthrough by setting up two PUF plugs in the air sampler chamber. Results indicated no problems with breakthrough for any target compound. Extraction efficiency was determined by spiking PUFs with a solution of four labeled organochlorine pesticides (which have been shown to behave similarly to PCBs and PBDEs) and treating as samples. Extraction efficiencies were above 90% for all compounds so there was no correction for loss due to extraction. Internal standards use accounted for any instrument signal variation.
Results

PBDEs

Figures 5-9 below show concentrations of PBDE congeners measured at the five sites in the study. At every site three congeners, BDE-047, BDE-099, and BDE-100 constituted virtually all of PBDEs measured. Figure 10 compares the PBDE congener profiles between the five sampling sites, showing that in all cases BDE-047 dominates (average 70%), followed by BDE-099 (average 24%) and BDE-100 (average 6%).

Numerous studies have reported similar finding with atmospheric concentrations being mostly composed of BDE-047, BDE-099 and BDE-100 (Standberg et al., 2001; Gouin et al., 2002; Lee et al., 2002; Li et al., 2011). This profile trend is similar to the pentaBDE commercial mixture. PentaBDE at one point was the most utilized out of the three main PBDE technical mixtures but was phased out in 2005, and since has been replaced with decaBDE technical mixture. Despite the shift of commercial use from pentaBDE to decaBDE tech mixtures, atmospheric levels at the time of this study were dominated by lighter congeners. This may be explained in two ways. It is possible that PBDEs measured in this study are the result of volatilization of PBDEs from older products containing the older pentaBDE technical mixture which has shown to have higher vapor pressure and higher stability in air over octaBDE and decaBDE tech mixtures (Wong et al., 2001). Alternatively, they are byproducts of photolitically degraded decaBDE technical mixture, as UV stability has shown to decreases with increased bromination (Wei et al., 2013).
Figure 10 also suggests that a similar source is contributing to the PBDE profiles among sampling sites regardless of varying land-use patterns. One would expect varying profiles with multiple or different sources. PBDE signature is not one of specific sources as in the case of PCBs, but rather one that is driven by consumerism and population density. Therefore it is no surprise to find highest and lowest concentrations of BDE-047, BDE-099 and BDE-100 in Port of Tampa and Palmetto, respectively, reflecting population sizes and densities. However, despite differences in land-use patterns around the sampling sites (e.g. Port of Tampa is the most industrial while Palmetto is least dense with an agricultural signature) the profiles are similar, indicating similar or even common sources.

![PBDEs at St.Petersburg](image)

**Figure 5:** Atmospheric levels of PBDEs in St.Petersburg.
**Figure 6:** Atmospheric levels of PBDEs in Safety Harbor.

**Figure 7:** Atmospheric levels of PBDEs in South Tampa.
Figure 8: Atmospheric levels of PBDEs in Port of Tampa.

Figure 9: Atmospheric levels of PBDEs in Palmetto.
Figure 10: PBDE profile distribution in Tampa Bay Area.

Figure 11 below summarizes the sum of PBDEs at the five sampling sites. Results show that concentrations in order of decreasing levels were as follows: Port of Tampa > South Tampa ~ Safety Harbour > St Petersburg > Palmetto. A two sample t-test assuming unequal variance indicated that Port of Tampa (Site 4) was the only site to show statistically significant differences to all the other sampling sites. Keeping in mind that PBDEs have no direct source it’s not surprising to find highest levels in the Port of Tampa. Being one of the most diverse ports in the nation and major economic engine for much of West Florida, the Port of Tampa is a large importer and exporter of construction material, petroleum, and fertilizer, as well as a hub for ship repair and cruise line businesses. Site 4 (Port of Tampa) is surrounded by a high-density urban area, which would explain the higher levels of PBDEs. Additionally, studies have also shown that ambient air near solid waste incinerators tends to have higher levels of PBDEs, especially of heavy natured congeners (Wang et al., 2010). Site 4 in Port of Tampa showed trace
amounts of BDE-153, BDE-154, and BDE-183 suggesting that the Hillsborough Counties solid waste incinerator plant, six miles North East of the sampling location, could be contributing to the elevated levels.

