SEASONAL AIR-WATER EXCHANGE OF TOXAPHENE IN LAKE MICHIGAN AND LAKE SUPERIOR

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Abstract

Studies from the turn of the century reported annual net volatilization of toxaphene from Lake Michigan and Lake Superior to the atmosphere. Net volatilization from Lake Superior was predicted to shift to net absorption before the year 2010. To measure current toxaphene concentrations and calculate instantaneous air-water fluxes, this study collected paired air-water samples in 2004 and 2005 on Lake Michigan and in 2006 on Lake Superior. Average(±SD) dissolved water concentrations were 380(±180) ng/m^3 for Lake Michigan and 730(±85) ng/m^3 for Lake Superior. Average gas-phase concentrations were 9.4(±4.1) pg/m^3 over Lake Michigan and 22(±20) pg/m^3 over Lake Superior. Instantaneous air-water fluxes averaged 240(±530) ng/m^2-season for Lake Michigan and 370(±1000) ng/m^2-season for Lake Superior. Mass budgets estimated a net export of 81(±30) kg/yr of toxaphene from Lake Michigan and 365(±64) kg/yr from Lake Superior. Half-lives were approximately 17 years for both lakes. These long residence times have prolonged toxaphene's elevated concentration in the upper Great Lakes, and will sustain it as a concerning contaminant in Lake Superior for well over 50 years.

Table of Contents

List of Tables

List of Figures

Chapter 1. Introduction

Toxaphene was first manufactured in the U.S. in 1947 by chlorinating pinenes ($C_{10}H_{16}$) and forming a complex mixture of hexa- to deca-chlorinated bornanes and camphenes (Buntln 1951). Upon entering the market, toxaphene quickly became a popular broad-spectrum pesticide. Its applications ranged from killing lampreys in streams to protecting cattle from scabies (Swackhamer 1999). The vast majority—over 85%—was used for the control of cotton insects like the boll weevil throughout the southeastern U.S. (Voldner and Li 1993). As DDT production decreased in the U.S. due to its diminishing efficacy and impending ban in 1972, toxaphene production increased in turn. By the end of the 1960's toxaphene had become the most heavily used pesticide in the country (Gianessi 1992). Before the beginning of its own phase out in 1982, over 300 million kg of toxaphene had been applied as a pesticide in the U.S (Voldner and Li 1995).

Up to 85% of toxaphene's total use in the U.S. occurred in the South, while only an estimated 1% occurred in the upper Midwest and Great Lakes Basin (Von Rumker 1974, MacLeod 2002). A smaller proportion was introduced into upper Midwestern lakes as a piscicide in efforts to control invasive species and make room for game fish (Rice and Evans 1984). In 1978, scientists were alarmed when Swain *et al.* (1978) documented elevated concentrations of organochlorine pesticides in fish tissues from Lake Siskiwit, an isolated and hydrologically distinct lake on Isle Royale. Since the island is 15 miles from the shore of Lake Superior, it was believed that Lake Siskiwit's seclusion had prevented its exposure to piscicides and agricultural runoff (Swain 1978). This suggested that the discovered chlorinated contaminants were highly mobile and had reached the Great Lakes region by long-range transport and atmospheric deposition; a realization that triggered an ongoing investigation into the atmospheric transport and air-water exchange of chlorinated compounds such as toxaphene.

Subsequent research revealed that approximately 70% (4 million kg) of the total toxaphene burden in the Great Lakes Basin was attributable to atmospheric transport originating outside of the region (MacLeod 2002). Even after a ban on toxaphene use, data from the 1990s showed ambient air concentrations in southern states to be up to 100 times greater than concentrations over the Great Lakes (Jantunen 2000). Further analysis of sediment samples from the upper Great Lakes found that concentration peaks in sediments concurred with peaks in toxaphene's agricultural use in southern states (Pearson 1997).

In contrast to other major contaminants, studies in the late 1990s revealed that toxaphene concentrations were highest in Lake Superior's water and biota relative to the other Great Lakes (Swackhamer 1999, Glassmeyer 1996). Measurements of average dissolved water concentrations in the mid-1990s found 1,120 ±180 ng/m^3 in Lake Superior, 380 ±120 ng/m^3 in Lake Michigan, and 470

±250 ng/m^3 in Lake Huron (Swackhamer 1999). Wet weight concentrations for lake trout in 1992 as reported by Glassmeyer *et al.* (2000) were 1,300 ±200 ng/g in Lake Superior, 490 ±50 ng/g in Lake Michigan, and 340 ±30 ng/g in Lake Huron. In particular, Lake Superior's trout concentrations were high enough to warrant the issuing of fish consumption advisories by the Ontario Ministry of the Environment and the U.S. Environmental Protection Agency (EPA).

Large quantities of Great Lakes fish are consumed by local communities and exported commercially throughout the U.S. and Canada. According to a 2002 survey of the Great Lakes Basin, over 4 million adults consume at least 1 meal of sport-caught fish from the Great Lakes each year and over 800,000 adults consume more than 24 (Imm 2005). Despite the benefits of a diet including fish, the consumption of contaminated Great Lakes fish has been linked to elevated levels of organochlorines in the blood and breast milk of humans (Hanrahan 1999, de Boer and Wester 1993, Falk 1999). Hazards to human health associated with toxaphene exposure have been deduced from toxicological studies of animals and case studies of habitually exposed workers or acute poisonings. A list of the identified health hazards includes the degeneration of the central nervous system, damage to the kidneys and liver, teratogenic effects such as immunosuppression, and an elevated risk of leukemia and lymphoma (de Geus 1999, ATSDR 2010).

Lake Superior's high levels of toxaphene contamination has been explained by its unique physical characteristics, namely its colder temperature, diminished productivity, and longer residence time relative to the other Great Lakes (James 2001, Quinn 1992). During the summers of 2005 and 2006, the surface water of Lake Superior was approximately 5 °C colder on average than Lake Michigan's (Schwab 1999). Colder water temperatures hinder a lake's primary productivity, which can in turn decrease the amount of a contaminant that becomes buried in the sediment (Swackhamer 1999). The cold also increases a lake’s absorption of toxaphene from the air by shifting the chemical’s equilibrium to more strongly favor the liquid phase (Bidleman 1989). Lake Superior’s volume is also larger than the rest of the Great Lakes combined (Quinn 1992). As a result, Lake Superior’s residence time is close to 180 years and more than 110 years longer than Lake Michigan’s (Quinn 1992). These reduced loss mechanisms explain how Lake Superior came to be the most contaminated of the Great Lakes and its continued slow removal of toxaphene.

As toxaphene use began declining during the end of the 1970's, air concentrations and the transport of toxaphene from the atmosphere to the Great Lakes began to diminish as well (Swackhamer 1999). Based on the dynamic mass budget of Swackhamer *et al.* (1999), the net annual air-water flux of Lake Superior reversed directions in 1980, when volatilization began dominating over absorption for the first time. Despite this, toxaphene has proven to be a highly persistent contaminant in the Great Lakes, and Lake Superior in particular. From 1982 to 1992 there were no observed changes in lipid concentrations in Lake Superior lake trout (Glassmeyer 2000), and the lake was still 200 to 1000% saturated with toxaphene when sampled in 1998 (James 2001).

Few updates to the literature have been made since the end of the 20th century, preventing the validation of the dynamic mass budget model of Swackhamer *et al.* (1999) and its prediction of Lake Superior shifting from net volatilization to net absorption. Additionally, seasonal patterns observed in dissolved toxaphene concentrations from the 1990s in Lake Michigan and Lake Superior have yet to be examined (James 2001). A further concern is whether the decontamination of the two lakes is continuing at the same rate. To address these questions a series of paired air and water samples were collected from across Lake Michigan and Lake Superior in the spring and summer. These concentration data were used to analyze within-lake variation, compare the seasonality of toxaphene levels, and calculate instantaneous mass fluxes at individual sampling sites. Estimated sedimentation and seasonal air-water fluxes were then combined to model toxaphene mass budgets for each lake.

Chapter 2. Experimental Methods

2.1. Atmospheric and water sampling

This study was performed in cooperation with the EPA's Great Lakes Aquatic Contaminant Survey (GLACS) water monitoring program. Researchers from the University of Minnesota gathered samples while aboard the EPA's *R/V Lake Guardian* during cruises lasting from 5 to 6 days. Sampling locations consisted of both near shore and open water sites and are indicated in Figure 2.1 (see Appendix A for site coordinates). These locations are historical sampling sites used by the EPA, U.S. Fish and Wildlife Service and other research facilities. The repeated use of these locations allows for the comparison of individual site concentrations across studies and over time.

Prior to sampling, glass fiber filters (GF/Fs) were combusted at 450 °C and placed in combusted aluminum foil. XAD-2 polymeric resin was rinsed by two sequential Soxhlet extractions: 24 hours of rinsing with dichloromethane (DCM) followed by 24 hours in methanol. Next, the resin was cleansed with MilliQ water and stored in a MilliQ bath. The glass columns were packed with the XAD-2 resin and refrigerated until required for sampling.

