

**The Occurrence and Environmental Fate of
Polybrominated Diphenyl Ethers and Glyphosate in the Atmosphere**

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Dedication

This dissertation is dedicated first to my parents, Yu Hsien-Li and Chang Cheng-Chi, whose good health allowed me to study in the U.S. without any concern. In addition, I sincerely appreciated my wife, Kuo Hsin-Ju, who had to overcome many difficulties here and did a great job on raising our little boy Shawn.

Finally, I would like to dedicate this dissertation to all of the friends and teachers who have helped and advised me during my Ph.D study.

Abstract

The net air-water exchange flux of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in the Great Lakes and the atmospheric presence of glyphosate and aminomethylphosphonic acid (AMPA) in the farm fields are reported here for the first time. Paired air and surface water samples were collected during May and July from Lake Michigan in 2005 and Lake Superior in 2006. Average atmospheric PCB and PAH concentrations and deposition were higher over Lake Michigan than Lake Superior and higher at nearshore urban than open-lake sites. Additionally, annual mass budgets of PCBs for the Great Lakes are presented by estimating atmospheric deposition, wastewater treatment plant discharge, burial of lake sediments, and lake water outflow. The results indicated that annual mass budget of \sum_6 PCB (BDE-47, 66, 100, 99, 154, and 153) for Lake Michigan was a net increase with 270 kg yr^{-1} . In contrast, the budget for Lake Superior approached equilibrium with a net increase of 14 kg yr^{-1} . Wet deposition was the major contributor (71-75%) of the total \sum_6 PCB inputs to both lakes. Glyphosate and AMPA were detected only in the particle phase of air samples in Mississippi and Iowa in 2007-2008. The frequency of glyphosate detection ranged from 61 to 100% (in air) and 63 to 92% (in rain). The highest concentrations of glyphosate and AMPA in both air and rain were found during the periods of intense glyphosate applications. Glyphosate and AMPA were removed efficiently from the air by particle scavenging in rainfall events. Based on annual mass budgets of glyphosate in Mississippi and Iowa study sites, less than 0.1% of the applied glyphosate moved into the atmosphere due to application spray drift (0.01%-0.05%), and wind erosion (<0.01%-0.02%).

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Chapter 1

Introduction

1.1 Background

PBDEs (polybrominated diphenyl ethers), a subset of the brominated flame retardants (BFRs), are used in thermoplastics, polyurethane foams, and textiles to reduce accidental ignition or fire (Alaee *et al.*, 2003). Like Polychlorinated biphenyls (PCBs), PBDEs also have 209 possible brominated congeners, but around 40 congeners are commonly found in the environment (Hites, 2004). The concern about environmental PBDEs is rising because of its accumulation, persistence, and risk for ecosystem and human health (Porterfield, 2000; Birnbaum and Staskal, 2004; Lema *et al.*, 2008; Herbstman *et al.*, 2010). Most PBDE studies focused on house dust, dietary ingestion, lake sediments, waste water treatment plant sludge, wildlife tissue, and human bodies (Li *et al.*, 2006; Song *et al.*, 2006; Batterman *et al.*, 2007; Wu *et al.*, 2007; Sjodin *et al.*, 2008; Stapleton *et al.*, 2008; Schreiber *et al.*, 2010), but the study of PBDEs in natural water bodies is relatively limited (Cetin and Odabasi, 2007; Oram *et al.*, 2008; Guan *et al.*, 2009).

Air-water exchange flow is an important pathway for semi-volatile organic compounds in natural water bodies (Baker and Eisenreich, 1990; Zhang *et al.*, 1999). However, no research has been conducted on net PBDE air-water exchange flux using paired air and surface water samples over the Great Lakes. For this reason PBDE mass budgets for the Great Lakes have not been established completely.

Unlike the semi-volatile PBDEs, glyphosate (N-phosphonomethyl-glycine) is a less volatile and very water soluble organic compound (Battaglin *et al.*, 2005). It is the

most widely used pesticide in the U.S. (Kiely *et al.*, 2004). Some studies indicated a link between glyphosate exposure and the risk of non-Hodgkin's lymphoma or human placental cell damage (De Roos *et al.*, 2005; Richard *et al.*, 2005). By far, most environmental research on glyphosate has focused on soil, crops, and water bodies (Vereecken, 2005; Peruzzo *et al.*, 2008; Green, 2009), but no one has looked for glyphosate and its degradate (aminomethylphosphonic acid, AMPA) in the atmosphere.

My long term goal is to minimize the human exposure from environmental PBDEs and glyphosate. The specific objective of my research, which is the next step toward this goal, is to construct the PBDE and glyphosate mass budgets in the environment. The first hypothesis is that the air-water exchange flux for PBDEs is the dominant source to Great Lakes water. The second hypothesis is that glyphosate is present in the atmosphere solely as the particle phase and comes from farmers' application during the growing season.

1.2 Significance

The goal of my PBDE research is to determine the net PBDE air-water exchange fluxes over the Great lakes by taking paired air and water samples. These fluxes will then be used to construct annual PBDE mass budgets which will in turn predict changes in PBDE levels in lake water. Furthermore, this thesis can provide insights into how to reduce PBDE loadings through either environmental management or engineering strategies by identifying the major sources and sinks. My glyphosate research is the first report of glyphosate and its major degradate (AMPA) levels in the atmosphere. Additionally, glyphosate mass budgets help elucidate the fate of applied glyphosate in the farm field.

From the public health point of view, people are concerned about environmental PBDEs because of their toxicity and accumulation in living organisms. For glyphosate, it's continuously increasing usage and potential toxicity of cooperative surfactants are the major concerns. Results from this study can lead to a better understanding of the environmental fate of PBDEs and glyphosate. Allowing the development of feasible methods to reduce the environmental loading of PBDEs and glyphosate which will help prevent environmental exposure from these chemicals. More specifically, this study provides a clear description of the distribution and direction of these two very different anthropogenic organic compounds in the environment. Next, people can determine what strategies are best to eliminate these pollutants' loading based on mass budgets in the environment, reducing human exposure. My PBDE study can be related to fish consumption advisories in the Great Lakes. Firstly, PBDE levels in the Great Lake water column were investigated. Based on a mass budget model, major PBDE inputs to the lakes were found in order to eliminate their inputs. By reducing the major sources of PBDEs the Great Lakes, water concentrations and subsequently PBDE concentrations in lake fish are expected to decline. Thus reducing the exposure pathway of PBDEs to people that eat Great Lakes fish.

Little research on the human exposure to environmental glyphosate has been carried out. This study gave the first data for researchers who are interested in environmental exposure or risk management on atmospheric glyphosate and AMPA. Although glyphosate is less toxic compared to PBDEs, a continuously increasing usage in farms may change a balance for the ecosystem. For instance, some researchers have found the emergence of glyphosate resistant weeds (Powles *et al.*, 1998) and

eutrophication (Vera *et al.*, 2010) in water bodies nearby strong glyphosate application. In addition, since the surfactants used in glyphosate herbicide have shown more toxic than glyphosate itself (Benachour and Se´ralini, 2009), this should also be taken into account in glyphosate research. Although only two chemicals were discussed in this study, the findings can represent and predict those behaviors of other atmospheric pollutants which have similar physical-chemical properties to PBDEs and glyphosate.

1.3 Specific Aims

- I. Determination of PBDE air-water exchange flux in Lake Michigan and Lake Superior
- II. Construction of PBDE mass budgets in Lake Michigan and Lake Superior
- III. Investigation of occurrence and fate of glyphosate and AMPA in the atmosphere

1.4 Summary

Paired air and surface water samples were collected at 11 sites over the upper Great Lakes (Lake Michigan in 2005 and Lake Superior in 2006) aboard the research vessel *Lake Guardian*. Air (gas and particle phase) and water (dissolved and particle phase) concentrations of six BDE congeners (BDE-47, 66, 100, 99, 154, and 153) were determinate and quantified by gas chromatography electron capture negative ionization mass spectrometry (GC-ECNI/MS). Additionally, gas phase concentrations of PBDEs at three representative sites (Sleeping Bear Dunes, Chicago, and Eagle Harbor) next to the shores of the upper Great lakes were taken from the IADN (Integrated Atmospheric Deposition Network) data in 2005-2006. Finally, the net air-water exchange fluxes and mass budgets of PBDEs were determined for the upper Great Lakes.

Atmospheric levels of glyphosate and its major degradation product (AMPA) in

air and rain were measured in three agricultural areas: the states of Mississippi, Iowa, and Indiana in 2007-2008 or 2004. This is the first report to provide insight into the sources and behavior of glyphosate and AMPA in the atmosphere.

In Chapter 2, the PBDE levels in surface water and air in the upper Great Lakes were reported. The net fluxes of PBDE air-water exchange in the upper Great Lakes were determined by a modification of the two-film model. Wet and dry depositions of PBDEs were also calculated through air PBDE concentrations, total washout ratios, annual precipitation rates, and dry particle deposition velocity. The differences of PBDE concentrations and atmospheric PBDE deposition were compared between Lake Michigan and Lake Superior, also nearshore and open-lake sites.

In Chapter 3, annual mass budgets of PBDEs in the upper Great Lakes were estimated by calculating the fluxes of atmospheric deposition, wastewater treatment plant (WWTP) discharge loadings, burial of lake sediments, and lake water outflow. In addition, seasonal patterns of the net PBDE air-water exchange fluxes, prediction of PBDE levels in lake water, and feasible approaches to reduce PBDE loadings in the lakes were discussed, respectively.

In Chapter 4, the concentrations and detection frequencies of glyphosate and AMPA in air and rain samples were reported for the study areas in Mississippi and Iowa in 2007-2008. The relationship between atmospheric glyphosate concentrations and glyphosate application rates was discussed. In addition, the temporal trend of AMPA fraction of the total glyphosate in air was examined.

In Chapter 5, the contribution of glyphosate spray drift and wind erosion of soil to air glyphosate was calculated. The removal efficiencies of glyphosate and AMPA from air

by rainfall scavenging were estimated. Finally, mass budgets of glyphosate in the farm fields were constructed. Pathways in the glyphosate mass budgets included application spray drift, wind erosion of soil, rainfall removal effect, degradation in soil, and transportation to streams and ground water.

Table 1-1 has summarized the physical-chemical characteristics and field sample results between PBDEs (BDE-47, 66, 100, 99, 154, and 153) in the Great Lakes and glyphosate in the farm fields.

Table 1-1. Summarized physical-chemical characteristics^{*}, field findings between PBDEs in the Great lakes and glyphosate in the farm fields

| | PBDEs | Glyphosate | Ratio (Gly/PBDE) |
|--|--|---|--|
| IUPAC name | Polybrominated diphenyl ethers | N-(phosphonomethyl) glycine | |
| Molecular weight | 486 to 644 | 169 (g mole ⁻¹) | 0.26 to 0.35 |
| Vapor pressure | 1.3×10 ⁻⁴ to 2.1×10 ⁻⁶ | 5.7×10 ⁻⁸ (Pa) | < 0.027 |
| Henry's law const. | 0.3-1.8 (Pa m ³ mole ⁻¹) | not available | |
| Water solubility | 1.5×10 ⁻⁵ to 8.7×10 ⁻⁷ | 10 to 15 (g L ⁻¹) | 6.7×10 ⁵ to 1.7×10 ⁷ |
| Log K _{OW} | 6.55 to 7.62 | -4.6 to -1.6 | 8 to 12 (difference) |
| Episode | banned in 2004 [#] | currently use | |
| Conc. in air (total) | 8.6 to 221 (pg m ⁻³) | <0.01 to 9.1 (ng m ⁻³) | 0.05 to 1,000 |
| Conc. in water | 1.5 to 122 (pg L ⁻¹) | not available | (Total conc.) |
| Conc. in rain | 0.41 to 41 (ng L ⁻¹) | <0.1 to 2.5 (µg L ⁻¹) | 2 to 240 |
| Particle ratio(ϕ) in the air | 5% to 11% | 100% | 10 to 20 |
| Total washout ratio | 1.4×10 ⁴ to 4.8×10 ⁵ | 9.3×10 ⁵ to 9.9×10 ⁵ | 2 to 70 |
| Source contribution to lake water (PBDEs) and the air (glyphosate) | 1. Air deposition (84% to 87%) 2. WWTPs (13% to 16%) | 1. Application spray drift (58% to 81%) 2. Wind erosion (19% to 42%) | |
| Contribution of the total mass outputs | 1. Net volatilization (0 to 50%) 2. Burial sediment (40% to 90%) 3. Lake water outflow (10%) | 1. Degradation in soil (> 96%) 2. Rainfall (< 1%) 3. Moving to streams (< 1%) | |

^{*} references of physical–chemical characteristics of PBDEs and glyphosate can be found in the following chapters; [#] only for penta and octa-BDE commercial formulation.

Chapter 2

Atmospheric Deposition of Polybrominated Diphenyl Ethers (PBDEs) to the Upper Great Lakes

Paired air and surface water samples were collected at 11 sites over the upper Great Lakes (Lake Michigan and Lake Superior) in 2005 and 2006. Total air concentrations (gas + particle phase) of \sum_6 PBDE were 72 ± 19 and 29 ± 11 pg m^{-3} over Lake Michigan and Lake Superior, respectively. Total surface water concentrations (dissolved + particle phase) of \sum_6 PBDE were 53 ± 7.3 pg L^{-1} in Lake Michigan and 41 ± 9.0 pg L^{-1} in Lake Superior. Estimated atmospheric deposition of \sum_6 PBDE including net air-water exchange, dry and wet deposition, ranged from 9.8 to 93 $\text{ng m}^{-2} \text{day}^{-1}$ and exhibited an average with 21 ± 4.0 $\text{ng m}^{-2} \text{day}^{-1}$. On average, net air-water exchange of PBDEs accounted for 74% of total atmospheric PBDE deposition. Average atmospheric PBDE concentrations and deposition were higher over Lake Michigan than Lake Superior and higher at nearshore urban sites than open-lake sites. This comparison suggests that atmospheric PBDE levels and deposition were associated with local PBDE emission from urban areas. Net volatilization of BDE-47 from Lake Superior and near equilibrium in Lake Michigan suggests that less brominated BDEs in the atmosphere have continuously declined since voluntary phase out of the penta-BDE technical formulation.

2.1 Introduction

PBDEs (polybrominated diphenyl ethers), a subset of the brominated flame retardants (BFRs), are composed of two aromatic rings linked by an ether bond and may contain one to ten bromine atoms. PBDEs were used as an additive in thermoplastics,

polyurethane foams, and textiles to reduce accidental ignition. Penta- (tetra-hexa bromines), octa- (hexa- octa bromines), and deca- (BDE-209) BDEs were three major technical formulations and have been used in the world market since the 1980s' (Alaee *et al.*, 2003; La Guardia *et al.*, 2006). Concern about PBDEs is rising because they are persistent and have been found to be increasing in the environment (Hale *et al.*, 2003).

Inhalation of house dust and dietary intake containing PBDE compounds are major potential human exposure pathways (Jones-Otazo *et al.*, 2005; Stapleton *et al.*, 2008; Frederiksen *et al.*, 2009). PBDE concentrations in human blood, milk, and tissue have exponentially increased with a doubling time of around 5 years since 1970 (Hites, 2004). PBDEs are structurally similar to human thyroid hormone allowing them to mimic their behavior in human bodies. For this reason PBDEs can be harmful by interfering with normal thyroid hormone function, which is important for early development stage of the human brain (Porterfield, 2000; Birnbaum and Staskal, 2004; Lema *et al.*, 2008). As a result, penta- and octa-BDE formulations, which are considered more bioavailable (Wu *et al.*, 2007; Sjodin *et al.*, 2008), were phased out in the European Union in August 2004. In the United States, the primary BFR manufacturer voluntarily stopped production of the penta- and octa-BDE formulations at the end of 2004 and regulations banning products containing deca-BDE have been implemented in the states of Maine and Washington in 2008 (Vonderheide *et al.*, 2008; Ward *et al.*, 2008).

Environmental PBDEs have been studied in urban areas (indoor or outdoor environment), rural and remote areas (lakes, atmosphere, and wildlife) (Hites, 2004; Anderson and MacRae, 2006; Su *et al.*, 2007; Oram *et al.*, 2008). Similar to other reported semi-volatile organic compounds (SVOCs), atmospheric deposition of PBDEs

can be a dominant route to a lake water in rural or remote areas because of their comparable physical-chemical characteristics (Shen *et al.*, 2006). Although the air-water exchange fluxes of PBDEs have been investigated at seashore (Cetin and Odabasi, 2007) and rivershore (Guan *et al.*, 2009) both of which were highly populated and industrialized, the details of air-water exchange flux of PBDEs over remote lake water have not been explored through field measurements. For this reason, a PBDE mass budget for the upper Great Lakes' environment cannot be understood completely until reliable air-water exchange fluxes of PBDEs are acquired.

A total of 100 samples of air and surface water were collected aboard the R/V *Lake Guardian* during May and July cruises over Lake Michigan in 2005 and Lake Superior in 2006. These samples are unique because they were collected from not only nearshore but open-lake sites, the first paired air and water samples, and comprehensive sampling sizes and volume. Furthermore, different categories of hydrophobic organic compounds including legacy and emergence chemicals were quantified through the techniques of solvent extraction, volume reduction, gas chromatography, and mass spectrometry. Previous studies have been unable to report reliable PBDE concentrations in water due to contamination issues in sampling media and laboratory contamination (these chemicals are present in many consumer products and the possibility for lab contamination is high). Due to our rigorous program of quality assurance and control we were able to produce quality dissolved phase PBDE concentrations. In this PBDE study, masses of six BDE congeners (BDE-47, 66, 100, 99, 154, and 153) which are most abundant in penta-BDE commercial formulation were reported. The PBDE data in lake water samples are particularly valuable because they were collected from both nearshore

and open-lake sites of the Great Lakes while minimizing the influence of analytical contamination. Consequently, these PBDE concentrations in lake water can be used to estimate the current PBDE levels in the Great Lakes, predict their levels in the future, and illustrate the mechanism of PBDE bioaccumulation between lake water and lake biota.

In this study, the net air-water exchange fluxes of individual BDE congeners over the lakes were estimated using a modification of the Whitman two-film model. Atmospheric dry and wet deposition were estimated according to the gas and particle-phase concentrations in air samples, assumed dry particle deposition velocity, and estimated total washout ratios. In addition, spatial variability in the atmospheric deposition of PBDEs was examined. This paper presents the first field measured air-water exchange fluxes of PBDEs over the upper Great Lakes.

2.2 Methods

Field Sampling. To investigate atmospheric deposition of PBDEs over the upper Great Lakes, paired air and surface water samples were collected during May and July cruises in Lake Michigan in 2005 and in Lake Superior in 2006. This study was executed as part of the U.S. EPA's Great Lakes Aquatic Contaminant Survey (GLACS) water monitoring program. A total of 50 surface water and 50 air samples were collected aboard the R/V *Lake Guardian* and sampling locations (numbers labeled) included both nearshore and open-lake sites (Figure 2-1). Surface water temperature and true wind speed were recorded concurrently onboard. During the Lake Michigan cruise in 2005, average surface water temperatures and true wind speed were 16.8 °C and 5.0 m sec⁻¹, respectively. During the Lake Superior cruise in 2006, surface water temperatures and true wind speed were 11.0 °C and 5.8 m sec⁻¹.

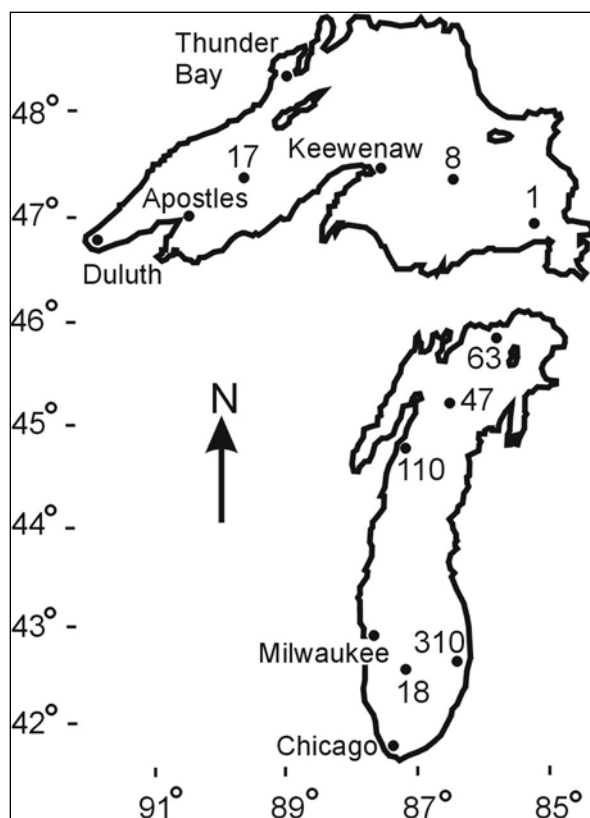


Figure 2-1. Sampling locations in Lake Michigan in 2005 and Lake Superior in 2006

Air was pulled for 12 consecutive hours through glass fiber filters (GF/Fs, Whatman, Florham Park, NJ) followed by a stainless steel cartridge containing cleaned XAD-2 resin (Supelco, Bellefonte, PA) by a high volume air sampler. The air sampler was situated on a boom that went out over the lake water away from the bow of the ship. The ship was always facing into the wind to diminish the sampling interference from the ship itself. The collected air volume (approximately 400 m³) was recorded by a Roots meter (Dresser, Huston, TX) during sampling. Approximately 800 L of surface water was collected from a depth of ~5 m by a peristaltic pump. Particle-phase PBDEs in water were collected by five parallel GF/Fs in a pentaplate apparatus. Subsequently, filtered water was pumped through a glass column (5 cm × 30 cm) filled with pre-cleaned

XAD-2 resin. While the filtered water was passing through the glass column, the flow rate was maintained around $1,000 \text{ mL min}^{-1}$ and was also monitored with a flow meter (Seametrics EM101, Kent, WA). The sampled GF/Fs were covered with aluminum foil and XAD-2 resin was transferred to combusted amber jars after the sampling was finished. All sampled XAD-2 resin and GF/Fs were placed into the freezer until laboratory analysis.

Sample Extraction, Cleanup, and Analysis. Air samples were Soxhlet-extracted with dichloromethane (DCM) for 16-24 hrs. Water samples were first Soxhlet-extracted using methanol for 16-24 hrs followed by 16-24 hrs using DCM. The methanol extracts were back-extracted into hexane to remove water and combined with their respective DCM extracts. All solvents were switched to hexane by rotary evaporation. Possible chromatographic interferences were removed by passing the extract through a combusted glass column (1 cm \times 50 cm) packed in order from bottom to top with 1 g of ashed sodium sulfate, 6 g of 2% water deactivated neutral alumina, 1 g of ashed sodium sulfate, 4.5 g slurry of 0% water deactivated silica, and 3 g of ashed sodium sulfate. The first fraction of the extract was eluted by $3 \times 33 \text{ mL}$ of hexane for polychlorinated biphenyl congener analysis. The second fraction was eluted by $3 \times 33 \text{ mL}$ of 40% DCM for PBDE congener analysis. Six PBDE congeners: 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), 2,3',4,4'-tetrabromodiphenyl ether (BDE-66), 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), 2,2',4,4',6-pentabromodiphenyl ether (BDE-100); 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153); and 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154) were quantified by monitoring m/z 79 and 81 through gas chromatography electron capture negative ionization mass

spectrometry (GC-ECNI/MS). The GC-ECNI was equipped with a 60 m DB-5 capillary column, helium carrier gas, methane ionization gas, and operated in the selective ion monitoring mode looking for the isotopes of bromine (79 and 81). The oven temperature was programmed from 110 °C for 1.9 min, 15 °C min⁻¹ to 210 °C, 2 °C min⁻¹ to 270 °C, 5 °C min⁻¹ to 305 °C, and held at 305 °C for 20 min. PBDE mass was determined by the Relative Response Factor (RRF) method using internal standard PCB-204 (m/z 428 and 430). More details of sample preparation, extraction, clean up and quantification are given elsewhere (Streets *et al.*, 2006).

Quality Assurance/Quality Control. To determine possible PBDE contamination from sample preparation through the laboratory analysis, both air and surface water field blanks including GF/Fs and XAD-2 resin were collected during each cruise. The masses (ng) of PBDEs in field blank GF/F matrix (average ± SE) were 0.55 ± 0.22 (BDE-47), 0.02 ± 0.02 (BDE-66), 0.07 ± 0.05 (BDE-100), 0.74 ± 0.33 (BDE-99), 0.03 ± 0.03 (BDE-154), and 0.04 ± 0.04 (BDE-153). The masses (ng) of PBDEs in field blank XAD-2 resin were 0.51 ± 0.24 (BDE-47), 0.05 ± 0.04 (BDE-66), 0.14 ± 0.05 (BDE-100), 0.57 ± 0.21 (BDE-99), < 0.001 (BDE-154), and < 0.001 (BDE-153). Assuming an average air sample of 400 m³, these blank masses would translate into concentrations of < 0.1 pg m⁻³ (BDE-66, 154, and 153) to 1.1 pg m⁻³ (BDE-99). Assuming an average water sample of 800 L, these blank masses would translate into concentrations of 0.1 pg L⁻¹ (BDE-154 and -153) to 3.1 pg L⁻¹ (BDE-99). Detailed PBDE masses found in field blanks are shown in supporting information.

One laboratory procedural blank was run with every four or five field samples to examine possible contamination during sample processing in the laboratory. The masses

of \sum_6 PBDE in all laboratory blanks (average \pm SE) were 1.2 ± 0.40 ng, which represents 2-3% of the measured gas and dissolved phases, respectively. PBDE surrogates (BDE-71 and 118) were also added in the round bottom flasks before DCM extraction in a Soxhlet apparatus. The PBDE surrogate recoveries were $115 \pm 3.6\%$ for BDE-71 and $122 \pm 4.7\%$ for BDE-118 in all air sample extraction. In all surface water sample extraction, the PBDE surrogate recoveries were $105 \pm 2.6\%$ for BDE-71 and $124 \pm 4.0\%$ for BDE-118. In every field sample and blanks, BDE-47 and 66 masses were corrected by BDE-71 recoveries; BDE-100, 99, 154, and 153 were corrected for BDE-118 recoveries. Since BDE-118 recoveries in four sequences of air samples were systematically high ($> 200\%$), those PBDE congener masses were only corrected by BDE-71 recoveries. The reported PBDE concentrations in this study were corrected by surrogate recoveries, procedural blanks, and field blanks.

Calculations of atmospheric PBDE deposition. Net flux ($\text{ng m}^{-2} \text{day}^{-1}$) of PBDE air-water exchange was determined using a modification of the two-film model (Whitman, 1923). This model (1) was first applied to evaluate the fluxes of gases across the air-sea interface (Liss and Slater, 1974). Afterward the fluxes of SVOCs between the atmosphere and surface water were also estimated by this model (Mackay and Leinonen, 1975; Baker and Eisenreich, 1990):

$$\text{Net air-water exchange flux} = K_{OL} (C_g - C_d H/RT) \quad (2-1)$$

Here, K_{OL} (m day^{-1}) is the overall mass transfer coefficient of PBDEs, C_g (ng m^{-3}) is gas the phase concentration of PBDEs in air, C_d (ng m^{-3}) is the dissolved phase concentration of PBDE in surface water, H ($\text{Pa m}^3 \text{mole}^{-1}$) is the Henry's law constant for each congener, R is the ideal gas constant ($8.314 \text{ Pa m}^3 \text{mole}^{-1} \text{K}^{-1}$), and T (K) is the surface water

temperature . A positive flux means net absorption from air to water; in contrast, a negative value means there is net volatilization of PBDEs from water to air. The overall mass transfer coefficient was estimated by the following equations, which used surface water temperature, true wind speeds, temperature corrected PBDE Henry's Law constants (Tittlemier *et al.*, 2002; Cetin and Odabasi, 2005), and mass transfer coefficients of PBDEs in air (k_a) (Chapra *et al.*, 2009) and in water (k_w) (Mackay and Yeun, 1983; Schwarzenbach *et al.*, 2003).

$$1/K_{OL} = (1/k_a) + (H/RTk_w) \quad (2-2)$$

$$k_a \text{ (cm s}^{-1}\text{)} = (0.2u_{10} + 0.3) / (MW_{\text{compound}}/MW_{\text{H}_2\text{O}})^{0.5 \times 0.67} \quad (2-3)$$

$$k_w \text{ (cm s}^{-1}\text{)} = 1.75 \times 10^{-4} \times u_{10} \times (6.1 + 0.63u_{10})^{0.5} / (MW_{\text{compound}}/MW_{\text{O}_2})^{0.5 \times 0.5} \quad (2-4)$$

Where u_{10} (m sec⁻¹) is the wind speed 10 m above the water surface. MW_{compound} , $MW_{\text{H}_2\text{O}}$, and MW_{O_2} are molecular weights of the PBDEs, water, and oxygen, respectively. Those parameters used to calculate the net flux of PBDE air-water exchange are given in Table 2-1.

Table 2-1. Parameters used to calculate air-water exchange fluxes of PBDEs in Lake Michigan and Lake Superior

| Para. | unit | BDE47 | BDE66 | BDE100 | BDE99 | BDE154 | BDE153 |
|---|---------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Lake Michigan in May in 2005 (N^a=5) | | | | | | | |
| H/RT ^b | | 1.3×10^{-4} | 4.2×10^{-5} | 3.3×10^{-5} | 5.7×10^{-5} | 1.8×10^{-5} | 3.1×10^{-5} |
| k _a ^c | cm s ⁻¹ | 3.7×10^{-1} | 3.7×10^{-1} | 3.5×10^{-1} | 3.5×10^{-1} | 3.4×10^{-1} | 3.4×10^{-1} |
| k _w ^d | cm s ⁻¹ | 1.2×10^{-3} | 1.2×10^{-3} | 1.2×10^{-3} | 1.2×10^{-3} | 1.1×10^{-3} | 1.1×10^{-3} |
| K _{ol} ^e | m day ⁻¹ | 308 ± 43 | 317 ± 43 | 301 ± 41 | 299 ± 41 | 289 ± 39 | 287 ± 39 |
| Lake Michigan in July in 2005 (N=6) | | | | | | | |
| H/RT | | 3.5×10^{-4} | 1.2×10^{-4} | 9.1×10^{-5} | 2.0×10^{-4} | 4.6×10^{-5} | 9.0×10^{-5} |
| k _a | cm s ⁻¹ | 4.3×10^{-1} | 4.3×10^{-1} | 4.1×10^{-1} | 4.1×10^{-1} | 3.9×10^{-1} | 3.9×10^{-1} |
| k _w | cm s ⁻¹ | 1.5×10^{-3} | 1.5×10^{-3} | 1.5×10^{-3} | 1.5×10^{-3} | 1.4×10^{-3} | 1.4×10^{-3} |
| K _{ol} | m day ⁻¹ | 339 ± 43 | 361 ± 44 | 345 ± 42 | 334 ± 41 | 333 ± 40 | 329 ± 40 |
| Lake Superior in May in 2006 (N=5) | | | | | | | |
| H/RT | | 7.3×10^{-5} | 2.8×10^{-5} | 2.1×10^{-5} | 3.4×10^{-5} | 1.2×10^{-5} | 2.0×10^{-5} |
| k _a | cm s ⁻¹ | 4.9×10^{-1} | 4.9×10^{-1} | 4.6×10^{-1} | 4.6×10^{-1} | 4.4×10^{-1} | 4.4×10^{-1} |
| k _w | cm s ⁻¹ | 1.8×10^{-3} | 1.8×10^{-3} | 1.8×10^{-3} | 1.8×10^{-3} | 1.7×10^{-3} | 1.7×10^{-3} |
| K _{ol} | m day ⁻¹ | 415 ± 61 | 421 ± 62 | 399 ± 59 | 398 ± 59 | 382 ± 56 | 381 ± 56 |
| Lake Superior in July in 2006 (N=5) | | | | | | | |
| H/RT | | 2.4×10^{-4} | 8.0×10^{-5} | 6.2×10^{-5} | 1.3×10^{-4} | 3.2×10^{-5} | 6.0×10^{-5} |
| k _a | cm s ⁻¹ | 4.2×10^{-1} | 4.2×10^{-1} | 4.0×10^{-1} | 4.0×10^{-1} | 3.8×10^{-1} | 3.8×10^{-1} |
| k _w | cm s ⁻¹ | 1.4×10^{-3} | 1.4×10^{-3} | 1.4×10^{-3} | 1.4×10^{-3} | 1.3×10^{-3} | 1.3×10^{-3} |
| K _{ol} | m day ⁻¹ | 338 ± 45 | 352 ± 44 | 336 ± 41 | 330 ± 42 | 323 ± 39 | 321 ± 40 |

^a Number of analyzed samples ^b Average dimensionless Henry Law constants (BDE-47, 100, 99, 154, 153) were calculated according to the research of Cetin and Odabasi. Henry Law constant of BDE-66 was estimated as one third of BDE-47's according to the study of Tittlemier *et al.*, ^c Average mass transfer coefficients of air films. ^d Average mass transfer coefficients of water films ^e Overall mass transfer coefficients (average ± SE).

Dry deposition of PBDEs was calculated using air concentrations in the particle phase ($C_{P,A}$) multiplied by dry particle deposition velocity (V_d) (Odabasi *et al.*, 1999; Raff and Hites, 2007). The V_d is a function of particle size and density, and ambient meteorological conditions (Zhang *et al.*, 2001). At an industrialized area in southern Sweden, the measured V_d for particle-bound PBDEs ranged from 0.4 cm sec⁻¹ (BDE-66) to 48.9 cm sec⁻¹ (BDE-209), and with an average of 2.7 cm sec⁻¹ for (BDE-47, 66, 100, 99, 154, and 153) (Ter Schure *et al.*, 2004b). Another reported V_d of PBDEs in Turkey (urban area), were 2.9 cm sec⁻¹ (BDE-209) to 6.4 cm sec⁻¹ (BDE-100) (Cetin and Odabasi, 2007). In this study, the V_d of particle-bound PBDEs is taken as 0.2 cm sec⁻¹ according to the report of atmospheric deposition of toxic chemicals to the Great Lakes (Hoff *et al.*, 1996). This choice of a much smaller V_d is justified given the remote areas of this study as opposed to the urban studies in Sweden and Turkey where larger particles (with higher deposition velocities) are expected to be more important. The dry deposition (ng m⁻² day⁻¹) of PBDEs in the upper Great Lakes water is calculated as:

$$\text{Dry deposition} = C_{P,A} \times 0.2 \text{ (cm sec}^{-1}\text{)} \times 10^{-2} \text{ (m cm}^{-1}\text{)} \times 86,400 \text{ (sec day}^{-1}\text{)} \quad (2-5)$$

Wet deposition is calculated through PBDE concentrations (Anderson and MacRae) in precipitation times the precipitation rate. Since precipitation samples were not collected in this study, the C_R was estimated through the total washout ratios (W_T) times total PBDE concentrations in air (C_A) as follows:

$$C_R = W_T C_A \quad (2-6)$$

$$W_T = W_G (1 - \phi) + W_P \phi \quad (2-7)$$

In equation 2-7, the total washout ratio (W_T) includes the gas phase washout ratio (W_G), the particle phase washout ratio (W_P), and the fraction of atmospheric

concentration associated with particle (ϕ) (Ligocki *et al.*, 1985). The total washout ratio values vary because atmospheric compounds have different physical-chemical properties and particle/gas distribution (Bidleman, 1988). In our study, the gas phase washout ratio was determined by RT/H (inverse of dimensionless Henry's law constant). The W_P values used here were taken as the total washout ratios of PBDEs at an industrialized area in southern Sweden (ter Schure *et al.*, 2004a). Since the PBDEs in their rain samples there were 99-100% bound to particle phase. The calculated total and gas washout are seen in Table 2-2. To simplify the calculation, the total washout ratio difference of PBDEs between rain and snow events was ignored. Then wet deposition of PBDE ($\text{ng m}^{-2} \text{day}^{-1}$) was calculated by total washout ratios (W_T) of individual PBDE congener, total air PBDE concentrations (C_A , pg m^{-3}), and annual precipitation (R , mm) as follows:

$$\text{Wet deposition} = W_T \times C_A \times R \times 10^{-6} / 365 \text{ (day yr}^{-1}\text{)} \quad (2-8)$$

Table 2-2. Calculated particle ratios in air (ϕ), estimated average gas washout ratios (W_G), and total washout ratios (W_T) of six PBDE congeners in Lake Michigan (LM) and Lake Superior (LS)

| | LM, May 2005 (N=5) | | | LM, July 2005 (N=6) | | | LS, May 2006 (N=5) | | | LS, July 2006 (N=5) | | |
|------|--------------------|-------------------|-------------------|---------------------|-------------------|-------------------|--------------------|-------------------|-------------------|---------------------|-------------------|-------------------|
| | ϕ | W_G | W_T | ϕ | V | V | ϕ | V | V | ϕ | V | V |
| BDE- | 0.0 | 8. | 5. | 0.0 | 4.6×10^3 | 4.9×10^4 | 0.3 | 1.3×10^4 | 2.2×10^5 | 0.6 | 4.8×10^3 | 3.3×10^5 |
| BDE- | 0.1 | 2.5×10^4 | 1.1×10^5 | 0.2 | 1.4×10^4 | 1.7×10^5 | 0.7 | 3.8×10^4 | 4.2×10^5 | 0.8 | 1.4×10^4 | 4.8×10^5 |
| BDE- | 0.1 | 3.2×10^4 | 8.4×10^4 | 0.0 | 1.1×10^4 | 3.1×10^4 | 0.1 | 4.9×10^4 | 1.4×10^5 | 0.2 | 1.9×10^4 | 1.6×10^5 |
| BDE- | 0.1 | 1.9×10^4 | 8.5×10^4 | 0.0 | 5.0×10^3 | 1.4×10^4 | 0.1 | 3.1×10^4 | 8.1×10^4 | N | 9.6×10^3 | 1.8×10^4 |
| BDE- | 0.1 | 5.7×10^4 | 1.3×10^5 | 0.0 | 2.1×10^4 | 4.0×10^4 | N | 8.6×10^4 | 8.9×10^4 | N | 3.5×10^4 | 3.9×10^4 |
| BDE- | 0.4 | 3.4×10^4 | 2.0×10^5 | 0.2 | 1.1×10^4 | 1.1×10^5 | N | 5.3×10^4 | 5.7×10^4 | N | 1.9×10^4 | 2.3×10^4 |

The particle washout ratios for BDE-47/66, BDE-100/99, and BDE-154/153 are set as 5.7×10^5 , 5.5×10^5 , and 4.5×10^5 , respectively (38.). ND: not detected.