Following Port of Tampa the two suburban sampling sites of South Tampa and Safety Harbor had the next highest levels of PBDEs, with the former having slightly higher levels that could possibly be attributed to its higher population density (4643>3302 inhabitants/sq.mi.). The urbanized down town site of St. Petersburg had the fourth lowest levels of PBDEs despite it being the most densely populated. The Palmetto site, located in a rural/agricultural area, had the lowest levels of PBDEs. Studies done on other coastal communities reported similar findings, with urbanized centers dominating the load over remote or agricultural sites (Zhang et al., 2008; Strandberg et al., 2001).

Figure 11: Atmospheric PBDE levels in Tampa Bay.
The overall PBDE range of 0.78-9.54 pg/m³ in Tampa Bay are comparable to ranges of 4.4-21 pg/m³ found in the rural sites of the Great Lakes and is significantly lower than the range of 33-77 pg/m³ found in urban sites around the Great Lakes (Strandberg et al., 2001). The PBDE levels in Tampa Bay measured in this study, as indicated in table 10 below, are lower than those reported for other areas around the world.

**Table 10:** PBDE level comparison between Tampa Bay and other locations.

<table>
<thead>
<tr>
<th>Sampling Locations</th>
<th>Congeners</th>
<th>Study Date</th>
<th>PBDE Ranges pg/m³</th>
<th>PBDE Mean pg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>St.Petersburg (Urban)</td>
<td>Σ14PBDE</td>
<td>2010</td>
<td>1.16-2.68</td>
<td>1.72</td>
</tr>
<tr>
<td>Port of Tampa (Industrial)</td>
<td>Σ14PBDE</td>
<td>2010</td>
<td>1.21-9.54</td>
<td>4.09</td>
</tr>
<tr>
<td>Safety Harbor (Sub-urban)</td>
<td>Σ14PBDE</td>
<td>2010</td>
<td>0.86-2.54</td>
<td>1.90</td>
</tr>
<tr>
<td>South Tampa (Sub-Urban)</td>
<td>Σ14PBDE</td>
<td>2010</td>
<td>1.37-3.63</td>
<td>1.95</td>
</tr>
<tr>
<td>Palmetto (Agricultural)</td>
<td>Σ14PBDE</td>
<td>2010</td>
<td>0.78-2.13</td>
<td>1.36</td>
</tr>
<tr>
<td>Great Lakes- Chicago (Urban)</td>
<td>Σ7PBDE</td>
<td>1997-1999</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Great Lakes- Sturgeon Point (Rural)</td>
<td>Σ7PBDE</td>
<td>1997-1999</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>Great Lakes- Sleeping Bear Dunes (Rural)</td>
<td>Σ7PBDE</td>
<td>1997-1999</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Great Lakes- Eagle Harbor (Remote)</td>
<td>Σ7PBDE</td>
<td>1997-1999</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>India (Urban)</td>
<td>Σ9PBDE</td>
<td>2006</td>
<td>2-181</td>
<td>34</td>
</tr>
<tr>
<td>India (Rural)</td>
<td>Σ9PBDE</td>
<td>2006</td>
<td>3-13</td>
<td>8</td>
</tr>
<tr>
<td>India (Wetlands)</td>
<td>Σ9PBDE</td>
<td>2006</td>
<td>1-6</td>
<td>3</td>
</tr>
<tr>
<td>Chicago</td>
<td>Σ13PBDE</td>
<td>2002-2003</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Toronto</td>
<td>Σ13PBDE</td>
<td>2002-2003</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>Σ10PBDE</td>
<td>2001</td>
<td>0.4-78.5</td>
<td>8.67</td>
</tr>
<tr>
<td>Antartica(King George)</td>
<td>Σ14PBDE</td>
<td>2009-2010</td>
<td>0.67-2.98</td>
<td>1.52</td>
</tr>
</tbody>
</table>
Figures 12-16 show concentrations of PCB homologs at each sampling site in this study. St. Petersburg and Port of Tampa PCB profiles were dominated by pentaCB>hexaCB congeners. South Tampa and Palmetto PCB profiles were dominated by lighter triCB congeners, while Safety Harbor showed an evenly distributed profile.