Water samples, ranging in volume between 750 to 1500 L, were collected at a depth of 3 meters using a submersible pump (see Appendix B for site specific volumes). In order to isolate the particle and dissolved phases, samples were passed through a prepared GF/F and then a glass column packed with XAD-2 resin. Air samples were taken by high volume air samplers and deployed on booms out over the front of the bow to limit contamination. Samples were pulled for 12 consecutive hours through two 8x10 inch series F GF/Fs and stored in stainless steel canisters containing cleansed XAD-2 resin. Flow rates were recorded using a Roots meter and used to measure total volume.

Following sampling, exposed GF/Fs were folded and placed back in combusted aluminum foil envelopes. Resin from each water sample was stored in a glass jar. Air sample canisters were placed in combusted aluminum foil and stored in steel tins sealed with PTFE tape. All envelopes, jars, and canisters were likewise placed inside plastic zip bags and stored at either 4 °C (water samples) or frozen (air samples) until ready for extraction.

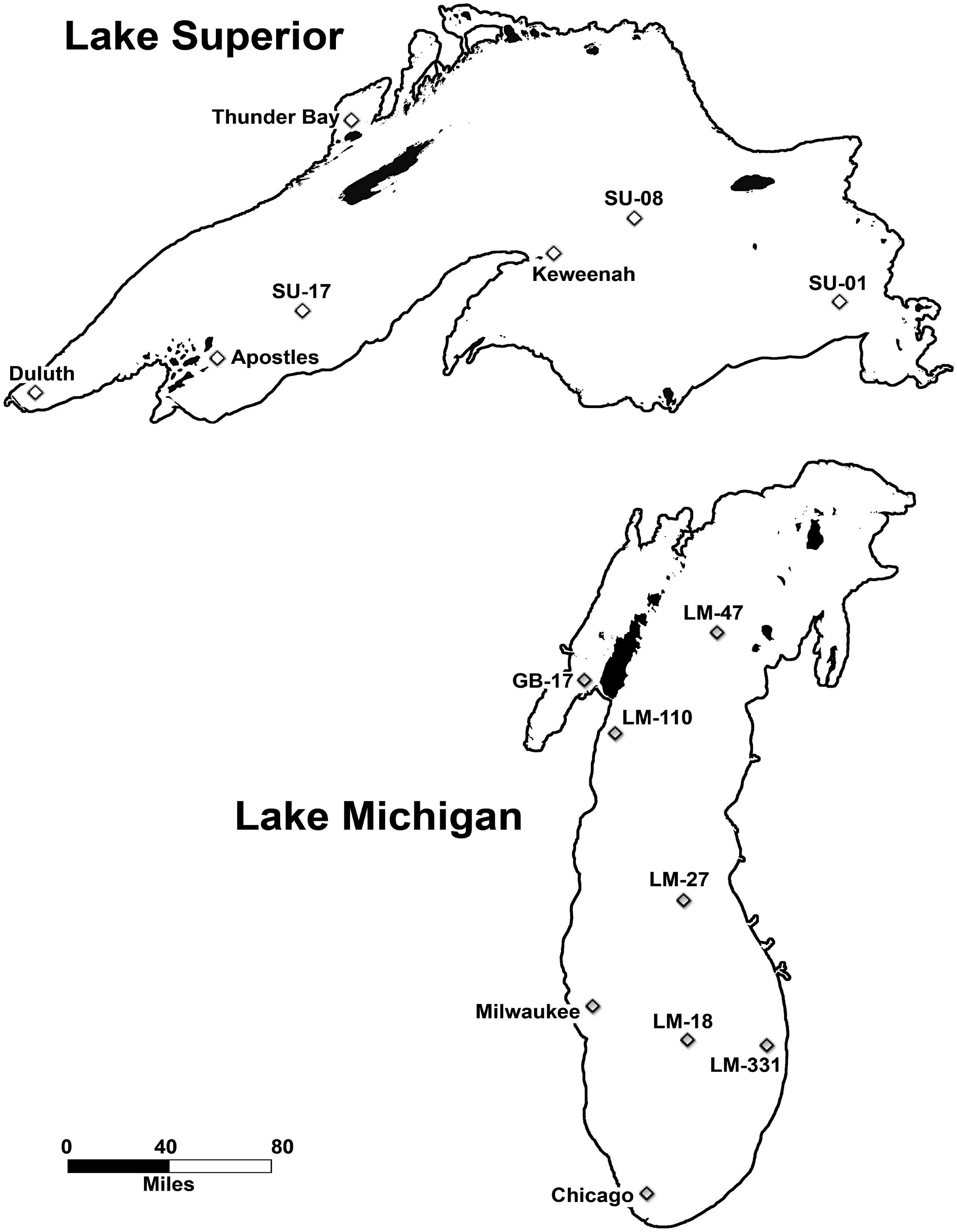

Figure 2.1. Map of sampling sites. Lake Michigan cruises occurred during July of 2004 and May of 2005. Lake Superior cruises occurred during May and July of 2006.

2.2. Extraction and Analysis

Extraction and analysis of the samples was conducted at the University of Minnesota. XAD-2 resin and GF/F samples were first Soxhlet extracted into a separatory funnel using 5 aliquots of 20 ml methanol. An additional 300 mL of methanol was added to the Soxhlet and run for 4 hours. The Soxhlet was then charged with 300 mL of DCM and run for 16-24 hours, after which 100 mL of Barnsted Nanopure water, 50 mL of saturated NaCl solution, and 50 mL of hexane were added to the funnel and mixed by agitation for 3 minutes.

Water was removed from the separatory funnel and the hexane drained into a flask containing 150 g Na_2SO_4. Two washes of 15 mL hexane were used to rinse the separatory funnel and the resulting rinsate added to the flask containing Na_2SO_4. Methanol extracts were reduced in volume to 10 to 15 mL using rotary evaporation. These were combined with the DCM extracts and solvent exchanged to hexane before being reduced in volume to approximately 1 mL.

Interfering compounds were removed on a glass column—1 x 30 cm—containing 3 g ashed sodium sulfate, 4.5 g 0% deactivated silica, and 6 g 2% deactivated alumina. Using 175 mL of 15% DCM in hexane, the column was eluted and the resulting rinsate labeled "F1". The column was eluted again using 50 mL of 40% DCM in hexane and the resulting rinsate labeled "F2". F1 extracts were solvent exchanged to hexane and volume reduced to approximately 1 mL, before stored in a freezer. Just prior to instrumental analysis, nitrogen gas steam was used to further volume reduce the F1 extracts to a few hundred microliters. PCB congener 204 was then added to each sample as an internal standard.

After PCB analysis, F1 and F2 extracts were combined for toxaphene analysis. A Hewlett-Packard 5973 coupled to a 5890A gas chromatograph analyzed the extracts by electron-capture, negative-ion, gas chromatographic / mass spectrometry (ECNI-GC/MS). This method was developed by Swackhamer *et al.* (1998) and was followed in this study with minor modifications. Using ECNI-GC/MS has been shown to be as sensitive as a gas chromatographic electron capture detector (GC-ECD), while also allowing for mass spectra confirmation criteria and the elimination of interferences from other chlorinated compounds such as chlordane and chlordene (Swackhamer 1998).

The column was a 60 m x 0.25 mm D8-5MS (J&W Scientific) with a 0.25 mm coating. Helium was used as the carrier gas and methane as the reagent. The temperature program was set to: 80 to 210 °C at 10 °C/min, 210 to 250 °C at 0.8 °C/min, 250 to 290 °C at 10 °C/min. The injection port and transfer line were both held at 270 °C, with a source temperature of 100 °C and a pressure of 1.0 Torr.

2.3. Quality Assurance

Each analysis series consisted of four field samples, one field blank, and one laboratory procedural blank. Before extraction, each sample and blank was first spiked with a $^{13}C_1$-chlordane recovery surrogate. Due to cis- and trans-nonachlor sharing a similar mass spectrum with toxaphene, analyses of the three were performed concurrently. Multiple procedural and field blanks exhibited several large toxaphene peaks. These mostly fell within the hepta-chlorinated range and had nearly identical elution times as the chlordane surrogate. In the cases when matching peaks were identified in both a sample and a blank from the same series, the peaks were removed from the sample's toxaphene total.

Several duplicate air and water samples were taken at various sites on both lakes to assess the precision of the extraction and analysis process. The average relative percent difference—absolute difference between the two samples divided by their average—was 22% in duplicate water samples and 30% in duplicate air samples.

Chapter 3. Results

3.1. Air Concentrations

Summaries of measured gas-phase concentrations are shown in Figures 3.1 and 3.2. For Lake Michigan, gas-phase air concentrations averaged 9 ±4 pg/m^3 in May of 2005. The air samples over Lake Superior averaged 12 ±9 pg/m^3 in May and 31 ±24 pg/m^3 in July of 2006. Site SU-08 on Lake Superior exhibited air concentrations that were more than double the mean during both seasons. One explanation of elevated air concentrations by Glassmeyer *et al.* (1999) suggests that spiraling wind patterns can cause an air parcel to recirculate over the open water of Lake Superior. An air parcel's prolonged exposure to volatilization from the surface of the lake would result in the accumulation of higher levels of toxaphene.