2.3 Results and Discussion

Concentrations of PBDEs in Air. Air and surface water concentrations (average \pm SE) of six PBDE congeners in Lake Michigan in 2005 and in Lake Superior in 2006 are shown in Table 2-3. All concentrations have been blank and recovery corrected. In Lake Michigan cruises, the total air concentrations (gas + particle phase) of \sum_6 PBDE congeners ranged from 33 to 222 pg m^{-3} , with an average of $72 \text{ pg m}^{-3} \pm 19$ at six sampling sites. The average fraction of \sum_6 PBDE associated with particle phase, ϕ , was 0.07 ± 0.03 . BDE-99 was the dominant congener in both gas (74%) and particle phase (67%) concentrations, followed by BDE-47 and BDE-100. Venier and Hites reported the average total air concentrations of \sum_6 PBDE (BDE-28, 47, 99, 100, 153, and 183) at Sturgeon Point and Chicago by Lake Michigan (2005-2006) was 6.6 and 43 pg m^{-3} , respectively (Venier and Hites, 2008a). Here our PBDE concentrations are about 2-7 times higher than their land based values near Lake Michigan. Another atmospheric PBDE deposition study at Izmir Bay in Turkey (urban area) (Cetin and Odabasi, 2007), found the average total air concentrations of \sum_6 PBDE (BDE-28, 47, 100, 99, 154, and 153) to be 46 and 187 pg m^{-3} in winter and summer in 2005, respectively. BDE-99 was also the major PBDE congener in both gas and particle-phase concentrations. Thus, the results of total air PBDE concentrations and dominant BDE congener at Izmir Bay were comparable to Lake Michigan.

During the Lake Superior cruises, the total air concentrations of \sum_6 PBDE ranged from 8.6 to 123 pg m^{-3} , with an average of $29 \text{ pg m}^{-3} \pm 9.6$ at five sampling sites. The average fraction of \sum_6 PBDE associated with particle phase, ϕ , was 0.18 ± 0.04 . BDE-99 and BDE-47 were the major congeners in both the gas (77%) and particle-phase (66%)

concentrations of \sum_6 PBDE, respectively. At Eagle Harbor site by Lake Superior (2005-2006), the average total air concentrations of \sum_6 PBDE (BDE-28, 47, 99, 100, 153, and 183) was 3.2 pg m^{-3} . Additionally Su *et al.* (2007) reported that the average \sum_6 PBDE concentrations in the Arctic atmosphere (2002-2004) were 5.8 pg m^{-3} , and BDE-47 and 99 were the dominant PBDE congeners. However, here our average total air PBDE concentrations in Lake Superior were 4-5 times higher than in the Arctic atmosphere.

Unlike the Baltic Sea and southern Sweden where particle phase PBDEs comprised more than 95% of total air PBDE concentrations (ter Schure *et al.*, 2004a; Ter Schure *et al.*, 2004b), gas phase PBDEs explained about 90% of total air PBDE concentrations in the upper Great Lakes. This suggests that PBDEs in less urbanized or more remote atmospheres could be comprised mostly of the gas phase rather than the particle phase.

The relationship between atmospheric temperature and gas PBDE concentrations (usually expressed as partial pressures) were examined according the equation of Clausius- Claperyon:

$$\ln P = - \Delta H/R (1/T) + \text{const} \quad (2-9)$$

Table 2-3. Concentrations of six PBDE congeners in air (pg m⁻³) and surface water (pg L⁻¹) in Lake Michigan and Lake Superior (average ± SE^a)

| | N ^b | BDE-47 | BDE-66 | BDE-100 | BDE-99 | BDE-154 | BDE-153 | ∑ ₆ PBDE |
|--|----------------|-----------|------------|-----------|-----------|------------|-----------|---------------------|
| Lake Michigan in May and July in 2005 | | | | | | | | |
| Air, gas phase | 10 | 9.1 ± 1.6 | 0.2 ± <0.1 | 7.1 ± 1.7 | 50 ± 15 | 0.9 ± 0.2 | 0.5 ± 0.2 | 68 ± 18 |
| Air, particle phase | 13 | 0.6 ± 0.2 | 0.1 ± <0.1 | 0.3 ± 0.1 | 2.5 ± 0.9 | 0.1 ± <0.1 | 0.2 ± 0.1 | 3.7 ± 1.3 |
| Water, dissolved phase | 12 | 30 ± 4.6 | 0.4 ± 0.1 | 2.8 ± 0.4 | 16 ± 2.4 | 0.6 ± 0.1 | 0.7 ± 0.1 | 51 ± 6.8 |
| Water, particle phase | 15 | 0.7 ± 0.2 | < 0.1 | 0.3 ± 0.1 | 0.5 ± 0.2 | 0.1 ± <0.1 | < 0.1 | 1.7 ± 0.5 |
| Lake Superior in May and July in 2006 | | | | | | | | |
| Air, gas phase | 12 | 2.6 ± 0.8 | 0.1 ± <0.1 | 2.0 ± 0.6 | 20 ± 7.4 | 0.7 ± 0.3 | 0.6 ± 0.3 | 26 ± 9.0 |
| Air, particle phase | 11 | 2.2 ± 0.6 | 0.3 ± 0.1 | 0.5 ± 0.1 | 0.4 ± 0.2 | < 0.1 | < 0.1 | 3.4 ± 0.6 |
| Water, dissolved phase | 14 | 25 ± 5.5 | 0.3 ± 0.1 | 2.5 ± 0.4 | 12 ± 2.0 | 0.3 ± 0.1 | 0.4 ± 0.1 | 41 ± 8.1 |
| Water, particle phase | 13 | 1.3 ± 0.7 | 0.1 ± <0.1 | 0.3 ± 0.1 | 0.6 ± 0.3 | 0.1 ± <0.1 | 0.3 ± 0.2 | 2.7 ± 1.0 |

^a Standard error. ^b Number of analyzed samples.

Where P is partial pressures of PBDE congeners (atm), ΔH is the phase transition energy of PBDE compound volatilizing from terrestrial or aquatic environment into the atmosphere (kJ/mole). The relationship between the inverse atmospheric temperature (1/K) and natural logarithmic partial pressures of PBDE congeners is shown in Figure 2-2. PBDE congener were shown a significant dependence ($p < 0.01$ or $0.05 > p > 0.01$) between temperature and partial pressures of PBDEs except BDE-66 ($p=0.07$). The ΔH value of individual BDE congener over the upper Greta Lakes water was calculated in Table 2-4. Compared with other published ΔH values, BDE-47 (55 ± 19 kJ/mole) in this study was comparable with Viener and Hites' study, 53 ± 5 kJ/mole, (Venier and Hites, 2008b), but smaller than Tittlemier's, 94.6 kJ/mole, (Tittlemier *et al.*, 2002). The ΔH values for the same organic compound may vary widely because of different sampling locations, sampling sizes, and the time of the year (Carlson and Hites, 2005).

Concentrations of PBDEs in Surface Water. In Lake Michigan, the total water concentrations (dissolved + particle phase) of \sum_6 PBDE ranged from 1.5 to 87 pg L^{-1} , with an average of 53 ± 7.3 pg L^{-1} . The average dissolved and particle phase concentrations of \sum_6 PBDE were 51 ± 6.8 and 1.7 ± 0.5 pg L^{-1} , respectively. In addition, BDE-47 was the dominant congener and comprised 59 and 41% of \sum_6 PBDE concentrations in the dissolved phase and particle-phase, respectively. In Lake Superior, the total water concentrations of \sum_6 PBDE ranged from 16 to 122 pg L^{-1} , with an average of 44 ± 9.1 pg L^{-1} at seven different sampling sites. The average dissolved and particle phase concentrations of \sum_6 PBDE were 41 ± 8.1 and 2.7 ± 1.0 pg L^{-1} , respectively. Likewise, BDE-47 was the major congener in dissolved (61%) and particle phase (48%) in Lake Superior.

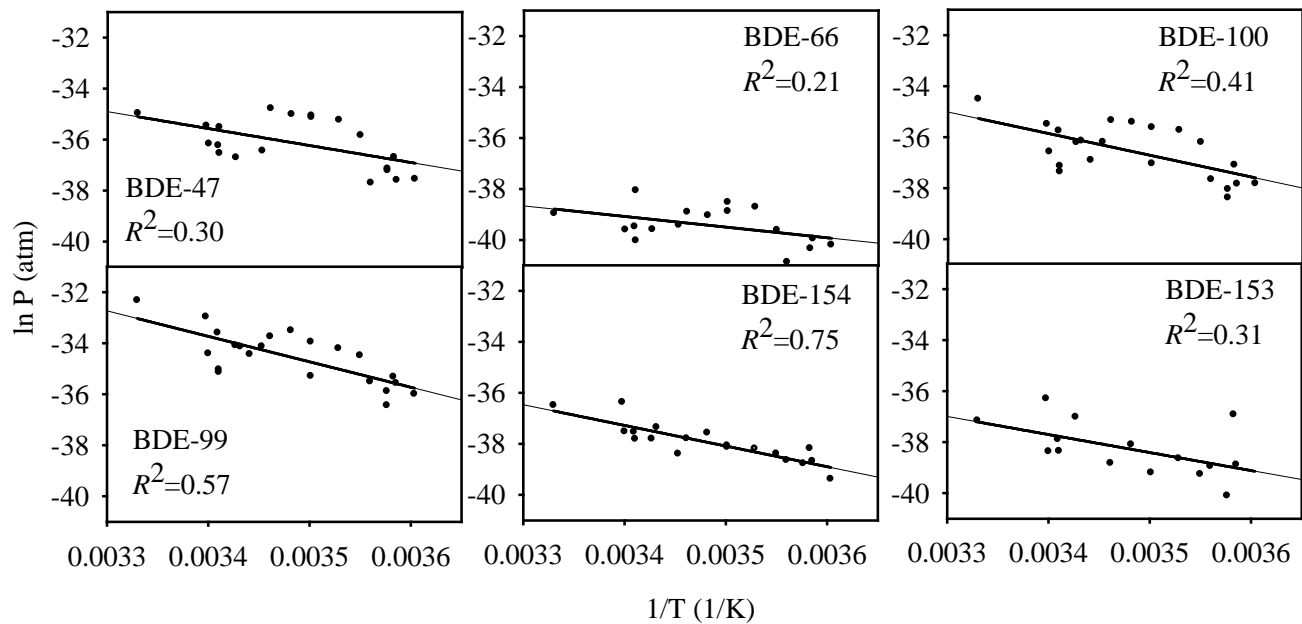


Figure 2-2. Relationship between the inverse atmospheric temperature and natural logarithmic partial pressures of PBDE congeners over the upper Great Lakes water

Table 2-4. Energy of phase transition (kJ/mol) relating atmospheric partial pressure of PBDEs to atmospheric temperature (1/K)

| | This study | | Venier and Hites (2008a) | | Tittlemier <i>et al.</i> (2002) | |
|---------|---------------------------|-------------------|---------------------------|-------------------|---------------------------------|-------------------|
| | ΔH^a (kJ/mole) | temp range (K) | ΔH^b (kJ/mole) | temp range (K) | ΔH^c (kJ/mole) | temp range (K) |
| BDE-47 | <i>55±19</i> | | 53±5 | 260-302 | 94.6 | |
| BDE-66 | 35±15 | | na | na | 97.8 | |
| BDE-100 | 71±19 | 277-298 | na | na | 102 | 323-423 |
| BDE-99 | 83±16 | | 44±8 | 260-302 | 108 | |
| BDE-154 | 67±9 | | na | na | 113 | |
| BDE-153 | <i>59±21</i> | | na | na | 110 | |

^a Coefficient ± standard error, plain, italics, and bold text present $p > 0.05$, $0.01 < p < 0.05$, and $p < 0.01$, respectively. ^b Coefficient ± standard error, all $p < 0.0001$. ^c Coefficients were determined using gas chromatographic retention time technique. na: data not available.

Limited studies have reported PBDE concentrations in natural water bodies. Cetin and Odabasi (2007) reported that the average total water concentrations of \sum_6 PBDE (BDE-28, 47, 100, 99, 154, and 153) ranged 99 to 237 pg L^{-1} at Izmir Bay in Turkey in 2005. Another average water concentration (dissolved + particle phase) of BDE-47 was reported as 55 pg L^{-1} at San Francisco Bay in the state of California from 2002-2006 (Oram *et al.*, 2008). Those PBDE concentrations in urban water bodies were 2-6 times greater than in the upper Great Lakes. Additionally, dissolved phase PBDEs comprised less than 50% of total water PBDE concentrations in those urban areas while, in this present study, \sum_6 BDE in the dissolved phase explained 95% of total water PBDE concentrations. This higher fraction of dissolved phase PBDEs in the Great Lakes suggests that lake surface water receives PBDEs largely from PBDE gas absorption. On the other hand, the overall higher water PBDE concentrations and lower dissolved phase contribution in urban water bodies may mostly result from burning of products containing PBDEs, storm runoff, municipal wastewater effluent, or higher biomass concentrations driving air-water exchange process (Dachs *et al.*, 1999).

Since BDE-47 (38.2%, w/w) and BDE-99 (48.6%, w/w) are the major congeners in penta-BDE technical formulation (DE-71) (La Guardia *et al.*, 2006), then BDE-47 and 99 are expected to be elevated in the environmental samples compared to other PBDE congeners. Additionally the coefficients of variance (Swackhamer *et al.*, 1988) for total \sum_6 PBDE concentrations in air sample (78%) were greater than in surface water samples (45%) in Lake Michigan. This suggests that PBDE concentrations in the atmosphere over the upper Great lakes are more site and temporally dependent than surface water. A similar CV comparison (108 and 77%) was observed between PBDE concentrations in air

and water samples, respectively, for Lake Superior.

Atmospheric Deposition of PBDEs. Fluxes ($\text{ng m}^{-2} \text{ day}^{-1}$) of net air-water exchange, dry deposition, and wet deposition of six PBDE congeners (BDE-47, 66, 100, 99, 154, and 153) in Lake Michigan in 2005 and in Lake Superior in 2006 are shown in Table 2-5. In Lake Michigan, the net flux of $\sum_6\text{PBDE}$ air-water exchange ranged from 8.1 to $72 \text{ ng m}^{-2} \text{ day}^{-1}$ and with an average of $24 \pm 10 \text{ ng m}^{-2} \text{ day}^{-1}$ at five sampling sites. On average, BDE-99, 100, and 47 contributed 83, 11, and 2.1% of $\sum_6\text{PBDE}$ gas absorption, respectively. In Lake Superior, the net flux of $\sum_6\text{PBDE}$ air-water exchange ranged from 1.5 to $21 \text{ ng m}^{-2} \text{ day}^{-1}$ and presented an average of $6.1 \pm 1.5 \text{ ng m}^{-2} \text{ day}^{-1}$ at five sampling sites. BDE-99 accounted for 96% of $\sum_6\text{PBDE}$ gas absorption, but BDE-47 showed net volatilization with an average flux of $0.8 \pm 0.5 \text{ ng m}^{-2} \text{ day}^{-1}$. Cetin and Odabasi (2007) reported the average net air-water exchange fluxes of BDE-47, 100, and 99 were 2.2, 2.2, and $6.5 \text{ ng m}^{-2} \text{ day}^{-1}$, respectively at Izmir Bay in Turkey. In this study (both lakes), the average net air-water exchange fluxes of BDE-47, 100, and 99 were -0.2, 1.7, and $13 \text{ ng m}^{-2} \text{ day}^{-1}$, respectively. A comparison of major PBDE congeners in air-water exchange flux between Izmir Bay (urban area) and the upper Great Lakes (rural versus remote areas) was not noticeably different. Likewise, the more volatile PBDE congeners (BDE-28 and 47) have shown negative fluxes (volatilization) at Izmir Bay and Peral River Delta in southern China (Guan *et al.*, 2009).

Table 2-5. Fluxes ($\text{ng m}^{-2} \text{day}^{-1}$) of air-water exchange, dry deposition, and wet deposition of PBDEs (average \pm SE) in Lake Michigan and Lake Superior

| | N | BDE-47 | BDE-66 | BDE-100 | BDE-99 | BDE-154 | BDE-153 | Σ_6PBDE |
|--|----------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|----------------------------------|
| Lake Michigan in May and July in 2005 | | | | | | | | |
| Air-water exchange | 6 | 0.5 ± 1.0 | $0.1 \pm < 0.1$ | 2.7 ± 0.7 | 20 ± 5.7 | 0.3 ± 0.1 | 0.2 ± 0.1 | 24 ± 5.8 |
| Dry deposition | 13 | $0.1 \pm < 0.1$ | < 0.1 | < 0.1 | 0.3 ± 0.2 | < 0.1 | < 0.1 | 0.4 ± 0.2 |
| Wet deposition | 10 | 0.9 ± 0.2 | $0.1 \pm < 0.1$ | 0.7 ± 0.2 | 3.7 ± 2.2 | $0.1 \pm < 0.1$ | 0.2 ± 0.1 | 5.8 ± 2.2 |
| Lake Superior in May and July in 2006 | | | | | | | | |
| Air-water exchange | 12 | -0.8 ± 0.6 | < 0.1 | 0.6 ± 0.3 | 5.8 ± 3.1 | 0.2 ± 0.1 | 0.2 ± 0.1 | 6.1 ± 3.1 |
| Dry deposition | 11 | 0.4 ± 0.1 | < 0.1 | $0.1 \pm < 0.1$ | $0.1 \pm < 0.1$ | < 0.1 | < 0.1 | 0.6 ± 0.1 |
| Wet deposition | 12 | 2.3 ± 0.6 | 0.3 ± 0.1 | 0.5 ± 0.2 | 0.8 ± 0.8 | < 0.1 | < 0.1 | 4.0 ± 1.0 |

Dry deposition of \sum_6 PBDE congeners in Lake Michigan ranged from 0.1 to 1.5 $\text{ng m}^{-2} \text{ day}^{-1}$, with an average of $0.4 \text{ ng m}^{-2} \pm 0.1 \text{ day}^{-1}$. On average, BDE-99 ($0.3 \text{ ng m}^{-2} \text{ day}^{-1}$) contributed 75% of the dry deposition flux to Lake Michigan. In Lake Superior, dry deposition of \sum_6 PBDE congeners ranged from 0.1 to 1.2 $\text{ng m}^{-2} \text{ day}^{-1}$, with an average of $0.6 \pm 0.1 \text{ ng m}^{-2} \text{ day}^{-1}$. BDE-47 ($0.4 \text{ ng m}^{-2} \text{ day}^{-1}$) was the dominant congener in dry deposition to Lake Superior. The reported average PBDE dry deposition at urban areas (ter Schure *et al.*, 2004a; Cetin and Odabasi, 2007): BDE -99 ($1.9\text{-}62 \text{ ng m}^{-2} \text{ day}^{-1}$) and BDE-47 ($2.9\text{-}42 \text{ ng m}^{-2} \text{ day}^{-1}$), was a factor of five to two orders of magnitude greater than observed here for upper Great Lakes. In addition, the average dry deposition of \sum_6 PBDE (BDE-28, 47, 99, 100, 153, and 183) at IADN sites in 2005-2006 ranged from 0.23 to 1.09 $\text{ng m}^{-2} \text{ day}^{-1}$. These values are not noticeably different from these estimates. This result suggests that PBDE dry deposition is positively correlated to population or industry.

Based on the calculated washout ratios and measured atmospheric concentrations for individual PBDE congeners, the \sum_6 PBDE concentrations in precipitation in Lake Michigan ranged from 0.8 to 21 ng L^{-1} and averaged $4.2 \pm 6.2 \text{ ng L}^{-1}$. In Lake Superior, PBDE concentrations in precipitation ranged from 0.6 to 4.3 ng L^{-1} and averaged $2.3 \pm 1.1 \text{ ng L}^{-1}$. However, the average \sum_6 PBDE (BDE-28, 47, 99, 100, 153, and 183) concentrations ranged from 0.41 to 0.54 ng L^{-1} at IADN sites near the upper Great Lakes. Compared with the above measurements, the estimated concentrations of PBDEs in precipitation were 4-10 times higher. This concentration difference in precipitation can be attributed to different sampling sites, periods, and errors from methodological calculations, but is directly related to higher air concentration measured in this study.

Annual precipitation rates were 692.4 and 621.7 mm for Lake Michigan in 2005 and Lake Superior in 2006, respectively (values obtained from the Great Lakes Environmental Research Laboratory database). Wet deposition of \sum_6 PBDE in Lake Michigan ranged from 1.6 to 20 ng m⁻² day⁻¹, with an average of 5.8 ± 1.7 ng m⁻² day⁻¹. On average, BDE-99 and 47 contributed 3.7 and 0.9 ng m⁻² day⁻¹, respectively. In Lake Superior, wet deposition of \sum_6 PBDE ranged from 1.0 to 7.3 ng m⁻² day⁻¹, with an average of 4.0 ± 0.5 ng m⁻² day⁻¹. BDE-47 and 99 contributed an average of 2.3 and 0.8 ng m⁻² day⁻¹, respectively. Venier and Hites also calculated the annual wet deposition of \sum_6 PBDE (BDE-28, 47, 99, 100, 153, and 183) in Lake Michigan and Lake Superior (2005-2006) was 11 and 1.0 ng m⁻² day⁻¹ (Venier and Hites, 2008a), respectively. Terschure *et al.*, (2004) reported the median wet deposition of \sum_6 PBDE was 6.6 ng m⁻² day⁻¹ at an urban site in southern Sweden, and BDE-47 and 99 accounted for 3.7 and 1.9 ng m⁻² day⁻¹, respectively. At a rural lake in southern Italy (Mariani *et al.*, 2008), the measured wet depositions of BDE-47 and -99 were 2.5 and 1.9 ng m⁻² day⁻¹, respectively, during a week in March in 2005. The estimated wet deposition of PBDEs in the upper Great Lakes was not noticeably different from those literature measurements (either urban or rural areas). In addition, the dominant congener in wet deposition in the upper Great Lakes was similar to those literature reports. The complete results of PBDE air-water exchange flux, dry deposition, and wet deposition at different sites can be found in Appendix A-2, A-3, and A-4.

PBDE Concentration and Deposition between Both Lakes. The average total air concentrations of \sum_6 PBDE in Lake Michigan (72 pg m⁻³) were significantly higher ($p < 0.05$) than in Lake Superior (29 pg m⁻³). This was because the gas phase concentrations

of \sum_6 PBDE in Lake Michigan (68 pg m^{-3}) were significantly greater ($p < 0.05$) than in Lake Superior (26 pg m^{-3}). This PBDE air concentration difference between the lakes was not surprising. The higher air PBDE concentrations in Lake Michigan were attributed to local PBDE emissions due to a more urbanized and industrialized lakeshore compared to Lake Superior. Although the average total surface water concentrations of \sum_6 PBDE in Lake Michigan (53 pg L^{-1}) were higher than in Lake Superior (44 pg L^{-1}), this difference was not statistically significant ($p = 0.52$). Any difference between Lake Michigan and Lake Superior water PBDE concentrations may be attributed to higher atmospheric PBDE deposition to Lake Michigan.

The average net flux of \sum_6 PBDE air-water exchange in Lake Michigan ($24 \text{ ng m}^{-2} \text{ day}^{-1}$) was significantly greater ($p < 0.05$) than in Lake Superior ($6.1 \text{ ng m}^{-2} \text{ day}^{-1}$). This difference between both lakes was attributed in the difference of PBDE concentrations in gas and dissolved phases, surface water temperature, and wind speed between both lakes. The net flux of BDE-99 air-water exchange explained the largest difference ($p < 0.05$) between Lake Michigan ($20 \text{ ng m}^{-2} \text{ day}^{-1}$) and Lake Superior ($5.8 \text{ ng m}^{-2} \text{ day}^{-1}$). For BDE-47, the average net flux of air-water exchange in Lake Superior was negative ($-0.8 \text{ ng m}^{-2} \text{ day}^{-1}$) compared to $0.5 \text{ ng m}^{-2} \text{ day}^{-1}$ in Lake Michigan ($p = 0.17$). That volatilization of BDE-47 reflected its over-saturation in Lake Superior water (Figure 2-3). A possible explanation for this net volatilization is that current BDE-47 concentrations in the gas phase have declined faster over Lake Superior compared to Lake Michigan, and PBDE concentrations in the air decline faster than the water.

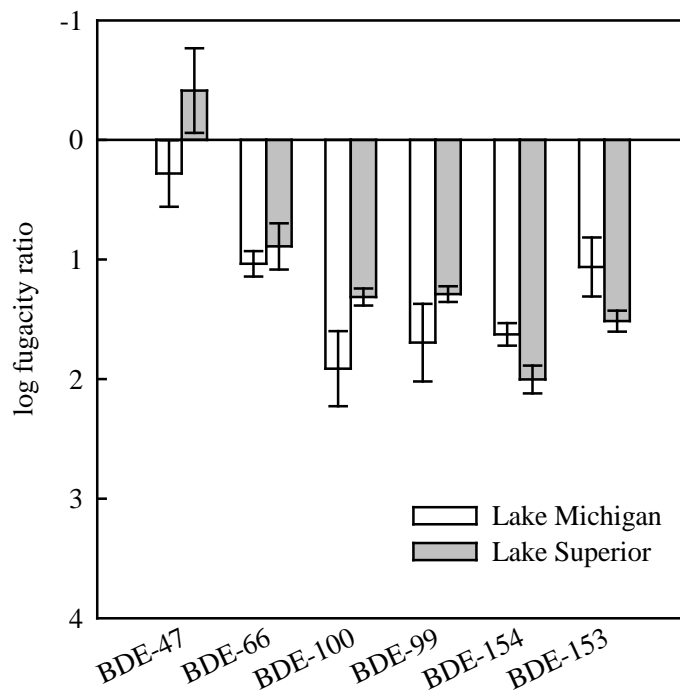


Figure 2-3. Fugacity of six PBDE congeners in Lake Michigan in 2005 and in Lake Superior in 2006. Error bars represent standard errors.

The average dry deposition of \sum_6 PBDE was not significantly different ($p = 0.34$) between Lake Michigan ($0.4 \text{ ng m}^{-2} \text{ day}^{-1}$) and Lake Superior ($0.6 \text{ ng m}^{-2} \text{ day}^{-1}$). This is due to slight differences in air particle phase concentrations of \sum_6 PBDE between both lakes. Likewise, the average wet deposition of \sum_6 PBDE in Lake Michigan ($5.8 \text{ ng m}^{-2} \text{ day}^{-1}$) was greater than in Lake Superior ($4.0 \text{ ng m}^{-2} \text{ day}^{-1}$) but this comparison was not statistically significantly ($p = 0.29$). This difference in wet deposition between both lakes resulted from different PBDE concentration levels in air and different washout ratios. As discussed earlier, the higher total air concentrations of \sum_6 PBDE in Lake Michigan than in Lake Superior caused higher wet deposition of PBDEs to Lake Michigan. On average, air-water exchange, wet deposition, and dry deposition have contributed (80, 19, and 1%)

and (57, 37, and 6%) of \sum_6 PBDE atmospheric deposition to Lake Michigan and Lake Superior, respectively.

PBDE Concentration and Deposition between Nearshore and Open-lake. In Lake Michigan, sampling sites GB17, Chicago, and Milwaukee are grouped into nearshore urban sites, and others are open-lake sites. The average total air concentrations of \sum_6 PBDE at nearshore sites (88 pg m^{-3}) were around 1.9 fold higher than at open-lake sites (47 pg m^{-3}) but this comparison was not statistically significantly ($p = 0.27$). Likewise, the average total surface water concentrations of \sum_6 PBDE at nearshore sites (65 pg L^{-1}) were 1.4 fold higher than at open-lake sites (46 pg L^{-1}), and this comparison was not statistically significantly either ($p = 0.20$). Analogous relationships (1.7-2.6 fold higher at nearshore sites than open-lake sites, not statistically significantly) were observed between nearshore and open lake sites for air-water exchange, dry deposition, and wet deposition.

In Lake Superior, sampling sites Duluth and Thunder Bay are classified as nearshore urban sites, and others are open-lake sites. The average total air concentrations of \sum_6 PBDE at nearshore sites (39 pg m^{-3}) were 1.9 fold greater than at open lake sites (21 pg m^{-3}) but this comparison was not statistically significantly ($p = 0.34$). Likewise, the average total surface water concentrations of \sum_6 PBDE at nearshore sites (59 pg L^{-1}) were 1.7 fold higher than at open-lake sites (35 pg L^{-1}), and that comparison was not statistically significantly ($p = 0.26$) either. The average net air-water exchange flux of \sum_6 PBDE was 2.0 fold higher at nearshore sites than open-lakes sites. The observed differences in atmospheric PBDE deposition between nearshore urban and open-lake sites (Figure 2-4) can be attributed to intense PBDE emission at urban areas compared to

open-lakes sites. The lack of statistical significance of PBDE levels and atmospheric deposition between nearshore and open-lake sites suggests continuously declining local PBDE emission. Furthermore, long range atmospheric transport of PBDEs is becoming more important to the upper Great Lakes.

2.4 Conclusions

Paired air and surface water samples were collected on aboard during May and July to determine the net PBDE air-water exchange flux in the upper Great Lakes for the first time. On average, the net \sum_6 PBDE air-water exchange fluxes accounted for 74% of the total atmospheric PBDE deposition, and wet and dry deposition fluxes explained the rest of the total atmospheric PBDE deposition. In Lake Michigan, the net flux of \sum_6 PBDE air-water exchange ranged from 8.1 to 72 $\text{ng m}^{-2} \text{day}^{-1}$ and with an average of $24 \pm 10 \text{ ng m}^{-2} \text{day}^{-1}$. On average, BDE-99,100, and 47 contributed 83, 11, and 2.1% of \sum_6 PBDE gas absorption, respectively. In Lake Superior, the net flux of \sum_6 PBDE air-water exchange ranged from 1.5 to 21 $\text{ng m}^{-2} \text{day}^{-1}$ and presented an average of $6.1 \pm 1.5 \text{ ng m}^{-2} \text{day}^{-1}$. BDE-99 accounted for 96% of \sum_6 PBDE gas absorption, but BDE-47 showed volatilization with an average flux of $0.8 \pm 0.5 \text{ ng m}^{-2} \text{day}^{-1}$. This volatilization of BDE-47 reflected its over-saturation in the Lake Superior water.

The average total air concentrations of \sum_6 PBDE in Lake Michigan (72 pg m^{-3}) were significantly higher ($p < 0.05$) than in Lake Superior (29 pg m^{-3}). Additionally, the average net flux of \sum_6 PBDE air-water exchange in Lake Michigan ($24 \text{ ng m}^{-2} \text{day}^{-1}$) was significantly greater ($p < 0.05$) than in Lake Superior ($6.1 \text{ ng m}^{-2} \text{day}^{-1}$). This comparison suggests that atmospheric PBDE levels and deposition were associated with local PBDE emission from urbanized activities.

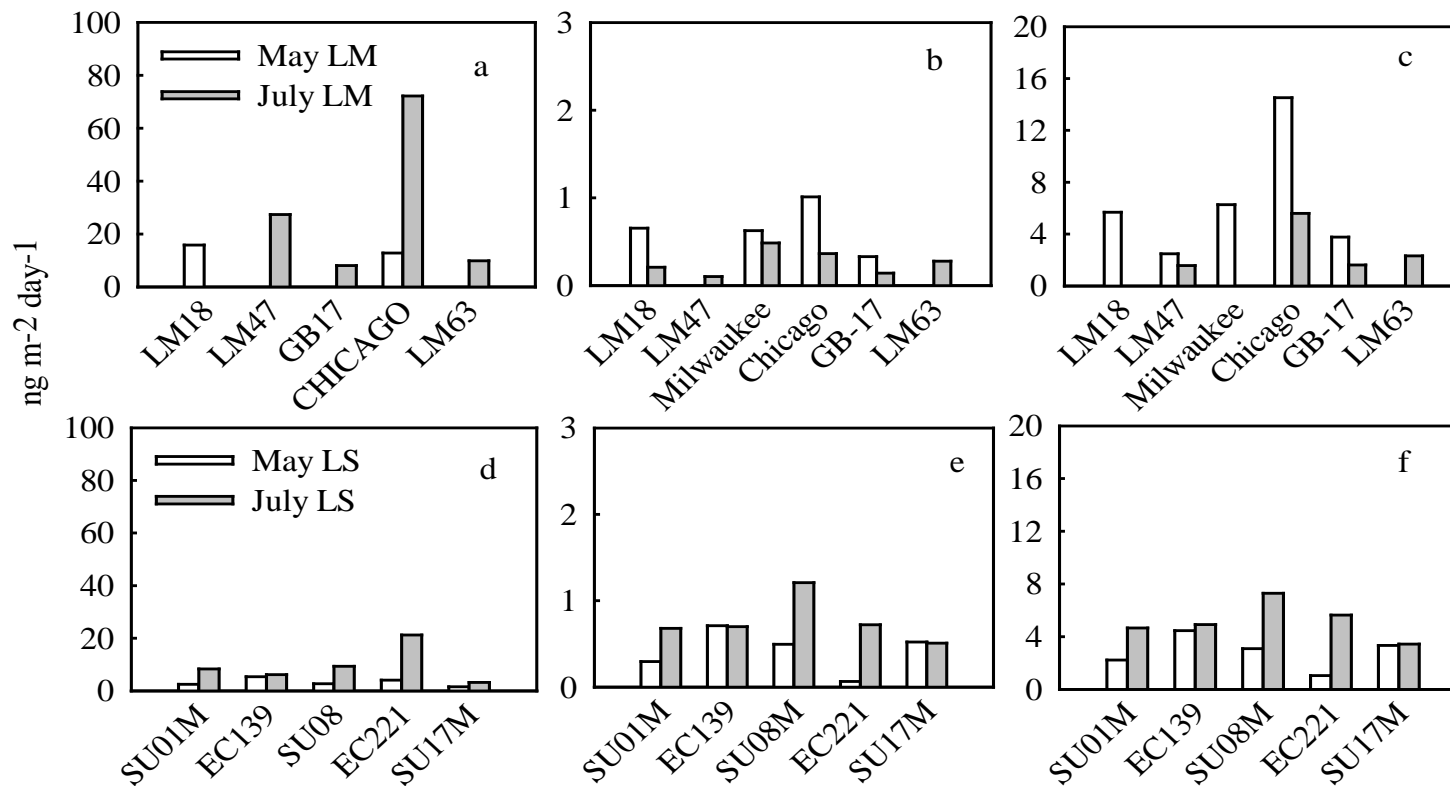


Figure 2-4. Atmospheric PBDE deposition at different locations in Lake Michigan and Lake Superior. (a), (d) present air-water exchange fluxes; (b), (e) present dry particle deposition; (c), (f) present wet deposition

Chapter 3

Mass Budgets of PBDEs in the Upper Great Lakes

The first estimates of annual mass budgets of polybrominated diphenyl ethers (PBDEs) for the upper Great Lakes are presented. Surface water samples were collected on board in Lake Michigan in 2005 and Lake Superior in 2006. Air samples were collected at three sites located next to the shores of the upper Great Lakes in 2005-2006 by the Integrated Atmospheric Deposition Network (IADN). Net air-water exchange flux was calculated from these air and water concentrations. Dry and wet depositions were measured by IADN in 2005-2006. Wastewater treatment plant's (WWTP) discharge was assumed to be the only point source of PBDEs to the lakes. Annual mass budget of the sum of six PBDE congeners ($\sum_6\text{PBDE}$) for Lake Michigan in 2005 showed a net increase with 270 kg yr^{-1} . In contrast, the mass budget for Lake Superior in 2006 approximately approached a balance (net increase of 14 kg yr^{-1}). Wet deposition accounted for 71-75% of the total $\sum_6\text{PBDE}$ inputs into the both lakes. The WWTP's discharge explained about 10% of the total $\sum_6\text{PBDE}$ inputs. The net $\sum_6\text{PBDE}$ air-water exchange flux showed small gas absorption (2.3 kg yr^{-1}) for Lake Michigan and volatilization (15 kg yr^{-1}) for Lake Superior. This net air-water exchange flux of $\sum_6\text{PBDE}$ also exhibited spatial and temporal variability. Net absorption was observed at near urban areas, while net volatilization occurred in the remote areas. PBDE air-water exchange flux exhibited an approaching equilibrium during spring and winter but higher flux between summer and fall. We estimated that the net annual fluxes in $\sum_6\text{PBDE}$ mass budgets are expected to 77 and -15 kg yr^{-1} for Lake Michigan and Lake Superior in 2009-2010, respectively. The

contribution of \sum_6 PBDE inputs from atmospheric deposition into the Great Lakes will decrease due to the declining PBDE levels in the atmosphere.

3.1 Introduction

Polybrominated diphenyl ethers, a subset of the brominated flame retardants (BFRs), are used in thermoplastics, polyurethane foams, and textiles to reduce accidental ignition or fire (Alaee *et al.*, 2003; Hale *et al.*, 2003). Like polychlorinated biphenyls (PCBs), PBDEs also have 209 possible brominated congeners but only around 40 congeners are commonly found in the environment (Palm *et al.*, 2002). Concern about environmental PBDEs is rising because they are persistent chemicals in the environment and accumulated in the ecosystem (Hites, 2004; Vonderheide *et al.*, 2008). Furthermore, research has shown that lower brominated PBDE congeners may interfere with the human thyroid hormone system (Porterfield, 2000). Thus, bans on the use of penta-BDE chemicals in manufacturing have been enacted or executed in the European countries and North America (Vonderheide *et al.*, 2008).