Figure 17 shows a comparison of these profiles among sampling sites, showing that the signature varies from site to site. Unlike PBDEs, PCB profiles suggest different sources contributing to atmospheric levels at the different sites. They also have a resemblance to PCB technical mixtures known as Aroclors. Between the 1930s and 1970s, nine PCB technical mixtures were used, each having a unique composition and application. Aroclors 1254 and 1248, which were the most widely used technical mixtures, are ones that are primarily composed of pentaCB congeners, while Aroclor 1016, only used for capacitors, is dominated by triCB congeners. Thus, the results suggest that the source of the PCBs measured in St. Petersburg and Port of Tampa is dominated by materials containing Aroclors 1254/1248 while the source of PCBs measured in South Tampa and Palmetto is dominated by materials containing Aroclor 1016.

The link between these Aroclor mixtures and sampling sites is further reinforced by an analysis of the specific congeners that compose the dominant homologs. The dominant congeners within the pentaCB homolog of both Aroclors 1254 and 1248 matched the profiles of observed at St. Petersburg and Port of Tampa - PCB-095, PCB-101, PCB-110, and PCB-118. Similarly for Aroclor 1016 and South Tampa and Palmetto, the triCB homolog is dominated by congeners PCB-018, PCB-028, PCB-031, and PCB-033. These
links reinforce the inference that local input of Aroclor 1254/1248 is contributing to the atmospheric levels of PCBs in St. Petersburg and Port of Tampa, and local input of Aroclor 1016 is seen in atmospheric levels in South Tampa and Palmetto.

**Figure 12:** Atmospheric levels of PCBs in St. Petersburg.

**Figure 13:** Atmospheric levels of PCBs in Safety Harbor.
**Figure 14:** Atmospheric levels of PCBs in South Tampa.

**Figure 15:** Atmospheric levels of PCBs in Port of Tampa.
Figure 16: Atmospheric Levels of PCBs in Palmetto.

Figure 17: PCB homologue composition in Tampa Bay sampling sites.

Figure 18 compares the total PCB load among the various sampling sites. Concentrations in decreasing order are the following: Port of Tampa > Palmetto > St. Petersburg > South.
Tampa > Safety Harbor. Levels at Port of Tampa were statistically different compared to all sites except Palmetto, St. Petersburg and Safety Harbor levels were statistically different as well.

![Mean $\sum_{56}$ PCBs](image)

**Figure 18:** Atmospheric PCB levels in Tampa Bay.

With the exception of Palmetto, the finding agree with other studies (Strandberg et al., 2001; Zhang et al., 2008), where PCB levels are elevated near industrial and urban centers. It was surprising to find such high concentrations of PCBs in the Palmetto site, which is located in a rural/agricultural area. Further inspection of data from Palmetto revealed a significant event occurred on June 15th, where concentration of PCBs increased by a factor of 10. At 1251 pg/m$^3$ this single event was the highest value obtained throughout the study. Figure 19 shows the total PCB load without the June 15th event for Palmetto. The adjusted concentration at this site made it statistically different
from Port of Tampa, once again highlighting how different the Port of Tampa is from the other sites. Despite the adjustment, Palmettos levels remained higher than that of two sub-urban locations of South Tampa and Safety Harbor, signaling possible input from an unknown nearby source.

![Mean Σ56 PCBs Corrected](image)

**Figure 19:** Atmospheric PCB levels in Tampa Bay without June 15th event.

The PCB profile of the June 15th event at Palmetto was compared with the profile of the other samples collected at this site. Figures 20 and 21 shows that the profiles are essentially identical, both dominated by triCB, with lesser quantities of tetraCB, pentaCB, etc.. Table 10 also points out the close homolog percent composition between Palmetto samples and the June 15th event, suggesting that input for both is coming from the same source. Different profiles would suggest an exceptional event and a different source for the June 15th event, one that is not reflective of the local atmosphere. Therefore the June 15th event is a spike in the local input, possible spike in Aroclor 1016 use or release due to some exceptional event on that day.
Figure 20: Palmetto PCB profile comparison

Figure 21: PCB profile of June 15\textsuperscript{th} event at Palmetto.
Table 11: Homolog % composition by concentration at Palmetto.