Lake Superior's average gas-phase concentration during the colder month of May was markedly lower than the average in July. This finding agrees with previous literature shown in Figure 3.3, which has consistently observed the highest gas-phase concentrations over the Great Lakes during the summer and the lowest concentrations during the winter. Measurements of gas-phase concentrations in 1997 by (Glassmeyer 1999) ranged from 0.2 to 2.9 pg/m^3 during the winter and from 6.6 to 15 pg/m^3 during the summer. Similarly, Burniston *et al.* (2005) found air concentrations that averaged 4.6 pg/m^3 in the winter and concentrations that averaged 19 pg/m^3 in the summer.

Lake Superior's average gas-phase concentrations were comparable to past literature values shown in Figure 3.3. The average of reported concentrations from 1993 to 1998 was 10 ±6 pg/m^3 in the spring and 31 ±19 pg/m^3 in the summer. Figure 3.3 also demonstrates that average concentrations in this study were as high as samples collected throughout the 1990s. The lack of a significant trend in historic concentrations suggests that concentrations in the air have remained steady since 1993. This may be attributable to increases in average air temperatures in the Great Lakes Basin and elsewhere. As warmer weather increases, the volatilization of toxaphene into the air from soil and water increases along with it. Based on data collected by the National Oceanic and Atmospheric Administration (NOAA) from 1979 to 2006, Austin and Colman (2007) estimated air temperatures were increasing over Lake Superior by 0.1 ±0.026 °C per year. After 13 years this rate would amount to an increase of 1.3 °C in average air temperatures.

The lingering of toxaphene's elevated air concentrations—long after its ban—demonstrates the persistence of some chlorinated contaminants. While it is no longer applied to cotton fields in the U.S., toxaphene that volatilizes from contaminated farmland continues to be transported to the Great Lakes (Li 2012). According to the mass budget model by Li *et al.* (2012), soils in the South still held over 29 million kg of toxaphene and had volatilized over 360 tons to the atmosphere in the year 2000.

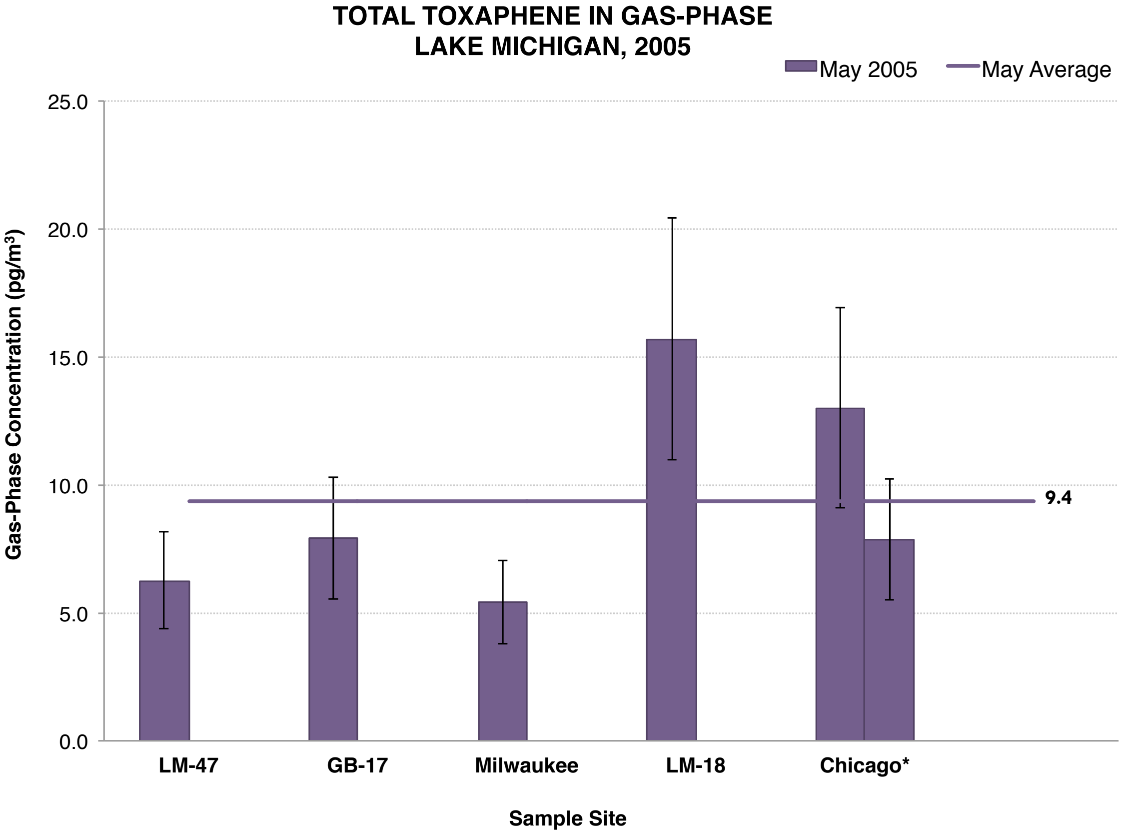

Figure 3.1. Gas-phase ($C_{a,g}$) toxaphene concentrations over Lake Michigan, May 2005. Sites are ordered from north to south. Error bars are based on the average percent difference in duplicate samples (30%). Starred (*) site indicates duplicate samples. Details listed in Table C.1.

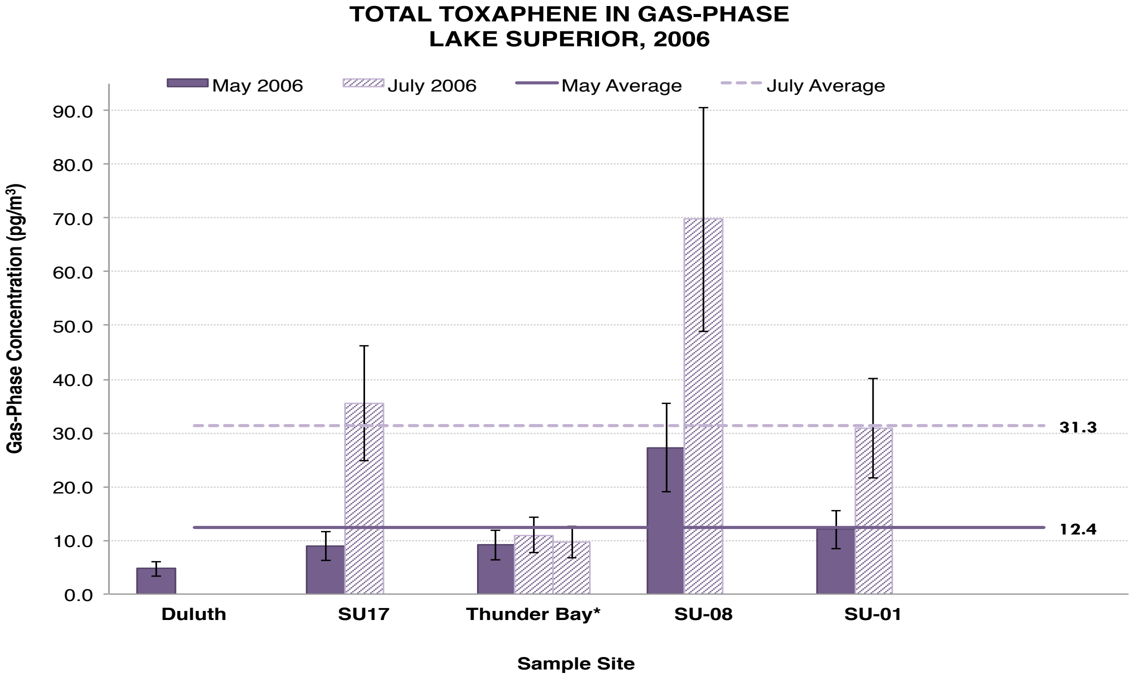

Figure 3.2. Gas-phase ($C_{a,g}$) toxaphene concentrations over Lake Superior, 2006. Sites are ordered from west to east. Error bars are based on the average percent difference in duplicate samples (30%). Starred (*) sites indicate duplicate samples. Details listed in Table C.2.