The Great Lakes' environment is significant because it provides a fundamental living function related to drinking and industrial water usage, commercial fishing, naval transportation, recreation, and habitats for over 33 million people and 130 globally rare, endangered, or at-risk species (Ward *et al.*, 2008). In order to monitor and manage anthropogenic pollutant loadings in the Great Lakes, various programs have been conducted since the 1980's. For instance, the integrated Atmospheric Deposition Network (IADN) has been in cooperation to monitor atmospheric pollution deposition at different sites near the Great Lakes' shores since 1990 cooperation with the United States and Canadian research institutions. Another program, Great Lakes Aquatic Contaminants

Survey (GLACS), also monitored emerging chemical levels at open-lake and near-shore sites in Lake Michigan and Lake Superior during 2004-2006 for both air and water samples.

The mass budget model is a straightforward tool used to determine the net flux and direction of a pollutant in an aquatic system (Pearson *et al.*, 1996). Although PBDE levels have been investigated in many environmental media such as lake sediment, lake water, riverbank soil, atmospheric environment, and wildlife (Song *et al.*, 2006; Batterman *et al.*, 2007; Venier and Hites, 2008a), studies of PBDE mass budgets have been limited. One California study researched the mass budget of PBDEs in San Francisco Bay to understand the local PBDE source inputs and the fate of the Bay area (Oram *et al.*, 2008). They found that BDE-47 (tetra-brominated BDE) loading was dominated by the source of wastewater effluent, and BDE-209 (deca-brominated BDE) was mainly contributed by runoff from the local tributaries. Another research study was conducted at the estuary by the Southern China Sea, which is heavily populated and industrialized. The riverine flux of PBDEs, 11 major BDE congeners including BDE-209, explained almost 85% of the annual mass input (Guan *et al.*, 2009). However, the annual mass budgets of PBDEs in the Great Lakes are not well understood because few investigations have been conducted on PBDE levels in lake water and loadings from point source inputs.

The main objective of this study is to establish the annual mass budgets of PBDEs in Lake Michigan and Lake Superior (the upper Great Lakes). Additionally, the estimated loadings of PBDEs from wastewater treatment plant (WWTP) and the seasonal patterns of air-water exchange fluxes are discussed for the first time. The results of the annual

PBDE mass budgets can predict changes in PBDE levels in lake water and provide insights into how to reduce PBDE loading through either environmental management or engineering strategies by identifying the major sources and sinks.

3.2 Methods

Annual PBDE mass budgets in the upper Great Lakes were constructed by calculating available annual fluxes of input and output PBDE mass. PBDE concentrations, fluxes in the atmosphere and the lake water were based on the results of both IADN and GLACS, respectively. Additionally, in order to calculate the atmospheric PBDEs' flux, the surface area of Lake Michigan and Lake Superior with 57,800 km² and 82,100 km² are used, respectively (Quinn, 1992).

Atmospheric Sampling and Analysis. Air and precipitation samples were collected every 12 days around Lake Michigan and Lake Superior by IADN. The IADN data used in the present study includes one urban site, at Chicago (CH), IL, one rural site, at Sleeping Bear Dunes (SB), MI near Lake Michigan, and one remote site at Eagle Harbor (EH), MI near Lake Superior. More details about sampling procedure and analytical methods for air and precipitation samples can be found elsewhere (Carlson *et al.*, 2004; Venier and Hites, 2008a).

Lake Water Sampling and Analysis. Water was sampled from Lake Michigan and Lake Superior during the spring and summer of 2005 (Lake Michigan) and 2006 (Lake Superior). Sampling and analytical methods are described in detail in Chang and Simcik (2010). In general, approximate 800 liter of lake water was filtered and extracted for a suite of hydrophobic organic containments including several PBDE congeners: 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), 2,3',4,4'-tetrabromodiphenyl ether

(BDE-66), 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), 2,2',4,4',6-peatabromodiphenyl ether (BDE-100), 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153), and 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154). Determination of PBDE congener was performed by monitoring m/z 79 and 81 through gas chromatography electron capture negative ionization mass spectrometry (GC-ECNI/MS). The quantification of PBDE congener mass was made relative to an internal standard (PCB-204). The GC-ECNI was equipped with a 60 m DB-5 capillary column, helium carrier gas, methane ionization gas, and operated in the selective ion monitoring mode. More details of sample preparation, extraction, clean up, and quantification are given elsewhere (Streets *et al.*, 2006).

PBDE Inputs. Net flux ($\text{ng m}^{-2} \text{ day}^{-1}$) of PBDE air-water exchange was determined using a modification of the two-film model (Whitman, 1923) as follows:

$$\text{Net air-water exchange flux} = K_{OL} (C_g - C_d H/RT) \quad (3-1)$$

where K_{OL} (m day^{-1}) is the overall mass transfer coefficient of PBDE, C_g (ng m^{-3}) is the gas phase concentration of PBDE in air, C_d (ng m^{-3}) is the dissolved phase concentration of PBDE in surface water, H ($\text{Pa m}^3 \text{ mole}^{-1}$) is PBDE Henry's law constant, R is the ideal gas constant ($8.314 \text{ Pa m}^3 \text{ mole}^{-1} \text{ K}^{-1}$), and T (K) is the temperature at surface water. A positive flux means the PBDE flux direction is from the atmosphere to water (gas absorption); in contrast, a negative value means the PBDE flux is from water to atmosphere (gas volatilization). Since the lake water samples were only collected in May and July in 2005 and 2006, the average water PBDE concentrations in May and July would be assumed to be constant for the entire year. Details about the parameters to calculate the net PBDE air-water exchange flux can be found in Appendix B-1.

Atmospheric wet and dry deposition of PBDEs into the upper Great Lakes was directly taken from Venier and Hites (2008a). Additionally, the influenced area of the atmospheric deposition of PBDEs from urban Chicago to the total area of Lake Michigan was assumed to be 5% based on the research of Venier and Hites (2008a), and Offenberg and Baker (1997). Consequently, atmospheric deposition at Sleeping Bear Dunes would explain the remaining area of Lake Michigan (95%). For Lake Superior, atmospheric PBDE deposition at Eagle Harbor represented the whole Lake Superior area.

Municipal wastewater treatment plant (WWTP) discharge was assumed to be the only PBDE point source input to the lakes. This annual input of PBDEs was estimated based on the reported PBDE concentrations in WWTP discharge multiplied by the annual WWTP discharge volume. Three studies in North America areas report PBDE concentrations in WWTP effluent were summarized by (Song *et al.*, 2006). The congener patterns and overall concentrations are similar despite different locations and plant capacities. Therefore, the average concentrations of five PBDE congeners (BDE-47, 100, 99, 154, and 153), 26.8 ng L^{-1} , was taken as representative of WWTP effluent around the Great Lakes. Additionally, annual WWTP discharge volume into the upper Great Lakes was estimated according to publicly owned treatment works (POTWs) discharge permits issued by the states of Michigan, Indiana, Illinois, Wisconsin, and Minnesota located around Lake Michigan and Lake Superior (personal communication). However, this legally allowed discharge volume is directly based on the facility capacity of WWTP instead of the actual WWTP discharge. Therefore, the actual annual discharge volume from WWTP into the upper Great Lakes may be lower than the numbers used in this paper. The WWTP discharge volume from Canadian cities around Lake Superior shores

used the actual WWTP discharge in the year 2009 from Thunder Bay, Ontario (personal communication). Other Canadian WWTP discharge volume into Lake Superior was ignored because the rest of the Canadian Lake Superior shoreline is far less populated. Details on WWTPs' discharge permits into Lake Michigan and Lake Superior can be found in Appendix B-2 and B-3.

PBDE Outputs. The annual outflow volume from Lake Michigan and Lake Superior was 8.0×10^{10} and $7.1 \times 10^{10} \text{ m}^3$, respectively (Quinn, 1992). The lake water outflow of PBDEs was estimated using the annual lake water outflow volume multiplied by the average water PBDE concentrations in the corresponding lakes. Annual burial of PBDEs in sediments of Lake Michigan and Lake Superior was taken from a study by Li *et al.* (2006) who reported total loadings and surface annual loading of \sum_9 PBDE (28, 47, 66, 85, 99, 100, 153, 154, and 183) in the Great lakes in 2002.

Model Limitations. While we feel that we have addressed the major loadings of PBDEs to the upper Great Lakes, other may be important. They include leaching from landfills, sedimentation re-suspension, tributary input from atmospheric PBDE deposition on the lake drainage basins, and discharge from industrial WWTPs. In addition, several factors may contribute to the errors and uncertainties including analysis bias between IADN and GLACS's laboratories, lake water concentrations of May and July representing the whole year's values, land based air concentrations instead of over lake based, and the estimated influence area from Chicago's urban air plume.

3.3 Results and Discussion

Concentrations. Table 3-1 summarizes the measured water and air \sum_6 PBDE concentrations in the upper Great Lakes in 2005 and 2006. The total water concentrations

of \sum_6 PBDE were 53 ± 24 and 44 ± 34 pg L^{-1} (mean \pm standard deviation) in Lake Michigan and Lake Superior, respectively. The average \sum_6 PBDE concentrations in Lake Michigan were about 1.2 times greater than in Lake Superior but it was not a statistically significant difference ($p > 0.05$). In individual BDE congeners, BDE-47 was dominant and comprised about 60% of \sum_6 PBDE in either dissolved phase or particle phase concentrations. Furthermore, \sum_6 PBDE in the dissolved phase concentrations comprised 93-97% of the total water \sum_6 PBDE concentrations.

Table 3-1. Concentrations^a of \sum_6 PBDE (average \pm SD) in the water and air in Lake Michigan in 2005 and in Lake Superior in 2006

| | Michigan | | Superior |
|------------------------------|-----------------|--------------|-----------------|
| C_d (pg L^{-1}) | 51 ± 23 | | 41 ± 30 |
| C_p (pg L^{-1}) | 1.7 ± 2.1 | | 2.7 ± 3.8 |
| | SB | CH | EH |
| C_g (pg m^{-3}) | 5.9 ± 8.3 | 27 ± 33 | 1.4 ± 1.2 |
| C_p (pg m^{-3}) | 3.8 ± 4.2 | 15 ± 7.6 | 1.6 ± 3.1 |

^a C_d , C_p , and C_g are labeled as concentrations in dissolved, particle, and gas phase
SB: Sleeping Bear Dunes, **CH**: Chicago, and **EH**: Eagle Harbor

Research of PBDE concentrations in natural water bodies is scarce. Compared with two published PBDE concentrations in urbanized water bodies, PBDE levels in this present study were 2-6 times lower than San Francisco Bay and Izmir Bay in Turkey (Cetin and Odabasi, 2007; Oram *et al.*, 2008). Besides the difference of water PBDE concentration magnitudes, PBDEs in dissolved phase typically comprised less than 50% of the total water PBDE concentrations in these urbanized water bodies. Thus, the lower water concentration and higher dissolved phase contribution of PBDEs in the upper Great Lakes were the differences compared to urbanized water bodies.

The average air concentrations of \sum_6 PBDE were higher in urban areas but relatively low in remote areas. The average total air concentrations (gas and particle phases) of \sum_6 PBDE at Chicago (42 pg m^{-3}) and Sleeping Bear Dunes (9.7 pg m^{-3}) were 14 and 3 times greater than that of \sum_6 PBDE at Eagle Harbor (3 pg m^{-3}), respectively. The fractions of the gas phase \sum_6 PBDE at CH, SB, and EH were 0.61, 0.64, 0.47 of the total air PBDE concentrations, but these fractions at three different study sites were not significantly different from each other (all $p > 0.05$). Compared with other atmospheric PBDE levels, the average total air concentrations of \sum_6 PBDE at Chicago were similar to urban areas of Izmir Bay in Turkey (Cetin and Odabasi, 2007) and the concentrations at Eagle Harbor were close to Arctic atmosphere (Su *et al.*, 2007).

Congener Profiles. In the penta-BDE formulation mixture (DE-71), the fractions of major BDE congeners, BDE-99, 47, and 100 were 0.44, 0.35, and 0.12, respectively (La Guardia *et al.*, 2006). Since the PBDE congener fractions in lake water were similar between Lake Michigan and Lake Superior, the reported fractions of PBDE congener were made from data of both of these lakes. The calculated fractions of BDE-99, 47, and

100 in lake water were 0.31 ± 0.08 , 0.59 ± 0.10 , and 0.06 ± 0.02 (mean \pm standard deviation), respectively. While comparing fraction changes of PBDE congeners from DE-71 to lake water, the average fraction of BDE-47 increased 24% but BDE-99 and 100 declined 13% and 6%, respectively. This result showed BDE-47, which is more volatile than the other five PBDE congeners, transported more successfully from products containing PBDE chemicals to the upper Great Lakes' water compared to BDE-99 and 100. Furthermore, the average fractions of BDE-47, 66, 100, 99, 154, and 153 in the dissolved phase were 0.59, 0.01, 0.06, 0.32, 0.01, and 0.01, respectively. In gas phase concentrations (data from Sleeping Bear Dunes and Eagle Harbor), the corresponding fractions of PBDE congeners were 0.57, 0.00, 0.07, 0.33, 0.01, and 0.02. The fraction patterns of PBDE congeners were very similar between lake water and the atmosphere, as shown in Figure 3-1. This observation suggests that the atmospheric transport of gas phase PBDEs may be the major contributor to the dissolved phase PBDEs in the upper Great Lakes.

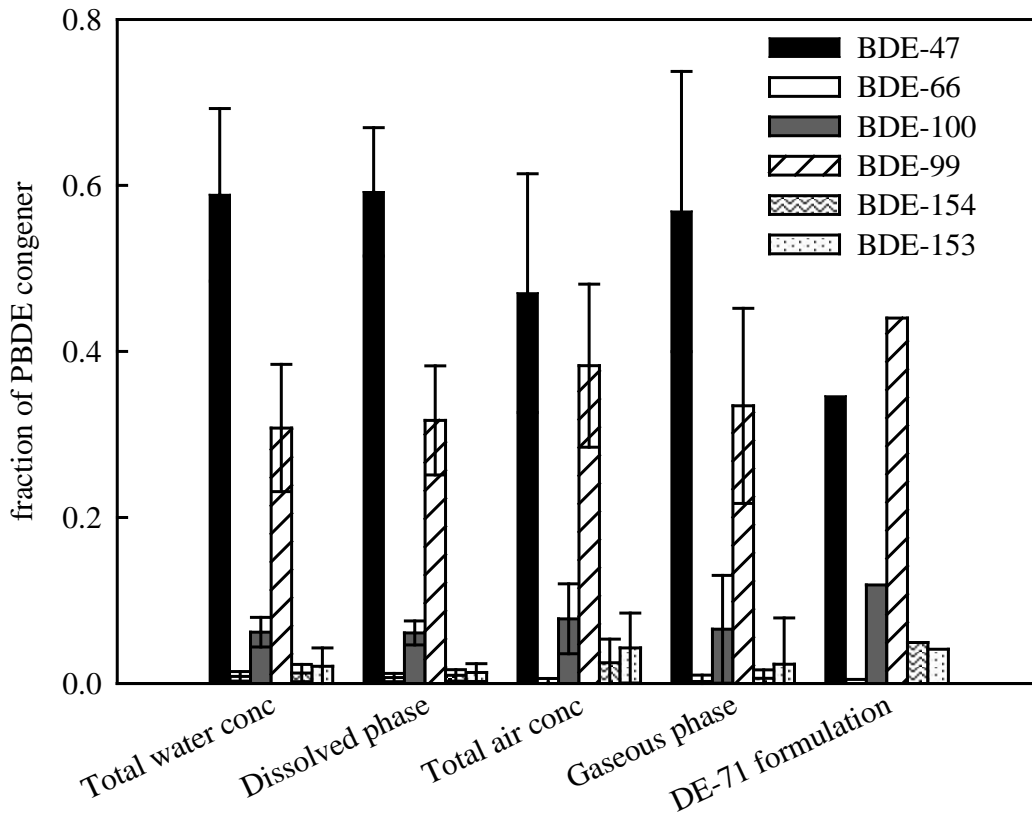


Figure 3-1. Fraction of BDE congeners of \sum_6 PBDE concentrations in lake water, air, and penta- BDE chemical formulation (DE-71). The error bars represent standard deviation.

Seasonal Patterns. In order to understand seasonal patterns of the net PBDE air-water exchange flux, the relationship between the net air-water exchange flux and gas phase concentrations of \sum_6 PBDE, air temperatures, and lake surface water temperatures were examined. Results showed that the direction and seasonal pattern of \sum_6 PBDE air-water exchange flux was site dependent. The general direction of the net \sum_6 PBDE air-water exchange flux was into the lake water column (gas absorption) at urban Chicago but was into the atmosphere (volatilization) at the remote area, Eagle Harbor. At a rural site, Sleeping Bear Dunes, both gas absorption and volatilization of \sum_6 PBDE were exhibited in a year. Since the dissolved phase BDE concentrations were not significantly

different between CH, SB, and EH (all $p > 0.1$), the direction difference of the net PBDE air-water exchange fluxes at the three sites is attributed to different gas phase BDE concentration levels among urban, rural, and remote areas. For instance, the average gas phase concentrations of \sum_6 PBDE at Chicago, Sleeping Bear Dunes, and Eagle Harbor were significantly different from each other (all $p < 0.01$). The high PBDE gas phase concentrations near Chicago showed a net PBDE deposition for most of the year except November to January. This observation, an elevated PBDE air-water exchange flux in Lake Michigan adjacent to the urban area of Chicago, agreed with the increased atmospheric PCB deposition into Southern Lake Michigan (Zhang *et al.*, 1999). In contrast, the lower PBDE gas phase concentrations at remote Eagle Harbor resulted in PBDE volatilization throughout the year. Using the Sleeping Bear Dunes air concentrations for the remainder of the lake, either absorption or volatilization of PBDE dominated depending on the time of year.

Aside from air concentrations, temperature also plays a large role in determining the direction and magnitude of net PBDE air-water exchange (Figure 3-2). In Lake Michigan, adjacent to Sleeping Bear Dunes in 2005, the net PBDE air-water exchange flux can be approximately divided into four temporal stages, as shown in Figure 3-2(A). First, the net flux of \sum_6 PBDE approached the state of equilibrium (equality between the flux of gas absorption and volatilization, -0.5 to $1.1 \text{ ng m}^{-2} \text{ day}^{-1}$) in the cold season from January to April. Next, elevated net gas absorption (about 5 to $9 \text{ ng m}^{-2} \text{ day}^{-1}$) occurred while the gas phase concentrations of PBDEs went up in the warmer season from May to mid-June, but water temperature remains relatively cold. Afterwards, a shift in direction of net air-water exchange flux (-1.7 to $1.4 \text{ ng m}^{-2} \text{ day}^{-1}$) occurred while surface water

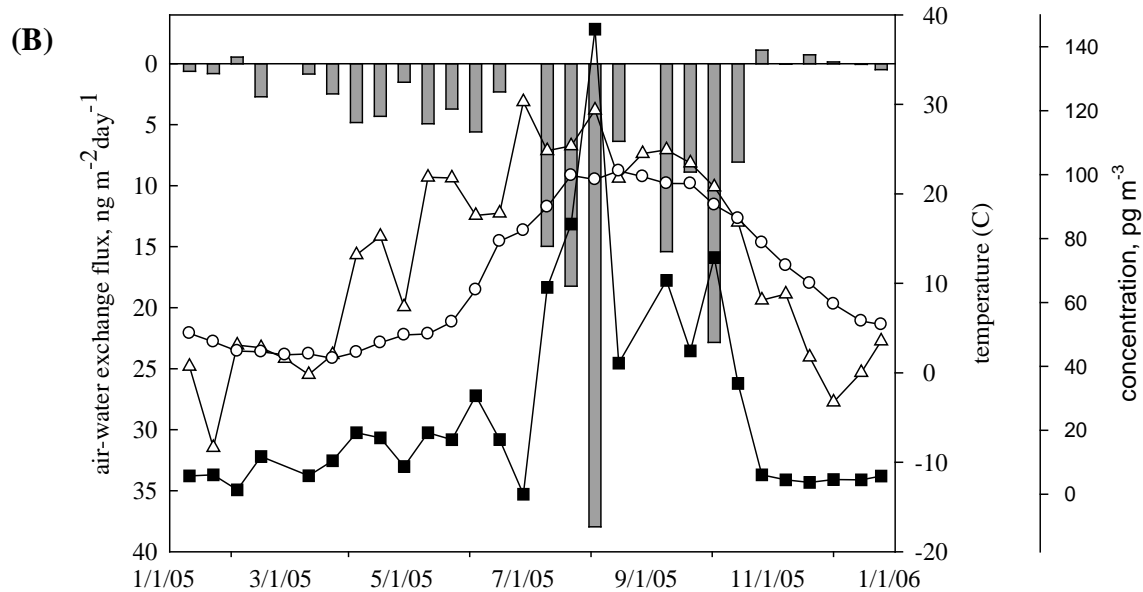
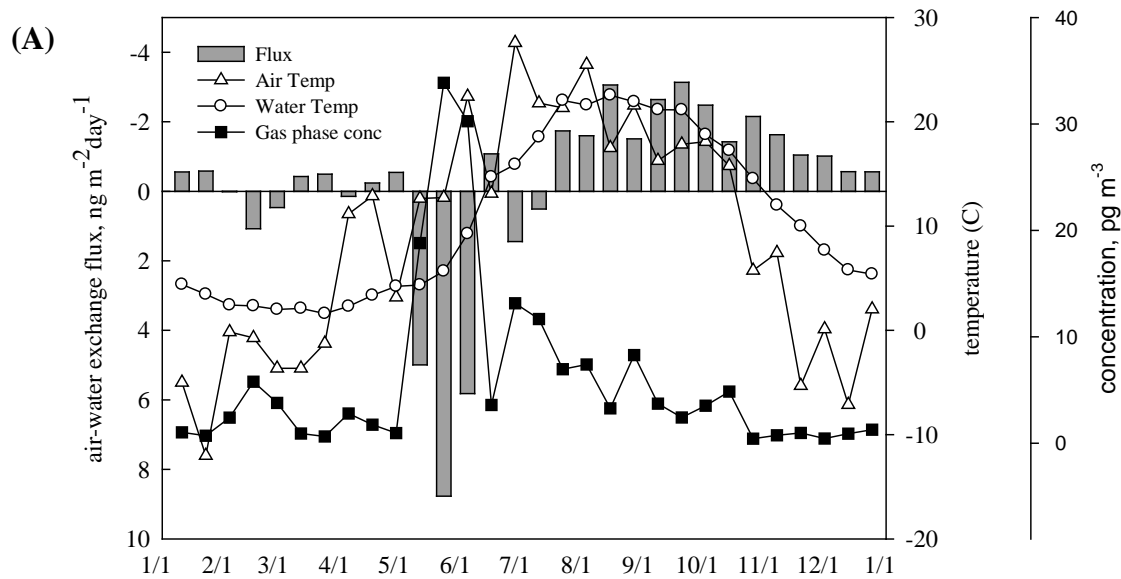
temperatures increased between mid-June and July. Finally, the net volatilization (-0.6 to $-3.1 \text{ ng m}^{-2} \text{ day}^{-1}$) dominated from the end of August to December.

Net PBDE air-water exchange in Lake Michigan adjacent to Chicago also exhibited four stages, as shown in Figure 3-2(B), but the timing and direction differ from the rest of the lake. First, the net flux of $\sum_6\text{PBDE}$ neared a state of equilibrium (-0.5 to $2 \text{ ng m}^{-2} \text{ day}^{-1}$) from January to mid-March. Second, the net flux of $\sum_6\text{PBDE}$ showed net gas absorption with a medium high magnitude (2 to $6 \text{ ng m}^{-2} \text{ day}^{-1}$) from mid-March to mid-June. Third, high gas phase concentrations of $\sum_6\text{PBDE}$ (40 to 140 pg m^{-3}) under high atmospheric temperatures caused a high gas absorption flux (6.4 to $38 \text{ ng m}^{-2} \text{ day}^{-1}$) from July to the end of October. Finally, the net air-water exchange flux of $\sum_6\text{PBDE}$ again approached equilibrium (-1.1 to $0.5 \text{ ng m}^{-2} \text{ day}^{-1}$) from November until December. At Chicago, the seasonal pattern of the net PBDE air-water exchange flux generally followed the pattern of atmospheric temperature. Elevated PBDE gas phase concentrations during warmer seasons caused a higher net atmospheric PBDE deposition. Lower PBDE gas phase concentrations during cold atmospheric temperatures might approach equilibrium.

Compared with Sleeping Bear Dunes and Chicago, the seasonal pattern of net PBDE air-water exchange flux in Lake Superior adjacent to Eagle Harbor was not as temporally distinguishable, as shown in Figure 3-2(C). Most of net PBDE air-water exchange showed volatilization in 2006, but three instances of small net absorption (about $0.2 \text{ ng m}^{-2} \text{ day}^{-1}$) might be driven by unusually high gas phase concentrations of BDE-47. However, these PBDE fluxes can be approximately divided to two temporal stages: net small and net medium volatilization. For example, the air-water exchange of $\sum_6\text{PBDE}$

exhibited net small volatilization (0 to $-0.5 \text{ ng m}^{-2} \text{ day}^{-1}$) while air and surface water temperatures were relatively low from January to June and November to December. In contrast, the PBDE fluxes reached net medium volatilization (-0.5 to $-1.5 \text{ g m}^{-2} \text{ day}^{-1}$) during the warmer ambient environment between July and October.

Besides location, gas phase concentrations, and ambient temperatures, the relationship between wind speed (m sec^{-1}) and the net air-water exchange flux of $\Sigma_6\text{PBDE}$ ($\text{ng m}^{-2} \text{ day}^{-1}$) were examined by Pearson correlation. The results showed positive or negative correlations at three study sites: urban Chicago ($r = 0.29$ and $p = 0.19$), Sleeping Bear Dunes ($r = -0.49$ and $p = 0.01$), and Eagle Harbor ($r = -0.26$ and $p = 0.28$), as shown in Figure 3-3. However, this correlation between wind speed and the net PBDE air-water exchange flux cannot present a simple linear relationship with statistical significance (all $p > 0.01$) because of the non-linear relationship between wind speed and mass transfer coefficients. The other reason is the interference caused by the uncertainty of the equilibrium term, $(C_g - C_d H/RT)$, which could be positive or negative at any given site in a year.



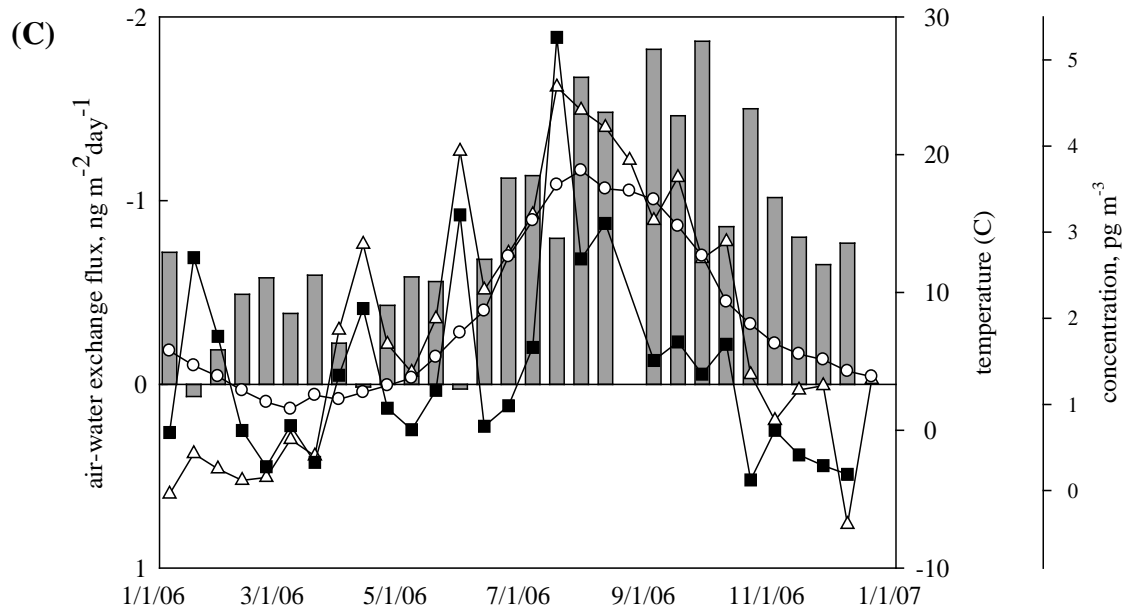


Figure 3-2. Seasonal patterns of net \sum_6 PBDE air-water exchange flux, air temperatures, lake surface water temperatures, and gas phase concentrations at Sleeping Bear Dunes (A), Chicago (B), and Eagle Harbor (C).

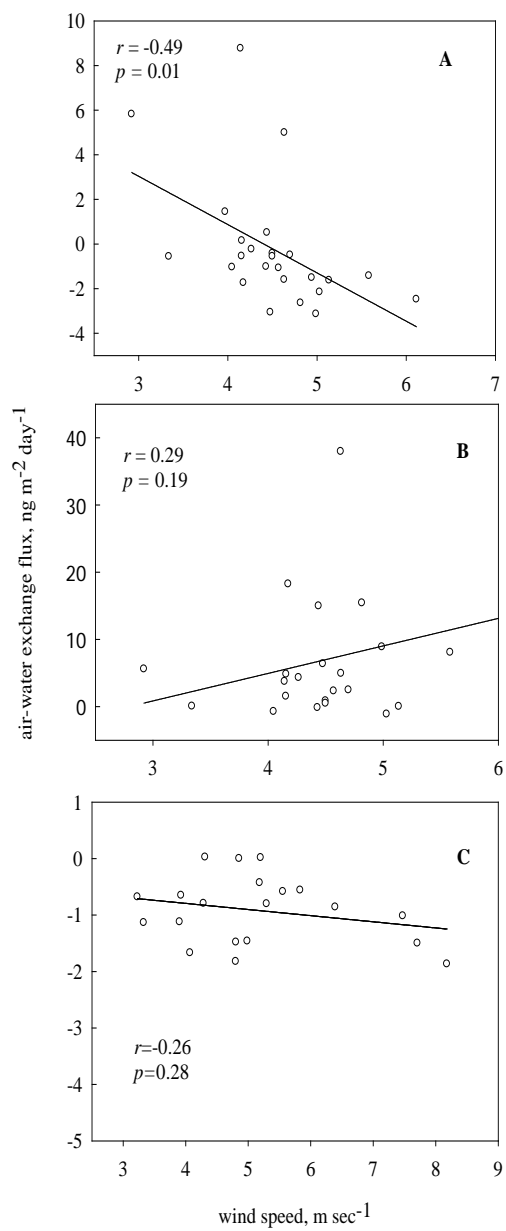


Figure 3-3. The Pearson correlation coefficients between wind speed and the net air-water exchange flux of Σ_6 PBDE at Sleeping Bear Dunes (A), Chicago (B), and Eagle Harbor (C).

PBDE loading from WWTPs. Compiled \sum_6 PBDE loadings from the WWTP discharge volume into the upper Great Lakes is given in Table 3-2. The estimated annual \sum_6 PBDE loadings to Lake Michigan and Lake Superior were 51 and 5.5 kg, respectively. For Lake Michigan, 257 WWTPs' discharge permits were recorded and ranged from $23 \text{ m}^3 \text{ day}^{-1}$ to $2.1 \times 10^6 \text{ m}^3 \text{ day}^{-1}$. Sorted by cities, the Milwaukee metropolitan area was the major contributor of WWTP discharge into Lake Michigan and accounted for about 40% of the total WWTP discharge into Lake Michigan. By states, the states of Wisconsin and Michigan explained 60% and 33% of the total WWTP discharge. Since WWTP discharging ($7.4 \times 10^6 \text{ m}^3 \text{ day}^{-1}$) from the Chicago metropolitan area do not enter Lake Michigan, the PBDE loading to Lake Michigan is greatly reduced.

In Lake Superior, 39 WWTP discharge permits were recorded and ranged from $38 \text{ m}^3 \text{ day}^{-1}$ to $2.6 \times 10^5 \text{ m}^3 \text{ day}^{-1}$. The city of Thunder Bay was the major contributor of WWTP discharge volume into Lake Superior and explained about 47% of the total WWTP discharge into Lake Superior. The state of Minnesota accounted for 45% of the total annual WWTPs' discharge volume. However, since the estimated WWTP discharge volume in this paper was based on the permit value, which was related to the capacity of the treatment facility, the actual WWTP discharge volume may have a lower value. In the Milwaukee metropolitan WWTP case, its actual treated wastewater discharge ranged from 6.5×10^5 to $7.9 \times 10^5 \text{ m}^3 \text{ day}^{-1}$ (in 2005-2009) and was only 31-38% of its permitted discharge. Therefore, the actual annual \sum_6 PBDE loading from WWTP discharge into the upper Great Lakes may have a factor of 0.3 to 1.0 of estimated \sum_6 PBDE loading presented in this study.

Table 3-2. Discharge volume ($\text{m}^3 \text{ day}^{-1}$) and loading (kg yr^{-1}) of $\sum_6\text{BDEs}$ from WWTPs into the receiving water bodies of Lake Michigan and Lake Superior

| state ^a | Lake Michigan | | | | Total |
|-----------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| | IL | IN | MI | WI | |
| numbers of WWTPs | 2 | 29 | 93 | 133 | 257 |
| discharge | 1.5×10^5 | 1.8×10^5 | 1.7×10^6 | 3.1×10^6 | 5.2×10^6 |
| $\sum_6\text{BDEs}$ loading | 1.5 | 1.8 | 17.1 | 30.6 | 51.0 |
| % of loading | 3 | 4 | 33 | 60 | 100 |

| state | Lake Superior | | | | Total |
|-----------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| | MI | WI | MN | Ontario | |
| numbers of WWTPs | 5 | 13 | 20 | 1 | 39 |
| discharge | 2.2×10^4 | 2.4×10^4 | 2.5×10^5 | 2.6×10^5 | 5.6×10^5 |
| $\sum_6\text{BDEs}$ loading | 0.2 | 0.2 | 2.4 | 2.6 | 5.5 |
| % of loading | 4 | 4 | 45 | 47 | 100 |

^a The states or province are labeled as follows: Illinois (IL), Indiana (IN), Michigan (MI), Wisconsin (WI), and Minnesota (MN).

Mass Budgets. Annual mass budgets of $\sum_6\text{PBDE}$ in Lake Michigan in 2005 and Lake Superior in 2006 are given in Figure 3-4. For Lake Michigan, there was a net annual increase of $\sum_6\text{PBDE}$ flux with $270 \pm 71 \text{ kg}$. Wet deposition was the major pathway of $\sum_6\text{PBDE}$ into Lake Michigan and accounted for about 75% of the total annual $\sum_6\text{PBDE}$ mass inputs. The second high input flux of $\sum_6\text{PBDE}$ into Lake Michigan was WWTP discharge ($51 \pm 18 \text{ kg yr}^{-1}$) and it explained about 16% of the total annual $\sum_6\text{PBDE}$ mass inputs. Here, an unanticipated result was that the pathway of the net $\sum_6\text{PBDE}$ air-water exchange flux was low at only $2.3 \pm 7.6 \text{ kg yr}^{-1}$. The reason for this is the air-water exchange flux of $\sum_6\text{PBDE}$ at Sleeping Bear Dunes showed approximate equilibrium or volatilization most of the time in 2005 except for May to July, but it represents 95% of the total Lake Michigan surface area. Nevertheless, the elevated gas absorption of $\sum_6\text{PBDE}$ at urban Chicago, which represents only 5% of the total Lake Michigan surface

area, still resulted in a net absorption of PBDEs to Lake Michigan as a whole.

In Lake Superior in 2006, the comparable fluxes between average \sum_6 PBDE mass inputs (43 kg yr^{-1}) and outputs (37 kg yr^{-1}) exhibited an approximately mass budget balance. Likewise, wet deposition ($31 \pm 7 \text{ kg yr}^{-1}$) was the main contributor of PBDEs input in Lake Superior. Because of the lower population living at the drainage basin of Lake Superior, \sum_6 PBDE flux ($5.5 \pm 1.9 \text{ kg yr}^{-1}$) from WWTPs discharge in Lake Superior was about one tenth of the flux ($51 \pm 18 \text{ kg yr}^{-1}$) from WWTP discharge in Lake Michigan. However, the WWTP discharge into Lake Michigan and Lake Superior contributed similar PBDE fractions of the total PBDE mass inputs, 16% and 13%, respectively. Unlike Lake Michigan, the net air-water exchange flux of \sum_6 PBDE in Lake Superior showed a net volatilization with $15 \pm 4.1 \text{ kg yr}^{-1}$. This volatilization of \sum_6 PBDE accounted for about 50% of the total PBDE mass output in Lake Superior. In the process of PBDE sedimentation, burial PBDE fluxes explained about 90% and 40% of the total PBDE mass outputs in Lake Michigan and Lake Superior, respectively. The lake water outflow of \sum_6 PBDE approximately accounted for about 10% of the total PBDE mass outputs in both lakes.