<table>
<thead>
<tr>
<th></th>
<th>∑Tri-CBs</th>
<th>∑Tetra-CBs</th>
<th>∑Penta-CBs</th>
<th>∑Hexa-CBs</th>
<th>∑Hepta-CBs</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 15th</td>
<td>60.52</td>
<td>23.45</td>
<td>10.62</td>
<td>4.40</td>
<td>1.01</td>
</tr>
<tr>
<td>original</td>
<td>53.71</td>
<td>21.88</td>
<td>12.80</td>
<td>9.22</td>
<td>2.40</td>
</tr>
<tr>
<td>No outlier</td>
<td>48.26</td>
<td>20.62</td>
<td>14.54</td>
<td>13.08</td>
<td>3.51</td>
</tr>
</tbody>
</table>

Table 12 below compares levels in this study with those reported for other locations. The data indicates that in general levels of PCBs in the air around Tampa Bay was similar to rural locations around the world, but lower than urban locations and higher than remote locations such as Antarctica.

Table 12: Comparison of PCB levels in Tampa Bay air with levels around the world.

<table>
<thead>
<tr>
<th>Sampling Locations</th>
<th>Congeners</th>
<th>Study Date</th>
<th>PCB Ranges pg/m3</th>
<th>PCB Mean pg/m3</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. Petersburg</td>
<td>∑56PCB</td>
<td>2010</td>
<td>81.87-423.80</td>
<td>248.71</td>
</tr>
<tr>
<td>Port of Tampa</td>
<td>∑56PCB</td>
<td>2010</td>
<td>176.93-778.82</td>
<td>452.18</td>
</tr>
<tr>
<td>Safety Harbor</td>
<td>∑56PCB</td>
<td>2010</td>
<td>41.96-230.93</td>
<td>85.36</td>
</tr>
<tr>
<td>South Tampa</td>
<td>∑56PCB</td>
<td>2010</td>
<td>81.43-557.21</td>
<td>181.41</td>
</tr>
<tr>
<td>Palmetto</td>
<td>∑56PCB</td>
<td>2010</td>
<td>61.18-1250.96</td>
<td>354.07</td>
</tr>
<tr>
<td>Great Lakes- Chicago (Urban)</td>
<td></td>
<td>1997-1999</td>
<td></td>
<td>3100.00</td>
</tr>
<tr>
<td>Great Lakes- Sturgeon Point (Rural)</td>
<td></td>
<td>1997-1999</td>
<td></td>
<td>530.00</td>
</tr>
<tr>
<td>Great Lakes- Sleeping Bear Dunes (Rural)</td>
<td></td>
<td>1997-1999</td>
<td></td>
<td>660.00</td>
</tr>
<tr>
<td>Great Lakes- Eagle Harbor (Remote)</td>
<td></td>
<td>1997-1999</td>
<td></td>
<td>140.00</td>
</tr>
<tr>
<td>India (Urban)</td>
<td>∑28PCB</td>
<td>2006</td>
<td>216-1077</td>
<td>662</td>
</tr>
<tr>
<td>India (Rural)</td>
<td>∑28PCB</td>
<td>2006</td>
<td>279-805</td>
<td>464</td>
</tr>
<tr>
<td>India (Wetlands)</td>
<td>∑28PCB</td>
<td>2006</td>
<td>120-320</td>
<td>238</td>
</tr>
<tr>
<td>Chicago</td>
<td>∑209PCB</td>
<td>2006-2007</td>
<td>75-5500</td>
<td>840</td>
</tr>
<tr>
<td>Chicago</td>
<td>∑48PCB</td>
<td>2002-2003</td>
<td></td>
<td>900</td>
</tr>
<tr>
<td>Toronto</td>
<td>∑48PCB</td>
<td>2002-2003</td>
<td></td>
<td>960</td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>∑18PCB</td>
<td>2001</td>
<td>1.6-21.3</td>
<td>7.40</td>
</tr>
<tr>
<td>Antartica(King George)</td>
<td>∑20PCB</td>
<td>2009-2010</td>
<td>1.66-6.50</td>
<td>4.34</td>
</tr>
</tbody>
</table>
Conclusion