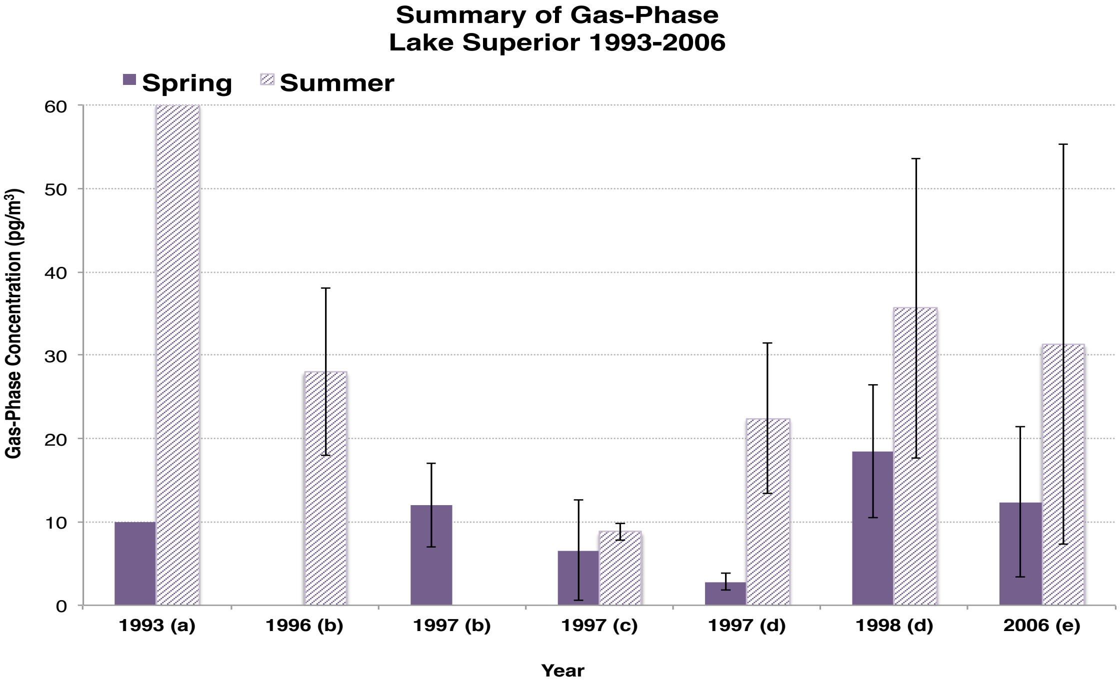

Figure 3.3. Summary of gas-phase ($C_{a,g}$) toxaphene concentrations over Lake Superior, 1993-2006. Error bars represent one standard deviation. [a] Hoff *et al.* (1993). [b] Jantunen *et al.* (2003). [c] Glassmeyer *et al.* (1999). [d] James *et al.* (2001). [e] This study.

3.2. Water Concentrations

Lake Michigan water samples, shown in Figure 3.4, ranged from 240 to 460 ng/m^3 with an average of 315 ng/m^3 in July of 2004, and ranged from 250 to 700 ng/m^3 with an average of 430 ng/m^3 in May of 2005. Shown in Figure 3.5, Lake Superior water samples in this study ranged from 460 to 1330 ng/m^3 with an average of 790 ng/m^3 in May, and ranged from 420 to 900 ng/m^3 with an average of 670 ng/m^3 in July of 2006. The 95% confidence interval of Lake Superior's average dissolved concentration (740 ±125 ng/m^3) in 2006 includes the prediction of 630 ng/m^3 made by the dynamic mass budget of Swackhamer *et al.* (1999). However, the model's underestimate suggests that it is overestimating outputs such as volatilization or underestimating annual inputs such as dry deposition.

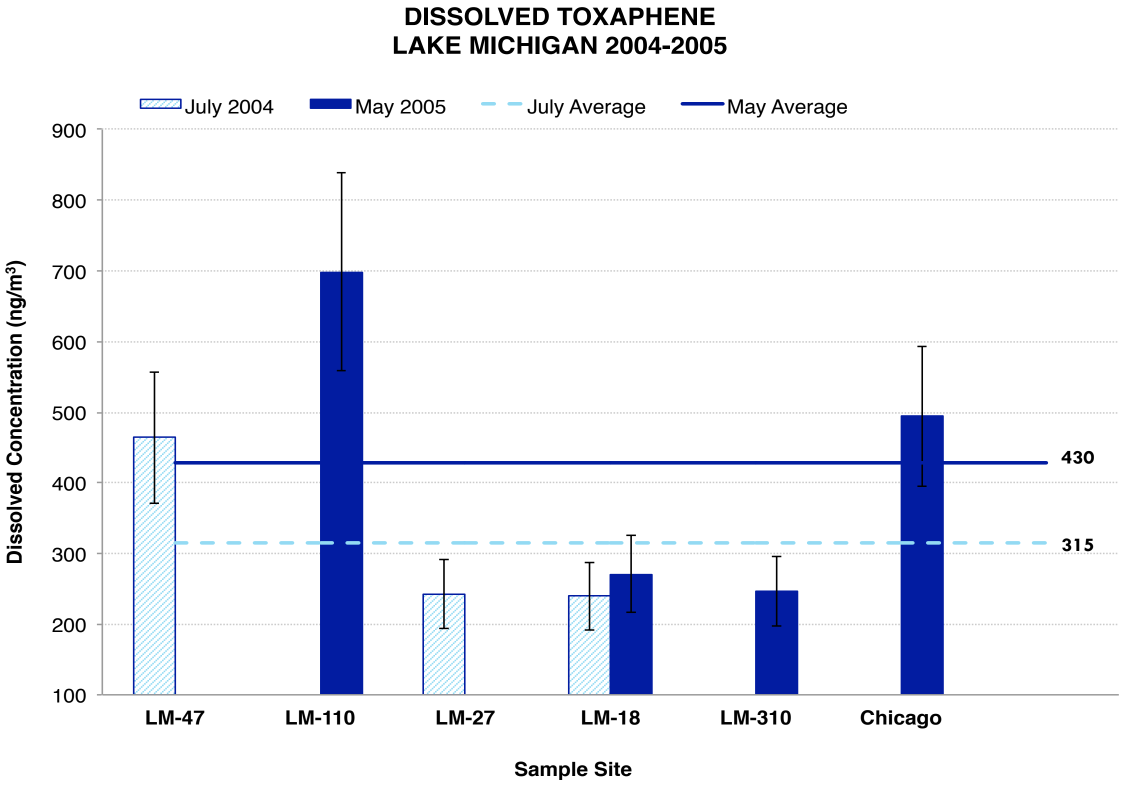

Figure 3.4. Dissolved water ($C_{w,d}$) toxaphene concentrations in Lake Michigan, 2004-2005. Error bars are based on the average percent difference in duplicate samples (20%). Details listed in Table C.4.

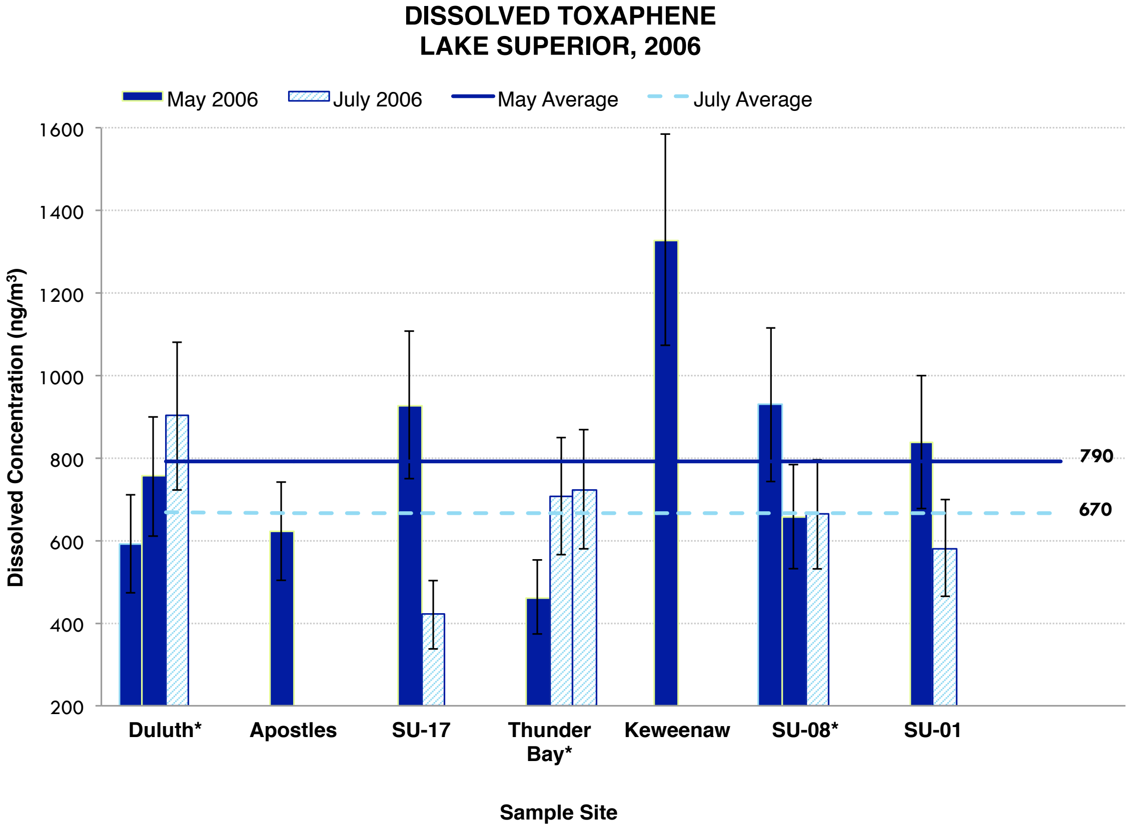

Figure 3.5. Dissolved water ($C_{w,d}$) toxaphene concentrations in Lake Superior, 2006. Error bars are based on the average percent difference in duplicate samples (20%). (*) sites indicate duplicate samples. Details listed in Table C.5.