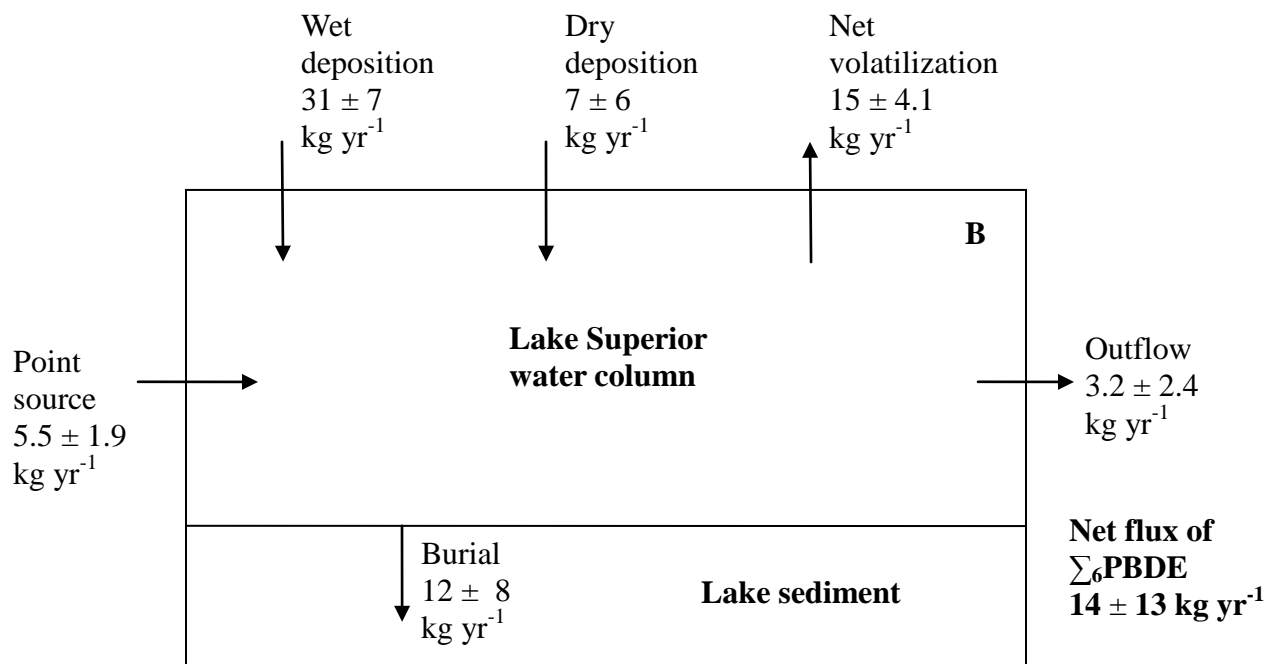
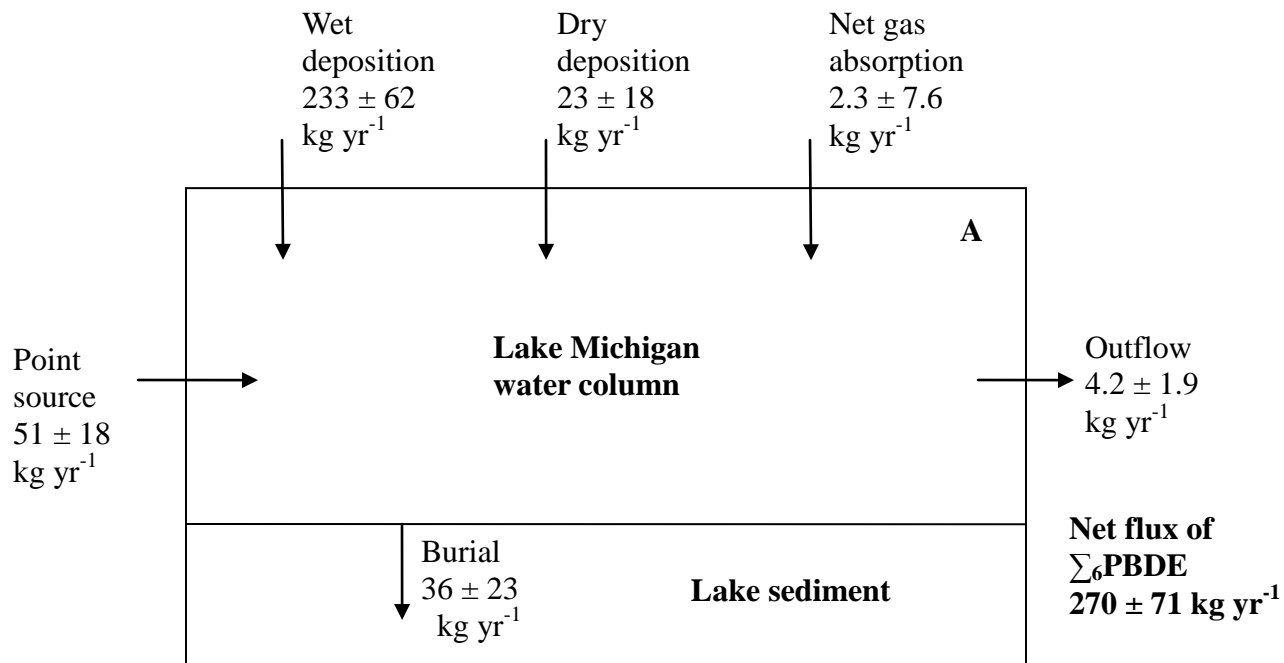


Figure 3-4. Annual mass budget of $\Sigma_6\text{PBDE}$ in Lake Michigan in 2005, (A) in Lake Superior in 2006, (B).

Octa- and deca- BDE compounds, which are higher brominated (8-10 bromines) and have relatively lower vapor pressure than penta-BDEs (Tittlemier *et al.*, 2002), were not counted in the mass budget because they were not quantified in the lake water samples. However, the concentrations of higher brominated BDEs, like BDE-209, were found to be much more enriched than the lower brominated BDEs in rain (Mariani *et al.*, 2008; Venier and Hites, 2008a), waste biosolid from WWTPs (La Guardia *et al.*, 2007), and lake sediment (Song *et al.*, 2004; Song *et al.*, 2005). Therefore, higher brominated BDEs can play a more important role than lower brominated BDEs in the fate of atmospheric dry deposition, surface erosion by storm water runoff, and burial in lake sediments. In order to get a complete picture of PBDE mass budgets in the Great Lakes, higher brominated BDEs should be considered in future studies.

Prediction of PBDE levels in Lake Water. The net annual increase in \sum_6 PBDE mass budget in Lake Michigan in 2005 suggests PBDE concentrations in lake water will increase in the following years, but the actual elevated magnitude is not easy to predict. An annual increase of 270 kg of \sum_6 PBDE in Lake Michigan in 2005 would not entirely correspond to a PBDE concentration increase in lake water. Similar to PCBs, PBDEs are lipophobic and preferably partition to particles and biota within the lake environment (Kelly *et al.*, 2008). Thus, one possible transport destination of net increased PBDEs was through partitioning between the lipid proportion of lake biota and lake water. Zhu and Hites (2004) have reported the PBDE concentrations in fish in the Great Lakes increased exponentially, doubling every 3-4 years. If the 3 years of doubling time for \sum_6 PBDE concentration is assumed, the average \sum_6 PBDE concentrations in lake trout may have an annual increase of about 0.04 to 0.2 mg kg⁻¹ in Lake Michigan based on the PBDE

concentration investigation of Lake Michigan's trout (2002-2004) by Street *et al.* (Streets *et al.*, 2006). In contrast, the net flux of \sum_6 PBDE mass budget in Lake Superior in 2006 was only 14 kg. This result suggests that input and output fluxes of \sum_6 PBDE in Lake Superior were approaching equilibrium. The potential increase of PBDE concentrations in its lake water was very limited in the following year. Even though the whole 14 kg of \sum_6 PBDE stayed in the Lake Superior water, it simply elevated about 1 pg L^{-1} of \sum_6 PBDE.

Further complicating the issue are the changing air and precipitation concentrations. Venier and Hites (2008b) estimated the total air concentrations of BDE-47 and 99 were decreasing with half-lives of about 2 years in the Great Lakes areas during 2005-2006. If this decreasing trend of atmospheric PBDE concentrations can completely translate into a decrease in atmospheric deposition, wet and dry deposition of \sum_6 PBDE may decline to 64 and 10 kg yr^{-1} in Lake Michigan and Lake Superior in 2009-2010, respectively. Therefore, annual PBDE flux from point source inputs may increase their proportion of the total PBDE mass inputs. Then the net annual fluxes in \sum_6 PBDE mass budgets will be 77 and -15 kg for Lake Michigan and Lake Superior in 2009-2010, respectively, if the PBDE fluxes from other pathways are assumed to be same as in the present study (2005-2006). As a result, the \sum_6 PBDE concentrations in lake water should have declined in Lake Superior but still increased in Lake Michigan in 2009- 2010 compared the levels of 2005-2006.

Feasible Approaches Reducing PBDE Loadings. Analyzing the mass budgets of \sum_6 PBDE in the upper Great lakes, atmospheric wet and dry deposition explained more than 80% of the total \sum_6 BDEs inputs. Therefore, reducing sources of PBDEs to atmosphere will efficiently reduce the atmospheric deposition of PBDEs into the lakes.

Phasing out of PBDE commercial formulation and products containing PBDEs should be the most direct strategy to reduce the levels of atmospheric PBDEs. Because point source loading of PBDEs (from WWTPs or landfills) accounted for the rest of PBDE input in the upper Great Lakes, improved removal efficiency of PBDEs in WWTPs' process, volatilization and leaching control of PBDEs in landfills would be helpful to reduce the PBDEs that are dispersed into the environment. Moreover, collecting and treatment in the initial period of storm water runoff should diminish the PBDEs loading into the lakes as well.

3.4 Conclusions

The total water concentrations of \sum_6 PBDE were 53 ± 24 and 44 ± 34 pg L^{-1} (mean \pm SD) in Lake Michigan and Lake Superior, respectively. The average \sum_6 PBDE concentrations in Lake Michigan were about 1.2 times greater than in Lake Superior but it was not a statistically significant difference ($p > 0.05$). Air samples were collected at three sites located by the shores of the upper Great Lakes in 2005-2006. The average total air concentrations (gas and particle phases) of \sum_6 PBDE at Chicago (42 pg m^{-3}) and Sleeping Bear Dunes (9.7 pg m^{-3}) were 14 and 3 times greater than that of \sum_6 BDEs at Eagle Harbor (3 pg m^{-3}), respectively.

Annual mass budget of \sum_6 PBDE for Lake Michigan in 2005 showed a net increase with 270 kg yr^{-1} . Nevertheless, that budget for Lake Superior in 2006 approximately approached a balance. Wet deposition accounted for 71-75% of the total \sum_6 PBDE inputs into the both lakes. The WWTP discharge explained about 10% of the total \sum_6 PBDE inputs. The net air-water exchange flux of \sum_6 PBDE showed small gas absorption (2.3 kg yr^{-1}) in Lake Michigan but volatilization (15 kg yr^{-1}) in Lake Superior.

The general direction of the net \sum_6 PBDE air-water exchange flux was into the lake water column (gas absorption) at urban Chicago but was into the atmosphere (volatilization) at the remote area, Eagle Harbor. At a rural site, Sleeping Bear Dunes, both gas absorption and volatilization of \sum_6 PBDE were exhibited in a year. In addition, the ambient temperature variance in a year will correspond to the direction and magnitude of the net PBDE air-water exchange flux.

We estimated that the net annual fluxes in \sum_6 PBDE mass budgets will be 77 and -15 kg yr^{-1} for Lake Michigan and Lake Superior in 2009-2010, respectively. The contribution of \sum_6 PBDE inputs from atmospheric deposition in the Great Lakes will decrease due to the declining PBDE levels in the atmosphere. However, that contribution from point source input in the Great Lakes may increase. Thus, phasing out of PBDE commercial formulation and products containing PBDEs, and preventing PBDE input from point source are feasible approaches to reduce PBDE loadings in the Great Lakes.

Chapter 4

The Occurrence of the Herbicide Glyphosate and Its Degradate Aminomethylphosphonic Acid in the Atmosphere

The atmospheric transport and fate of glyphosate, the most widely used herbicide in the United States, is not well understood. This is the first study to measure ambient levels of glyphosate and its major degradation product aminomethylphosphonic acid (AMPA) in air and rain in three agricultural areas. Concurrent, weekly integrated air (particle phase and vapor phase) and rain samples were collected during the growing seasons in agricultural areas in Mississippi and Iowa. Only rain samples were collected in Indiana. In air samples, glyphosate and AMPA were detected only in the particle phase. The frequency of glyphosate detection ranged from 61 to 100% (in air) and 63 to 92% (in rain). The concentrations of glyphosate ranged from <0.01 to 9.1 ng m^{-3} and <0.1 to $2.5 \text{ } \mu\text{g L}^{-1}$ in air and rain samples, respectively. The highest concentrations of glyphosate and AMPA in both air and rain were found during the periods of intense glyphosate applications in both Mississippi and Iowa. The frequency of detection, median, and maximum concentration of glyphosate in air were similar or greater to the other high-use herbicides (trifluralin, atrazine, metolachlor) observed in the Mississippi River basin, whereas its concentration in rain was greater than these other herbicides. Additionally, AMPA as a fraction of total glyphosate in air was lower during application seasons and then increased after the last glyphosate applications each year. These changes are due to biodegradation of glyphosate to AMPA in the soil which results in decreasing glyphosate and proportionally increasing AMPA concentrations as the time since last application

increases

4.1 Introduction

Although the use of pesticides in agriculture has significantly increased crop yields, there are concerns about their environmental occurrence and fate (Harner *et al.*, 1999; Tilman *et al.*, 2002; Juraske *et al.*, 2007). Approximately 400 million kilograms of pesticides (A.I., active ingredients) were used in the U.S. in 2001. The agricultural sector accounted for about 76% of this use. Within U.S. agriculture in 2001, herbicides, insecticides, fungicides and other pesticides accounted for 64%, 11%, 6% and 19%, respectively (Kiely *et al.*, 2001).

Some fraction of applied pesticide moves away from the target, and a variety of pesticides have been observed in different environmental media, including natural water bodies, soil, and the atmosphere (Coupe *et al.*, 2000; Capel *et al.*, 2008). In the atmosphere, some semi-volatile persistent pesticides (i.e., dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexanes (HCHs), trifluralin, and metolachlor) have been observed to be transported regionally and to remote areas (MacDonald *et al.*, 2000; Waite *et al.*, 2005; Yao *et al.*, 2006). The extent of the pesticide flux from the landscape to the atmosphere is affected by the amount and method of application, meteorological conditions, and physical-chemical characteristics of the pesticide. Pesticides can be introduced into the atmosphere as spray drift, by volatilization, and by wind erosion of soil with their associated pesticides. The removal of pesticides from the local atmosphere include deposition (wet or dry), photochemical reaction, and advective transport (Foreman *et al.*, 2000; Thurman *et al.*, 2000). In the atmosphere, pesticides are distributed between particle and vapor phases based on the

chemical's vapor pressure, ambient temperature, and concentration of suspended particle matter (Gioia *et al.*, 2005).

Glyphosate (N-(phosphonomethyl) glycine), a broad spectrum, nonselective, and post-emergence herbicide, is the most widely used pesticide in the U.S. (Kiely *et al.*, 2004; Baylis *et al.*, 2000). Genetically modified crops have become increasingly popular since 1996 (James 2004; Dill *et al.*, 2008) and it is estimated that 91% of the soybeans, 22% of the corn, and 23% of the cotton crop hectares in the U.S. were planted as herbicide-tolerant varieties in 2009 (USDA 2009). The popularity of genetically-modified varieties has increased the use of glyphosate. Pure glyphosate is a crystalline solid with high water solubility (12 g L⁻¹) (Franz *et al.*, 1997), low vapor pressure (5.7×10^{-8} Pa at 25°C) (Battaglin *et al.*, 2005) and four pKa's (0.31, 2.6, 5.6 and 10.6) (Smith and Raymond 1988; Sprankle *et al.*, 1975). From a human health perspective, glyphosate is classified as "carcinogenic category E" due to evidence of non-carcinogenicity for humans (USEPA 1993). But, some studies suggested a link between glyphosate exposure and the risk of non-Hodgkin's lymphoma or human placental cell damage (De Roos *et al.*, 2005; Richard *et al.*, 2005).

The mean half-life of glyphosate in soil has been reported as 32 days in forests and row crops (Segawa 1995; Giesy *et al.*, 2000), but varies considerably as a function of microbial activity, pH and temperature (Mallat and Barcelo 1998). In the environment, glyphosate is degraded to aminomethylphosphonic acid (AMPA). The half-life of AMPA is largely unknown, but is thought to be greater than glyphosate because it has been observed to accumulate in soil. Both glyphosate and AMPA have been detected in natural waters near agricultural areas (Vereecken 2005; Peruzzo *et al.*, 2008). However, very

little work has been done on the atmospheric transport of glyphosate. One study reported that air concentrations of glyphosate were below $15.7 \mu\text{g m}^{-3}$ during silvicultural spraying periods (Jauhiainen *et al.*, 1991). Thus, the occurrence and behavior of atmospheric glyphosate is still largely unknown even though glyphosate is the most widely used herbicide in the world (Dill *et al.*, 2008; Duke and Powles 2008).

Glyphosate and AMPA were quantified in the ambient atmosphere of three agricultural areas in the United States (Mississippi, Iowa, and Indiana). Field sampling and laboratory extraction methods for glyphosate and AMPA in air were developed. Concurrent, weekly integrated, air (particle and vapor phase), and rain samples were collected during two growing seasons in Mississippi and Iowa. Rain was collected only during one growing season in Indiana. The field samples and spiked samples in laboratory were used to quantify particle/vapor distribution of glyphosate, the mechanisms of introduction the atmosphere, and their removal efficiency by rainfall. This paper presents the first report of glyphosate and AMPA in the ambient air and rain. An overall mass budget model for glyphosate is developed for the study area in Mississippi. This mass budget model allows for a comparison of the fluxes of glyphosate into and out of the atmosphere to its fluxes to surface and ground waters and its loss due to soil degradation.

4.2 Methods

Sampling Sites. Air and rainfall samples were collected weekly during the crop growing seasons near Pace, Mississippi, and Blairsburg, Iowa in 2007 and 2008. In addition, weekly rainfall samples were also collected near Mohawk, Indiana, in 2004. The major crops grown near the sampling sites at Mississippi, Iowa, and Indiana were

soybean/rice, soybean/corn, and soybean/corn, respectively. Typical growing months for major crops were from March to October in Mississippi and April to September in Iowa and Indiana. The meteorological information during sampling periods was acquired from National Oceanic and Atmospheric Administration National Weather Service (NOAA). The summaries of agricultural activities and meteorological data for the three study areas are presented in the Supporting Material Table 4-1.

Preparation of Sample. Glass-fiber filters (GFFs, 90 mm, GF/F, Whatman), used for collecting atmospheric particle-phase samples, were baked at 550°C for 12 h, cooled to room temperature and wrapped in aluminum foil before use. Polyurethane foam plugs (PUFs, Tisch Environmental, Village of Cleves, OH), used for collecting vapor-phase samples, were washed with Alconox laboratory soap and thoroughly rinsed with deionized water, dried, then rinsed with acetone three times and squeezed to remove the excess. The acetone rinsed PUFs were then extracted with acetone in a Soxhlet apparatus for 24 h, and then with a mixture of acetone:hexane (1:1 by volume) for another 24 h. Finally, the PUFs were placed in a desiccator under a vacuum for 48 h to eliminate any residual solvent. The cleaned PUFs were then placed in clean glass jars, covered with aluminum foil, and capped prior to use.

Table 4-1. Summary of agricultural activities and environmental characteristics of study watersheds near Pace, Mississippi, Blairsburg, Iowa, and Mohawk, Indiana.

| | Mississippi | Iowa | Indiana |
|--|-------------------------|-----------------|-----------------|
| Area of watershed (hectare) | 1,383 | 3,100 | 1,787 |
| Land in row crops (%) | 99 | 97 | 87 |
| Major crops | Soybeans, rice | Soybeans, corn | Soybeans, corn |
| Typical growing season | February to July | April to August | April to August |
| Month of major glyphosate application | February-July | June-July | May-July |
| Glyphosate application rate on one field per time (kg ha ⁻¹ , mean ± S.D.) | 1.05 ± 0.21 | 0.82 ± 0.10 | -- |
| Mean watershed glyphosate application rate during growing season (kg ha ⁻¹ yr ⁻¹) | 2.00 | 0.52 | 0.58 |
| Total annual glyphosate application ^a (kg) in 2007 or 2004 | 2,800 | 1,475 | 1,040 |
| Total annual glyphosate application ^a (kg) in 2008 | 2,750 | 1,719 | -- |
| Method of glyphosate application | Aircraft and Ground rig | Ground rig | Ground rig |
| Mean temperature (°C) (April to September in 2007 and 2008 or 2004) | 25-26 | 18-22 | 22 |
| Accumulative precipitation (mm) (April to September in 2007 or 2004) | 443 | 545 | 661 |
| Accumulative precipitation (mm) (April to September in 2008) | 716 | 1,159 | -- |
| Mean wind speed (m sec ⁻¹) (April to September in 2007) | 2.5 | 4.0 | -- |
| Mean wind speed (m sec ⁻¹) (April to September in 2008) | 2.9 | 3.9 | -- |

^a Glyphosate applications are reported for the watersheds of Tommie Bayou near Pace, Mississippi (USGS site # 07288636), for 2007 and 2008, South Fork of the Iowa River near Blairsburg, Iowa (USGS site # 05451080), for 2007 and 2008, and Leary-Weber Ditch near Mohawk, Indiana (USGS site # 03361638), for 2004. -- Not applicable.

Field Sampling. The air stream inflow of high-volume air samplers (Tisch Environmental, Village of Cleves, OH; Thermo Scientific, Waltham, MA) were mounted at approximately 1.5 m above ground level at the sampling sites. The air samplers were turned on once each hour for a fixed time period (either 5 or 10 min). Each air sample was an integration of air over a seven day period. The air samplers were operated at flow rates from 0.15 to 0.37 m³ min⁻¹. The GFFs and PUFs in the samplers were replaced every Tuesday during the study period and both were stored frozen until extraction in the laboratory. The flow rates of the air samplers were calibrated with a volumetric air flow meter (Roots meter, Dresser, Huston, TX) before and after the sampling. The rainfall samples were collected using modified rainfall samplers, which was covered during dry periods and collected wet deposition only. The rainfall was collected in a Teflon-lined container which drained into a refrigerated, clean, glass carboy. The details of rainfall sampling can be found in Vogel *et al.*, 2008. The weekly-integrated rainfall samples were collected on the same schedule as the air samples.

Extraction. The GFF samples were slowly pulverized inside a 50 mL polypropylene (PP) tube (mixing tube) with a clean, wide, stainless steel drill bit. Next, 20 mL of hydrochloric acid (HCl, pH=2) was added to this mixing tube, which was then capped and placed on a shaker for 21 h. The free solution was decanted into another 50 mL PP tube (composite tube). Ten mL of potassium hydroxide (KOH, pH=11) was then added to the mixing tube which was again shaken for 24 h. The contents of both tubes were filtered through a cellulose nitrate filter (0.45 µm pore diameter, 47 mm filter diameter) under vacuum. The filtered extract was poured into a third, pre-weighed PP tube and weighed again to measure the extract volume. The PUF was extracted by adding

50 mL organic-free water (Millipore, Billerica, MA) into its storage jar. The PUF was squeezed with the bottom of a cleaned glass cylinder and the water decanted into a clean glass jar. This process was repeated three times. The final volume of the aqueous PUF extract was determined by weight. A subsample (approximate 50 mL) of the PUF extract was decanted into a cleaned PP tube and frozen until analyzed. The collected rain sample was filtered through a Supor membrane filter (0.45 μm pore diameter, Pall Corporation, East Hills, NY) and transferred to an amber glass bottle. All of the final extracts from the air and filtered rain samples were shipped on ice to the USGS Organic Geochemistry Laboratory (Lawrence, KS) for glyphosate and AMPA analysis.

Analysis. Glyphosate and AMPA were derivitized with 9-fluorenylmethylchloroformate and then analyzed by Hewlett Packard liquid chromatography/mass spectrometer (HPLC/MS). The HPLC/MS was equipped with automatic on-line solid-phase extraction (SPE) cartridges. A mobile phase gradient from 95% of 5 mM ammonium acetate in reagent water to 100% of acetonitrile was used for LC column elution. The molecular and fragment ions were 390 and 168 for glyphosate, and 332, 110, and 136 for AMPA. Method detection limits (MDLs) were 0.084 and 0.078 $\mu\text{g L}^{-1}$ for glyphosate and AMPA, respectively. More detailed information can be found in Lee *et al.*, 2002 (Lee *et al.*, 2002). The masses (ng) of glyphosate and AMPA from extracted air samples were divided by air sampling volume (m^3) to obtain the air concentrations.

Spiked Recoveries. A spiked recovery experiment was conducted to validate the efficiency of the extraction procedure for glyphosate and AMPA from the GFFs and PUFs. Two clean GFFs and two cleaned PUFs were spiked with a 25 μg of glyphosate and 25

μg of AMPA in aqueous solution (0.5 mg mL^{-1}). The water was allowed to evaporate. The extraction procedures for GFF and PUF were conducted as described above. A spiked recovery experiment was also conducted to validate the efficiency of the sampling procedure for glyphosate and AMPA on the GFFs and PUFs. Two clean GFFs were spiked with $1 \mu\text{g}$ of glyphosate and $1 \mu\text{g}$ of AMPA in aqueous solution (0.01 mg mL^{-1}). A cleaned PUF was mounted in the air sampler downstream of the GFF. The sampler was turned on for 24 h indoors at 25°C (average 186 m^3 of air sampled). The GFF and PUF were removed from the air sampler and extracted as described above.

Quality Assurance/Quality Control. Several field blanks, laboratory procedural blanks, and spiked matrix were measured in this study. Air sample volumes ranged from 300 to $1,000 \text{ m}^3$. A typical GFF extract volume was 50 mL. Since the MDL for glyphosate and AMPA in aqueous solution were about $0.08 \mu\text{g L}^{-1}$, the MDLs for glyphosate and AMPA concentrations for air samples are estimated to be in the range of $0.004\text{--}0.013 \text{ ng m}^{-3}$. The laboratory procedural and field blanks for glyphosate and AMPA masses on GFFs and in PUFs were all $<0.011 \mu\text{g}$. The resulting air concentrations of glyphosate and AMPA in air based on these blanks would be $0.011\text{--}0.036 \text{ ng m}^{-3}$. Therefore, the method reporting limit (MRL) of glyphosate and AMPA in air samples was set at 0.01 ng m^{-3} , and MRL of glyphosate and AMPA in rain samples was $0.1 \mu\text{g L}^{-1}$. The reported concentrations were not blank corrected.

Percentage AMPA of Total Glyphosate. The percentage AMPA from total atmospheric (air and rain) glyphosate is defined as following:

$$\text{AMPA as a percent of total glyphosate in air} = \left[\frac{C_{\text{air AMPA}}}{C_{\text{air glyphosate}} + C_{\text{air AMPA}}} \right] \times 100$$

$$\text{AMPA as a percent of total glyphosate in rain} = \left[\frac{C_{\text{rain AMPA}}}{(C_{\text{rain glyphosate}} + C_{\text{rain AMPA}})} \right] \times 100$$

where:

$C_{\text{air glyphosate}}$: concentrations of glyphosate in air, ng m^{-3}

$C_{\text{air AMPA}}$: concentrations of AMPA in air, ng m^{-3}

$C_{\text{rain glyphosate}}$: concentrations of glyphosate in rainfall, $\mu\text{g L}^{-1}$

$C_{\text{rain AMPA}}$: concentrations of AMPA in rainfall, $\mu\text{g L}^{-1}$

4.3 Results and Discussion

Validation of Extraction Methods. The extraction efficiency recoveries of glyphosate and AMPA from the GFFs were 83% and 101%, and 104% and 122%, respectively. The recoveries of glyphosate and AMPA from the PUFs were 78 and 81%, and 83 and 85%, respectively. These results indicate that both extraction procedures worked acceptably. In the sampling efficiency recovery study, neither glyphosate nor AMPA were detected in the PUF matrix after running the air sampler. The spiked GFF recoveries after running the air sampler were 76 and 138%, and 38 and 42% for glyphosate and AMPA, respectively. The absence of glyphosate and AMPA on the PUF in the laboratory sampling efficiency study was confirmed in the field. The concentrations of vapor-phase glyphosate and AMPA were analyzed with six field PUF samples, chosen because the particle-phase glyphosate concentrations in these samples spanned the range of measured concentrations. Neither glyphosate nor AMPA were detected in any of these selected PUFs, suggesting that glyphosate and AMPA are only in the particle phase in the atmosphere. Therefore, the total glyphosate and total AMPA concentrations in air are equal to their particle-phase concentrations (as measured on the GFF).

Glyphosate Application. Based on interviews with the applicators in the watersheds, glyphosate was applied from February to July in the Mississippi study area and from May to July in the Iowa study area. In Mississippi, the timing and seasonal pattern of glyphosate application was similar for 2007 and 2008 (Figure 4-1). However in Iowa, the glyphosate application was extended one month longer in 2008 compared to 2007 due to very large rain events in late May and early June which delayed planting and herbicide application (Figure 4-2).

Frequency of Glyphosate and AMPA Detection. A total of 87 air and 80 rainfall samples were collected from three agricultural areas in Mississippi, Iowa, and Indiana during the growing seasons of 2004, 2007, and 2008. Glyphosate was observed in >60% of the air and rain samples in at all three sites. AMPA was also observed in >60% of the air samples and usually >50% of the rain samples at all three sites (Table 4-1). The frequencies of glyphosate and AMPA detection in rain were both 92% in Indiana in 2004. No air sample was collected during this part of the study, so no comparison can be made. Both glyphosate and AMPA occurred more frequently in air in Mississippi as compared to Iowa. The frequency of glyphosate and AMPA detection in rain was about the same as in air for Mississippi, whereas in Iowa, the frequency of glyphosate detection in rain was similar to in air, but the frequency of detection of AMPA was less in rain compared to air.

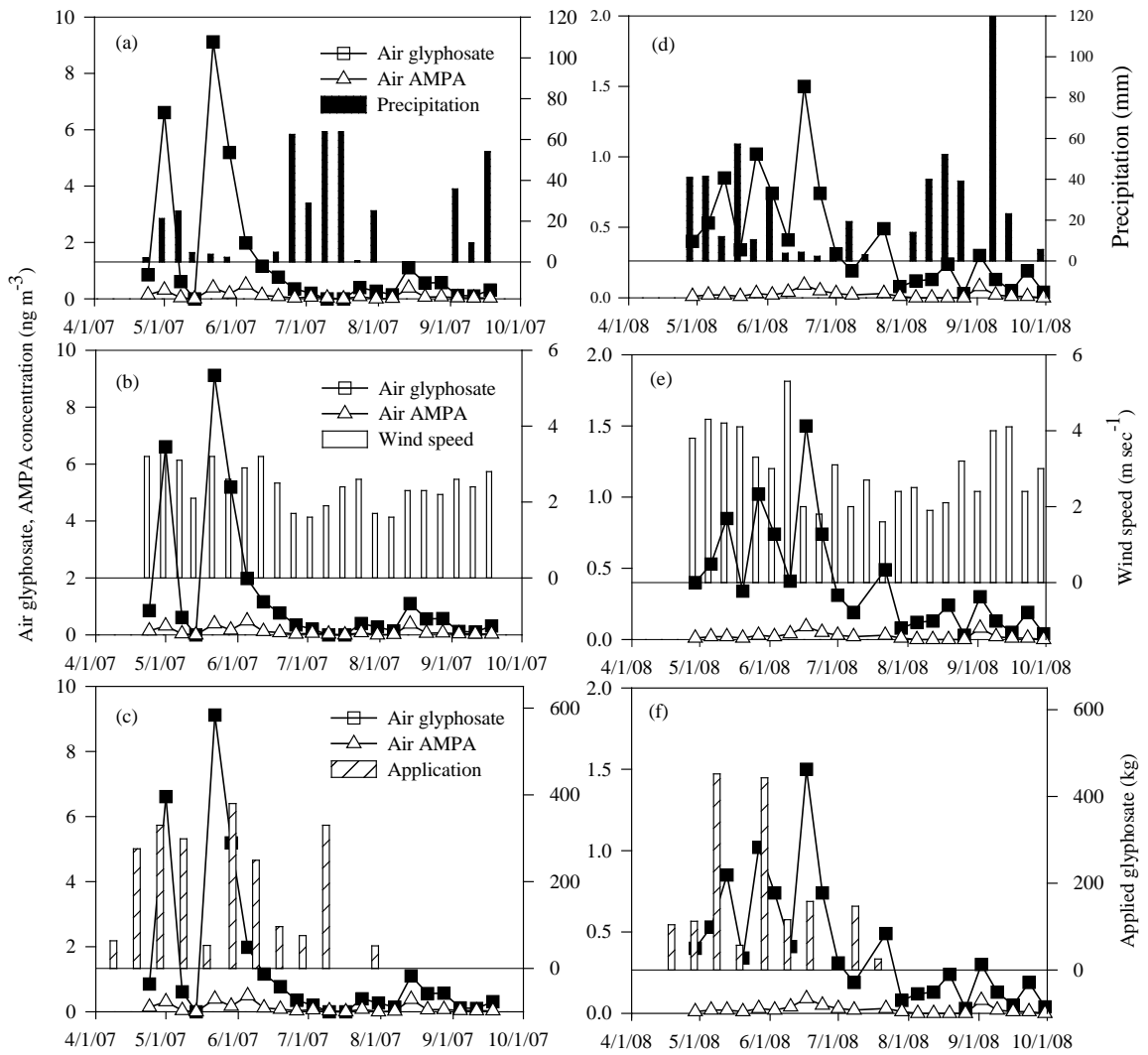


Figure 4-1. Concentrations of glyphosate and (AMPA in air (ng m⁻³), weekly rainfall (mm), wind speed (m sec⁻¹), and applied glyphosate (kg) for the Tommie Bayou watershed near Pace, Mississippi, in 2007 (a, b, and c) and 2008 (d, e, and f)

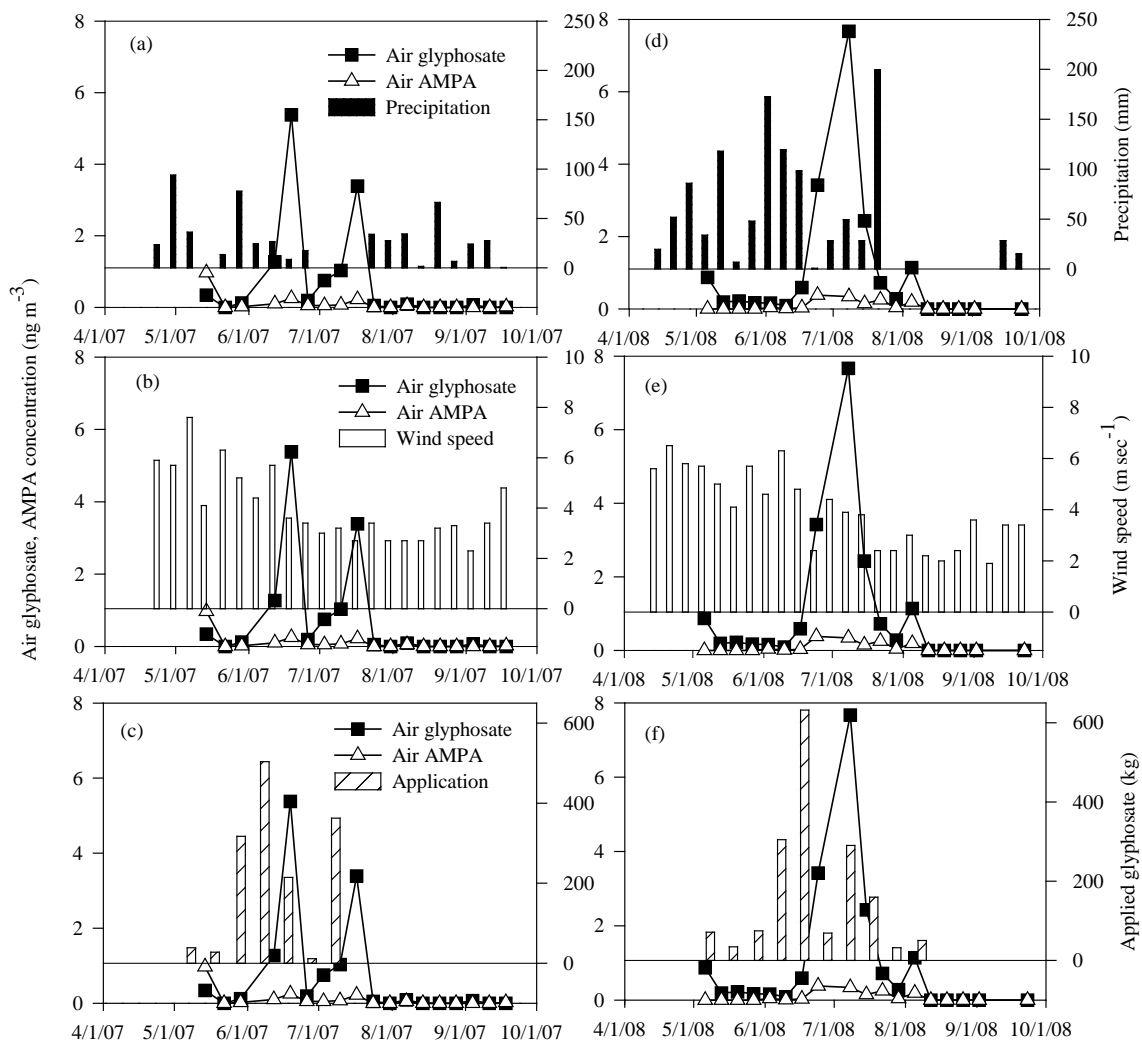


Figure 4-2. Concentrations of glyphosate and (AMPA in air (ng m⁻³), weekly rainfall (mm), wind speed (m sec⁻¹), and applied glyphosate (kg) for the South Fork of the Iowa River watershed at Blairsburg, Iowa, in 2007 (a, b, and c) and 2008 (d, e, and f)

Table 4-2: Concentrations of glyphosate and AMPA in air and rain and AMPA as a fraction of total glyphosate in air and rain near Pace, Mississippi, Blairsburg, Iowa, and Mohawk, Indiana

| Compounds | Statistic | Mississippi: | | Iowa: | | Mississippi: | | Iowa: | | Indiana: |
|----------------------------------|---------------------|--------------|-------|-------|-------|--------------|------|-------|------|----------|
| | | Air | | Air | | Rain | | Rain | | Rain |
| | | 2007 | 2008 | 2007 | 2008 | 2007 | 2008 | 2007 | 2008 | 2004 |
| Glyphosate | Median | 0.48 | 0.24 | 0.08 | 0.22 | 0.20 | 0.15 | 0.20 | <0.1 | 0.14 |
| | Maximum | 9.1 | 1.5 | 5.4 | 7.7 | 1.9 | 1.6 | 2.5 | 1.8 | 1.1 |
| | Minimum | <0.01 | <0.01 | <0.01 | <0.01 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| | SD ^a | 1.8 | 0.36 | 1.4 | 1.9 | 0.57 | 0.39 | 0.72 | 0.47 | 0.32 |
| | % of D ^b | 86 | 100 | 61 | 72 | 73 | 68 | 71 | 63 | 92 |
| | N ^c | 22 | 27 | 18 | 18 | 11 | 19 | 14 | 24 | 12 |
| AMPA | Median | 0.06 | 0.02 | 0.02 | 0.04 | 0.10 | <0.1 | <0.1 | <0.1 | <0.1 |
| | Maximum | 0.49 | 0.09 | 0.97 | 0.38 | 0.30 | 0.48 | 0.20 | 0.24 | 0.47 |
| | Minimum | <0.01 | <0.01 | <0.01 | <0.01 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| | SD | 0.18 | 0.02 | 0.23 | 0.12 | 2.0 | 0.14 | 0.08 | 0.06 | 0.13 |
| | % of D | 86 | 70 | 56 | 61 | 73 | 74 | 36 | 50 | 92 |
| | N | 22 | 27 | 18 | 18 | 11 | 19 | 14 | 24 | 12 |
| AMPA/Total glyphosate | Median | 0.11 | 0.05 | 0.07 | 0.10 | 0.25 | 0.33 | 0.00 | 0.13 | 0.34 |
| | Maximum | 1.00 | 0.22 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| | Minimum | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 |
| | SD | 0.25 | 0.07 | 0.32 | 0.32 | 0.32 | 0.35 | 0.30 | 0.31 | 0.25 |

Concentration units: air: ng m⁻³; rain: µg L⁻¹)

^a SD = standard deviation

^b % OF D = frequency of detection (in percent)

^c N = number of samples

Air concentrations – Mississippi. In 2007, glyphosate and AMPA concentrations in air ranged from <0.01 to 9.1 ng m⁻³ and <0.01 to 0.49 ng m⁻³, respectively (Figure 4-1a). The median concentrations of glyphosate and AMPA in air were 0.48 and 0.06 ng m⁻³, respectively. Two spikes in glyphosate concentration (6.6 and 9.1 ng m⁻³) occurred in May, and a few smaller spikes occurred in July and August. For AMPA, three small concentration spikes (0.31, 0.39, and 0.49 ng m⁻³) occurred from May to June and one occurred in August. In 2008, both glyphosate and AMPA had lower air concentrations than in 2007. The glyphosate concentration in air ranged from <0.01 to 1.5 ng m⁻³, whereas the concentration of AMPA in air ranged from <0.01 to 0.09 ng m⁻³ (Figure 4-1d). The median concentrations of glyphosate and AMPA in air were 0.24 and 0.02 ng m⁻³, respectively. There were four glyphosate concentration spikes from May to July, 2008, and a few smaller AMPA concentration spikes (about 1.0 ng m⁻³) after the middle of July.