Ambient air concentrations of PBDEs in Tampa Bay were found to be lower than levels from many areas around the world. They were significantly lower compared to coastal counterparts in the Great Lakes and coastal India. Mean $\sum_{14}$ PBDE levels were highest in Port of Tampa (4.09 pg/m$^3$), followed by South Tampa (1.95 pg/m$^3$), Safety Harbor (1.90 pg/m$^3$), St. Petersburg (1.72 pg/m$^3$), and Palmetto (1.36 pg/m$^3$). PCB levels were lower than values reported for urban areas around the world, higher than values for remote locations, and generally in the same range for values reported for rural areas. Mean $\sum_{56}$ PCB levels in Tampa Bay from highest to lowest levels are the following: Port of Tampa (452.18 pg/m$^3$), Palmetto (354.07 pg/m$^3$), St. Petersburg (248.71 pg/m$^3$), South Tampa (181.41 pg/m$^3$), Safety Harbor (85.36 pg/m$^3$).

Port of Tampa proved to be a significant source of both pollutants. This industrial location showed statistically significant differences in concentrations of both PBDEs and PCBs to all other sampling sites. The results also showed statistically significant differences for PCBs between urban St. Petersburg and sub-urban Safety Harbor. It was surprising to find no statistical distinction between urban St. Petersburg and sub-urban South Tampa or agricultural Palmetto. It was also surprising to see no statistical distinction in PBDEs levels between highly dense urban St. Petersburg and Palmetto, South Tampa or Safety Harbor.

Agricultural Palmetto which had the lowest PBDE levels had the second highest levels of PCBs in Tampa Bay. Further examination unveiled a local spike that occurred on the sampling event of June 15th. During this event ambient air PCB concentration in Palmetto
was recorded at 1250.96 pg/m³, an increase by a factor of 10. PCB profiles of both the June 15th spike and ambient levels in Palmetto were matching, signaling that this spiked event was not distinct but one that is representative of the local input.

PBDE profiles at all Tampa Bay sampling location were alike, with BDE-047 being dominant followed by BDE-099 and BDE-100. Despite varying land use, the uniform profiles suggest a similar source contributing to the levels across Tampa Bay. On the other hand PCB profiles varied from site to site suggesting different sources contributing to local levels. PentaCB dominated profiles of St.Petersburg and Port of Tampa, showing a similarity to Aroclor 1254/1248 while triCB dominated profiles of Palmetto and South Tampa, showing a similarity to Aroclor 1016.
Chapter Three: PBDE Degradation with Zero-valent Bimetallic Systems

Introduction

Nano- and micro-scale particle technology has garnered renewed research interest because of its enhanced reactivity, and economic and environmental feasibility (Geiger and Carvalho-Knighton, 2009). The enhanced reactivity of these materials has yielded a scientific renaissance leading to research on systems that had previously proven nearly impossible to degrade safely. Materials that may have lacked reactivity at the macro-size have become useful remediation tools as nanoscale particles. Noble metals that would have never been used due to economics are now becoming feasible alternatives for field applications because of the low mass required when incorporated with nanoparticle base metals. In addition, the complexities of matrices that are innate to environmental remediation make these small particles of particular interest for improved emplacement technologies.

Recent interest in dehalogenation of waste by the use of zero valent metals (ZVMs) has brought much focus upon halogenated hydrocarbons. ZVM have been proven to be effective against trichloroethylene (TCE) and perchloroethylene (PCE). A study by Keum and Li (2005) also included promising data in debromination of PBDEs by the use of zero valent iron. In a 40 day study, 90% BDE-209 was converted in lower substituted congeners dominated mainly by triBDEs and tetraBDEs (Keum, 2005). The use of zero valent metals to treat PBDEs is new and still requires numerous studies to explore its
feasibility. However, it has proven effective with PCBs (Devor, 2008) and ultimately is projected onto PBDEs due to their chemical and structural similarities. As a result of its corrosive nature, extensive pre-treatment and anaerobic storage, iron is not an ideal metal for this type of remediation. Magnesium, much like iron, can remediate but does not require such extensive treatment. It also exhibits a higher oxidation potential with 2.372V in comparison to Fe 0.44V, therefore having a greater electropotential driving force.

\[
\begin{align*}
\text{Mg}^{2+} + 2e^- & \rightarrow \text{Mg}^0 & E^0 & = -2.37V \\
\text{Fe}^{2+} + 2e^- & \rightarrow \text{Fe}^0 & E^0 & = -0.44V
\end{align*}
\]