In contrast to the greater atmospheric concentrations observed during summer months, both lakes demonstrated higher average dissolved water concentrations in the spring. Data from James *et al.* (2001) demonstrated the same trend between seasons. In samples collected from Lake Superior in 1998, water concentrations showed a statistically significant ($p<0.05$) decrease of 290 ng/m^3 between the spring and summer. The net effects of lake mixing and summer stratification are one possible explanation for this disparity. Because spring samples are generally collected before the lakes become stratified, their surfaces are able to mix freely with deeper waters and water concentrations in the lakes remain uniform throughout. In contrast, summer samples are collected after the lakes have been stratified for some time. Due to the epilimnion's resulting isolation, the surface layers of the lakes become depleted of toxaphene through the processes of volatilization and particle settling. Lake Michigan's earlier date of stratification could explain the more extreme difference in its average spring and summer water concentrations (30% in Lake Michigan and 15% in Lake Superior). Assuming an average thermocline depth of 10 meters in the summer, as seen for Lake Superior in Austin and Allen (2011), the observed reduction in summer concentrations would correspond to toxaphene exports of 50 kg from Lake Michigan and 100 kg from Lake Superior. In terms of air-water fluxes, these exports amount to -1,500 ng/m^2-season for Lake Michigan and -1,200 ng/m^2-season for Lake Superior.

Historic water concentrations, shown in Figure 3.6, indicate that dissolved water concentrations from 1993 to 2006 have declined in Lake Superior but remained steady in Lake Michigan. The decrease in Lake Superior's average concentration from 1993 to 2006 corresponds to a total mass loss of 5.7 metric tons and a loss rate of -440 kg/yr. Assuming first order exponential decay, the best fit equation through the average concentrations from 1993 and 2006 has a decay constant(±SE) of 0.042 ±0.012. This corresponds to a half-life for toxaphene in Lake Superior ranging from 13 to 23 years, a range just below the 18 to 31 years estimated from fish concentrations in Glassmeyer *et al.* (1999).

For Lake Michigan, the slope of the line running from the average concentration in 1995 to the average concentration in 2005 is negligible (< 1 ng/m^3-yr) and suggests that Lake Michigan is nearing a steady state in which its total toxaphene imports are equal to its exports. While contradicting the calculated volatilization rates of over 400 kg/yr seen in James *et al.* (2001), this conclusion agrees with the model by Swackhamer *et al.* (1999) showing Lake Michigan approaching equilibrium near the end of the 1990s.

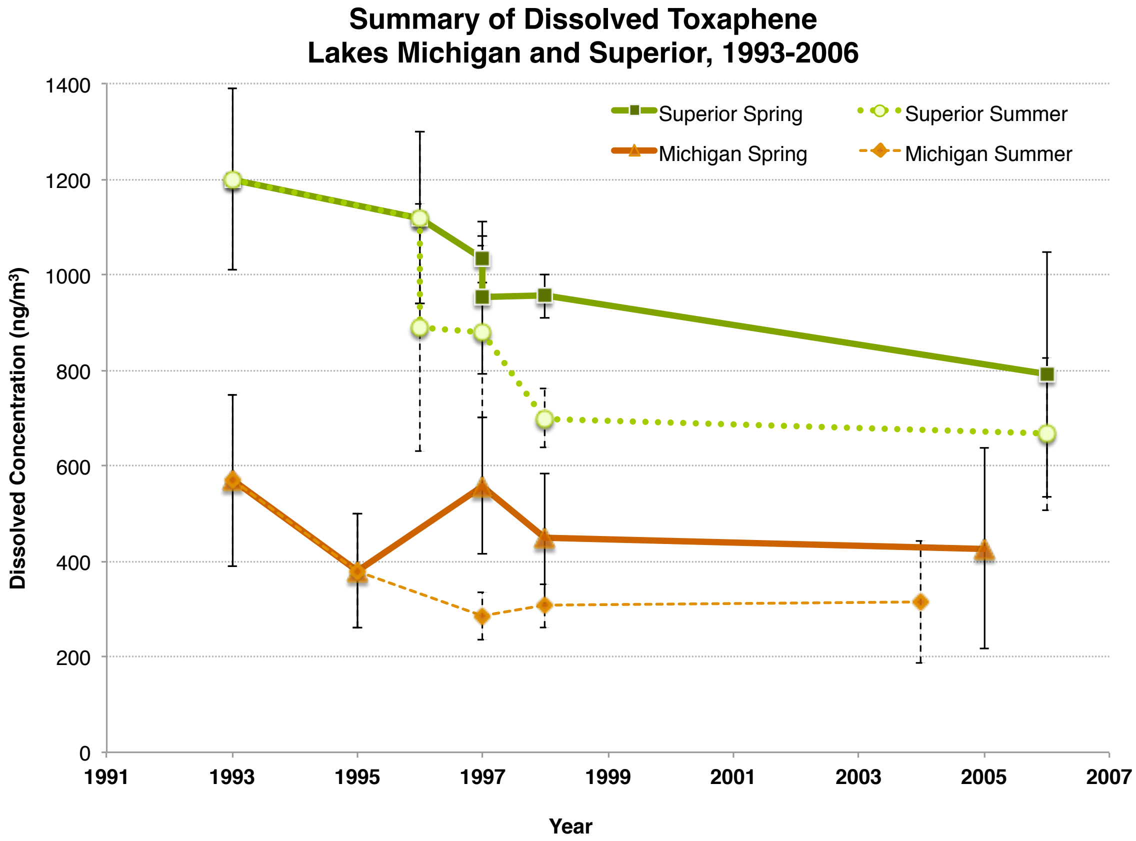

Figure 3.6. Summary of dissolved water ($C_{w,d}$) toxaphene concentrations in Lakes Michigan and Superior, 1993-2006. Error bars represent one standard deviation. Years with one data point represent average annual concentrations. See Tables C.6 and C.7 for references.

3.3. Air-Water Flux

Toxaphene in the atmosphere is mostly in the vapor phase and has a low Henry's law constant in comparison to other chlorinated contaminants (Glassmeyer 2000). These unique characteristics cause gas absorption to dominate over other atmospheric inputs of toxaphene to the Great Lakes (Swackhamer 1999). The stagnant two-film model developed by Whitman is commonly used when describing organic contaminant transport across the air-water interface (Achman 1993). In Whitman's model, a compound's total resistance to mass transfer is determined by the sum of its resistances in both the air and water layers (Whitman 1923). For toxaphene, however, the air-side resistance is much greater than the water-side resistance. This allows for toxaphene's overall mass transfer coefficient (K_{ol}) to be approximated solely by its air-side mass transfer coefficient (James 2001). Therefore, the instantaneous flux of toxaphene can be calculated by multiplying its air-side mass transfer coefficient ($k_{a,tox}$) by the air-water concentration gradient:

$$Flux_{into\ Lake} = k_{a,tox} \times \left(C_{a,g} - C_{w,d} \times H'\right) \tag{1}$$

where $k_{a,tox}$ (m/s) is the air-side mass transfer coefficient, $C_{a,g}$ (ng/m^3) is the gas phase air concentration, $C_{w,d}$ (ng/m^3) is the dissolved water concentration, H' is the unitless Henry's law constant, and $Flux_{into\ Lake}$ is in units of ng/m^2•sec, as in James *et al.* (2001). Fluxes from this study are best described as daily fluxes since air samples were drawn for 6 to 10 hours and water samples were pumped for 1 to 2 hours. A negative flux indicates volatilization from the water to the atmosphere.

The air-side mass transfer coefficient ($k_{a,tox}$) is correlated with the mass transfer of water and accordingly varies with the air-water interface temperature and wind speed (Achman 1993). The relationship of $k_{a,tox}$ to water can be approximated as:

$$k_{a,tox} = k_{a,water}\left(\frac{D_{a,tox}}{D_{a,water}}\right)^{n} \tag{2}$$

where $k_{a,water}$ (m/s) is the air-side mass transfer coefficient for water, D_a (cm^2/sec) is a compound's molecular diffusivity in air, and the constant n is 0.61 (Schwarzenbach et al. 1992, Smith et al. 1980). The air-side mass transfer coefficient for water ($k_{a,water}$) can be approximated directly from the wind speed over a lake (Schwarzenbach 1992):

$$k_{a,water} = 0.002 \times u_{10} + 0.003 \tag{3}$$

where u_{10} (m/s) is the wind speed at a reference height of 10 m. The wind speeds used in the calculations for this study were averages based on the hourly wind speed measurements taken over the course of a site's entire sampling period.