Air concentrations – Iowa. In contrast to the Mississippi site, the magnitude and pattern of glyphosate and AMPA concentrations in air in Iowa were more consistent between 2007 and 2008. In 2007, glyphosate and AMPA in air ranged from <0.01 to 5.4 ng m⁻³ and 0.01 to 0.97 ng m⁻³, respectively (Figure 4-2a). The median concentrations of glyphosate and AMPA in air were 0.08 ng m⁻³ and 0.02 ng m⁻³, respectively. Two major spikes in concentrations of glyphosate and AMPA in air occurred in mid-June and mid-July. These correspond to the local period of application in 2007 for soybeans and corn. After July, neither glyphosate nor AMPA were detected at high levels (>0.1 ng m⁻³) in the air. In 2008, glyphosate and AMPA concentrations in air ranged from <0.01 to 7.7 ng m⁻³ and <0.01 to 0.38 ng m⁻³, respectively (Figure 4-2d). The median air glyphosate and AMPA concentrations were 0.22 and 0.04 ng m⁻³. There was a sustained, elevated

concentration ($>0.5 \text{ ng m}^{-3}$) of glyphosate in air from mid-June to mid-July. The application period in 2008 was shifted to a few weeks later as compared to 2007 due to large rain events, flooded fields, and saturated soils that occurred from late May into early June. A few smaller concentration spikes of AMPA in air occurred from mid-June to mid-August. After the end of July, both glyphosate and AMPA in air remained at low concentration levels.

Rain concentrations. In Mississippi in 2007, the glyphosate and AMPA concentrations in rain ranged from <0.1 to $1.9 \mu\text{g L}^{-1}$ and <0.1 to $0.3 \mu\text{g L}^{-1}$, respectively, with median rain concentrations of 0.20 and $0.10 \mu\text{g L}^{-1}$ (Figure 4-3a). A few elevated concentrations ($>1.0 \mu\text{g L}^{-1}$) of glyphosate in rain occurred in May and June (1.4 , 1.9 , and $1.8 \mu\text{g L}^{-1}$), but only one relatively high concentration of AMPA was observed ($0.3 \mu\text{g L}^{-1}$ in early June). In 2008, the glyphosate and AMPA concentrations in rain ranged from <0.1 to $1.6 \mu\text{g L}^{-1}$ and <0.1 to $0.48 \mu\text{g L}^{-1}$, respectively, and with rain median concentrations of 0.15 and $<0.1 \mu\text{g L}^{-1}$. Only one elevated concentration of glyphosate was measured in rain ($1.6 \mu\text{g L}^{-1}$), but there were 3 weeks in July and August in which an elevated concentration of AMPA in rain ($>0.4 \mu\text{g L}^{-1}$) was observed.

In Iowa in 2007, the glyphosate and AMPA concentrations in rain ranged from <0.1 to $2.5 \mu\text{g L}^{-1}$ and <0.1 to $0.2 \mu\text{g L}^{-1}$, respectively (Figure 4-3b) with median concentrations of $0.2 \mu\text{g L}^{-1}$ and $<0.1 \mu\text{g L}^{-1}$. Two elevated glyphosate concentrations in rain (1.6 and $2.5 \mu\text{g L}^{-1}$) were observed in June and July. In 2008, the glyphosate and AMPA concentrations in rain ranged from <0.1 to $1.8 \mu\text{g L}^{-1}$ and <0.1 to $0.24 \mu\text{g L}^{-1}$, respectively with a median concentrations of $<0.1 \mu\text{g L}^{-1}$. One relatively high rain glyphosate ($1.8 \mu\text{g L}^{-1}$) and rain AMPA ($0.2 \mu\text{g L}^{-1}$) occurred in early July, but there was

not significant rain in late June of this year.

Rain samples were collected from April to August in Indiana in 2004. Glyphosate and AMPA in rain ranged from <0.1 to $1.1 \mu\text{g L}^{-1}$ and <0.1 to $0.5 \mu\text{g L}^{-1}$, with median concentrations of 0.1 and $0.1 \mu\text{g L}^{-1}$ (Table 4-2). Two weekly rain samples had elevated concentrations of glyphosate (1.1 and $0.7 \mu\text{g L}^{-1}$, end of April and mid-May). One elevated AMPA concentration in rain ($0.5 \mu\text{g L}^{-1}$) occurred in mid-July.

AMPA as A Fraction of Total Glyphosate in Air. Although AMPA as a fraction of total glyphosate in air ranged from 0 to 100%, the median fractions ranged from 0.05 to 0.11 for both years at both locations (Table 4-2). In general, AMPA as a fraction of total glyphosate in air was lower during application seasons and then increased after the last glyphosate applications each year. These changes are due to biodegradation of glyphosate to AMPA in the soil (Forlani *et al.*, 1999) which results in decreasing glyphosate and proportionally increasing AMPA concentrations as the time since last application increases (Figure 4-4).

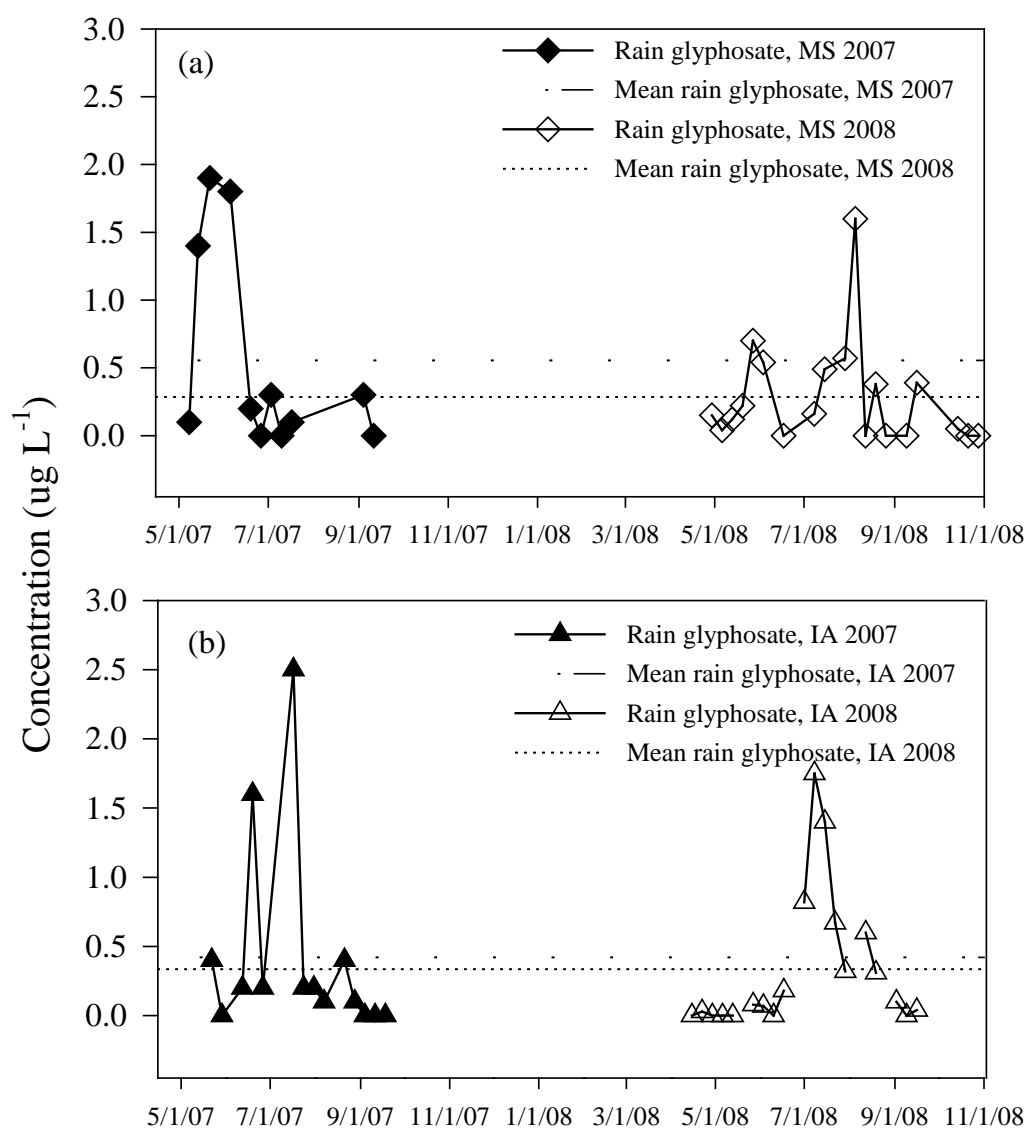


Figure 4-3. Concentrations of glyphosate in rain in 2007 and 2008 in (a) Mississippi and (b) Iowa.

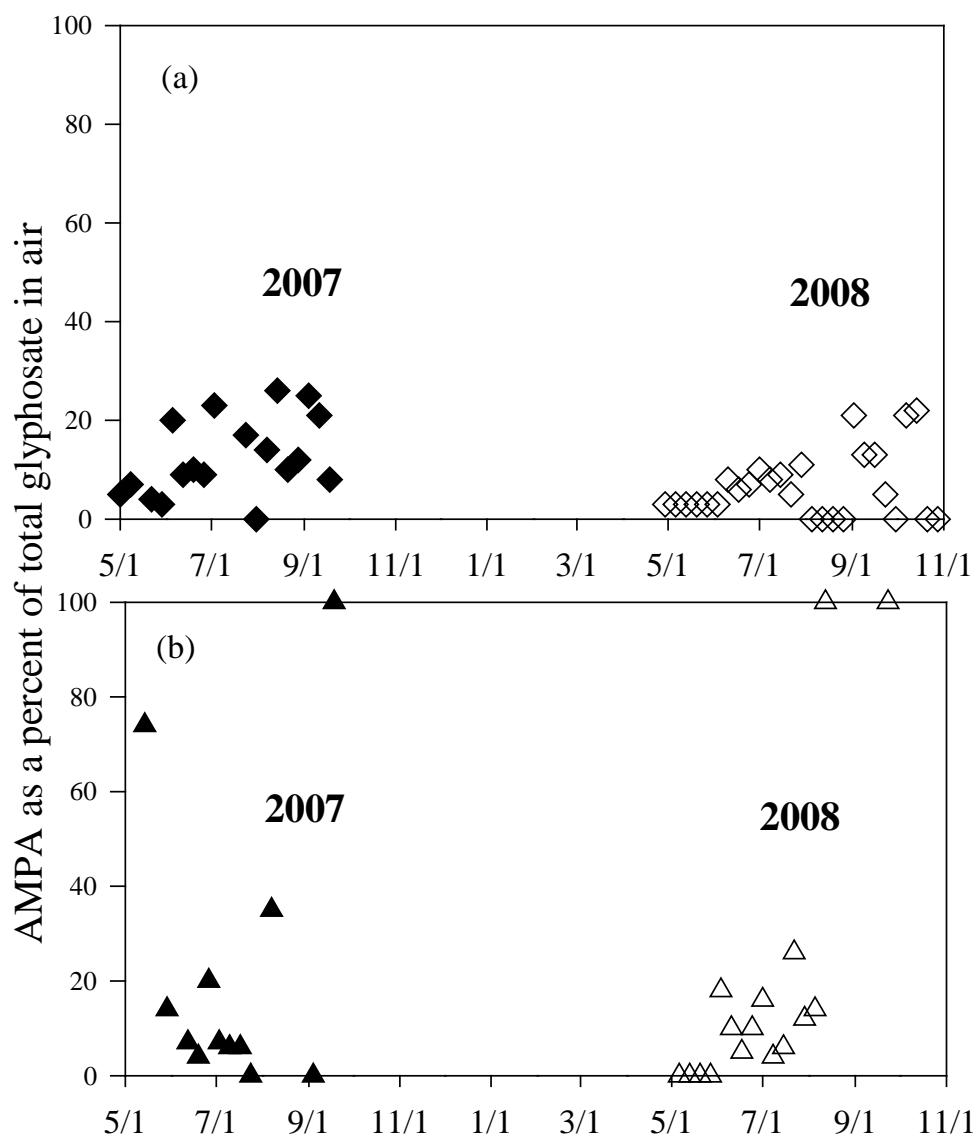


Figure 4-4. AMPA as a percent of total glyphosate in air in (a) Mississippi and (b) Iowa.

Comparison with Other Herbicides. Compared with other current-use herbicides, the frequencies of detection and median concentrations of glyphosate in both air and rain were not substantially different, but maximum concentrations of glyphosate were greater. For instance the frequency of detection in air for glyphosate (61–100%) is similar to other observations for trifluralin (100%), atrazine (67–74%), and metolachlor (81–100%) in the Mississippi River basin (Majewski *et al.*, 2008). The median concentration of glyphosate in air in Mississippi and Iowa (0.26 ng m^{-3}) was comparable to the median concentrations of trifluralin (0.81 ng m^{-3}), atrazine (0.05 ng m^{-3}), and metolachlor (0.21 ng m^{-3}) (Majewski *et al.*, 2008). However, the maximum concentration of glyphosate in air (9.1 ng m^{-3}) was greater than the maximum concentrations of trifluralin (5.5 ng m^{-3}), atrazine (2.8 ng m^{-3}), and metolachlor (1.5 ng m^{-3}). Likewise, the frequency of detection of glyphosate in rain (63–92%) was similar to trifluralin (10–69%), atrazine (75–95%), and metolachlor (94–100%) (Vogel *et al.*, 2008). But, the median and maximum concentrations of glyphosate in rain ($0.10, 2.5 \mu\text{g L}^{-1}$, respectively) were substantially greater than atrazine ($0.02, 0.83 \mu\text{g L}^{-1}$), metolachlor ($0.02, 0.25 \mu\text{g L}^{-1}$), and much greater than trifluralin ($0.01, 0.02 \mu\text{g L}^{-1}$) in rain (Vogel *et al.*, 2008).

Application Rates of Glyphosate. Based on the applicator interviews, the whole-watershed normalized application rate of glyphosate in the Mississippi and Iowa area were 1.97 and $0.52 \text{ kg ha}^{-1} \text{ yr}^{-1}$, respectively (Table 4-1). The higher glyphosate application rate in Mississippi did not correspond to a higher concentration (either maximum or median) of glyphosate and AMPA in air or rain. However, this application difference (around four-fold higher in Mississippi than Iowa) did reflect the higher frequency of glyphosate and AMPA detection in air and rain in Mississippi.

Timing of Glyphosate Application. The highest concentrations of glyphosate and AMPA in both air and rain were found during the periods of intense glyphosate applications in both Mississippi and Iowa. At both study locations, the highest air concentrations were observed in the weeks during the application season when there was little or no rainfall (Figure 4-1, 4-2). These conditions gave a strong source of glyphosate to the air, but no strong removal mechanism from the air. For glyphosate concentrations in rain samples, the intense period of application occurred in June and July in Iowa study area and the peaks also occurred during this same time frame. In contrast to the application pattern in Iowa, the glyphosate application in Mississippi was more uniform over a longer period of time from April to July. Likewise, the peaks of glyphosate concentrations in rain in Mississippi corresponded to the same time period (Figure 4-3).

4.4 Conclusions

Glyphosate and AMPA were detected only in the particle phase in air samples. The highest concentrations of glyphosate and AMPA in both air and rain were found during the periods of intense glyphosate applications in both Mississippi and Iowa. In addition, the higher glyphosate application rate in Mississippi did not correspond to a higher concentration of glyphosate and AMPA in air or rain. However, the longer period of glyphosate application did reflect the higher frequency of glyphosate and AMPA detection in air and rain in Mississippi than Iowa.

The frequency of detection, median, and maximum concentration of glyphosate in air were similar or greater to the other high-use herbicides (trifluralin, atrazine, metolachlor) observed in the Mississippi River basin, whereas its concentration in rain was greater than these other herbicides. Additionally, AMPA as a fraction of total

glyphosate in air was lower during application seasons and then increased after the last glyphosate applications each year. These changes should be due to biodegradation of glyphosate to AMPA in the soil which results in decreasing glyphosate and proportionally increasing AMPA concentrations as the time since last application increases.

Chapter 5

The Fate of the Herbicide Glyphosate and Its Degradate Aminomethylphosphonic Acid in the Atmosphere

There was no simple relation between the weekly integrated concentrations of glyphosate or AMPA in air and weekly wind speed at either Mississippi or Iowa study areas. Based on a mass budget model, the median wind contribution to the total glyphosate in air were similar in 2007 (41%) and 2008 (42%) in Iowa, whereas the modeled median wind contributions were generally lower and different in 2007 (34%) and 2008 (19%) in Mississippi. This result agreed with a higher wind speed (mean \pm SD) in Iowa (4.0 ± 1.4 m sec⁻¹) than in Mississippi (2.7 ± 0.8 m sec⁻¹) during the sampling period. Glyphosate and AMPA were removed from the air by particle scavenging by rainfall; a 30 mm rainfall in a week was estimated to remove >90% of both compounds from air. Their total washout ratios were determined to be in the range of 8.0×10^4 to 5.1×10^6 . Based on annual glyphosate mass budgets for the Mississippi and Iowa study areas in 2007-2008, less than 0.1% of the applied glyphosate moved into the atmosphere due to application spray drift (0.01%-0.05%), and wind erosion (<0.01%-0.02%). Most of the applied glyphosate (96%-99% of the applied glyphosate) degraded in soil by microbiological activity. Wet deposition (0.02%-0.57%) and transport to the streams (0.15%-0.39%) explained the rest of the applied glyphosate. Neither glyphosate nor AMPA was found in ground water samples.

5.1 Introduction

Following the previous chapter that describes glyphosate and AMPA occurrence

in the atmosphere, the fate of glyphosate and AMPA in farm fields are discussed in this chapter. There was no clear relation observed between weekly wind speed and weekly integrated concentrations of glyphosate and AMPA because other factors, like application timing and rain events might interfere the affect of wind erosion. According to field samples and laboratory observation, glyphosate and AMPA were only found in gas phase not in gas phase. Therefore, glyphosate applications spray drift and wind erosion of soil were assumed to be the only two sources of atmospheric glyphosate. In order to solve individual contribution between application and wind erosion, a mass balance model was developed. The model showed the wind erosion of soil may contribute 40% of total air glyphosate in Iowa study area, and about 20-30% of total air glyphosate in Mississippi study site. The results suggest glyphosate in the atmosphere was mainly contributed from application spray drift. Additionally, air glyphosate in Iowa where experienced a higher wind speed showed a higher wind contribution compared with Mississippi.

Besides quantifying the source contribution of atmospheric glyphosate, the removal efficiencies of glyphosate in the air were also determined. Examining the removal percentages of total air glyphosate by rain scavenging and weekly rainfall accumulation, the fitting curves approximately shows a logarithmic relationship. This relationship suggests that small amount or initial period of rainfall was able to efficiently scavenge glyphosate and AMPA from the atmosphere. In addition, wet deposition and total rain washout ratios of glyphosate and AMPA were calculated based on their concentrations in rain and air samples.

Finally, a general picture of annual glyphosate mass flows in study farm fields which includes application spray drift, wind erosion, rain scavenging, transportation to

streams or groundwater, and degradation in soil was present. The results shows less than 0.1% of applied glyphosate went to the atmosphere due to application spray drift and wind erosion. About 0.02-1% of applied glyphosate were found in wet deposition and surrounding streams. More than 96% of applied glyphosate should still stay in soil and be degraded by soil microbes.

The main objective in this chapter is to estimate source contribution and removal efficiency of glyphosate and AMPA in the atmosphere. Additionally, annual mass flows of glyphosate in study farm areas are constructed based on field samples and model estimation.

5.2 Methods

A Mass Balance Model of Glyphosate in The Air. The contribution of glyphosate and AMPA in the air due to application spray drift and wind erosion was estimated using a mass balance model. The model employs a 2,000 m tall column of air with a base of 1 m × 1 m conducting the following assumptions:

- (1) The only two sources of glyphosate to air are spray drift from application and wind erosion of soil with its associated glyphosate. Wind erosion of soil is the only source of AMPA to the atmosphere.
- (2) The transformation (biodegradation) of glyphosate to AMPA occurs only in the soil. There is no photo-oxidation of glyphosate in the atmosphere.
- (3) The ratio of glyphosate concentration in soil to AMPA concentration in soil (S) decreases weekly from 5.1 (first week after application) to 0.1 (12th week after application). This is based on the logarithmic fitting of field observations reported by Grunewald *et al.*, 2001. The wind erosion produces air particles with the same glyphosate

to AMPA ratio as found in the soil.

The input of total glyphosate in the air due application and wind erosion is

$$M_{\text{glyphosate+AMPA}} = M_{\text{application}} + M_{\text{wind}} \quad (5-1)$$

where, $M_{\text{glyphosate+AMPA}}$ is the mass of total glyphosate (glyphosate + AMPA) in the control volume in the air, $M_{\text{application}}$ is the mass of total glyphosate in the control volume of air contributed by application, and M_{wind} is the mass of total glyphosate in the control volume in the air contributed by wind erosion. Therefore,

$$M_{\text{glyphosate+AMPA}} = (C_{\text{air glyphosate}} + C_{\text{air AMPA}}) \times A \times H \quad (5-2)$$

where, $C_{\text{air glyphosate}}$ is the concentration of glyphosate in air (ng m^{-3}), $C_{\text{air AMPA}}$ is the concentration of AMPA in air (ng m^{-3}), A is the base area of air column (1 m^2) and H is the assumed height of air column (well mixed and around low cloud height, 2000 m).

The mass of total glyphosate in air attributed to wind erosion effect is

$$M_{\text{wind}} = (C_{\text{air AMPA}} + (S \times C_{\text{air AMPA}})) \times A \times H \quad (5-3)$$

where S is the ratio of glyphosate to AMPA concentration in the soil at that time step ($C_{\text{soil glyphosate}} / C_{\text{soil AMPA}}$).

$M_{\text{application}}$ is calculated as the difference between $M_{\text{glyphosate+AMPA}}$ and M_{wind} .

The percent contributions of application spray drift and wind erosion to total mass glyphosate in air are obtained by the following equations:

$$\%_{\text{application}} = M_{\text{application}} / (M_{\text{application}} + M_{\text{wind}}) \times 100\% \quad (5-4)$$

$$\%_{\text{wind}} = M_{\text{wind}} / (M_{\text{application}} + M_{\text{wind}}) \times 100\% \quad (5-5)$$

Glyphosate Removal by Rain. Glyphosate and AMPA exist only in the particle

phase in the atmosphere, thus their removal by rain scavenging is very important (Offenberg and Baker 1997). The weekly removal of total glyphosate in air by rain is calculated as:

$$M_{\text{rain}} = (C_{\text{rain glyphosate}} + C_{\text{rain AMPA}}) \times R \times A \times CF_1, \quad (5-6)$$

where $C_{\text{rain glyphosate}}$ is the concentration of glyphosate in rainfall ($\mu\text{g L}^{-1}$), $C_{\text{rain AMPA}}$ is the concentration of AMPA in rainfall ($\mu\text{g L}^{-1}$), R is the total weekly rainfall (mm), A is the area (1 m^2) and CF_1 is a unit conversion factor ($10^3 \text{ ng } \mu\text{g}^{-1}$). From this, the percent of the weekly integrated mass of total glyphosate in air that is removed by rainfall is

$$WR_{\text{rain}} = M_{\text{rain}} / (M_{\text{glyphosate+AMPA}} + M_{\text{rain}}) \times 100\% \quad (5-7)$$

Additionally, the total washout ratios (W_T) of glyphosate and AMPA in air scavenged by rain were calculated by the method presented by Ligocki *et al.*, (1985).

$$W_{T(\text{glyphosate})} = C_{\text{rain glyphosate}} / C_{\text{air glyphosate}} \times CF_2 \quad (5-8)$$

$$W_{T(\text{AMPA})} = C_{\text{rain AMPA}} / C_{\text{air AMPA}} \times CF_2 \quad (5-9)$$

where CF_2 is the conversion factor = $10^3 \text{ ng } \mu\text{g}^{-1} \times 10^3 \text{ L m}^{-3}$

Wet Deposition of Glyphosate and AMPA. The wet deposition (WD, $\mu\text{g m}^{-2}$) of glyphosate and AMPA from the atmosphere (Table5-1) was calculated as:

$$WD_{\text{glyphosate}} = C_{\text{rain glyphosate}} \times R \quad (5-10)$$

$$WD_{\text{AMPA}} = C_{\text{rain AMPA}} \times R \quad (5-11)$$

5.3 Results and Discussion

Wind Speed Effect. All of the AMPA and some fraction of the glyphosate observed in the air are likely due to wind erosion of soil particles. Conceptually then, wind speed should influence their concentrations in the air, but there was no simple relation between the weekly integrated concentrations of glyphosate or AMPA in air and

the mean, maximum, and 95th percentile of the weekly wind speed at either site. There were positive correlations between the mean, maximum, and 95th percentile of the weekly wind speed and the logarithm of both glyphosate and AMPA concentrations in air in Mississippi in 2007, but no correlations for the other sites and years, as shown in Figure 5-1.

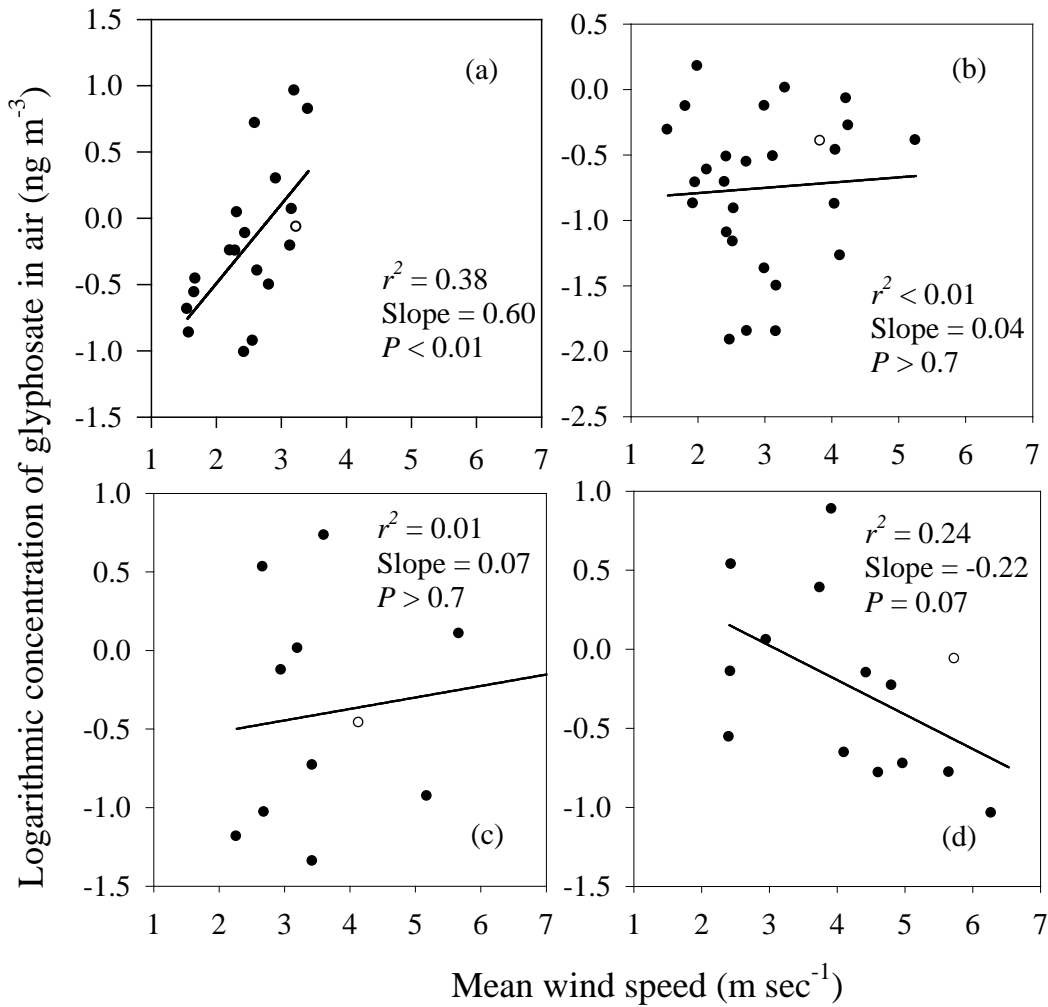


Figure 5-1. Mean wind speed (m sec⁻¹) versus logarithmic concentration of glyphosate in air: (a) Mississippi, 2007 (b) Mississippi, 2008 (c) Iowa, 2007, and (d) Iowa, 2008

For Iowa, the modeled median wind contribution to total glyphosate in air were similar in 2007 (41%) and 2008 (42%), whereas the modeled median wind contributions for Mississippi were generally lower and different for the 2 years (2007: 34% and 2008 19%), as shown in Figure 5-2. The greater contributions from wind erosion to total glyphosate in air in Iowa can be attributed to a higher wind speed (mean \pm SD) in Iowa (4.0 ± 1.4 m sec⁻¹) than in Mississippi (2.7 ± 0.8 m sec⁻¹) during the sampling period.

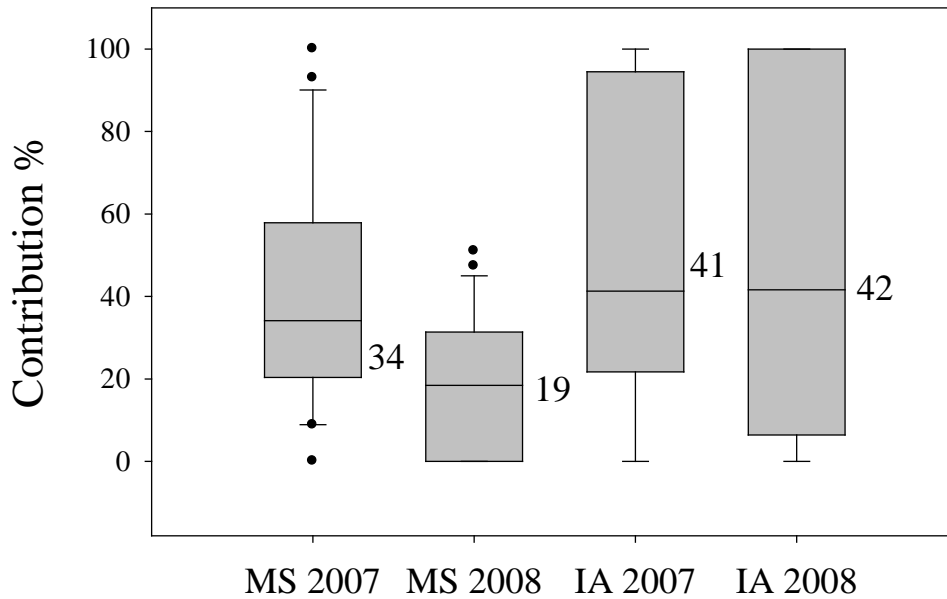


Figure 5-2. Modeled percent of the total mass of glyphosate in air contributed by wind erosion of soil particles in Mississippi (MS) and Iowa (IA), in 2007 and 2008. Within each box, value of median contribution is shown as solid line and number. The 95th, 90th, 75th, 25th, 10th, and 5th percentiles contributions are represented by upper point, upper error bar, upper edge of box, lower edge of box, lower error bar and lower point, respectively.

Rain Removal. Using the concurrent weekly air and rain concentrations of total glyphosate and the weekly rainfall amount, the relationship between weekly rainfall and percent of total glyphosate in air removed by rainfall shows a logarithmic relationship for both Mississippi and Iowa (Figure 5-3). This logarithmic relationship suggests that a very small amount of rainfall was able to efficiently scavenge the glyphosate and AMPA from the atmosphere. Based on the logarithmic fitting of the observed data, 30 mm of cumulative weekly rainfall removes about 90% of total glyphosate from the air. This is not unexpected for a chemical that is completely in the particle phase in the atmosphere.

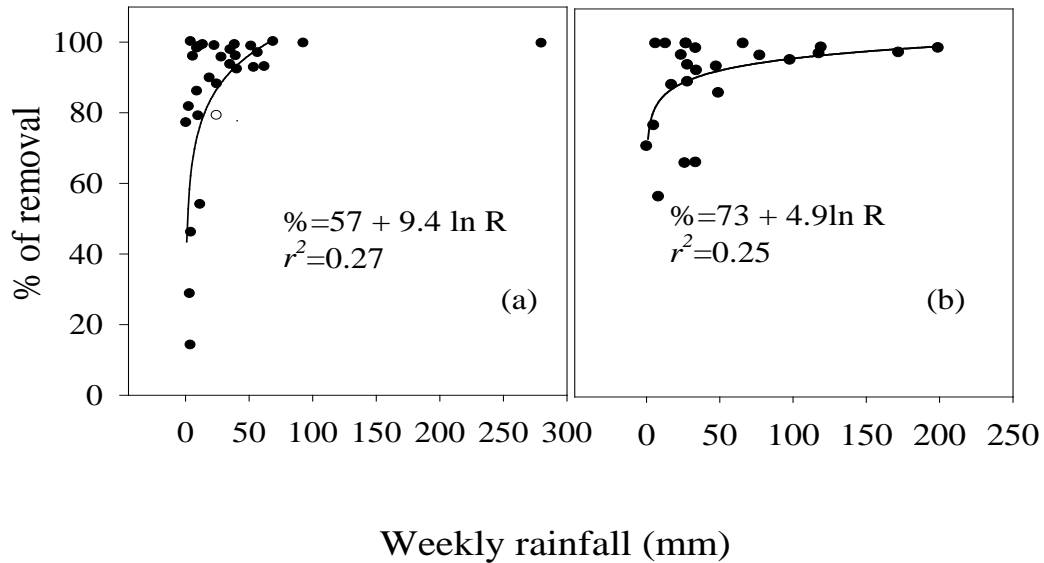


Figure 5-3. Correlation between weekly rainfall amount and percent of total glyphosate in air removed by rain: (a) Mississippi, 2007–2008 (b) Iowa, 2007–2008

Among the two study locations and the 2 years, there were 54 weeks that had paired air and rain samples; 90% of these paired samples yielded W_T values between 8.0×10^4 to 5.1×10^6 for both glyphosate and AMPA. Six pairs had W_T values in the range of 6.6×10^6 to 1.6×10^7 . If these six outliers are not included, the means of W_T for glyphosate were not significantly different between Mississippi (9.9×10^5) and Iowa (9.3×10^5) (t-test, $p=0.87$). Likewise, the means of the W_T for AMPA were not significantly different from Mississippi (2.0×10^6) and Iowa (1.3×10^6) (t-test, $p=0.12$), as shown in Table 5-1.