Zero-valent magnesium and iron form hydrogen gas by reacting with a protic solvent, as seen below.

\[
\begin{align*}
2 \text{ Mg}^0 & \rightarrow 2 \text{ Mg}^{2+} + 4e^- \\
2 \text{ ROH} & \rightarrow 2\text{H}^+ + 2\text{R}^- \\
2\text{H}^+ + 2e^- & \rightarrow \text{H}_2 (g)
\end{align*}
\]

As seen previously with zero-valent iron treatment of halogenated hydrocarbons, the hydrogen gas goes on to replace the halogen of the toxin (Devor et al., 2008).

The objective of the following study is to test feasibility of zero-valent metals (ZVM) for degradation of PBDEs. As seen effective with PCBs several bimetallic systems were tested on 2,2’,4,4’-tetrabromodiphenyl ether (BDE-047) to determine optimum system. In addition, rate and kinetic studies on BDE-047 were conducted, as well as identification of byproducts and degradation pathway.
Method

*Chemicals and Reagents*

2,2’,4,4’- tetrabromodiphenyl ether (BDE-47, CAS No:5436-43-1)) were purchased from Accustandard, Inc. Palladium coated magnesium, 0.08% based on weight, ball milled March 13th of 2007 were obtained from UCF industrial chemistry labs. Methanol and toluene solvents utilized in the experiment were all obtained from Fischer scientific, Inc, and were all optima grade.

*Palladium Coated Magnesium*

Magnesium (~ 4 µm) was obtained from Hart Metals, Inc (Tamaqua, PA). 1% palladium on graphite was obtained from Engelhard (Iselin, NJ), while 10% palladium on graphite was obtained from Acros Organics. A ~0.08 wt% palladium-magnesium mixture was prepared by ball-milling 78g Mg with 7g of 1% palladium on graphite in a stainless steel canister (inner dimensions 5.5 cm by 17 cm) with 16 steel ball bearings (1.5 cm diameter, at a total mass of 261.15g). The material was milled for 30 minutes using a Red Devil 5400 series paint mixer. A 0.8% palladium-magnesium mixture was prepared in a similar fashion using 10% palladium on graphite.

*Treatment of BDE-047 by Zerovalent Mg/Pd*

Five mL of 20 ppm BDE-047 in methanol (20mg/L) were placed in a septum sealed (PTFE lined) vial containing 0.25 grams of 0.08% Mg/Pd. During the reaction period the vials were placed on a shaker table (Cole Parmer 51704 Series) until appropriate extraction time. Control vials were set up without Mg/Pd, and the experiment was set up in duplicates.
**Extraction and Analysis**

Extraction was performed at 0, 0.25, 0.50, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5 hours of reaction with the palladized metal. The extraction process included placing 5 ml of Toluene (Optima) in the vials and shaking for approximately 2 minutes followed by extraction of 4 mL through a syringe filter (Puradisc 25mm with 0.45 µm pore size). To the extracted 4 ml of 50/50 methanol/toluene 2 ml of deionized water was applied and again shaken for a minute. Afterwards the vial was placed in a centrifuge for two minutes, at which point the top layer was pulled off using glass pipettes and placed in an autosampler vial for analysis. All samples were analyzed by Shimadzu GC-17A/MS-QP5000 equipped with DB-XLB column (30m length, 0.25mm I.D., 0.25µm Film) and an autosampler. Mobile phase consisted of helium with a column flow of 1.3 mL/min, injection port temperature was set at 260°C with a mass spectrometer interface of 225°C. Oven temperature ramp was held for 2 minutes at 80°C, followed by a 30°C/min ramp to 200°C, and finally a 5°C/min ramp to 320°C.

An extended study was set up by following the same parameters but extending reaction time to 24 hours. For kinetic analysis, a secondary study was set up with similar parameters as well but was slowed down by reducing the amount of 0.08% Mg/Pd to 0.10g.