Diffusivities for water vapor and toxaphene in air were calculated using the Fuller, Schettler, and Giddings (FSG) method:

$$D_{a,tox} = \frac{0.001 \times T^{1.75} \times \sqrt{M_r}}{P \times \left(\sqrt[3]{V_{air}} + \sqrt[3]{V_{tox}}\right)^2} \tag{4}$$

where $D_{a,tox}$ is the diffusion coefficient of toxaphene in air, T (Kelvin) is the air-water interface temperature, P (atm) is the pressure, M_r is the unitless mass ratio of the molecular weights of air and toxaphene, and V_{air} and V_{tox} are the molar volumes of air and toxaphene (Fuller 1966).

The Henry's law constant for toxaphene varies with interface temperature, and experimental observation has derived the relationship:

$$H' = \frac{10^{10.42 - 3209/T}}{R \times T} \tag{5}$$

where R (Pa•m^3/mol•K) is the gas constant and T is the air-water interface temperature in Kelvin (Jantunen and Bidleman 2000).

Calculated instantaneous mass fluxes were multiplied by the number of seconds in 3 months to convert from units of ng/m^2•second into ng/m^2•season. The seasonal fluxes for sites with paired air and water samples are shown in Figures 3.7 and 3.8. The average of Lake Michigan fluxes was -236 ±145 ng/m^2•season in the spring of 2005. For Lake Superior, fluxes averaged -488 ±110 ng/m^2•season in the spring and -246 ±190 ng/m^2•season in the summer of 2006. The uncertainties in the fluxes, shown as error bars in Figures 3.7 and 3.8, were estimated by propagating the uncertainty in wind speeds, duplicate air and water samples, and Henry's law constants.

The near shore site at Chicago on Lake Michigan demonstrated a higher volatilization of toxaphene than the open water site at LM-18. Similarly, the near shore sites of Duluth and Thunder Bay on Lake Superior demonstrated the greatest volatilization during the spring and summer respectively. In contrast, the open water site at SU-08 exhibited a net absorption of toxaphene during both seasons. This disparity between near shore and open water sites was predominantly driven by variation in temperature. Near shore sites on average exhibited warmer surface water temperatures during both seasons. The average of the Thunder Bay and Duluth sites for both sampling periods was 11 °C, whereas the average of the open water sites was only 9.9 °C. In addition to being colder than near shore sites, site SU-08's higher air concentrations during both sampling periods further reduced its volatilization of toxaphene.

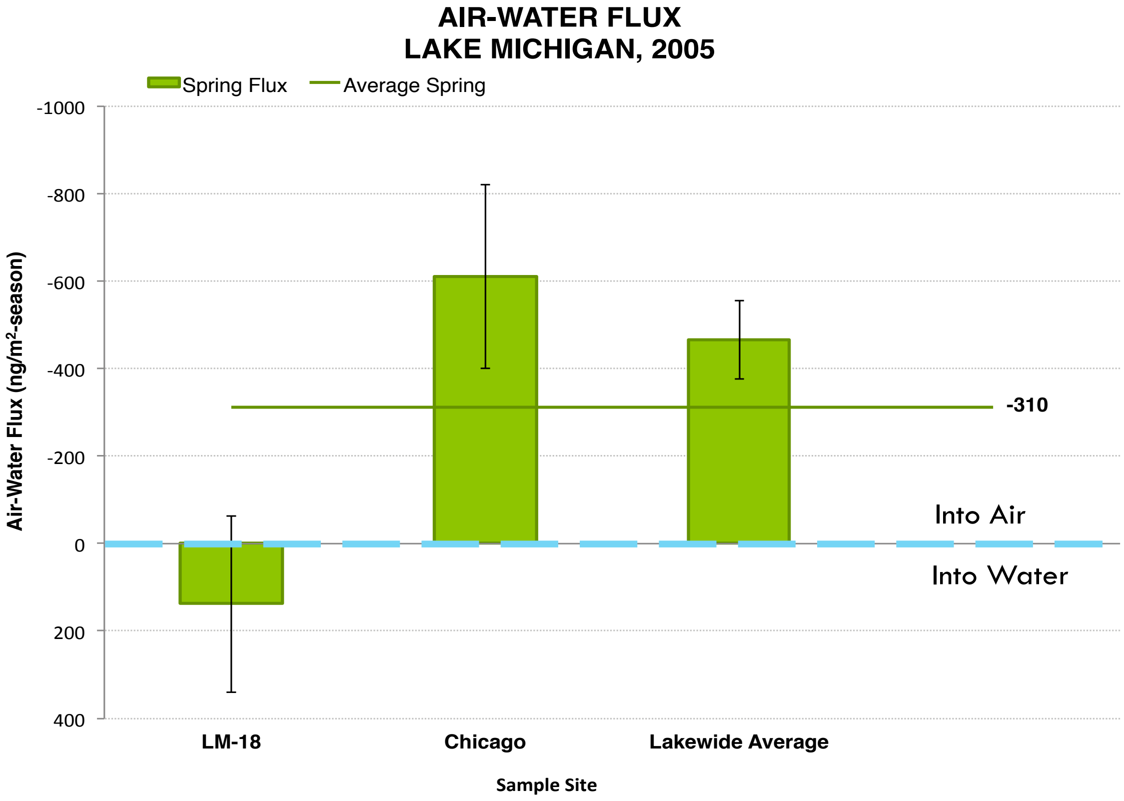

Figure 3.7. Seasonal air-water toxaphene fluxes for Lake Michigan, spring 2005. Error bars represent the propagation of uncertainty in wind speeds, Henry's law constants, and duplicate air and water samples. Details listed in Table C.9.

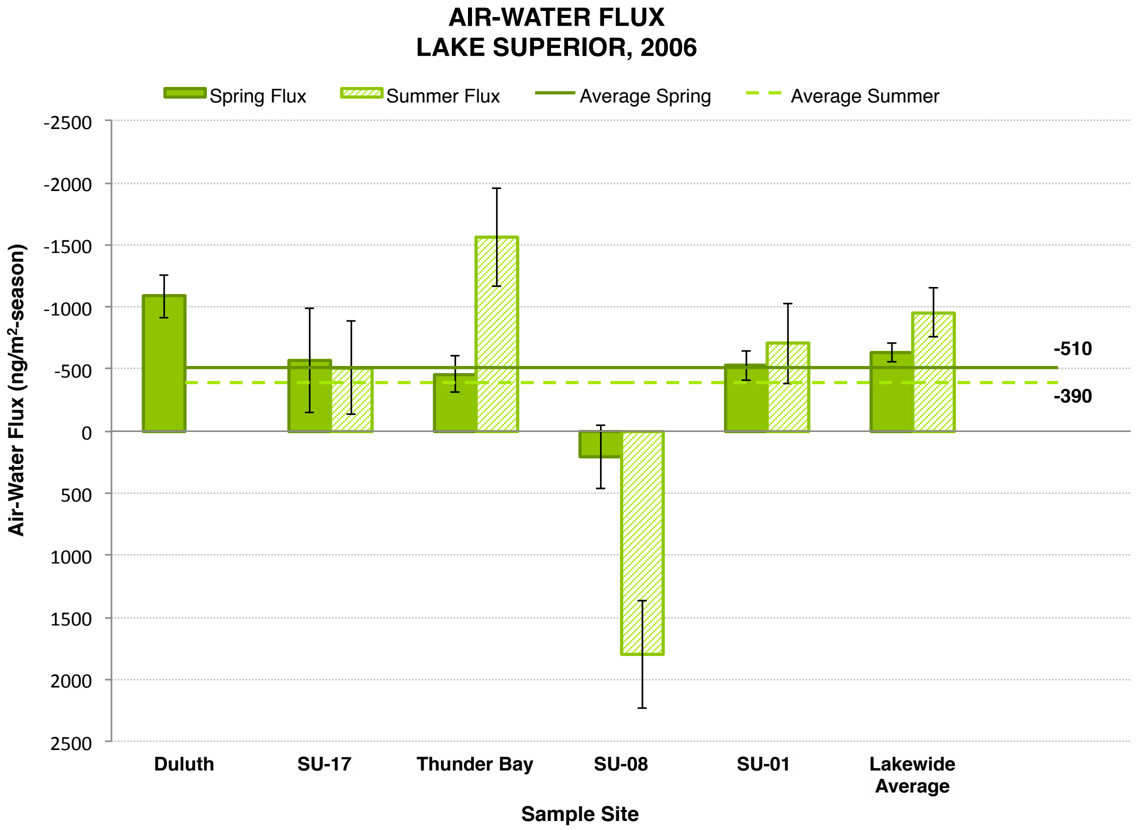

Figure 3.8. Seasonal air-water toxaphene fluxes for Lake Superior, spring and summer 2006. Error bars represent propagation of uncertainty in wind speeds, Henry's law constants, and duplicate air and water samples. Details listed in Table C.10.

Previous studies have calculated fluxes based on lakewide averages for each parameter. For comparison, Figures 3.7 and 3.8 also include fluxes labeled "Lakewide Average". These fluxes were calculated based on values corresponding to the average for each parameter within a given lake and season. Compared to the average of sites with paired air-water data, the "Lakewide Average" fluxes were greater in magnitude. Both lakes were calculated to have average seasonal fluxes of toxaphene from the water to the air. Despite Lake Superior's colder temperature and higher air concentrations, it was shown to be volatilizing 200 ng/m^2•season more than Lake Michigan in the spring. The larger magnitude of fluxes in Lake Superior's was a result of its greater wind speeds and higher dissolved toxaphene concentrations.