Table 5-1. Wet deposition and total washout ratios ($\times 10^6$) of glyphosate and AMPA from the atmosphere near Pace, Mississippi, and Blairsburg, Iowa

| Year | Mississippi | | Iowa | |
|-------------------|---|----------------|-----------------|----------------|
| | Glyphosate | AMPA | Glyphosate | AMPA |
| | Wet deposition ($\mu\text{g m}^{-2}$, mean \pm SD) | | | |
| 2007 ^a | 3.9 \pm 4.1 | 2.1 \pm 3.2 | 5.1 \pm 7.3 | 1.7 \pm 3.9 |
| 2008 ^b | 5.5 \pm 7.6 | 5.2 \pm 11 | 16 \pm 35 | 2.4 \pm 5.0 |
| | Total washout ratio (mean \pm SD) | | | |
| 2007–2008 | 0.99 \pm 0.24 | 2.0 \pm 0.33 | 0.93 \pm 0.94 | 1.3 \pm 0.94 |
| number of samples | 16 | 13 | 14 | 10 |

^a: sampling dates in 2007: Mississippi: 4/17–9/18; Iowa: 4/17–9/18

^b: sampling dates in 2008: Mississippi: 4/22–10/28; Iowa: 4/8–10/28

These calculated W_T for glyphosate and AMPA (8.0×10^4 to 5.1×10^6) are one to two orders of magnitude higher than for the C_{13} - C_{16} n-alkanes, which are also observed to be 100% in the particle phase in the atmosphere ($W_T = 1.5 \times 10^4$ - 2.3×10^4 , Ligocki *et al.*, 1985). The observed difference of washout ratios between glyphosate and AMPA and the n-alkanes can be attributed to the different sampling approaches (W_T for glyphosate and AMPA are based on weekly integrated air and rain samples whereas the n-alkanes are

based on single storm event air and rain samples), and meteorological conditions (rainfall intensity and duration).

In Pace, Mississippi, the total wet deposition of glyphosate during the growing seasons was 0.60 and 1.5 kg in 2007 and 2008, respectively. For AMPA, the total wet deposition was 0.52 and 1.3 kg in 2007 and 2008, respectively. The total wet deposition of glyphosate equaled 0.02 and 0.05% of the mass of glyphosate applied in the watershed in 2007 and 2008, respectively. Although, the total amount of glyphosate applied to the watershed in Mississippi were about same in 2007 and 2008 (2,700 kg A.I.), the total wet deposition in 2008 for both glyphosate (2.4 fold) and AMPA (2.5 fold) was greater because of more rainfall (Table 4-1).

In Blairsburg, Iowa, the total wet deposition of glyphosate during the growing seasons was 2.2 and 9.9 kg in 2007 and 2008, respectively, whereas the total wet deposition of glyphosate AMPA was 0.72 and 1.5 kg in 2007 and 2008, respectively. The total wet deposition of glyphosate equaled 0.15 and 0.58% of mass of glyphosate applied in the watershed in 2007 and 2008, respectively. The total amount of glyphosate applied to this watershed was 1,500 kg A.I. in 2007 and 1,700 kg A.I. in 2008. The total wet deposition was greater for both glyphosate (4.5 fold) and AMPA (2.0 fold) in 2008 than in 2007. This can be attributed to more rainfall and a greater glyphosate application rate in 2008 than in 2007 (Table 4-1).

Mass Budgets of Glyphosate. When glyphosate, or any pesticide, is applied to a field, there are limited number of processes that control its behavior and fate. Some pesticides may not reach the soil and remain in air (spray drift). Once on the soil, some glyphosate can undergo biodegradation to AMPA and eventually be mineralized and

some can be introduced into the atmosphere from the wind erosion of soil particles. Some can be taken up by the plants and some can move off the field to surface or ground waters. In the air, glyphosate can be deposited on the soil through either dry particle deposition or rainfall scavenging. Since there was no vapor-phase glyphosate found, vapor dissolution into the rain is not a loss mechanism from the atmosphere. Based on the literature, photo-degradation of glyphosate is also unlikely (Rueppel *et al.*, 1977).

An annual mass budget was estimated from field observations and modeling results reported here to quantify the importance of the atmosphere to the overall fate of glyphosate for the Tommie Bayou watershed near Pace, Mississippi, in 2007 (Figure 5-4). The mass of glyphosate introduced into the atmosphere from application spray drift and the erosion of soil particles was estimated to be about 0.02 and <0.01% of the applied glyphosate, respectively. The mass measured in wet deposition was nearly equal (0.02% of application). Most applied glyphosate was estimated to biodegrade in the soil (>98% of application using a half-life of 20 days). Coupe *et al.*, (2010 in review) estimated that 0.15% of the applied glyphosate moved into streams, and there was no evidence from the field samples that glyphosate moved to the ground water. Annual mass budgets for the study areas in Mississippi in 2008 and Iowa in 2007-2008 are shown in Table 5-2.

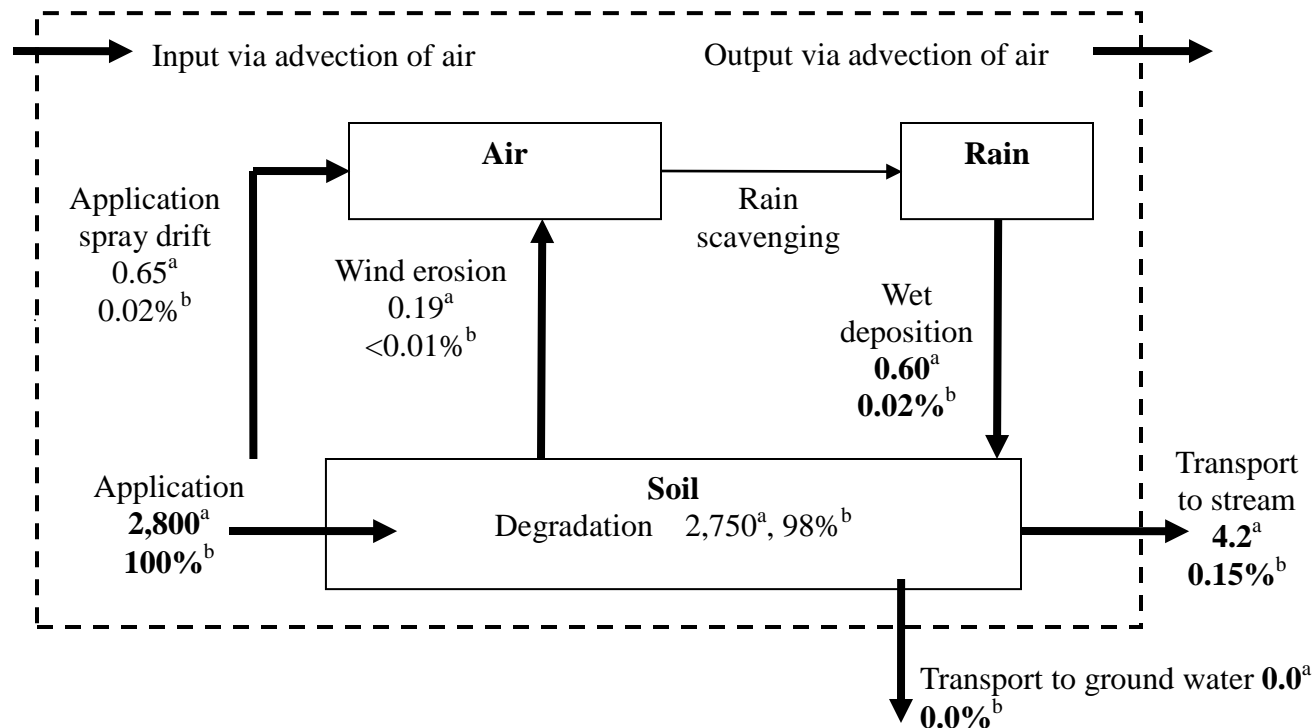


Figure 5-4. Annual mass budget of glyphosate in the Tommie Bayou watershed near Pace, Mississippi, for 2007.

Then numbers present the ^(a) annual loads of glyphosate (kg yr⁻¹) through each of the pathways and ^(b) percentage of applied glyphosate (%). The values in bold type are based on field measurements; the values in regular type are based on model estimates. The solid arrows represent the transport arrows. The solid boxes represent environmental compartments that can store (at least temporarily) glyphosate. The dashed box represents the area of the Tommie Bayou watershed from the bottom of the root zone to the cloud level in the atmosphere. In order to calculate the percent of application for each transport arrow, the assumption is made that the input via

advection in air is equal to the output via advection in air. The premise of this assumption is based on the short residence time of the air over the watershed compared to all of the other transport processes and that there is a large agricultural area surrounding Tommie Bayou that receives similar amounts of glyphosate, so that the regional concentration is the same as above the Tommie Bayou watershed.

Table 5-2. Mass budgets of glyphosate at watersheds of Tommie Bayou near Pace, Mississippi, and South Fork of the Iowa River near Blairsburg, Iowa

| kg yr ⁻¹ | Mississippi | | Iowa | |
|---------------------------|-------------|-------|-------|-------|
| | 2007 | 2008 | 2007 | 2008 |
| Glyphosate application | 2,800 | 2,750 | 1,475 | 1,719 |
| Wet deposition | 0.60 | 1.45 | 2.20 | 9.85 |
| Application spray drift | 0.65 | 0.21 | 0.59 | 0.81 |
| Wind erosion | 0.19 | 0.05 | 0.20 | 0.37 |
| Soil degradation | 2,750 | 2,718 | 1,430 | 1,645 |
| Transport to stream | 4.2 | 10.6 | 2.5 | 3.2 |
| Transport to ground water | 0 | 0 | 0 | 0 |

5.4 Conclusions

There was no simple relation between the weekly integrated concentrations of glyphosate or AMPA in air and weekly wind speed at either Mississippi or Iowa study areas. This suggests that atmospheric glyphosate and AMPA were influenced by not only wind speed but also other factors. In Iowa study area, the modeled median wind contribution to total glyphosate in air were similar in 2007 (41%) and 2008 (42%), whereas the modeled median wind contributions for Mississippi study area were generally lower in 2007 (34%) and 2008 (19%). This result agreed with a higher average wind speed in Iowa ($4.0 \pm 1.4 \text{ m sec}^{-1}$) than in Mississippi ($2.7 \pm 0.8 \text{ m sec}^{-1}$) during the sampling period. Air glyphosate and AMPA were removed effectively by rainfall; a 30 mm rainfall in a week was estimated to remove >90% of both compounds from air. Based on annual glyphosate mass budgets for Mississippi and Iowa study areas in 2007 and 2008, less than 0.1% of the applied glyphosate moved into the atmosphere due to application spray drift (0.01%-0.05%), and wind erosion (<0.01%-0.02%). About

96%-99% of the applied glyphosate degraded in soil by microbiological activity. Wet deposition (0.02%-0.57%) and transport to streams (0.15%-0.39%) explained the rest of the applied glyphosate. Neither glyphosate nor AMPA was transported into ground water.

Chapter 6

Conclusion

6.1 Finding

Difference between PBDEs and Glyphosate. Since PBDEs and glyphosate are very different in physical-chemical characteristics, use scenarios, applied products, and toxic potentials, these differences can cause their different occurrence, fate, and concerns in the environment. PBDEs are semi-volatile and hydrophobic organic chemicals but glyphosate is a much less volatile and relatively water soluble organic compound. Comparing the major differences of physical-chemical characteristics between PBDEs and glyphosate, vapor pressure of glyphosate is about 3% of PBDEs' (at 25°C), and water solubility of glyphosate is a 6-7 order higher than PBDEs'. Additionally, the log of the octanol- water partition coefficient (K_{ow}) for glyphosate is a factor of 8-12 lower than PBDEs'.

For use scenario, glyphosate is the currently most used herbicide ingredient in the world and its use has been continuously increasing since 1997. In contrast, PBDE chemicals were added in electronic or upholstery products to reduce fire incidents since the 1980', but their use has been declined while penta- and octa BDE commercial formulation were phased out in 2004. The only currently used PBDE product, deca-BDE (BDE-209), may also be phased out in 2012. However, environmental PBDEs are still ubiquitous because many products containing PBDEs are still in use or discarded in the environment.

Atmospheric Occurrence. Due to its very low vapor pressure, glyphosate in the atmosphere was only found in the particle phase. Besides, the concentration levels of air glyphosate in farms were related to glyphosate application and rain events. In contrast,

PBDEs in the gas phase above the Great Lakes presented more than 90% of the total air PBDE concentrations. The total PBDE concentrations in air were strongly affected by the urbanization and atmospheric temperature. Furthermore, since glyphosate is currently used but penta-BDEs were phase out in 2004, the maximum concentrations of air glyphosate found in this study were about 40 fold greater than that of air PBDEs' in the Great Lakes. For total rain washout ratios, the ratios of glyphosate were greater 2-70 folds than PBDEs estimates. These higher washout ratios in glyphosate can be attributed to greater air particle phase fraction (almost one) of glyphosate than PBDEs' (0.05-0.1).

Atmospheric Deposition. Gas absorption and wet deposition were the dominant PBDE inputs to the Great Lakes. These PBDE inputs to lake water were influenced by both spatial locations and temperature variances. Atmospheric deposition of PBDEs at nearby urban areas was present greater net gas absorption than rural or remote areas. The net air-water exchange flux of PBDEs also showed net gas absorption around summer and fall (hotter seasons) but net volatilization or close to equilibrium at winter and spring (colder seasons). Unlike PBDEs, since glyphosate in the atmosphere was only present in particle phase, wet and dry deposition of glyphosate should be the major mechanisms to remove glyphosate from air. Although the current data cannot exam how far air glyphosate transports away the target site, the ability of horizontal transportation in the atmosphere should be limited.

6.2 Impacts

Environment. In annual mass budgets of PBDEs in the Great Lakes, wet deposition was the major input source. Burial of lake sediments or volatilizations of PBDEs were major PBDE outputs from lake water. This net increase of PBDEs in lake

water might accumulate in lake biota through food web because of its higher K_{ow} . In contrast, most applied glyphosate may stay or be degraded in soil. Only less than 1% of applied glyphosate will be moved to air, rain, or surrounding streams. However, will the continuously increasing usage of glyphosate cause the spread of glyphosate resistant weed or eutrophication in nearby water bodies? These possibilities should be taken into account in the future.

Public Health. Exposure to high levels of PBDEs is the major public health concern. When PBDE levels in the atmosphere and point sources of PBDEs into lakes are diminished, PBDE exposure to humans from lakes will also decline. According to an assessment from Integrated Risk Information System (IRIS), USEPA, the oral reference dose is 10^{-4} mg/kg-day for BDE-47. That is about 0.05 mg ingestion of BDE-47 for a person weighing 70 kg per week. Additionally, the Minnesota Department of Health has advised that people can safely eat one meal of lake trout whose size is less than 10 cm in Lake Superior per week (fish consumption advisory). This would correspond to between 0.01 and 0.05 mg of BDE-47 exposure based on the PBDE concentration of Lake Michigan's trout (2002-2004) reported by Streets et al. (Streets et al., 2006). Although BDE-47 exposure from lake fish consumption referenced above is not greater than oral reference of IRIS, people may still exceed the suggested oral PBDE reference while they eat lake fish under the advice but also receive exposure from other pathways such as house dust with high levels of PBDEs.

Due to its lower toxicity, there is no published exposure reference of glyphosate. The public health concern of glyphosate is human exposure under an intense application or accidental oral ingestion. Although more than 98% of applied glyphosate will be

degraded in farm soil based on our estimates, the large amount of glyphosate that is applied may be still influence the environment. For instance, the Pesticide Illness Surveillance from the California Environmental Protection Agency has shown glyphosate-related incidents rank as one of the highest reports of currently used pesticides (California Department of Pesticide Regulation). Thus human exposure during an intensive glyphosate application event should be prevented. Additionally, the increasing usage of glyphosate may cause eutrophication in nearby water bodies. This eutrophication can deteriorate water quality and affect the health of biota in surrounding streams or lakes. Finally, due to an uncertain toxicity of surfactants in glyphosate herbicide, the impact of the surfactants on the environment and human health should be studied in the future.

6.3 Future Studies

PBDEs. First, the surface water samples should be taken at different sites to monitor current PBDE levels in the Great Lakes. This trend of PBDE concentrations in lake water can be compared with the trend of PBDE concentrations in lake fish. This comparison should be able to provide useful information about PBDE bioaccumulation between lake water and lake fish. Additionally, atmospheric deposition of PBDEs in the dominant pathway in the Great Lakes based on the mass budget results. Thus, reducing emission of urban PBDEs into the atmosphere will diminish PBDE loading in the lakes. Besides phasing out of PBDE products, if other environmental management policy may be significant to reduce PBDE emission to the atmosphere? For example, recycle policy of waste product containing PBDE chemicals, appropriate disposal sites for waste biosolid sludge from WWTPs, and prevent open dumping burning may be able to reduce

PBDE emission to the atmosphere. Finally, due to the declining PBDE concentrations in the atmosphere, point source of PBDEs from WWTPs or stormwater runoff may become an important role. Thus, the methods to eliminate PBDE concentrations in point sources before entering the lakes may be a significant topic in the future.

Glyphosate. First, air and rain samples may be collected continuously in 12-24 hrs before and after a rain or application event. Then the results can better elucidate the variation of air glyphosate affected by rain and application events, individually. Since air concentrations of glyphosate in this study were presented as weekly-integrated, rain and application events in a same week might have confounded the occurrence of air glyphosate. For instance, the total washout ratios of glyphosate can be calculated based on a single rain event rather than using weekly accumulated rain amounts. Additionally, the influential scale of applied glyphosate in farms is not clear yet. Does an intense application of glyphosate in farms affect air glyphosate levels at nearby cities? However, the answer may involve multiple factors, such as meteorological conditions, application tools, frequencies and amounts of application. Finally, dry deposition estimation of glyphosate should be conducted in farms. The data of dry deposition flux will fill out the gap of this present glyphosate study. The dry deposition should be a significant pathway to remove glyphosate from air because air glyphosate is present only in particle phase. Table 6-1 summarized a qualitative comparison between PBDEs and glyphosate in the environment.

Table 6-1. The qualitative comparison between PBDEs and glyphosate in the environment

| | PBDEs in lakes | Glyphosate in farms |
|---|---|--|
| Current finding and concern | | |
| Dominant phase | Gas | Particle |
| Major influential factor | <ol style="list-style-type: none"> 1. Ambient temperature 2. Urbanization | <ol style="list-style-type: none"> 1. Application events 2. Rain events |
| Major removal mechanism | <ol style="list-style-type: none"> 1. Wet deposition 2. Gas absorption | <ol style="list-style-type: none"> 1. Wet deposition 2. Dry deposition |
| Influential distance | Long range | Locally |
| Environmental concern | Bioaccumulation | <ol style="list-style-type: none"> 1. Glyphosate resistant weed 2. Eutrophication |
| Public health concern | Lake fish consumption | Human exposure study |
| Future trend and concern | | |
| | PBDEs in lakes | Glyphosate in farms |
| Air concentration | Declining | Increasing |
| Concentrations in lake water or streams | Concentrations may still increase in Lake Michigan but decrease in Lake Superior in 2009-2010 | Concentrations may increase in water bodies nearby glyphosate application areas |
| Research interests | <ol style="list-style-type: none"> 1. Lake water monitoring 2. Prevent urban emission to the atmosphere 3. Reduce loading from point sources | <ol style="list-style-type: none"> 1. Single rain and application event 2. Spatial influence 3. Dry deposition estimation |

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Appendix A: Air-water exchange fluxes of PBDEs

A-1: Analyzed mass (ng) of six PBDE congeners in field blank samples

| medium, matrix | BDE-47 | BDE-66 | BDE-100 | BDE-99 | BDE-154 | BDE-153 | Σ_6 PBDE |
|---|-----------------|--------|---------|-----------------|---------|---------|-----------------|
| Lake Michigan in May in 2005 | | | | | | | |
| Air, XAD-2 | nd ^a | nd | 0.213 | 0.304 | nd | nd | 0.517 |
| Air, GFF | 0.118 | nd | nd | 0.096 | nd | nd | 0.214 |
| Water, XAD-2 | | | | na ^b | | | |
| Water, GFF | 1.040 | nd | nd | 1.866 | nd | nd | 2.906 |
| Lake Michigan in July in 2005 | | | | | | | |
| Air, XAD-2 | 0.636 | 0.038 | 0.078 | 0.881 | nd | nd | 1.633 |
| Air, GFF | 0.263 | nd | 0.068 | nd | nd | nd | 0.331 |
| Water, XAD-2 | | | | na | | | |
| Water, GFF | 1.352 | 0.160 | 0.337 | 1.850 | 0.178 | 0.292 | 4.169 |
| Lake Superior in May in 2006 | | | | | | | |
| Air, XAD-2 | | | | na | | | |
| Air, GFF | nd | nd | nd | nd | nd | nd | nd |
| Water, XAD-2 | 0.633 | 0.216 | 0.142 | 0.491 | nd | nd | 1.482 |
| Water, GFF | | | | na | | | |
| Lake Superior in July in 2006 | | | | | | | |
| Air, XAD-2 | nd | nd | 0.005 | nd | nd | nd | 0.005 |
| Air, GFF | nd | nd | nd | 0.125 | nd | nd | 0.125 |
| Water, XAD-2 | 1.270 | nd | 0.283 | 1.193 | nd | nd | 2.746 |
| Water, GFF | 1.050 | nd | 0.118 | 1.011 | nd | nd | 2.179 |
| average concentrations ^c in field blanks | | | | | | | |
| Air, XAD-2, pg m ⁻³ | 0.5 | <0.1 | 0.2 | 1.0 | <0.1 | <0.1 | 1.8 |
| Air, GFF, pg m ⁻³ | 0.2 | <0.1 | <0.1 | 0.1 | <0.1 | <0.1 | 0.4 |
| Water, XAD-2, pg L ⁻¹ | 1.2 | 0.1 | 0.3 | 1.1 | <0.1 | <0.1 | 2.6 |
| Water, GFF, pg L ⁻¹ | 1.4 | 0.1 | 0.2 | 2.0 | 0.1 | 0.1 | 3.9 |
| ^a Not detected. ^b Not analyzed. ^c Air and surface water volume collected in field samples were assumed 400 m ³ and 800 L, respectively. | | | | | | | |

A-2. Air-water exchange flux ($\text{ng m}^{-2} \text{day}^{-1}$) of individual BDE congener in Lake Michigan and Lake Superior

| Site | BDE-47 | BDE-66 | BDE-100 | BDE-99 | BDE-154 | BDE-153 | $\Sigma_6\text{PBDE}$ |
|--------------------------------------|--------|--------|---------|--------|---------|---------|-----------------------|
| Lake Michigan in May in 2005 | | | | | | | |
| LM18 | 2.7 | 0.1 | 2.3 | 10.3 | 0.2 | 0.1 | 15.8 |
| Chicago | 2.0 | 0.1 | 1.8 | 8.9 | 0.1 | 0.0 | 12.8 |
| Lake Michigan in July in 2005 | | | | | | | |
| LM47 | 1.6 | 0.1 | 2.6 | 22.4 | 0.4 | 0.3 | 27.4 |
| GB17 | -1.0 | 0.0 | 0.9 | 7.5 | 0.2 | 0.4 | 8.1 |
| Chicago | -1.7 | 0.1 | 7.6 | 64.6 | 1.0 | 0.5 | 72.1 |
| LM63 | -0.4 | 0.0 | 1.2 | 8.9 | 0.1 | 0.0 | 9.8 |
| Lake Superior in May in 2006 | | | | | | | |
| SU01M | 0.1 | 0.0 | 0.2 | 2.0 | 0.1 | 0.1 | 2.5 |
| EC139 | 0.2 | 0.0 | 0.5 | 4.3 | 0.2 | 0.1 | 5.4 |
| SU08M#1 | 0.4 | 0.0 | 0.3 | 2.5 | 0.1 | 0.0 | 3.3 |
| SU08M#2 | 0.5 | 0.0 | 0.2 | 1.4 | 0.0 | 0.0 | 2.1 |
| EC221 | -1.4 | 0.0 | 0.7 | 3.7 | 0.2 | 0.8 | 4.1 |
| SU17M | 0.2 | 0.0 | 0.2 | 1.2 | 0.0 | 0.0 | 1.5 |
| Lake Superior in July in 2006 | | | | | | | |
| SU08M | -1.8 | 0.0 | 0.9 | 10.3 | 0.0 | 0.0 | 9.4 |
| SU01M | -1.9 | 0.0 | 1.2 | 8.7 | 0.3 | 0.0 | 8.3 |
| EC221 | -4.4 | 0.0 | 1.8 | 22.3 | 0.8 | 0.8 | 21.2 |
| EC139#1 | 0.1 | 0.0 | 0.4 | 4.5 | 0.3 | 0.2 | 5.6 |
| EC139#2 | 1.9 | 0.2 | 0.6 | 4.1 | 0.0 | 0.0 | 6.8 |
| SU17M | -3.0 | 0.0 | 0.6 | 5.1 | 0.3 | 0.1 | 3.2 |

A-3. Dry deposition ($\text{ng m}^{-2} \text{day}^{-1}$) of individual BDE congener in Lake Michigan and Lake Superior

| Site | BDE-47 | BDE-66 | BDE-100 | BDE-99 | BDE-154 | BDE-153 | $\Sigma_6\text{PBDE}$ |
|--------------------------------------|--------|--------|---------|--------|---------|---------|-----------------------|
| Lake Michigan in May in 2005 | | | | | | | |
| LM18M | 0.1 | 0.0 | 0.0 | 0.3 | 0.0 | 0.1 | 0.7 |
| LM47M | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.1 |
| Milwaukee | 0.1 | 0.0 | 0.1 | 0.4 | 0.0 | 0.0 | 0.6 |
| Chicago #1 | 0.3 | 0.0 | 0.1 | 1.0 | 0.0 | 0.0 | 1.5 |
| Chicago #2 | 0.3 | 0.0 | 0.0 | 0.2 | 0.0 | 0.0 | 0.6 |
| GB-17 | 0.1 | 0.0 | 0.0 | 0.2 | 0.0 | 0.0 | 0.3 |
| Lake Michigan in July in 2005 | | | | | | | |
| LM47M | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.1 |
| GB17 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.1 |
| Chicago #1 | 0.0 | 0.0 | 0.1 | 0.4 | 0.0 | 0.0 | 0.5 |
| Chicago #2 | 0.1 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.3 |
| LM63 | 0.1 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.3 |
| Milwaukee | 0.0 | 0.0 | 0.0 | 0.5 | 0.0 | 0.0 | 0.5 |
| LM18M | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.2 |
| Lake Superior in May in 2006 | | | | | | | |
| SU01M | 0.0 | 0.1 | 0.0 | 0.2 | 0.0 | 0.0 | 0.3 |
| EC139 | 0.4 | 0.0 | 0.1 | 0.2 | 0.0 | 0.0 | 0.7 |
| SU08M#1 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 |
| SU08M#2 | 0.5 | 0.0 | 0.1 | 0.3 | 0.0 | 0.0 | 0.9 |
| EC221 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 |
| SU17M | 0.4 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.5 |
| Lake Superior in July in 2006 | | | | | | | |
| SU08M | 1.1 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 1.2 |
| SU01M | 0.5 | 0.0 | 0.1 | 0.1 | 0.0 | 0.0 | 0.7 |
| EC221 | 0.5 | 0.1 | 0.2 | 0.0 | 0.0 | 0.0 | 0.7 |
| EC139#1 | 0.4 | 0.1 | 0.2 | 0.0 | 0.0 | 0.0 | 0.7 |
| SU17M | 0.3 | 0.0 | 0.2 | 0.0 | 0.0 | 0.0 | 0.5 |

A-4. Wet deposition ($\text{ng m}^{-2} \text{day}^{-1}$) of individual BDE congener in Lake Michigan and Lake Superior

| Site | BDE-47 | BDE-66 | BDE-100 | BDE-99 | BDE-154 | BDE-153 | $\Sigma_6\text{PBDE}$ |
|--------------------------------------|--------|--------|---------|--------|---------|---------|-----------------------|
| Lake Michigan in May in 2005 | | | | | | | |
| LM18M | 1.0 | 0.2 | 0.7 | 3.1 | 0.2 | 0.3 | 5.7 |
| LM47M | 0.1 | 0.0 | 0.6 | 1.6 | 0.2 | 0.0 | 2.5 |
| Milwaukee | 1.1 | 0.0 | 1.0 | 4.1 | 0.1 | 0.0 | 6.3 |
| Chicago #1 | 2.7 | 0.2 | 2.0 | 13.1 | 0.4 | 1.3 | 19.7 |
| Chicago #2 | 2.1 | 0.0 | 0.7 | 6.2 | 0.2 | 0.2 | 9.4 |
| GB-17 | 0.6 | 0.0 | 0.6 | 2.5 | 0.1 | 0.0 | 3.8 |
| Lake Michigan in July in 2005 | | | | | | | |
| LM47M | 0.1 | 0.0 | 0.3 | 1.1 | 0.1 | 0.0 | 1.6 |
| GB17 | 0.1 | 0.1 | 0.3 | 1.0 | 0.0 | 0.1 | 1.6 |
| Chicago | 1.2 | 0.1 | 1.0 | 3.2 | 0.1 | 0.0 | 5.6 |
| LM63 | 0.3 | 0.1 | 0.3 | 1.3 | 0.1 | 0.2 | 2.3 |
| Lake Superior in May in 2006 | | | | | | | |
| SU01M | 0.0 | 0.6 | 0.1 | 1.4 | 0.1 | 0.0 | 2.2 |
| EC139 | 2.5 | 0.2 | 0.4 | 1.3 | 0.0 | 0.0 | 4.5 |
| SU08M#1 | 0.0 | 0.5 | 0.1 | 0.3 | 0.1 | 0.0 | 1.0 |
| SU08M#2 | 3.1 | 0.2 | 0.3 | 1.6 | 0.0 | 0.0 | 5.2 |
| EC221 | 0.3 | 0.1 | 0.1 | 0.3 | 0.1 | 0.1 | 1.0 |
| SU17M | 2.3 | 0.0 | 0.6 | 0.4 | 0.0 | 0.0 | 3.3 |
| Lake Superior in July in 2006 | | | | | | | |
| SU08M | 6.3 | 0.0 | 0.5 | 0.5 | 0.0 | 0.0 | 7.3 |
| SU01M | 2.6 | 0.2 | 0.6 | 1.1 | 0.1 | 0.0 | 4.7 |
| EC221 | 2.7 | 0.4 | 1.1 | 1.2 | 0.1 | 0.1 | 5.6 |
| EC139 #1 | 2.4 | 0.6 | 0.9 | 0.6 | 0.1 | 0.0 | 4.6 |
| EC139 #2 | 3.6 | 0.5 | 0.7 | 0.5 | 0.0 | 0.0 | 5.3 |
| SU17M | 1.6 | 0.2 | 1.2 | 0.4 | 0.1 | 0.0 | 3.4 |

Appendix B: Mass budgets of PBDEs

B-1. The estimated parameters for calculating the air-water exchange of individual BDE congeners in the upper Great Lakes

| Lake Michigan in 2005 | | | | | | | |
|------------------------------|--------------|---------------|---------------|----------------|---------------|----------------|----------------|
| Para. | Stat. | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 |
| K_{OL} | Max | 380 | 398 | 379 | 372 | 365 | 362 |
| | Min | 226 | 233 | 221 | 219 | 212 | 211 |
| | Average | 306 | 316 | 301 | 298 | 289 | 288 |
| | SD | 29 | 30 | 29 | 28 | 28 | 27 |
| K_a | Max | 4.7E-01 | 4.7E-01 | 4.5E-01 | 4.5E-01 | 4.3E-01 | 4.3E-01 |
| | Min | 2.7E-01 | 2.7E-01 | 2.6E-01 | 2.6E-01 | 2.5E-01 | 2.5E-01 |
| | Average | 3.7E-01 | 3.7E-01 | 3.5E-01 | 3.5E-01 | 3.4E-01 | 3.4E-01 |
| | SD | 3.7E-02 | 3.7E-02 | 3.5E-02 | 3.5E-02 | 3.3E-02 | 3.3E-02 |
| K_w | Max | 1.7E-03 | 1.7E-03 | 1.6E-03 | 1.6E-03 | 1.6E-03 | 1.6E-03 |
| | Min | 7.2E-04 | 7.2E-04 | 7.0E-04 | 7.0E-04 | 6.7E-04 | 6.7E-04 |
| | Average | 1.2E-03 | 1.2E-03 | 1.2E-03 | 1.2E-03 | 1.1E-03 | 1.1E-03 |
| | SD | 1.8E-04 | 1.8E-04 | 1.7E-04 | 1.7E-04 | 1.7E-04 | 1.7E-04 |
| H' | Max | 3.6E-04 | 1.2E-04 | 9.4E-05 | 2.1E-04 | 4.8E-05 | 9.3E-05 |
| | Min | 6.0E-05 | 2.0E-05 | 1.6E-05 | 2.3E-05 | 9.0E-06 | 1.4E-05 |
| | Average | 1.6E-04 | 5.4E-05 | 4.3E-05 | 8.2E-05 | 2.2E-05 | 4.1E-05 |
| | SD | 1.1E-04 | 3.6E-05 | 2.8E-05 | 6.5E-05 | 1.4E-05 | 2.8E-05 |

Lake Superior in 2006

| Para. | Stat. | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 |
|-----------------|---------|---------|---------|---------|---------|---------|---------|
| K _{OL} | Max | 501 | 514 | 488 | 484 | 468 | 466 |
| | Min | 240 | 249 | 237 | 235 | 227 | 226 |
| | Average | 346 | 354 | 337 | 334 | 323 | 322 |
| | SD | 61 | 61 | 57 | 58 | 55 | 55 |
| K _a | Max | 6.0E-01 | 6.0E-01 | 5.7E-01 | 5.7E-01 | 5.4E-01 | 5.4E-01 |
| | Min | 2.9E-01 | 2.9E-01 | 2.8E-01 | 2.8E-01 | 2.6E-01 | 2.6E-01 |
| | Average | 4.1E-01 | 4.1E-01 | 3.9E-01 | 3.9E-01 | 3.8E-01 | 3.8E-01 |
| | SD | 7.1E-02 | 7.1E-02 | 6.7E-02 | 6.7E-02 | 6.4E-02 | 6.4E-02 |
| K _w | Max | 2.4E-03 | 2.4E-03 | 2.4E-03 | 2.4E-03 | 2.3E-03 | 2.3E-03 |
| | Min | 8.1E-04 | 8.1E-04 | 7.8E-04 | 7.8E-04 | 7.5E-04 | 7.5E-04 |
| | Average | 1.4E-03 | 1.4E-03 | 1.4E-03 | 1.4E-03 | 1.3E-03 | 1.3E-03 |
| | SD | 3.7E-04 | 3.7E-04 | 3.6E-04 | 3.6E-04 | 3.4E-04 | 3.4E-04 |
| H' | Max | 2.7E-04 | 8.9E-05 | 6.9E-05 | 1.4E-04 | 3.6E-05 | 6.8E-05 |
| | Min | 6.0E-05 | 2.0E-05 | 1.5E-05 | 2.2E-05 | 8.9E-06 | 1.4E-05 |
| | Average | 1.2E-04 | 4.0E-05 | 3.2E-05 | 5.6E-05 | 1.7E-05 | 3.0E-05 |
| | SD | 6.7E-05 | 2.2E-05 | 1.7E-05 | 3.8E-05 | 8.8E-06 | 1.7E-05 |

K_{OL}: total mass transfer coefficient, m day⁻¹; K_a and K_w: mass transfer coefficient in air and water, cm sec⁻¹; H': dimensionless Henry's Law constant