**Results**

Several different bimetallic systems were explored in a preliminary study in order to determine the ideal system for further extensive study of BDE-047 (Figure 22). This congener is one of the most persistent PBDE congeners in the environment,
Figure 22: 2,2’,4,4’- tetrabromodiphenyl ether

The bimetallic systems utilized were 1%, 10% and 30% Mg/Pd, Fe/Ni, Fe/Pd, Mg, and acid washed µFe. Three hour studies were set up for each system to determine degradation percent of the parent compound as shown in Figure 23.

<table>
<thead>
<tr>
<th>Bimetallic System</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08% Mg/Pd</td>
<td>69.39</td>
</tr>
<tr>
<td>0.8% Mg/Pd</td>
<td>75.01</td>
</tr>
<tr>
<td>2.4% Mg/Pd</td>
<td>N/A</td>
</tr>
<tr>
<td>Fe/Ni</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Fe/Pd</td>
<td>1.94</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;1</td>
</tr>
<tr>
<td>microFe (acid-washed)</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Figure 23: BDE-47 degradation by various systems in a three hour study.
In the initial studies, 0.08% Mg/Pd proved to be the most effective with 75.01% degradation of 20ppm BDE-047 in methanol in three hours. 2.4% Mg/Pd showed the highest potential in terms of degradation rates, however due to its reactive and vigorous nature it was difficult to work with due to high heats and large pressure build ups and was omitted.

A five hour study of 20ppm BDE-047 in methanol reacting with 0.10g of 0.08% Mg/Pd proved to be effective in degrading congener 47. The results showed 80% degradation within the first 30 minutes followed by 99% within the remaining 4.5 hours as shown in Figure 24.

![Figure 24: Degradation of BDE-47 with Mg/Pd in Methanol with 0.08% Pd](image)

The reaction proved to be a step-wise debromination, the parent BDE-47 debrominates down into tri substituted congeners, then a di- and mono-, and finally into bare diphenyl ether.
The exact byproduct congeners were not identified, but have been limited down based on their parent congeners bromine orientation, 2,4,4’-tribromodiphenyl ether (BDE-028) or 2,2’,4-tribromodiphenyl ethers (BDE-017) for the tri substituted congeners, 2,4-dibromodiphenyl ethers (BDE-007), 2,4’-dibromodiphenyl ether (BDE-008), 4,4’-dibromodiphenyl ether (BDE-015) for di substituted congeners and finally to either 2-monobromodiphenyl ether (BDE-001) or 4-monobromodiphenyl ether (BDE-003) for the mono substituted congeners as shown in Figures 28 and 29. Identification of congeners will be of focus in future studies in hopes of determining stereo selectivity of ortho, para, and meta oriented bromines, and determining major and minor byproducts.

Figure 25: GC-MS chromatogram of BDE-47 degradation
The hydrogen gas produced from the zero-valent magnesium reacts with the toxin and substitutes the bromines through an unknown mechanism, as can be seen below (Devor, 2008).

\[
M^0 + 2\text{CH}_3\text{OH} \rightarrow M^{2+} + \text{H}_2 + 2\text{CH}_3\text{O}^-
\]

\[
Pd
\]

\[
2\text{RBr} + \text{H}_2 \rightarrow 2\text{RH} + \text{Br}_2
\]

\[
\text{H}_2 + 2\text{Br}_2 \rightarrow 2\text{HBr}
\]

After 45 minutes the degradation rate began to slowdown. This can be attributed to competition for active sites by two factors. As previously seen in degradation of PCBs
with Mg/Pd systems (Devor, 2008), the parent toxin competes for active sites on the metal. Once the active sites have been saturated the reaction is halted until the degraded parent toxins departs the active site. The newly formed byproducts then are also competing and are favored on the reaction site. Figure 30 below supports this theory. The initial byproduct, either 2, 4, 4’-tribromodiphenyl ether (BDE-028) or 2, 2’, 4-tribromodiphenyl ether (BDE-017), concentration maximizes around 45 minutes of reaction time and steadily starts degrading by the Mg/Pd system. This result directly correlates with the slowdown of the parent congener 2, 2’, 4, 4’- tetrabromodiphenyl ether (BDE-047) around 45 minutes, indicating that lower substituted congeners may already be formed on the active sites of the metal and do not leave until diphenyl ether is formed.