Shown in Figure 3.8, the average volatilization from Lake Superior during the spring surpassed that of the summer. This might be expected since the water concentrations are higher and the air concentrations are lower in the spring. However, warmer water temperatures during the summer can increase toxaphene's Henry's law constant more than enough to make up for the change in concentrations. James *et al.* (2001) observed this in 1997 and 1998 in both Lake Michigan and Lake Superior. During an unusually warm summer in 1998, in which August water temperatures reached 4 to 5 °C above the year before, volatilization in the summer was three times greater than in the spring. (James 2001)

Summaries of Lake Michigan and Lake Superior fluxes documented in previous literature are shown in Figures 3.9 and 3.10. The average seasonal fluxes for both lakes in 1997 and 1998 were much greater in magnitude than those observed in this study. The elevated fluxes seen in James *et al.* (2001) are mostly due to the study's use of mass transfer coefficients from Hoff *et al.* (1993), which were based on Lake Superior wind speeds averaging more than 9 m/s. In comparison, this study observed average wind speeds of 4 m/s on Lake Michigan in 2005 and 6 m/s on Lake Superior in 2006. Nevertheless, the declining flux magnitudes support the earlier conclusion based on Figures 3.3 and 3.6 that water concentrations in Lake Superior are declining faster than air concentrations. As this trend continues, the volatilization of toxaphene from Lake Superior will continue to decrease each year as the lake approaches equilibrium with the air.

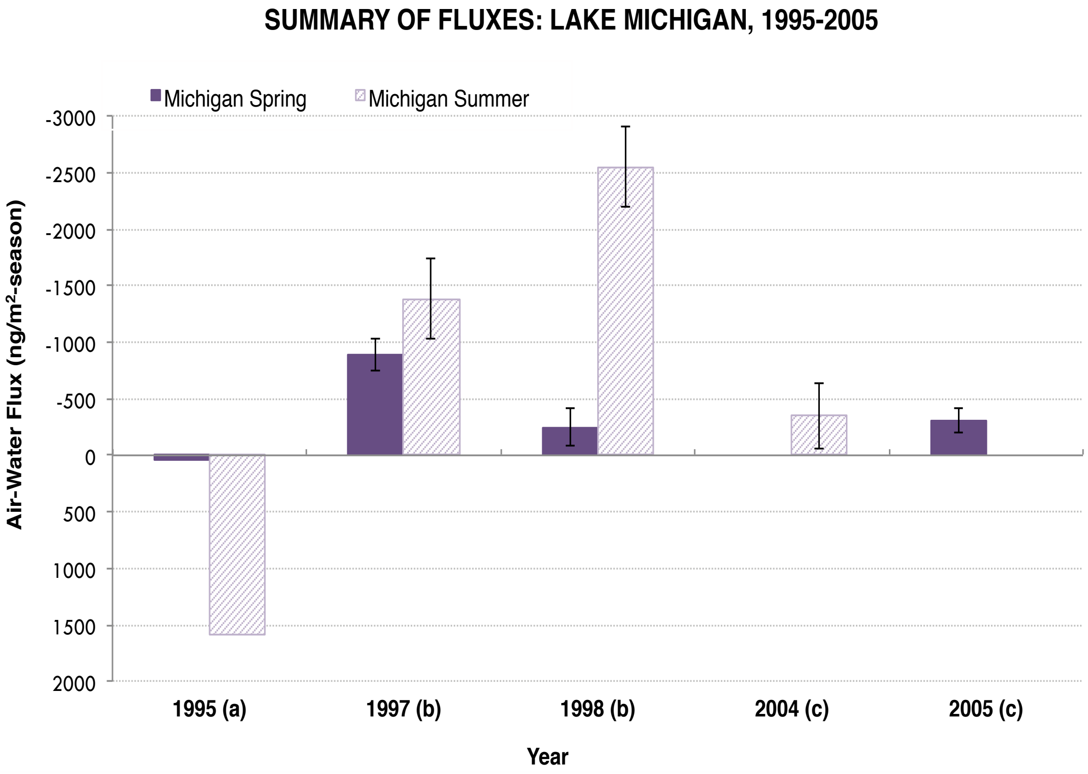

Figure 3.9. Summary of seasonal air-water toxaphene fluxes for Lake Michigan, 1995-2005. Details listed in Table C.10.

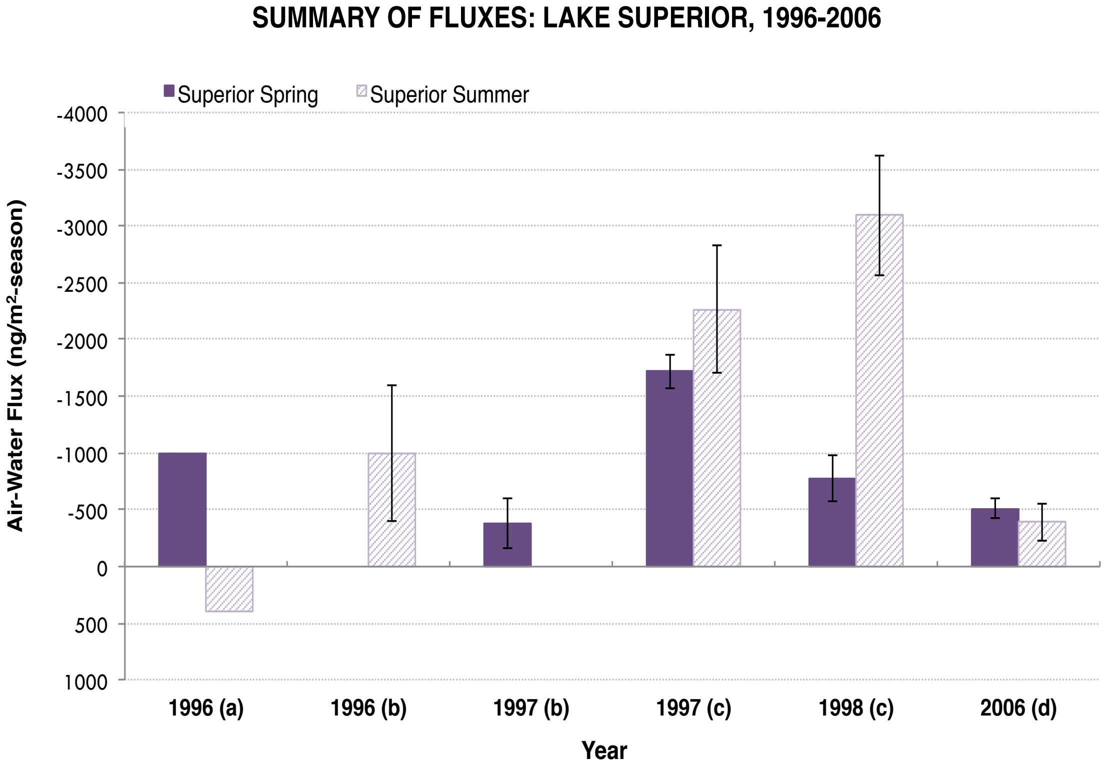

Figure 3.10. Summary of seasonal air-water toxaphene fluxes for Lake Superior, 1996-2006. Details listed in Table C.11.

3.4. Suspended Particle Concentrations

Toxaphene in water exists in both a dissolved and particle-bound phase. The proportion of a lake's total toxaphene inventory in the particle phase depends on the lake's concentration of suspended particulate matter (SPM) and the fraction of organic carbon (*foc*) making up the particles (Achman, 1993). Because only the dissolved portion of toxaphene is available for air-water exchange, volatilization is mediated by the partitioning of toxaphene between the suspended particles and water (Achman 1993). The majority of Lake Michigan and Lake Superior's toxaphene inventory is in the dissolved phase. Based on the water samples in this study, the percent of each lake's total toxaphene inventory stored in particles averaged 2 ±0.9% for Lake Michigan and 3 ±0.5% for Lake Superior.

Toxaphene particle concentrations ($C_{w,p}$) and SPM content for Lake Michigan and Lake Superior are shown in Tables 3.1 and 3.2. There was not a significant difference observed in toxaphene particulate concentrations or SPM content between seasons. In Lake Michigan, toxaphene particulate concentrations ($C_{w,p}$) averaged 8 ±6 ng/g in July of 2004 and 20 ±13 ng/g in May of 2005. In Lake Superior, toxaphene particulate concentrations ($C_{w,p}$) averaged 36 ±18 ng/g in May and 50 ±42 ng/g in July of 2006. The SPM content of both lakes was similar, averaging 0.55 ±0.10 mg/L in Lake Michigan and 0.61 ±0.17 mg/L in Lake Superior. Shown in Figure 3.2, Lake Superior's average SPM content was influenced by the high concentrations measured at the near shore sites of Duluth and Thunder Bay.