B-2. WWTP daily discharge permits into Lake Michigan issued in 2001-2009

| WWTPs | m ³ day ⁻¹ |
|--|----------------------------------|
| State of Illinois | |
| NORTH SHORE SANITARY DISTRICT | 67,373 |
| NORTH SHORE SANITARY DISTRICT | 83,270 |
| State of Indiana | |
| LAGRANGE WWTP | 6,813 |
| SYRACUSE WWTP | 3,974 |
| WOLCOTTVILLE MUNICIPAL STP | 946 |
| ANGOLA WWTP | 6,435 |
| NAPPANEE WWTP, CITY OF | 7,192 |
| TOPEKA WWTP, TOWN OF | 1,136 |
| CROMWELL WWTP | 568 |
| ALBION WWTP | 1,287 |
| ASHLEY WWTP, TOWN OF | 1,514 |
| CHESTERTON WWTP, TOWN OF | 17,411 |
| FREMONT WASTEWATER TREATMENT PLANT | 2,271 |
| LIGONIER WASTEWATER TREATMENT PLANT | 5,678 |
| MICHIGAN CITY - J.B. GIFFORD WWTP | 56,775 |
| MIDDLEBURY WWTP, TOWN OF | 2,650 |
| PORTAGE MUNICIPAL WWTP | 18,925 |
| WAKARUSA MUNICIPAL WWTP | 1,893 |
| CROWN POINT WWTP, CITY OF | 15,519 |
| BRISTOL WWTP | 2,839 |
| MILFORD MUNICIPAL WWTP | 946 |
| MILLERSBURG WWTP | 454 |
| TURKEY CREEK REGIONAL SEWER DISTRICT | 1,400 |
| ADAMS LAKE REG.SEWER DIST. | 261 |
| NEW PARIS CONSERVANCY DISTRICT | 780 |
| DEEP RIVER WATER PARK WWTP | 114 |
| NATURE WORKS CONSERVANCY DIST. | 1,325 |
| LAGRANGE CO REGIONAL UTILITY DISTRICT - REGION B | 2,839 |
| HOBART WASTEWATER TREATMENT PLANT | 18,168 |
| STEBEN LAKES RWD | 3,785 |
| LAGRANGE CO SEWER DIST REGION A | 454 |
| State of Wisconsin | |
| KIEL WASTEWATER TREATMENT FACI | 3,263 |
| KEWAUNEE WASTEWATER TREATMENT | 2,195 |
| GRAFTON VILLAGE WATER & WASTEWE | 8,138 |

| | |
|--------------------------------|---------|
| CEDARBURG WASTEWATER TREATMENT | 11,355 |
| BRILLION WASTEWATER TREATMENT | 2,702 |
| NICHOLS WASTEWATER TREATMENT F | 189 |
| CEDAR GROVE WASTEWATER TRTMNT | 1,590 |
| REDGRANITE WASTEWATER TREATMEN | 379 |
| ALGOMA WASTEWATER TREATMENT FA | |
| MARION WASTEWATER TREATMENT FA | 908 |
| FREDONIA MUNICIPAL SEWER AND W | 2,271 |
| CAMPBELLSPORT WASTEWATER TREAT | 2,006 |
| FREEDOM SANITARY DISTRICT NO 1 | 671 |
| MANAWA WASTEWATER TREATMENT FA | 1,079 |
| SURING WASTEWATER TREATMENT FA | 379 |
| NEW HOLSTEIN WASTEWATER TREATM | 5,034 |
| WEYAUWEGA WASTEWATER TREATMENT | 1,923 |
| GREEN BAY METROPOLITAN SEWERAG | 198,713 |
| RIPON WASTEWATER TREATMENT FAC | 7,570 |
| BLACK CREEK WASTEWATER TREATME | 1,798 |
| STURGEON BAY UTILITIES WWTF | 10,674 |
| BERLIN WASTEWATER TREATMENT FA | 5,678 |
| BOWLER WASTEWATER TREATMENT FA | |
| HILBERT WASTEWATER TREATMENT F | 643 |
| REEDSVILLE WASTEWATER TREATMEN | 606 |
| MISHICOT WASTEWATER TREATMENT | 712 |
| FRANCIS CREEK VILLAGE | |
| STOCKBRIDGE WASTEWATER TREATME | 189 |
| RANDOM LAKE SEWAGE TREATMENT P | 1,703 |
| FAIRWATER VILLAGE | 189 |
| CLINTONVILLE WASTEWATER TREATM | 3,785 |
| SAUKVILLE VILLAGE SEWER UTILIT | 3,785 |
| HOWARDS GROVE WASTEWATER TRTMT | 1,060 |
| IOLA VILLAGE | 821 |
| KEWASKUM VILLAGE | 3,785 |
| DENMARK WASTEWATER TREATMENT F | 1,893 |
| SEYMOUR WASTEWATER TREATMENT F | 2,188 |
| GREEN LAKE WASTEWATER TREATMEN | 1,070 |
| JACKSON (VILLAGE) WASTEWATER T | 3,293 |
| VALDERS WASTEWATER TREATMENT F | 568 |
| LUXEMBURG VILLAGE | 1,514 |
| WINNECONNE WASTEWATER TREATMEN | 1,874 |
| WABENO SANITARY DISTRICT #1 | 379 |
| WHITELAW WASTEWATER TREATMENT | 379 |

| | |
|--------------------------------|---------|
| PRINCETON WASTEWATER TREATMENT | 1,048 |
| GILLETT WASTEWATER TREATMENT F | 1,249 |
| SISTER BAY WASTEWATER TREATMEN | 1,136 |
| COLEMAN WASTEWATER TREATMENT F | 1,060 |
| ST NAZIANZ WASTEWATER TREATMEN | 492 |
| OOSTBURG WASTEWATER TREATMENT | 1,064 |
| TIGERTON WASTEWATER TREATMENT | 379 |
| WRIGHTSTOWN SANITARY DISTRICT | 38 |
| WRIGHTSTOWN SANITARY DISTRICT | 151 |
| WALDO WASTEWATER UTILITY | 379 |
| WRIGHTSTOWN SEWER & WATER UTIL | 1,136 |
| BIRNAMWOOD WASTEWATER TREATMEN | |
| GRESHAM WASTEWATER TREATMENT F | 579 |
| CHILTON WASTEWATER TREATMENT F | 3,312 |
| CAROLINE SANITARY DISTRICT 1 | |
| OCONTO UTILITY COMMISSION WWTF | 6,662 |
| OCONTO FALLS WASTEWATER TREATM | 1,893 |
| HORTONVILLE WASTEWATER TREATME | 1,855 |
| AMHERST WASTEWATER TREATMENT F | 530 |
| APPLETON WASTEWATER TREATMENT | |
| BELGIUM WASTEWATER TREATMENT F | 1,363 |
| CASCO WASTEWATER TREATMENT FAC | 265 |
| GBMSD - DE PERE WWTF | 53,747 |
| FOND DU LAC WATER POLLUTION CO | 43,528 |
| MARKESAN WASTEWATER TREATMENT | 1,461 |
| GRAND CHUTE-MENASHA WEST SEWER | 14,762 |
| MONTELLO WASTEWATER TREATMENT | 1,136 |
| NEWBURG VILLAGE | 848 |
| NEW LONDON WASTEWATER TREATMEN | 4,145 |
| OAKFIELD WASTEWATER TREATMENT | 1,154 |
| OMRO WASTEWATER TREATMENT FACI | 2,044 |
| OSHKOSH WASTEWATER TREATMENT F | 75,700 |
| RACINE WASTEWATER UTILITY | 113,550 |
| SHEBOYGAN WASTEWATER TREATMENT | 69,606 |
| WEST BEND CITY | 34,065 |
| NEENAH MENASHA SEWER COMMISSIO | 68,130 |
| FREMONT ORIHULA WOLF RIVER JOI | 379 |
| MARINETTE WASTEWATER UTILITY | 16,086 |
| ROCKDALE WASTEWATER TREATMENT | 95 |
| TWO RIVERS WASTEWATER TREATMEN | 16,654 |
| SEVASTOPOL SD NO 1 WWTF | 295 |

| | |
|--------------------------------|---------|
| ST CLOUD VILLAGE UTILITY COMMI | 167 |
| BEAR CREEK WASTEWATER TREATMEN | |
| SHIOCTON WASTEWATER TREATMENT | 568 |
| KRAKOW SANITARY DISTRICT | 379 |
| HOLLAND SD 1 WASTEWATER TREATM | 757 |
| ROSENDALE WASTEWATER TREATMENT | 522 |
| WITTENBERG VILLAGE | 946 |
| WOLF TREATMENT PLANT | 11,355 |
| LAONA SANITARY DISTRICT #1 | 405 |
| KENOSHA WASTEWATER TREATMENT F | 105,980 |
| SOUTH MILWAUKEE WASTEWATER TRE | 22,710 |
| FORESTVILLE WASTEWATER TREATME | 303 |
| POTTER WASTEWATER TREATMENT FA | 151 |
| NIAGARA WASTEWATER TREATMENT F | 1,476 |
| YORKVILLE SEWER UTILITY DISTRI | 568 |
| PLYMOUTH CITY UTIL COMMISSION | 6,245 |
| WAUPACA WASTEWATER TREATMENT F | 4,731 |
| RIDGEWAY COUNTRY CLUB INC WWTF | 23 |
| PESHTIGO JOINT WASTEWATER TREA | 17,600 |
| EDEN WASTEWATER TREATMENT FACI | 568 |
| PLEASANT PRAIRIE UTILITY DISTR | 1,514 |
| MADELINE SANITARY DISTRICT | 575 |
| ASHLAND SEWAGE UTILITY | 6,056 |
| DALE SANITARY DISTRICT NO 1 WW | 227 |
| CLEVELAND WASTEWATER TREATMENT | 568 |
| SAUK COUNTY HEALTH CARE CENTER | 159 |
| SHERWOOD WASTEWATER TREATMENT | 189 |
| HEART OF VALLEY MSD WW TRTMNT | 20,818 |
| CASCADE WASTEWATER TREATMENT F | 633 |
| EAGLE LAKE SEWER UTILITY | 1,514 |
| GIBBSVILLE SANITARY DISTRICT | 114 |
| EMERALD GLENWOOD TNS SAN DIST | 47 |
| POY SIPPI SD WASTEWATER TREATM | 182 |
| FRIESLAND WASTEWATER TREATMENT | |
| AURORA SANITARY DISTRICT # 1 | |
| LARSEN WINCHESTER SD WWTF | 189 |
| LITTLE SUAMICO SANITARY DISTRI | 186 |
| OXFORD WASTEWATER TREATMENT FA | 227 |
| FOREST JUNCTION SANITARY DISTR | 110 |
| BUTTE DES MORTS CONSOLIDATED S | |
| GRAND VIEW SANITARY DISTRICT | |

| | |
|--------------------------------|-----------|
| MOUNT CALVARY WASTEWATER TREAT | 643 |
| STOCKBRIDGE-MUNSEE COMMUNITY | 76 |
| MILWAUKEE METRO SEW DIST COMBI | 2,081,750 |
| WILD ROSE WASTEWATER TREATMENT | |
| BRIGHTON DALE COUNTY PARK | 38 |
| CRIVITZ WASTEWATER TREATMENT F | 454 |
| NORTHERN MORAINÉ UTILITY COMM | |
| State of Michigan | |
| ALLEGAN WWTP | 4,542 |
| BELLAIRE WWTP | 809 |
| BETSIE LAKE UA WWTP | 2,176 |
| BOYNE CITY WWTP | 3,407 |
| BRONSON WWTP | 1,893 |
| CARSON CITY WWSL | 1,711 |
| CHAIN OF LAKES SA WWTP | 606 |
| CHARLEVOIX WWTP | 3,785 |
| DENTON TWP WWTP | 2,650 |
| DIMONDALE/WINDSOR WWTP | 1,893 |
| EATON RAPIDS WWTP | 4,542 |
| ELSIE WWSL | 1,438 |
| FOWLerville WWSL | 3,028 |
| GRAND LEDGE WWTP | 5,678 |
| GRANT WWTP | 379 |
| GUN LAKE WWTP | 4,542 |
| HANDY TWP WWTP | 3,217 |
| HART WWTP | 2,763 |
| HARTFORD WWTP | 1,325 |
| HASTINGS WWTP | 7,570 |
| HOUGHTON LAKE WWTP | 7,930 |
| HOWARD CITY WWTP | 2,763 |
| JONESVILLE WWTP | 2,271 |
| KALAMAZOO LAKE WWTP | 3,785 |
| KENT CITY WWTP | 757 |
| LAKEVIEW WWTP | 829 |
| LAKEWOOD WW AUTH WWTP | 16,276 |
| LAWTON WWTP | 757 |
| LESLIE WWTP | 1,779 |
| MOLINE WWTP | 946 |
| NASHVILLE WWTP | 1,514 |
| NEWAYGO WWTP | 1,514 |
| NORTH HOUGHTON CO W&SA CSO | 537 |

| | |
|------------------------------|---------|
| NORWAY WWTP | 1,893 |
| OTSEGO WWTP | 2,839 |
| PAW PAW WWTP | 6,435 |
| PLAINWELL WWTP | 4,921 |
| QUINCY WWTP | 757 |
| REED CITY WWTP | 3,596 |
| SPARTA WWTP | 3,028 |
| ST JOSEPH CSO | |
| SUNFIELD WWSL | 310 |
| VERMONTVILLE WWTP | 371 |
| WILLIAMSTON WWTP | 2,460 |
| ALBION WWTP | 15,140 |
| BATTLE CREEK WWTP | 68,130 |
| BELDING WWTP | 19,682 |
| BENTON HARBOR-ST JOSEPH WWTP | 57,911 |
| BIG RAPIDS WWTP | 9,084 |
| BUCHANAN WWTP | 5,678 |
| CADILLAC WWTP | 12,112 |
| CHARLOTTE WWTP | 6,813 |
| COLDWATER WWTP | 12,112 |
| COOPERSVILLE WWTP | 3,407 |
| DELHI TWP WWTP | 15,140 |
| DELTA TWP WWTP | 22,710 |
| DOWAGIAC WWTP | 9,463 |
| EAST LANSING WWTP | 70,969 |
| ESCANABA WWTP | 8,327 |
| GALIEN RIVER SD AUTH WWTP | 11,355 |
| GRAND HAVEN-SPRING LAKE WWTP | 25,246 |
| GRAND RAPIDS WWTP | 224,829 |
| GRANDVILLE WWTP | 16,654 |
| GREENVILLE WWTP | 5,678 |
| HILLSDALE WWTP | 7,570 |
| HOLLAND WWTP | 45,420 |
| IONIA WWTP | 15,140 |
| IRON MOUNTAIN-KINGSFORD WWTP | 24,981 |
| JACKSON WWTP | 71,915 |
| KALAMAZOO WWTP | 202,498 |
| LANSING WWTP | 132,475 |
| LEONI TWP WWTP | 11,355 |
| LOWELL WWTP | 5,375 |
| LUDINGTON WWTP | 28,388 |

| | |
|-----------------------------|---------|
| MANISTEE WWTP | 4,921 |
| MANISTIQUE WWTP | 5,678 |
| MARSHALL WWTP | 11,355 |
| MASON WWTP | 5,678 |
| MENOMINEE WWTP | 12,112 |
| MUSKOGON CO WWMS METRO WWTP | 178,652 |
| NILES WWTP | 21,953 |
| PAW PAW LAKE AREA WWTP | 8,327 |
| PETOSKEY WWTP | 9,463 |
| PORTAGE LAKE AUTHORITY WWTP | 11,734 |
| SOUTH HAVEN WWTP | 8,289 |
| SOUTHERN CLINTON CO WWTP | 18,925 |
| ST JOHNS WWTP | 7,192 |
| STURGIS WWTP | 10,598 |
| THREE RIVERS WWTP | 10,409 |
| TRAVERSE CITY WWTP | 32,173 |
| WEST IRON CO SA WWTP | 7,570 |
| WYOMING WWTP | 83,270 |
| ZEELAND WWTP | 6,245 |

B-3. WWTP daily discharge permits into Lake Superior issued in 2001-2009

| WWTPs | m³ day⁻¹ |
|--------------------------------------|---------------------------------------|
| State of Michigan | |
| BESSEMER AREA SA WWTP | 2,650 |
| KI SAWYER WWTP-MARQUETTE CO | 2,460 |
| MUNISING WWTP | 3,531 |
| RICHMOND TWP WWTP-MARQUETTE CO | 204 |
| GOGEBIC-IRON WW AUTHORITY WWTP | 12,869 |
| State of Wisconsin | |
| MELLEN CITY OF | 530 |
| MONTREAL CITY OF | 2,460 |
| WASHBURN CITY OF | 946 |
| SUPERIOR SEWAGE DISPOSAL SYSTE | 18,925 |
| KNIGHT TOWN OF | 121 |
| MAPLE SCHOOL DISTRICT | 104 |
| PORT WING TOWN OF | 93 |
| ELCHO SANITARY DISTRICT # 1 | 227 |
| SUPERIOR, VILLAGE OF | 204 |
| DRUMMOND SANITARY DISTRICT #1 | 151 |
| SAXON SANITARY DISTRICT #2 | 53 |
| Whitecap Mountains Sanitary District | 189 |
| SCHOOL DISTRICT OF SUPERIOR | 104 |
| State of Minnesota | |
| AURORA | 3,444 |
| BEAVER BAY | 151 |
| BIWABIK | 802 |
| BUHL-KINNEY | 731 |
| CHISHOLM | 2,725 |
| EVELETH | 3,785 |
| FLOODWOOD | 400 |
| GILBERT | 1,893 |
| GRAND MARAIS | 3,747 |
| HOYT LAKES | 2,574 |
| IRON JUNCTION | 38 |
| MCKINLEY | 108 |
| MEADOWLANDS | 95 |
| MOUNTAIN IRON | 2,082 |
| SILVER BAY | 3,478 |
| SILVER CREEK TOWNSHIP | 231 |

| | |
|-----------------------|---------|
| HIBBING-SOUTH | 17,033 |
| TWO HARBORS | 6,056 |
| VIRGINIA | 16,276 |
| WESTERN LAKE SSD | 183,194 |
| City in Canada | |
| THUNDER BAY | 262,679 |

Appendix C: Concentrations of individual BDE congener from GLACS

C-1. Air concentrations

| Lake Michigan Air | | Gas phase PBDE pg m⁻³ | | | | | | |
|--------------------------|---------------|--|----------------|---------------|----------------|----------------|----------|--|
| Site and date | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | Σ | |
| LM18M 5-28-05 | 11 | 0.3 | 6.4 | 29 | 0.5 | 0.3 | 47 | |
| LM47M 5-30-05 | 5.8 | 0.1 | 4.0 | 22 | 0.5 | 0.2 | 33 | |
| Milwaukee 5-27-05 | 16 | 0.3 | 9.4 | 46 | 0.8 | 0.3 | 73 | |
| Chicago #1 5-28-05 | 12 | 0.3 | 7.1 | 38 | 0.6 | 0.2 | 57 | |
| Chicago #2 5-28-05 | 12 | 0.4 | 1.7 | 9.8 | 0.6 | 0.0 | 25 | |
| GB17 5-31-05 | 13 | 0.2 | 8.6 | 58 | 1.0 | 0.6 | 81 | |
| LM47M 7-28-05 | 3.7 | 0.1 | 6.0 | 52 | 1.0 | 0.7 | 63 | |
| GB17 7-30-05 | 2.3 | 0.1 | 3.8 | 31 | 0.8 | 1.7 | 40 | |
| Chicago #1 7-26-05 | 13 | 0.2 | 21 | 181 | 2.8 | 1.4 | 219 | |
| LM63 7-29-05 | 3.0 | 0.2 | 3.9 | 30 | 0.4 | 0.0 | 38 | |
| | | Particle phase PBDE pg m⁻³ | | | | | | |
| Site and date | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | Σ | |
| LM18M 5-28-05 | 0.8 | 0.2 | 0.3 | 1.9 | 0.2 | 0.4 | 3.8 | |
| LM47M 5-30-05 | 0.0 | 0.0 | 0.2 | 0.4 | 0.1 | 0.0 | 0.8 | |
| Milwaukee 5-27-05 | 0.8 | 0.0 | 0.4 | 2.4 | 0.0 | 0.0 | 3.6 | |
| Chicago #1 5-29-05 | 2.4 | 0.2 | 1.6 | 12.0 | 0.4 | 1.6 | 18.1 | |
| Chicago #2 5-29-05 | 1.7 | 0.0 | 0.6 | 5.8 | 0.1 | 0.2 | 8.5 | |
| GB-17 5-31-05 | 0.4 | 0.0 | 0.3 | 1.2 | 0.0 | 0.0 | 1.9 | |
| LM47M 7-28-05 | 0.0 | 0.0 | 0.0 | 0.6 | 0.0 | 0.0 | 0.6 | |
| GB17 7-30-05 | 0.0 | 0.1 | 0.0 | 0.7 | 0.0 | 0.0 | 0.8 | |
| Chicago #1 7-26-05 | 0.0 | 0.1 | 0.4 | 1.7 | 0.0 | 0.0 | 2.2 | |
| Chicago #2 7-26-05 | 0.0 | 0.0 | 0.3 | 2.3 | 0.0 | 0.0 | 2.6 | |
| LM63 7-29-05 | 0.3 | 0.1 | 0.0 | 0.9 | 0.1 | 0.2 | 1.6 | |
| Milwaukee 7-25-05 | 0.0 | 0.0 | 0.1 | 2.7 | 0.0 | 0.0 | 2.8 | |
| LM18M 7-25-05 | 1.1 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 1.2 | |

| Lake Superior Air | | Gas phase PBDE pg m⁻³ | | | | | |
|--------------------------|---------------|---|----------------|---------------|----------------|----------------|----------|
| Site and date | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | Σ |
| SU01M 5-16-06 | 1.0 | 0.1 | 0.8 | 7.6 | 0.3 | 0.3 | 10 |
| EC139 5-17-06 | 0.9 | 0.0 | 0.9 | 8.0 | 0.3 | 0.3 | 11 |
| SU08M #1 5-17-06 | 1.6 | 0.0 | 0.6 | 5.5 | 0.3 | 0.0 | 8.1 |
| SU08M #2 5-17-06 | 1.5 | 0.0 | 0.5 | 3.2 | 0.0 | 0.1 | 5.2 |
| EC221 5-13-06 | 2.4 | 0.1 | 1.6 | 9.6 | 0.6 | 1.9 | 16 |
| SU17M 5-14-06 | 1.0 | 0.1 | 0.8 | 5.0 | 0.2 | 0.0 | 7.0 |
| SU08M 7-20-06 | 0.0 | 0.0 | 1.9 | 23 | 0.0 | 0.0 | 25 |
| SU01M 7-19-06 | 0.0 | 0.0 | 4.1 | 303 | 1.2 | 0.0 | 35.7 |
| EC221 7-17-06 | 7.9 | 0.0 | 7.7 | 97 | 3.2 | 3.5 | 119 |
| EC139 #1 7-20-06 | 2.8 | 0.1 | 1.2 | 13 | 0.8 | 0.5 | 18 |
| EC139 #2 7-20-06 | 7.7 | 0.6 | 1.5 | 11 | 0.0 | 0.0 | 21 |
| SU17M 7-18-06 | 3.9 | 0.1 | 2.6 | 23 | 1.0 | 0.4 | 31 |
| | | Particulate phase PBDE pg m⁻³ | | | | | |
| Site and date | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | Σ |
| SU01M 5-16-06 | 0.0 | 0.6 | 0.0 | 1.1 | 0.0 | 0.0 | 1.7 |
| EC139 5-17-06 | 2.5 | 0.2 | 0.4 | 1.0 | 0.0 | 0.0 | 4.1 |
| SU08M #1 5-17-06 | 0.0 | 0.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.5 |
| SU08M #2 5-17-06 | 3.2 | 0.2 | 0.3 | 1.5 | 0.0 | 0.0 | 5.2 |
| EC221 5-13-06 | 0.3 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.4 |
| SU17M 5-14-06 | 2.4 | 0.0 | 0.5 | 0.1 | 0.0 | 0.0 | 3.0 |
| SU08M 7-20-06 | 6.5 | 0.0 | 0.5 | 0.0 | 0.0 | 0.0 | 7.0 |
| SU01M 7-19-06 | 2.7 | 0.2 | 0.6 | 0.4 | 0.0 | 0.0 | 3.9 |
| EC221 7-17-06 | 2.7 | 0.4 | 1.0 | 0.1 | 0.0 | 0.0 | 4.2 |
| EC139 #1 7-20-06 | 2.4 | 0.6 | 0.9 | 0.1 | 0.0 | 0.0 | 4.0 |
| SU17M 7-18-06 | 1.6 | 0.1 | 1.3 | 0.0 | 0.0 | 0.0 | 2.9 |

C-2. Water concentrations

**Lake Michigan
Water**

Dissolved phase PBDE pg L⁻¹

| Site and date | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | Σ |
|----------------------|---------------|---------------|----------------|---------------|----------------|----------------|----------|
| LM18M 5-28-05 | 31 | 0.5 | 2.3 | 18 | 0.6 | 0.7 | 54 |
| Chicago 5-29-05 | 31 | 0.8 | 3.2 | 33 | 1.0 | 1.7 | 70 |
| LM310 5-31-05 | 30 | 0.5 | 3.4 | 16 | 1.1 | 0.8 | 53 |
| LM110 6-1-05 | 25 | 0.7 | 2.0 | 22 | 0.8 | 0.8 | 51 |
| LM47M 7-29-05 | 0.4 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.6 |
| GB17 7-30-05 | 19 | 0.1 | 2.6 | 9.7 | 0.8 | 0.9 | 33 |
| Chicago 7-26-05 | 41 | 0.3 | 4.5 | 21 | 0.7 | 0.0 | 68 |
| LM63M 7-29-05 | 16 | 0.1 | 2.2 | 12 | 0.3 | 0.3 | 31 |
| Milwaukee 7-25-05 | 61 | 1.0 | 3.5 | 16 | 0.0 | 0.6 | 83 |
| LM18M #1 7-25-05 | 43 | 0.7 | 3.7 | 17 | 0.5 | 0.7 | 66 |
| LM18M #2 7-25-05 | 45 | 0.6 | 4.4 | 22 | 0.8 | 1.1 | 74 |
| LM110 7-29-05 | 21 | 0.0 | 1.9 | 8.6 | 0.3 | 0.7 | 32 |

Particle phase PBDE pg L⁻¹

| Site and date | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | Σ |
|-------------------------|---------------|---------------|----------------|---------------|----------------|----------------|----------|
| LM18M 5-28-05 | 3.5 | 0.0 | 1.0 | 1.7 | 0.3 | 0.0 | 6.6 |
| Milwaukee 5-27-05 | 1.6 | 0.0 | 0.9 | 2.1 | 0.4 | 0.0 | 5.1 |
| Chicago 5-29-05 | 0.8 | 0.0 | 0.4 | 0.1 | 0.0 | 0.0 | 1.3 |
| GB17 penta#1 5-31-05 | 1.4 | 0.0 | 0.8 | 0.0 | 0.0 | 0.0 | 2.1 |
| GB17 penta#2 5-31-05 | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 0.0 | 0.3 |
| LM310 5-30-05 | 0.6 | 0.0 | 0.7 | 0.3 | 0.0 | 0.0 | 1.6 |
| LM110 6-01-05 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| LM47M 7-29-05 | 0.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.9 |
| GB17 7-30-05 | 0.0 | 0.0 | 0.5 | 1.7 | 0.0 | 0.0 | 2.2 |
| Chicago 7-26-05 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| LM63M 7-29-05 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Milwaukee 7-25-05 | 1.2 | 0.1 | 0.3 | 2.1 | 0.0 | 0.7 | 4.3 |
| LM18M #1 7-25-05 | 0.3 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.4 |
| LM18M #2 7-25-05 | 0.0 | 0.0 | 0.0 | 0.0 | 0.2 | 0.0 | 0.2 |
| LM110 7-29-05 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

| Lake Superior Water | | Dissolved phase PBDE pg L⁻¹ | | | | | |
|----------------------------|---------------|---|----------------|---------------|----------------|----------------|----------|
| Site and date | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | Σ |
| SU01M 5-16-06 | 11 | 0.2 | 1.8 | 7.9 | 0.0 | 0.8 | 22 |
| EC139 5-18-06 | 6.8 | 0.0 | 0.9 | 5.9 | 0.2 | 0.3 | 14 |
| SU08M #1 5-16-06 | 12 | 0.3 | 1.8 | 7.7 | 0.5 | 0.8 | 23 |
| SU08M #2 5-17-06 | 6.8 | 0.0 | 0.6 | 5.4 | 0.3 | 0.3 | 13 |
| EC221 5-13-06 | 49 | 0.5 | 4.5 | 25 | 0.8 | 1.3 | 81 |
| SU17M 5-14-06 | 18 | 0.4 | 3.0 | 10 | 0.0 | 0.0 | 32 |
| SUFO 5-15-06 | 15 | 0.0 | 1.7 | 8.4 | 0.2 | 0.4 | 26 |
| SUFE 5-14-06 | 25 | 0.2 | 2.7 | 12 | 0.0 | 0.0 | 40 |
| SU08M 7-20-06 | 22 | 0.0 | 2.2 | 11 | 0.6 | 0.4 | 36 |
| SU01M 7-19-06 | 28 | 0.5 | 1.3 | 7.8 | 0.1 | 0.2 | 37 |
| EC221 7-17-06 | 79 | 1.3 | 5.9 | 32 | 1.1 | 1.4 | 121 |
| EC139 #1 7-20-06 | 15 | 0.3 | 1.9 | 8.4 | 0.2 | 0.2 | 26 |
| EC139 #2 7-21-06 | 17 | 0.3 | 1.9 | 8.9 | 0.3 | 0.0 | 29 |
| SU17M 7-18-06 | 49 | 0.5 | 4.2 | 19 | 0.4 | 0.0 | 73 |

| | | Particle phase PBDE pg L⁻¹ | | | | | |
|----------------------|---------------|--|----------------|---------------|----------------|----------------|----------|
| Site and date | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | Σ |
| SU01M 5-16-06 | 0.0 | 0.0 | 0.5 | 0.0 | 0.0 | 0.0 | 0.5 |
| EC139 5-18-06 | 1.6 | 0.2 | 0.5 | 1.3 | 0.3 | 0.5 | 4.3 |
| SU08M #1 5-16-06 | 0.0 | 0.3 | 0.2 | 0.0 | 0.0 | 0.0 | 0.5 |
| SU08M #2 5-17-06 | 0.0 | 0.2 | 0.3 | 0.0 | 0.5 | 1.2 | 2.2 |
| EC221 5-13-06 | 1.0 | 0.0 | 0.4 | 0.7 | 0.0 | 0.4 | 2.4 |
| SUFO 5-15-06 | 1.5 | 0.0 | 0.0 | 2.4 | 0.0 | 1.8 | 5.8 |
| SU08M 7-20-06 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.0 | 0.1 |
| SU01M 7-19-06 | 0.2 | 0.0 | 0.2 | 0.0 | 0.1 | 0.1 | 0.7 |
| EC221 7-17-06 | 0.1 | 0.0 | 0.0 | 0.8 | 0.0 | 0.0 | 0.9 |
| EC139 #1 7-20-06 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| EC139 #2 7-21-06 | 0.0 | 0.0 | 0.3 | 0.2 | 0.0 | 0.0 | 0.5 |
| SU17M 7-18-06 | 3.0 | 0.2 | 0.3 | 0.0 | 0.0 | 0.2 | 3.7 |

Appendix D: Gas phase concentrations and the net air-water exchange fluxes of BDE congeners at IADN sites

D-1. Gas phase concentrations

| Chicago Date | Gas phase PBDE pg m ⁻³ | | | | | | Σ |
|-----------------|-----------------------------------|--------|---------|--------|---------|---------|-------|
| | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | |
| 01-11-05 | 5.1 | 0.0 | 0.2 | 0.5 | 0.0 | 0.0 | 5.7 |
| 01-23-05 | 3.4 | 0.0 | 0.7 | 1.9 | 0.0 | 0.0 | 6.0 |
| 02-04-05 | 0.7 | 0.0 | 0.1 | 0.5 | 0.0 | 0.0 | 1.4 |
| 02-16-05 | 7.9 | 0.0 | 1.0 | 2.9 | 0.0 | 0.0 | 11.8 |
| 02-28-05 | NA | NA | NA | NA | NA | NA | NA |
| 03-12-05 | 3.5 | 0.0 | 0.5 | 1.6 | 0.1 | 0.1 | 5.8 |
| 03-24-05 | 8.7 | 0.0 | 0.0 | 1.7 | 0.1 | 0.0 | 10.5 |
| 04-05-05 | 16.5 | 0.0 | 0.7 | 2.0 | 0.0 | 0.1 | 19.2 |
| 04-17-05 | 15.1 | 0.0 | 0.7 | 1.9 | 0.0 | 0.0 | 17.6 |
| 04-29-05 | 7.1 | 0.0 | 0.5 | 1.0 | 0.0 | 0.1 | 8.7 |
| 05-11-05 | 15.5 | 0.0 | 1.2 | 2.5 | 0.1 | 0.0 | 19.2 |
| 05-23-05 | 13.5 | 0.0 | 1.1 | 2.4 | 0.1 | 0.0 | 17.1 |
| 06-04-05 | 24.0 | 0.0 | 1.4 | 4.9 | 0.2 | 0.3 | 30.8 |
| 06-16-05 | 14.5 | 0.0 | 0.3 | 2.3 | 0.0 | 0.0 | 17.1 |
| 06-28-05 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 07-10-05 | 54.3 | 0.0 | 3.2 | 7.2 | 0.0 | 0.0 | 64.7 |
| 07-22-05 | 70.2 | 0.0 | 4.3 | 9.7 | 0.3 | 0.0 | 84.5 |
| 08-03-05 | 126.0 | 1.3 | 5.4 | 12.9 | 0.0 | 0.0 | 145.5 |
| 08-15-05 | 33.0 | 0.0 | 3.4 | 4.6 | 0.0 | 0.0 | 41.0 |
| 08-27-05 | NA | NA | NA | NA | NA | NA | NA |
| 09-08-05 | 53.6 | 1.7 | 3.7 | 7.9 | 0.0 | 0.0 | 66.9 |
| 09-20-05 | 33.9 | 0.0 | 3.0 | 7.6 | 0.3 | 0.1 | 44.9 |
| 10-02-05 | 63.1 | 0.0 | 3.2 | 7.7 | 0.0 | 0.0 | 74.0 |
| 10-14-05 | 29.1 | 0.0 | 2.0 | 3.6 | 0.0 | 0.0 | 34.7 |
| 10-26-05 | 5.4 | 0.0 | 0.2 | 0.5 | 0.0 | 0.0 | 6.1 |
| 11-07-05 | 4.1 | 0.0 | 0.0 | 0.4 | 0.0 | 0.0 | 4.5 |
| 11-19-05 | 2.7 | 0.0 | 0.3 | 0.8 | 0.0 | 0.0 | 3.7 |
| 12-01-05 | 3.0 | 0.0 | 0.0 | 1.6 | 0.0 | 0.0 | 4.6 |
| 12-13-05 | 3.6 | 0.0 | 0.0 | 0.9 | 0.0 | 0.0 | 4.5 |
| 12-25-05 | 4.2 | 0.0 | 0.2 | 1.2 | 0.0 | 0.0 | 5.7 |

| Sleeping Bear Dunes Date | Gas phase PBDE $\mu\text{g m}^{-3}$ | | | | | | Σ |
|--------------------------------|-------------------------------------|--------|---------|--------|---------|---------|----------|
| | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | |
| 01-11-05 | 0.8 | 0.0 | 0.1 | 0.2 | 0.0 | 0.0 | 1.0 |
| 01-23-05 | 0.4 | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 0.7 |
| 02-04-05 | 1.1 | 0.0 | 0.2 | 0.9 | 0.1 | 0.2 | 2.4 |
| 02-16-05 | 3.5 | 0.0 | 0.3 | 2.0 | 0.0 | 0.0 | 5.8 |
| 02-28-05 | 1.6 | 0.1 | 0.3 | 1.4 | 0.1 | 0.1 | 3.8 |
| 03-12-05 | 0.4 | 0.0 | 0.0 | 0.4 | 0.0 | 0.0 | 0.9 |
| 03-24-05 | 0.3 | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 0.6 |
| 04-05-05 | 2.0 | 0.0 | 0.2 | 0.6 | 0.0 | 0.0 | 2.8 |
| 04-17-05 | 1.3 | 0.0 | 0.1 | 0.4 | 0.0 | 0.0 | 1.7 |
| 04-29-05 | 0.5 | 0.0 | 0.1 | 0.3 | 0.0 | 0.0 | 0.9 |
| 05-11-05 | 8.3 | 0.3 | 1.8 | 7.3 | 0.5 | 0.6 | 18.8 |
| 05-23-05 | 14.6 | 0.5 | 3.3 | 13.6 | 0.8 | 1.0 | 33.9 |
| 06-04-05 | 22.9 | 1.0 | 1.8 | 4.4 | 0.1 | 0.1 | 30.3 |
| 06-16-05 | 2.6 | 0.0 | 0.1 | 0.9 | 0.0 | 0.0 | 3.6 |
| 06-28-05 | 7.6 | 0.2 | 1.3 | 3.9 | 0.1 | 0.1 | 13.2 |
| 07-10-05 | 5.5 | 0.0 | 1.1 | 4.5 | 0.2 | 0.3 | 11.7 |
| 07-22-05 | 3.9 | 0.0 | 0.7 | 2.1 | 0.1 | 0.1 | 7.0 |
| 08-03-05 | 4.5 | 0.0 | 0.8 | 1.9 | 0.0 | 0.2 | 7.4 |
| 08-15-05 | 1.8 | 0.0 | 0.3 | 1.2 | 0.0 | 0.1 | 3.3 |
| 08-27-05 | 4.4 | 0.2 | 0.8 | 2.7 | 0.1 | 0.1 | 8.3 |
| 09-08-05 | 2.2 | 0.0 | 0.4 | 1.1 | 0.0 | 0.0 | 3.7 |
| 09-20-05 | 1.3 | 0.0 | 0.3 | 0.8 | 0.0 | 0.0 | 2.4 |
| 10-02-05 | 2.2 | 0.0 | 0.3 | 1.0 | 0.0 | 0.0 | 3.5 |
| 10-14-05 | 2.6 | 0.0 | 0.5 | 1.7 | 0.0 | 0.1 | 4.9 |
| 10-26-05 | 0.3 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.4 |
| 11-07-05 | 0.6 | 0.0 | 0.0 | 0.2 | 0.0 | 0.0 | 0.7 |
| 11-19-05 | 0.6 | 0.0 | 0.1 | 0.3 | 0.0 | 0.0 | 1.0 |
| 12-01-05 | 0.3 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.4 |
| 12-13-05 | 0.5 | 0.0 | 0.0 | 0.4 | 0.0 | 0.0 | 0.9 |
| 12-25-05 | 0.8 | 0.0 | 0.1 | 0.4 | 0.0 | 0.0 | 1.3 |

| Eagle Harbor | Gas phase PBDE pg m ⁻³ | | | | | | |
|--------------|-----------------------------------|--------|--------|---------|--------|---------|---------|
| | Date | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 |
| 01-06-06 | 0.4 | 0.0 | 0.0 | 0.2 | 0.0 | 0.0 | 0.7 |
| 01-18-06 | 1.3 | 0.0 | 0.3 | 1.0 | 0.0 | 0.1 | 2.7 |
| 01-30-06 | 0.8 | 0.0 | 0.0 | 1.0 | 0.0 | 0.0 | 1.8 |
| 02-11-06 | 0.3 | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 0.7 |
| 02-23-06 | 0.2 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.3 |
| 03-07-06 | 0.4 | 0.0 | 0.0 | 0.4 | 0.0 | 0.0 | 0.8 |
| 03-19-06 | 0.2 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.3 |
| 03-31-06 | 0.9 | 0.0 | 0.1 | 0.2 | 0.0 | 0.1 | 1.3 |
| 04-12-06 | 1.5 | 0.0 | 0.1 | 0.5 | 0.0 | 0.0 | 2.1 |
| 04-24-06 | 0.7 | 0.0 | 0.0 | 0.2 | 0.0 | 0.0 | 1.0 |
| 05-06-06 | 0.4 | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 0.7 |
| 05-18-06 | 0.6 | 0.0 | 0.1 | 0.4 | 0.0 | 0.0 | 1.2 |
| 05-30-06 | 1.9 | 0.0 | 0.3 | 0.9 | 0.0 | 0.1 | 3.2 |
| 06-11-06 | 0.4 | 0.0 | 0.1 | 0.2 | 0.0 | 0.0 | 0.7 |
| 06-23-06 | 0.6 | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 1.0 |
| 07-05-06 | 1.1 | 0.0 | 0.2 | 0.4 | 0.0 | 0.0 | 1.7 |
| 07-17-06 | 2.7 | 0.0 | 0.5 | 1.8 | 0.1 | 0.1 | 5.3 |
| 07-29-06 | 1.6 | 0.0 | 0.2 | 0.8 | 0.1 | 0.0 | 2.7 |
| 08-10-06 | 1.9 | 0.0 | 0.3 | 0.9 | 0.0 | 0.0 | 3.1 |
| 08-22-06 | NA | NA | NA | NA | NA | NA | NA |
| 09-03-06 | 1.2 | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 1.5 |
| 09-15-06 | 1.1 | 0.0 | 0.2 | 0.5 | 0.0 | 0.0 | 1.7 |
| 09-27-06 | 1.0 | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 1.4 |
| 10-09-06 | 1.0 | 0.0 | 0.1 | 0.4 | 0.0 | 0.1 | 1.7 |
| 10-21-06 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.1 |
| 11-02-06 | 0.6 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.7 |
| 11-14-06 | 0.3 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.4 |
| 11-26-06 | 0.0 | 0.0 | 0.0 | 0.2 | 0.0 | 0.1 | 0.3 |
| 12-08-06 | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.1 | 0.2 |
| 12-20-06 | NA | NA | NA | NA | NA | NA | NA |