![Byproduct Formation](image)

**Figure 27:** Plot of tribrominated diphenyl ether byproduct formation.

An additional experiment was set up with altered parameters to focus on the kinetics. The 0.08% Mg/Pd concentration was lowered from 0.10g to 0.05g and the first 60 minutes where the focus of the reaction. The first order, second order and zero order kinetic plots are shown in Figure 28.
Figure 28: Degradation kinetic comparison of BDE-47.
The reaction follows 1st order degradation with an $R^2$ value of 0.9485 however it is followed by very close 2nd order degradation with an $R^2$ value of 0.9483. With such close results further studies are needed to confirm these findings.

Unlike previous studies published that indicate impartial debromination resulting in more hazardous byproducts, the use of Mg/Pd proved to undergo complete debromination to diphenyl ether within 30 minutes as shown in Figure 29. This is promising as previous remediation techniques like microbial, photolytic, and zero-valent Fe were not able to achieve complete debromination.

![Chromatogram and MS fragmentation for Diphenyl Ether.](image)

**Figure 29:** Chromatogram and MS fragmentation for Diphenyl Ether.

One final parameter examined was the production of dibenzofuran. Dibenzofuran is a volatile hazardous air pollutant that can be found as a byproduct of smoking. It is believed that this toxin is not necessarily a byproduct of BDE-47 but rather a product of thermal degradation on GC-MS. Due to the nature of the instrumentation, it is crucial to inject samples at high temperatures, however with such sensitive compounds exceeding
threshold temperatures, a breakdown of the byproducts into dibenzofuran is inevitable. A significant amount of dibenzofuran was also detected as shown in Figure 30.

![Chromatogram and MS fragmentation of Dibenzofuran](image)

**Figure 30:** Chromatogram and MS fragmentation of Dibenzofuran

Extensive modification of the instruments methods minimized the formation of dibenzofuran but did not eliminate it, further analysis using cold-on-column injection will be needed to truly determine the source of dibenzofuran.

An additional extended study was set up to observe how dibenzofuran and diphenyl ether faiured up against the Mg/Pd bimetallic system. The five hour study was extended to 24 hours. The concentration of both compounds reached maximum concentrations at 5 hours and was designated as initial to obtain percent degradation. Table 11 and Figure 31 show the ratio change resulted in 75.63% degradation for dibenzofuran and 55.60% degradation for diphenyl ether. This illustrated that Mg/Pd bimetallic systems are capable of degrading dibenzofuran effectively.
Table 13: Percent degradation of Dibenzofuran and Diphenyl Ether

<table>
<thead>
<tr>
<th></th>
<th>C/C0</th>
<th>C/C0</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 hours</td>
<td>24 hours</td>
<td></td>
</tr>
<tr>
<td>Dibenzofuran</td>
<td>1</td>
<td>0.24</td>
<td>75.6</td>
</tr>
<tr>
<td>Diphenyl Ether</td>
<td>1</td>
<td>0.44</td>
<td>55.6</td>
</tr>
</tbody>
</table>

Figure 31: Chromatogram of diphenyl ether and dibenzofuran degradation.

Conclusion

Treatment of one of the most persistent BDE congeners, BDE-47, by Mg/Pd bimetallic systems proved to be an effective way of remediation. In a five hour study 99% of BDE-47 was debrominated, with 80% of remediation taking place within the first 30 minutes. The slowdown is attributed to competition for active sites on magnesium by the parent toxin (BDE-47) as well as newly formed byproducts. The remediation reaction followed a step-wise debromination path with pseudo 1st order kinetics. Unlike other studies utilizing zero-valent metals, Mg/Pd also proved to be capable of obtaining complete...
debromination to diphenyl ether. Dibenzofuran formation was detected however it is believed to be produced by thermal degradation on the GC-MS. Extended studies indicated that Mg/Pd bimetallic systems can remediate dibenzofuran if it were to be present.

In improving Mg/Pd remediation technologies, future research will focus on several factors that will help optimize conditions for enhanced liquid membrane remediation and possible future applications. The established congener library on the GC-MS will be utilized to determine major and minor byproducts. In addition, studies on BDE-1, BDE-2, and BDE-3 will be conducted to determine stereo selectivity of ortho, meta, and para positioned bromines. Finally, select congeners in different solvent systems will be explored to determine the exact path and mode of debromination.
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