D-2. Net air-water exchange flux

| Chicago | Air-water exchange flux ng m⁻² day⁻¹ | | | | | | | |
|----------------|---|---------------|---------------|----------------|---------------|----------------|----------------|----------|
| | Date | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | Σ |
| | 01-11-05 | 0.72 | 0.00 | 0.03 | -0.11 | 0.00 | 0.00 | 0.63 |
| | 01-23-05 | 0.28 | 0.00 | 0.19 | 0.34 | 0.00 | 0.00 | 0.81 |
| | 02-04-05 | -0.51 | 0.00 | 0.02 | -0.05 | 0.00 | 0.01 | -0.54 |
| | 02-16-05 | 1.77 | 0.00 | 0.27 | 0.69 | 0.00 | 0.00 | 2.71 |
| | 02-28-05 | NA | NA | NA | NA | NA | NA | NA |
| | 03-12-05 | 0.40 | 0.00 | 0.12 | 0.28 | 0.03 | 0.03 | 0.85 |
| | 03-24-05 | 2.14 | 0.00 | -0.02 | 0.34 | 0.02 | 0.00 | 2.47 |
| | 04-05-05 | 4.25 | 0.00 | 0.17 | 0.38 | 0.01 | 0.02 | 4.82 |
| | 04-17-05 | 3.83 | 0.00 | 0.17 | 0.32 | 0.00 | 0.00 | 4.32 |
| | 04-29-05 | 1.36 | 0.00 | 0.10 | 0.06 | 0.00 | 0.01 | 1.52 |
| | 05-11-05 | 4.05 | 0.00 | 0.34 | 0.52 | 0.02 | 0.00 | 4.92 |
| | 05-23-05 | 3.04 | 0.00 | 0.28 | 0.39 | 0.01 | 0.00 | 3.72 |
| | 06-04-05 | 4.46 | -0.01 | 0.29 | 0.75 | 0.05 | 0.05 | 5.60 |
| | 06-16-05 | 2.38 | -0.01 | 0.04 | -0.07 | -0.01 | -0.01 | 2.31 |
| | 06-28-05 | NA | NA | NA | NA | NA | NA | NA |
| | 07-10-05 | 13.13 | -0.02 | 0.87 | 1.00 | -0.01 | -0.02 | 14.96 |
| | 07-22-05 | 15.90 | -0.02 | 1.13 | 1.20 | 0.06 | -0.02 | 18.24 |
| | 08-03-05 | 33.79 | 0.38 | 1.52 | 2.29 | -0.01 | -0.02 | 37.96 |
| | 08-15-05 | 5.80 | -0.02 | 0.89 | -0.27 | -0.01 | -0.02 | 6.36 |
| | 08-27-05 | NA | NA | NA | NA | NA | NA | NA |
| | 09-08-05 | 12.94 | 0.53 | 1.04 | 0.93 | -0.01 | -0.02 | 15.41 |
| | 09-20-05 | 7.09 | -0.02 | 0.86 | 0.84 | 0.09 | 0.02 | 8.88 |
| | 10-02-05 | 20.35 | -0.02 | 1.10 | 1.44 | -0.01 | -0.02 | 22.84 |
| | 10-14-05 | 7.36 | -0.02 | 0.62 | 0.12 | -0.01 | -0.02 | 8.06 |
| | 10-26-05 | -0.44 | -0.01 | 0.01 | -0.65 | -0.01 | -0.01 | -1.12 |
| | 11-07-05 | 0.56 | -0.01 | -0.05 | -0.45 | -0.01 | -0.01 | 0.03 |
| | 11-19-05 | -0.54 | -0.01 | 0.04 | -0.21 | 0.00 | -0.01 | -0.73 |
| | 12-01-05 | -0.23 | -0.01 | -0.03 | 0.13 | 0.00 | -0.01 | -0.15 |
| | 12-13-05 | 0.12 | 0.00 | -0.02 | -0.03 | 0.00 | 0.00 | 0.06 |
| | 12-25-05 | 0.36 | -0.01 | 0.05 | 0.09 | 0.00 | 0.00 | 0.49 |

| Sleeping Bear Dunes | | Air-water exchange flux ng m-2 day-1 | | | | | | |
|--------------------------------|---------------|---|----------------|---------------|----------------|----------------|----------|--|
| Date | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | Σ | |
| 01-11-05 | -0.47 | 0.00 | 0.00 | -0.08 | 0.00 | 0.00 | -0.55 | |
| 01-23-05 | -0.54 | 0.00 | -0.01 | -0.02 | 0.00 | 0.00 | -0.58 | |
| 02-04-05 | -0.26 | 0.00 | 0.05 | 0.16 | 0.02 | 0.04 | 0.01 | |
| 02-16-05 | 0.53 | 0.00 | 0.07 | 0.49 | 0.00 | 0.00 | 1.08 | |
| 02-28-05 | -0.06 | 0.04 | 0.08 | 0.32 | 0.04 | 0.04 | 0.47 | |
| 03-12-05 | -0.44 | 0.00 | -0.01 | 0.03 | 0.00 | 0.01 | -0.42 | |
| 03-24-05 | -0.47 | 0.00 | -0.01 | -0.02 | 0.00 | 0.01 | -0.49 | |
| 04-05-05 | 0.02 | 0.00 | 0.06 | 0.06 | 0.00 | 0.00 | 0.15 | |
| 04-17-05 | -0.24 | 0.00 | 0.01 | -0.01 | 0.00 | 0.00 | -0.24 | |
| 04-29-05 | -0.51 | 0.00 | 0.00 | -0.03 | 0.00 | 0.00 | -0.54 | |
| 05-11-05 | 1.92 | 0.09 | 0.55 | 2.11 | 0.15 | 0.17 | 4.99 | |
| 05-23-05 | 3.53 | 0.14 | 0.91 | 3.69 | 0.23 | 0.27 | 8.77 | |
| 06-04-05 | 4.39 | 0.22 | 0.38 | 0.80 | 0.03 | 0.01 | 5.82 | |
| 06-16-05 | -0.91 | -0.01 | -0.01 | -0.13 | 0.00 | -0.01 | -1.08 | |
| 06-28-05 | 0.40 | 0.05 | 0.32 | 0.64 | 0.02 | 0.01 | 1.44 | |
| 07-10-05 | -0.63 | -0.01 | 0.28 | 0.74 | 0.06 | 0.07 | 0.51 | |
| 07-22-05 | -1.71 | -0.01 | 0.14 | -0.18 | 0.01 | 0.01 | -1.74 | |
| 08-03-05 | -1.55 | -0.01 | 0.16 | -0.21 | -0.01 | 0.03 | -1.60 | |
| 08-15-05 | -2.54 | -0.02 | 0.00 | -0.50 | -0.01 | 0.00 | -3.06 | |
| 08-27-05 | -1.76 | 0.04 | 0.18 | 0.00 | 0.03 | 0.00 | -1.51 | |
| 09-08-05 | -2.24 | -0.01 | 0.07 | -0.44 | -0.01 | -0.02 | -2.64 | |
| 09-20-05 | -2.59 | -0.02 | 0.04 | -0.54 | -0.01 | -0.02 | -3.14 | |
| 10-02-05 | -2.11 | -0.01 | 0.03 | -0.36 | -0.01 | -0.02 | -2.48 | |
| 10-14-05 | -1.53 | -0.01 | 0.11 | -0.01 | -0.01 | 0.02 | -1.42 | |
| 10-26-05 | -1.70 | -0.01 | -0.04 | -0.39 | 0.00 | -0.01 | -2.15 | |
| 11-07-05 | -1.31 | -0.01 | -0.03 | -0.27 | 0.00 | -0.01 | -1.63 | |
| 11-19-05 | -0.89 | -0.01 | 0.01 | -0.15 | 0.00 | -0.01 | -1.04 | |
| 12-01-05 | -0.83 | 0.00 | -0.02 | -0.15 | 0.00 | 0.00 | -1.01 | |
| 12-13-05 | -0.51 | 0.00 | -0.01 | -0.04 | 0.00 | 0.00 | -0.56 | |
| 12-25-05 | -0.54 | 0.00 | 0.00 | -0.01 | 0.00 | 0.00 | -0.56 | |

| Eagle Harbor | | Air-water exchange flux ng m-2 day-1 | | | | | |
|---------------------|---------------|---|----------------|---------------|----------------|----------------|----------|
| Date | BDE 47 | BDE 66 | BDE 100 | BDE 99 | BDE 154 | BDE 153 | Σ |
| 01-06-06 | -0.63 | 0.00 | -0.02 | -0.06 | 0.00 | 0.00 | -0.72 |
| 01-18-06 | -0.25 | 0.00 | 0.07 | 0.21 | 0.01 | 0.02 | 0.07 |
| 01-30-06 | -0.38 | 0.00 | -0.02 | 0.21 | 0.00 | 0.00 | -0.19 |
| 02-11-06 | -0.49 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | -0.49 |
| 02-23-06 | -0.51 | 0.00 | 0.00 | -0.07 | 0.00 | 0.00 | -0.58 |
| 03-07-06 | -0.41 | 0.00 | -0.01 | 0.04 | 0.00 | 0.01 | -0.39 |
| 03-19-06 | -0.52 | 0.00 | -0.01 | -0.06 | 0.00 | 0.00 | -0.59 |
| 03-31-06 | -0.25 | 0.00 | 0.03 | -0.03 | 0.01 | 0.02 | -0.22 |
| 04-12-06 | -0.06 | 0.00 | 0.03 | 0.05 | 0.00 | 0.00 | 0.02 |
| 04-24-06 | -0.37 | 0.00 | -0.02 | -0.03 | 0.00 | 0.00 | -0.43 |
| 05-06-06 | -0.56 | 0.00 | -0.02 | -0.01 | 0.00 | 0.01 | -0.58 |
| 05-18-06 | -0.60 | 0.00 | 0.03 | 0.00 | 0.00 | 0.01 | -0.56 |
| 05-30-06 | -0.18 | 0.00 | 0.07 | 0.12 | 0.01 | 0.01 | 0.03 |
| 06-11-06 | -0.60 | 0.00 | 0.01 | -0.09 | 0.00 | 0.00 | -0.68 |
| 06-23-06 | -0.94 | 0.00 | -0.02 | -0.16 | 0.00 | 0.00 | -1.12 |
| 07-05-06 | -0.95 | -0.01 | 0.01 | -0.19 | 0.00 | 0.00 | -1.14 |
| 07-17-06 | -1.01 | -0.01 | 0.11 | 0.06 | 0.02 | 0.03 | -0.79 |
| 07-29-06 | -1.45 | -0.01 | 0.02 | -0.24 | 0.01 | -0.01 | -1.67 |
| 08-10-06 | -1.33 | -0.01 | 0.05 | -0.19 | 0.00 | 0.00 | -1.48 |
| 08-22-06 | NA | NA | NA | NA | NA | NA | NA |
| 09-03-06 | -1.44 | -0.01 | -0.05 | -0.32 | 0.00 | -0.01 | -1.82 |
| 09-15-06 | -1.25 | -0.01 | 0.01 | -0.21 | 0.01 | -0.01 | -1.46 |
| 09-27-06 | -1.51 | -0.01 | -0.05 | -0.29 | 0.00 | -0.01 | -1.87 |
| 10-09-06 | -0.82 | -0.01 | 0.03 | -0.10 | 0.02 | 0.03 | -0.86 |
| 10-21-06 | -1.27 | -0.01 | -0.01 | -0.21 | 0.00 | 0.00 | -1.50 |
| 11-02-06 | -0.83 | 0.00 | -0.03 | -0.15 | 0.00 | 0.00 | -1.02 |
| 11-14-06 | -0.67 | 0.00 | -0.02 | -0.11 | 0.00 | 0.01 | -0.80 |
| 11-26-06 | -0.60 | 0.00 | -0.01 | -0.05 | 0.00 | 0.02 | -0.65 |
| 12-08-06 | -0.68 | 0.00 | -0.02 | -0.08 | 0.00 | 0.02 | -0.77 |
| 12-20-06 | NA | NA | NA | NA | NA | NA | NA |

Appendix E: Glyphosate and AMPA

E-1. Concentrations in Mississippi

| Mississippi in 2007 | | TSP | Rain glyphosate | Rain AMPA | Air glyphosate | Air AMPA |
|---------------------|----------|----------------------|----------------------|----------------------|--------------------|--------------------|
| begin | end | $\mu\text{g m}^{-3}$ | $\mu\text{g L}^{-1}$ | $\mu\text{g L}^{-1}$ | ng m^{-3} | ng m^{-3} |
| 04-17-07 | 04-24-07 | 210 | | | 0.85 | 0.14 |
| 04-24-07 | 05-01-07 | 155 | | | 6.61 | 0.31 |
| 05-01-07 | 05-08-07 | 171 | 0.10 | 0.10 | 0.61 | 0.04 |
| 05-07-07 | 05-14-07 | 167 | 1.40 | 0.10 | 0.00 | 0.00 |
| 05-15-07 | 05-22-07 | | 1.90 | 0.10 | 9.12 | 0.39 |
| 05-22-07 | 05-29-07 | 189 | | | 5.19 | 0.17 |
| 05-29-07 | 06-05-07 | 107 | 1.80 | 0.30 | 1.98 | 0.49 |
| 06-05-07 | 06-12-07 | 120 | | | 1.16 | 0.12 |
| 06-12-07 | 06-19-07 | 179 | 0.20 | 0.10 | 0.77 | 0.08 |
| 06-19-07 | 06-26-07 | 80 | 0.00 | 0.00 | 0.35 | 0.03 |
| 06-26-07 | 07-03-07 | 85 | 0.30 | 0.10 | 0.20 | 0.06 |
| 07-03-07 | 07-10-07 | 82 | 0.00 | 0.10 | 0.00 | 0.03 |
| 07-10-07 | 07-17-07 | | 0.10 | 0.10 | 0.00 | 0.00 |
| 07-17-07 | 07-24-07 | 92 | | | 0.40 | 0.08 |
| 07-24-07 | 07-31-07 | 90 | | | 0.27 | 0.00 |
| 07-31-07 | 08-07-07 | 115 | | | 0.14 | 0.02 |
| 08-07-07 | 08-14-07 | 123 | | | 1.10 | 0.38 |
| 08-14-07 | 08-21-07 | 122 | | | 0.56 | 0.06 |
| 08-21-07 | 08-28-07 | 143 | | | 0.57 | 0.07 |
| 08-28-07 | 09-04-07 | 116 | 0.30 | 0.00 | 0.12 | 0.04 |
| 09-04-07 | 09-11-07 | 95 | 0.00 | 0.00 | 0.10 | 0.03 |
| 09-11-07 | 09-18-07 | 99 | | | 0.31 | 0.03 |

| Mississippi in 2008 | | TSP | Rain glyphosate | Rain AMPA | Air glyphosate | Air AMPA |
|----------------------------|----------|----------------------|----------------------------|----------------------|---------------------------|---------------------|
| begin | end | $\mu\text{g m}^{-3}$ | $\mu\text{g L}^{-1}$ | $\mu\text{g L}^{-1}$ | ng m^{-3} | ng m^{-3} |
| 04-22-08 | 04-29-08 | 25 | 0.15 | 0.09 | 0.40 | 0.01 |
| 04-29-08 | 05-06-08 | 33 | 0.04 | 0.05 | 0.53 | 0.02 |
| 05-06-08 | 05-13-08 | 41 | 0.12 | 0.05 | 0.85 | 0.02 |
| 05-13-08 | 05-20-08 | 28 | 0.22 | 0.16 | 0.34 | 0.01 |
| 05-20-08 | 05-27-08 | 36 | 0.70 | 0.06 | 1.02 | 0.03 |
| 05-27-08 | 06-03-08 | 38 | 0.54 | 0.08 | 0.74 | 0.02 |
| 06-03-08 | 06-10-08 | 23 | | | 0.41 | 0.04 |
| 06-10-08 | 06-17-08 | 117 | 0.00 | 0.04 | 1.50 | 0.09 |
| 06-17-08 | 06-24-08 | 55 | | | 0.74 | 0.05 |
| 06-24-08 | 07-01-08 | 37 | | | 0.31 | 0.03 |
| 07-01-08 | 07-08-08 | 31 | 0.16 | 0.03 | 0.19 | 0.02 |
| 07-08-08 | 07-15-08 | 27 | 0.49 | 0.40 | 0.28 | 0.03 |
| 07-15-08 | 07-22-08 | 50 | | | 0.49 | 0.03 |
| 07-22-08 | 07-29-08 | 4 | 0.57 | 0.04 | 0.08 | 0.01 |
| 07-29-08 | 08-05-08 | 37 | 1.60 | 0.48 | 0.12 | 0.00 |
| 08-05-08 | 08-12-08 | 30 | 0.00 | 0.00 | 0.13 | 0.00 |
| 08-12-08 | 08-19-08 | 31 | 0.38 | 0.35 | 0.24 | 0.00 |
| 08-19-08 | 08-26-08 | 24 | 0.00 | 0.11 | 0.03 | 0.00 |
| 08-26-08 | 09-02-08 | 37 | | | 0.30 | 0.08 |
| 09-02-08 | 09-09-08 | 22 | 0.00 | 0.17 | 0.13 | 0.02 |
| 09-09-08 | 09-16-08 | 26 | 0.39 | 0.00 | 0.05 | 0.01 |
| 09-16-08 | 09-23-08 | 53 | | | 0.19 | 0.01 |
| 09-23-08 | 09-30-08 | 51.5 | | | 0.04 | 0.00 |
| 09-30-08 | 10-07-08 | 92.2 | | | 0.07 | 0.02 |
| 10-07-08 | 10-14-08 | 31.5 | 0.05 | 0.00 | 0.01 | 0.00 |
| 10-14-08 | 10-21-08 | 47.6 | 0.00 | 0.00 | 0.01 | 0.00 |
| 10-21-08 | 10-28-08 | 30.3 | 0.00 | 0.00 | 0.01 | 0.00 |

E-2. Concentrations in Iowa

| Iowa in 2007 | | TSP | Rain glyphosate | Rain AMPA | Air glyphosate | Air AMPA |
|---------------------|----------|----------------------|----------------------------|----------------------|---------------------------|---------------------|
| begin | end | $\mu\text{g m}^{-3}$ | $\mu\text{g L}^{-1}$ | $\mu\text{g L}^{-1}$ | ng m^{-3} | ng m^{-3} |
| 04-17-07 | 04-24-07 | 66 | | | | |
| 04-24-07 | 05-01-07 | 54 | | | | |
| 05-01-07 | 05-08-07 | 64 | | | | |
| 05-08-07 | 05-14-07 | 95 | | | 0.34 | 0.97 |
| 05-14-07 | 05-22-07 | 70 | 0.40 | 0.10 | 0.00 | 0.00 |
| 05-22-07 | 05-29-07 | 47 | 0.00 | 0.10 | 0.12 | 0.02 |
| 06-05-07 | 06-12-07 | 32 | 0.20 | 0.00 | 1.27 | 0.10 |
| 06-12-07 | 06-19-07 | 67 | 1.60 | 0.10 | 5.38 | 0.25 |
| 06-19-07 | 06-26-07 | 52 | 0.20 | 0.00 | 0.19 | 0.05 |
| 06-26-07 | 07-03-07 | 63 | | | 0.75 | 0.05 |
| 07-03-07 | 07-10-07 | 57 | | | 1.03 | 0.07 |
| 07-10-07 | 07-17-07 | 68 | 2.50 | 0.20 | 3.39 | 0.22 |
| 07-17-07 | 07-24-07 | 50 | 0.20 | 0.00 | 0.05 | 0.00 |
| 07-24-07 | 07-31-07 | 53 | 0.20 | 0.00 | 0.00 | 0.00 |
| 07-31-07 | 08-07-07 | 67 | 0.10 | 0.00 | 0.09 | 0.05 |
| 08-07-07 | 08-14-07 | 61 | | | 0.00 | 0.00 |
| 08-14-07 | 08-21-07 | 20 | 0.40 | 0.20 | 0.00 | 0.00 |
| 08-21-07 | 08-28-07 | 44 | 0.10 | 0.00 | 0.00 | 0.00 |
| 08-28-07 | 09-04-07 | 49 | 0.00 | 0.00 | 0.07 | 0.00 |
| 09-04-07 | 09-11-07 | 47 | 0.00 | 0.00 | 0.00 | 0.00 |
| 09-11-07 | 09-18-07 | 63 | 0.00 | 0.00 | 0.00 | 0.02 |

| Iowa in 2008 | | TSP | Rain glyphosate | Rain AMPA | Air glyphosate | Air AMPA |
|---------------------|----------|----------------------|----------------------------|----------------------|---------------------------|---------------------|
| begin | end | $\mu\text{g m}^{-3}$ | $\mu\text{g L}^{-1}$ | $\mu\text{g L}^{-1}$ | ng m^{-3} | ng m^{-3} |
| 04-08-08 | 04-15-08 | | 0.00 | 0.00 | | |
| 04-15-08 | 04-22-08 | | 0.03 | 0.00 | | |
| 04-22-08 | 04-29-08 | | 0.00 | 0.00 | | |
| 04-29-08 | 05-06-08 | 137 | 0.00 | 0.02 | 0.87 | 0.00 |
| 05-06-08 | 05-13-08 | 8 | 0.00 | 0.03 | 0.19 | 0.00 |
| 05-13-08 | 05-20-08 | 29 | | | 0.22 | 0.00 |
| 05-20-08 | 05-27-08 | 18 | 0.08 | 0.02 | 0.17 | 0.00 |
| 05-27-08 | 06-03-08 | 10 | 0.07 | 0.02 | 0.16 | 0.04 |
| 06-03-08 | 06-10-08 | 9 | 0.00 | 0.00 | 0.09 | 0.01 |
| 06-10-08 | 06-17-08 | 10 | 0.18 | 0.00 | 0.59 | 0.03 |
| 06-17-08 | 06-24-08 | 19 | | | 3.42 | 0.38 |
| 06-24-08 | 07-01-08 | 13 | 0.82 | 0.10 | 0.70 | 0.14 |
| 07-01-08 | 07-08-08 | | 1.75 | 0.24 | 7.67 | 0.34 |
| 07-08-08 | 07-15-08 | 15 | 1.40 | 0.10 | 2.43 | 0.15 |
| 07-15-08 | 07-22-08 | 10 | 0.67 | 0.10 | 0.72 | 0.25 |
| 07-22-08 | 07-29-08 | 13 | 0.32 | 0.07 | 0.28 | 0.04 |
| 07-29-08 | 08-05-08 | 12 | | | 1.14 | 0.19 |
| 08-05-08 | 08-12-08 | 12 | 0.60 | 0.10 | 0.00 | 0.11 |
| 08-12-08 | 08-19-08 | 15 | 0.31 | 0.09 | 0.00 | 0.00 |
| 08-19-08 | 08-26-08 | 4 | | | 0.00 | 0.00 |
| 08-26-08 | 09-02-08 | | 0.10 | 0.00 | 0.00 | 0.00 |
| 09-02-08 | 09-09-08 | | 0.00 | 0.00 | | |
| 09-09-08 | 09-16-08 | | 0.04 | 0.03 | | |
| 09-16-08 | 09-23-08 | 42.4 | | | 0.00 | 0.08 |
| 09-23-08 | 09-30-08 | | 0.00 | 0.00 | | |
| 09-30-08 | 10-07-08 | | 0.07 | 0.00 | | |
| 10-07-08 | 10-14-08 | | 0.00 | 0.00 | | |
| 10-14-08 | 10-21-08 | | 0.00 | 0.00 | | |
| 10-21-08 | 10-28-08 | | 0.02 | 0.00 | | |

E-3. Rain concentrations in Indiana

| Indiana in 2004 | Rain glyphosate | Rain AMPA |
|------------------------|----------------------------|----------------------|
| collection day | $\mu\text{g L}^{-1}$ | $\mu\text{g L}^{-1}$ |
| 04-27-04 | 1.09 | 0.07 |
| 05-12-04 | 0.67 | 0.21 |
| 05-18-04 | 0.15 | 0.06 |
| 05-25-04 | 0.04 | 0.06 |
| 06-08-04 | 0.12 | 0.08 |
| 06-15-04 | 0.10 | 0.08 |
| 06-29-04 | 0.24 | 0.17 |
| 07-06-04 | 0.20 | 0.07 |
| 07-20-04 | 0.20 | 0.47 |
| 08-03-04 | 0.06 | 0.02 |
| 08-17-04 | 0.11 | 0.04 |
| 08-24-04 | <0.01 | 0.03 |
| 06-07-05 | 0.03 | 0.00 |
| 11-08-04 | <0.01 | <0.01 |

E-4. Glyphosate application (kg) in the study areas in Mississippi and Iowa

| date | MS in 2007 | MS in 2008 | IA in 2007 | IA in 2008 |
|--------------|-------------------|-------------------|-------------------|-------------------|
| Feb. 01 - 10 | 258 | 0 | 0 | 0 |
| Feb. 11 - 20 | 0 | 222 | 0 | 0 |
| Feb. 21 - 28 | 69 | 536 | 0 | 0 |
| Mar. 01 - 10 | 128 | 122 | 0 | 0 |
| Mar. 11 - 20 | 96 | 171 | 0 | 0 |
| Mar. 21 - 31 | 0 | 34 | 0 | 0 |
| Apr. 01 - 10 | 64 | 0 | 0 | 0 |
| Apr. 11 - 20 | 275 | 104 | 0 | 0 |
| Apr. 21 - 30 | 330 | 112 | 0 | 0 |
| May 01 - 10 | 299 | 452 | 39 | 71 |
| May 11 - 20 | 53 | 57 | 28 | 34 |
| May 21 - 31 | 380 | 443 | 317 | 75 |
| June 01 - 10 | 249 | 116 | 503 | 305 |
| June 11 - 20 | 96 | 158 | 215 | 632 |
| June 21 - 30 | 75 | 0 | 11 | 69 |
| July 01 - 10 | 330 | 147 | 362 | 290 |
| July 11 - 20 | 0 | 25 | 0 | 160 |
| July 21 - 30 | 52 | 0 | 0 | 32 |
| Aug. 01 - 10 | 0 | 0 | 0 | 50 |

E5. Wind speed and precipitation

| Mississippi study area | | Temp. | Wind speed | Precipitation | Wind speed | Precipitation |
|------------------------|----------|-------|------------|---------------|---------------------|---------------|
| begin | end | °C | MPH | in | m sec ⁻¹ | mm |
| 04-17-07 | 04-24-07 | 19 | 7.2 | 0.1 | 3.2 | 2.0 |
| 04-24-07 | 05-01-07 | 21 | 7.6 | 0.8 | 3.4 | 21.3 |
| 05-01-07 | 05-08-07 | 24 | 7.0 | 1.0 | 3.1 | 24.9 |
| 05-08-07 | 05-15-07 | 25 | 4.8 | 0.2 | 2.1 | 4.6 |
| 05-15-07 | 05-22-07 | 20 | 7.2 | 0.2 | 3.2 | 3.8 |
| 05-22-07 | 05-29-07 | 25 | 5.8 | 0.1 | 2.6 | 2.3 |
| 05-29-07 | 06-05-07 | 26 | 6.5 | 0.0 | 2.9 | 0.0 |
| 06-05-07 | 06-12-07 | 28 | 7.1 | 0.0 | 3.2 | 0.5 |
| 06-12-07 | 06-19-07 | 28 | 5.5 | 0.2 | 2.5 | 4.8 |
| 06-19-07 | 06-26-07 | 27 | 3.8 | 2.5 | 1.7 | 62.5 |
| 06-26-07 | 07-03-07 | 28 | 3.5 | 1.1 | 1.6 | 28.7 |
| 07-03-07 | 07-10-07 | 26 | 4.3 | 3.7 | 1.9 | 93.2 |
| 07-10-07 | 07-17-07 | 27 | 5.4 | 2.7 | 2.4 | 69.3 |
| 07-17-07 | 07-24-07 | 27 | 5.9 | 0.0 | 2.6 | 0.5 |
| 07-24-07 | 07-31-07 | 28 | 3.7 | 1.0 | 1.7 | 25.1 |
| 07-31-07 | 08-07-07 | 30 | 3.5 | 0.0 | 1.6 | 0.0 |
| 08-07-07 | 08-14-07 | 31 | 5.2 | 0.0 | 2.3 | 0.0 |
| 08-14-07 | 08-21-07 | 31 | 5.1 | 0.0 | 2.3 | 0.0 |
| 08-21-07 | 08-28-07 | 30 | 5.0 | 0.0 | 2.2 | 0.0 |
| 08-28-07 | 09-04-07 | 28 | 5.7 | 1.4 | 2.6 | 35.8 |
| 09-04-07 | 09-11-07 | 29 | 5.4 | 0.4 | 2.4 | 9.4 |
| 09-11-07 | 09-18-07 | 23 | 6.3 | 2.1 | 2.8 | 54.1 |
| 04-22-08 | 04-29-08 | 20 | 8.6 | 1.6 | 3.8 | 40.9 |
| 04-29-08 | 05-06-08 | 19 | 9.5 | 1.6 | 4.3 | 41.4 |
| 05-06-08 | 05-13-08 | 21 | 9.4 | 0.5 | 4.2 | 11.9 |
| 05-13-08 | 05-20-08 | 20 | 9.1 | 2.3 | 4.1 | 57.2 |
| 05-20-08 | 05-27-08 | 26 | 7.4 | 0.4 | 3.3 | 10.4 |
| 05-27-08 | 06-03-08 | 26 | 6.7 | 1.4 | 3.0 | 35.6 |
| 06-03-08 | 06-10-08 | 28 | 11.8 | 0.2 | 5.3 | 3.8 |
| 06-10-08 | 06-17-08 | 27 | 4.5 | 0.2 | 2.0 | 4.3 |
| 06-17-08 | 06-24-08 | 25 | 4.1 | 0.1 | 1.8 | 2.3 |
| 06-24-08 | 07-01-08 | 27 | 7.0 | 0.1 | 3.1 | 1.3 |
| 07-01-08 | 07-08-08 | 27 | 4.4 | 0.8 | 2.0 | 19.3 |
| 07-08-08 | 07-15-08 | 29 | 6.1 | 0.1 | 2.7 | 3.0 |
| 07-15-08 | 07-22-08 | 29 | 3.5 | 0.0 | 1.6 | 0.0 |
| 07-22-08 | 07-29-08 | 31 | 5.5 | 0.0 | 2.4 | 0.0 |
| 07-29-08 | 08-05-08 | 30 | 5.7 | 0.6 | 2.5 | 14.0 |

| | | | | | | |
|----------|----------|----|-----|------|-----|-------|
| 08-05-08 | 08-12-08 | 27 | 4.3 | 1.6 | 1.9 | 39.9 |
| 08-12-08 | 08-19-08 | 26 | 4.8 | 2.1 | 2.1 | 52.1 |
| 08-19-08 | 08-26-08 | 27 | 7.1 | 1.5 | 3.2 | 39.1 |
| 08-26-08 | 09-02-08 | 28 | 5.4 | 0.1 | 2.4 | 3.0 |
| 09-02-08 | 09-09-08 | 24 | 9.1 | 11.0 | 4.0 | 280.4 |
| 09-09-08 | 09-16-08 | 27 | 9.2 | 0.9 | 4.1 | 23.1 |
| 09-16-08 | 09-23-08 | 23 | 5.4 | 0.0 | 2.4 | 0.0 |
| 09-23-08 | 09-30-08 | 28 | 6.7 | 0.2 | 3.0 | 5.6 |
| 09-30-08 | 10-07-08 | 20 | 5.7 | 0.0 | 2.5 | 0.0 |
| 10-07-08 | 10-14-08 | 22 | 7.1 | 0.3 | 3.2 | 6.4 |
| 10-14-08 | 10-21-08 | 19 | 5.6 | 0.5 | 2.5 | 11.4 |
| 10-21-08 | 10-28-08 | 14 | 6.1 | 0.4 | 2.7 | 9.4 |

| Iowa study area | | Temp. | Wind speed | Precipitation | Wind speed | Precipitation |
|-----------------|----------|-------|------------|---------------|---------------------|---------------|
| begin | end | °C | MPH | in | m sec ⁻¹ | mm |
| 04-17-07 | 04-24-07 | 15 | 13.1 | 0.9 | 5.9 | 23.4 |
| 04-24-07 | 05-01-07 | 17 | 12.8 | 3.7 | 5.7 | 94.0 |
| 05-01-07 | 05-08-07 | 18 | 16.9 | 1.4 | 7.6 | 36.3 |
| 05-08-07 | 05-14-07 | 22 | 9.3 | 0.0 | 4.1 | 0.0 |
| 05-14-07 | 05-22-07 | 20 | 14.2 | 0.5 | 6.3 | 13.5 |
| 05-22-07 | 05-29-07 | 19 | 11.6 | 3.1 | 5.2 | 77.7 |
| 05-29-07 | 06-05-07 | 20 | 9.8 | 1.0 | 4.4 | 24.4 |
| 06-05-07 | 06-12-07 | 21 | 12.7 | 1.1 | 5.7 | 26.7 |
| 06-12-07 | 06-19-07 | 25 | 8.1 | 0.3 | 3.6 | 8.6 |
| 06-19-07 | 06-26-07 | 23 | 7.7 | 0.7 | 3.4 | 17.5 |
| 06-26-07 | 07-03-07 | 23 | 6.6 | 0.0 | 3.0 | 0.0 |
| 07-03-07 | 07-10-07 | 28 | 7.2 | 0.0 | 3.2 | 0.0 |
| 07-10-07 | 07-17-07 | 23 | 6.0 | 0.0 | 2.7 | 0.0 |
| 07-17-07 | 07-24-07 | 25 | 7.7 | 1.3 | 3.4 | 34.0 |
| 07-24-07 | 07-31-07 | 23 | 6.1 | 1.1 | 2.7 | 27.4 |
| 07-31-07 | 08-07-07 | 23 | 6.0 | 1.4 | 2.7 | 34.5 |
| 08-07-07 | 08-14-07 | 25 | 6.0 | 0.1 | 2.7 | 1.5 |
| 08-14-07 | 08-21-07 | 23 | 7.3 | 2.6 | 3.2 | 66.3 |
| 08-21-07 | 08-28-07 | 22 | 7.4 | 0.3 | 3.3 | 6.6 |
| 08-28-07 | 09-04-07 | 20 | 5.1 | 1.0 | 2.3 | 24.1 |
| 09-04-07 | 09-11-07 | 20 | 7.7 | 1.1 | 3.4 | 27.4 |
| 09-11-07 | 09-18-07 | 14 | 10.6 | 0.0 | 4.8 | 0.5 |
| 04-08-08 | 04-15-08 | 3 | 12.6 | 0.8 | 5.6 | 19.8 |
| 04-15-08 | 04-22-08 | 11 | 14.6 | 2.0 | 6.5 | 51.8 |
| 04-22-08 | 04-29-08 | 9 | 12.9 | 3.4 | 5.8 | 85.9 |
| 04-29-08 | 05-06-08 | 11 | 12.8 | 1.3 | 5.7 | 34.0 |
| 05-06-08 | 05-13-08 | 13 | 11.1 | 4.7 | 5.0 | 118.1 |
| 05-13-08 | 05-20-08 | 15 | 9.2 | 0.3 | 4.1 | 6.9 |
| 05-20-08 | 05-27-08 | 16 | 12.7 | 1.9 | 5.7 | 48.0 |
| 05-27-08 | 06-03-08 | 15 | 10.3 | 6.8 | 4.6 | 172.5 |
| 06-03-08 | 06-10-08 | 22 | 14.0 | 4.7 | 6.3 | 119.6 |
| 06-10-08 | 06-17-08 | 21 | 10.8 | 3.9 | 4.8 | 98.3 |
| 06-17-08 | 06-24-08 | 21 | 5.5 | 0.0 | 2.4 | 0.8 |
| 06-24-08 | 07-01-08 | 21 | 9.9 | 1.1 | 4.4 | 28.4 |
| 07-01-08 | 07-08-08 | 23 | 8.8 | 2.0 | 3.9 | 49.5 |
| 07-08-08 | 07-15-08 | 23 | 8.4 | 1.1 | 3.8 | 28.4 |
| 07-15-08 | 07-22-08 | 24 | 5.4 | 7.9 | 2.4 | 199.4 |
| 07-22-08 | 07-29-08 | 21 | 5.4 | 0.0 | 2.4 | 0.0 |

| | | | | | | |
|----------|----------|----|-----|-----|-----|------|
| 07-29-08 | 08-05-08 | 25 | 6.6 | 0.0 | 3.0 | 0.0 |
| 08-05-08 | 08-12-08 | 21 | 5.0 | 0.0 | 2.2 | 0.0 |
| 08-12-08 | 08-19-08 | 20 | 4.4 | 0.0 | 2.0 | 0.0 |
| 08-19-08 | 08-26-08 | 20 | 5.4 | 0.0 | 2.4 | 0.0 |
| 08-26-08 | 09-02-08 | 21 | 7.9 | 0.0 | 3.6 | 0.0 |
| 09-16-08 | 09-23-08 | 19 | 7.5 | 0.6 | 3.4 | 15.2 |