Table 3.1. Suspended particle ($C_{w,p}$) toxaphene concentrations with paired SPM, POC, K_d, K_{oc}, and $C_{w,oc}$ values for Lake Michigan, 2004-2005.

	$C_{w,p}$		SPM		POC		K_d		K_{oc}		$C_{w,oc}$	
Lake Michigan sample site[a]	**July-04 (ng/g)**	**May-05 (ng/g)**	**July-04 (mg/L)**	**May-05 (mg/L)**	**July-04 (mg/L)**	**May-05 (mg/L)**	**July-04 (L/kg)**	**May-05 (L/kg)**	**July-04 (L/kg)**	**May-05 (L/kg)**	**July-04 (ng/g)**	**May-05 (ng/g)**
LM-47	14	--	0.6	--	0.22	--	3.0E+04	--	7.8E+04	--	36	--
GB-17	--	32	--	1.4	--	0.32	--	--	--	--	--	135
LM-110	--	13	--	0.2	--	0.17	--	1.9E+04	--	2.4E+04	--	17
LM-27	3	--	0.5	--	0.16	--	1.1E+04	--	3.2E+04	--	8	--
Milwaukee	--	11	0.4	--	0.15	0.21	--	--	--	--	--	--
LM-18	7	39	0.2	0.4	0.13	0.20	3.0E+04	1.5E+05	4.5E+04	2.7E+05	11	74
LM-310	--	17	--	0.5	--	0.23	--	6.6E+04	--	1.4E+05	--	35
Chicago	--	7	0.5	0.4	0.20	0.13	--	1.3E+04	--	4.1E+04	--	20
Average	8	20	0.4	0.6	0.17	0.21	2.4E+04	6.1E+04	5.1E+04	1.2E+05	18	56
SD	*6*	*13*	*0.1*	*0.5*	*0.03*	*0.07*	*1.1E+04*	*6.1E+04*	*2.4E+04*	*1.1E+05*	*15*	*50*

POC Particulate organic carbon. [a] Sites listed from north to south. -- Sample not collected.

Table 3.2. Suspended particle ($C_{w,p}$) toxaphene concentrations with paired SPM, POC, K_d, K_{oc}, and $C_{w,oc}$ values for Lake Superior, 2006.

	$C_{w,p}$		SPM		POC		K_d		K_{oc}		$C_{w,oc}$	
Lake Superior sample site[a]	**May-06 (ng/g)**	**July-06 (ng/g)**	**May-06 (mg/L)**	**July-06 (mg/L)**	**May-06 (mg/L)**	**July-06 (mg/L)**	**May-06 (L/kg)**	**July-06 (L/kg)**	**May-06 (L/kg)**	**July-06 (L/kg)**	**May-06 (ng/g)**	**July-06 (ng/g)**
Duluth	25	67	2.0	1.0	0.65	0.23	3.7E+04	7.4E+04	1.1E+05	3.2E+05	78	290
SU-17	--	8	0.4	0.4	0.09	0.15	--	1.9E+04	--	4.8E+04	--	20
Thunder Bay	66	115	0.6	1.2	0.26	0.35	1.4E+05	1.6E+05	3.0E+05	5.3E+05	140	384
Keweenaw	31	--	0.4	--	0.10	--	2.3E+04	--	8.4E+04	--	111	--
SU-08	23	22	0.2	0.2	0.08	0.18	2.9E+04	3.3E+04	6.5E+04	3.1E+04	52	21
SU-01	37	41	0.4	0.2	0.11	0.15	4.3E+04	7.1E+04	1.5E+05	7.7E+04	123	44
Average	36	50	0.64	0.58	0.22	0.21	5.5E+04	7.1E+04	1.4E+05	2.0E+05	101	152
SD	*18*	*42*	*0.7*	*0.5*	*0.22*	*0.08*	*5.0E+04*	*5.5E+04*	*9.5E+04*	*2.2E+05*	*36*	*172*

POC Particulate organic carbon. [a] Sites listed from west to east. -- Sample not collected.

The observed water-particle distribution coefficient (K_d) controlling toxaphene's partitioning between the two phases is defined as:

$$K_d, L/kg = \frac{C_{w,p}}{C_{w,d}} \times \left(\frac{\mathrm{L} \times 10^3 \times \mathrm{g} \times 10^3}{\mathrm{m}^3 \times \mathrm{kg}} \times 10^6 \right) \tag{6}$$

where $C_{w,p}$ is in units of ng/g, $C_{w,d}$ is in ng/m^3, and K_d is in L/kg (Hites and Eisenreich 1987). Average log K_d values for both lakes were within 5% of each other and averaged 4.7 L/kg. Since the toxaphene concentration of particulate matter has been shown to depend on its fraction of organic carbon content (Achman, 1993), the water-particle distribution coefficient is often normalized to organic carbon. The result is the organic carbon-water distribution coefficient (K_{oc}) calculated as:

$$K_{oc} = \frac{K_d}{foc} \tag{7}$$

where foc is the fraction of organic carbon in the particulate matter (Schwarzenbach 1992). In Lake Michigan, the average log K_{oc} value across both seasons was 4.96 L/kg and in Lake Superior 5.24 L/kg. These average observed log K_{oc} values agree well with the range of previously reported values summarized in ATSDR (2010) and with the value of 5.32 L/kg reported by EPA (2009).

The annual sedimentation of toxaphene was calculated for each lake by first estimating its lakewide organic carbon burial rate. For Lake Superior, this study used the organic carbon burial rate of 0.48 Tg/yr reported in Cotner *et al.* (2004). For Lake Michigan, organic carbon burial was estimated by combining the average mass sedimentation rate (0.018 ±0.005 g/cm^2-yr) found in Doskey *et al.* (2001) and Li *et al.* (2006) with the average organic carbon fraction in buried sediments (4 ±1%) documented in Simcik *et al.* (1994) and Doskey *et al.* (2001). The resulting lakewide organic carbon sedimentation rate for Lake Michigan was 0.41 Tg/yr. Toxaphene sedimentation was then calculated by multiplying the organic carbon sedimentation rates of each lake by their respective average organic carbon toxaphene concentrations ($C_{w,oc}$), which are shown in Tables 3.1 and 3.2. The calculated toxaphene sedimentation rates were 19 ±6 kg/yr for Lake Michigan and 61 ±21 kg/yr for Lake Superior.

In comparison to estimates for the mid-1990s by Swackhamer *et al.* (1999), toxaphene sedimentation rates in this study were 92% less for Lake Michigan and 32% less for Lake Superior. While the magnitude of sedimentation decrease in Lake Superior is proportional to its 35% decrease in water concentration since 1996, the difference between Lake Michigan's calculated sedimentation rates is unexpected due to the lake's similar water concentration in 1995 and 2005. This discrepancy can be explained by the differences in methodology between this study and Swackhamer *et al.* (1999). The mid-1990s calculations used sediment concentrations from 1991 to 1992 and particle sedimentation rates found in Pearson *et al.* (1997). The toxaphene concentration of Lake Michigan's sediment in Pearson *et al.* (1997) averaged nearly 3 times that of Lake Superior's. In contrast, this study observed an average toxaphene concentration in Lake Superior's suspended particles that was approximately 3 times higher than Lake

Michigan's. While the rate of organic carbon burial relative to surface area was 36% higher in Lake Michigan than Lake Superior, this difference was not great enough to increase Lake Michigan's toxaphene sedimentation to the level seen in Lake Superior.

3.5. Toxaphene Mass Budgets

To construct toxaphene mass budgets, lakewide averages were calculated for each parameter across all four seasons. To model dissolved water concentrations over the course of the year, the average summer concentrations (from Figures 3.4 and 3.5) were used for both the summer and fall, while the average spring concentrations were used for both the spring and winter. This decision was based on the assumption that the lakes remained relatively well mixed during the winter and spring, but were stratified during the summer and much of the fall.

In the atmosphere toxaphene exists in both a vapor and particle phase, with temperature controlling its partitioning between the two phases (Jantunen 2000). This relationship has been described by the Clausius-Claypeyron equation, which specifies a compound's transition from the gas-phase to the particle phase in response to a change in temperature (Hoff 1993):

$$\ln P = \frac{-\Delta H}{R \times T} + constant \tag{8}$$

where P (atm) is the partial pressure of the compound, ΔH is the phase transition energy, R is the gas constant, and T (Kelvin) is the air temperature. When this equation was fitted to the air measurements of James *et al.* (2001), the value of ΔH was 76 ±10 kJ/mol and the constant was -2.76. This study used the resulting equation along with air temperature data from the NOAA National Weather Service to estimate average air concentrations over both lakes during all four seasons.

Air-water fluxes were then estimated for each season by combining the calculated average air and water concentrations with the average wind speeds and surface water temperatures collected by NOAA. The resulting fluxes for Lakes Michigan and Superior are plotted in Figure 3.11 and show Lake Superior's annual volatilization rate to be nearly three times that of Lake Michigan's. Figure 3.11 also depicts fall as the season when volatilization is at its greatest in both lakes. This is primarily due to average surface temperatures in the fall remaining as high as those in the summer, while the average concentration of toxaphene in the air drops to nearly half of its summer concentration.

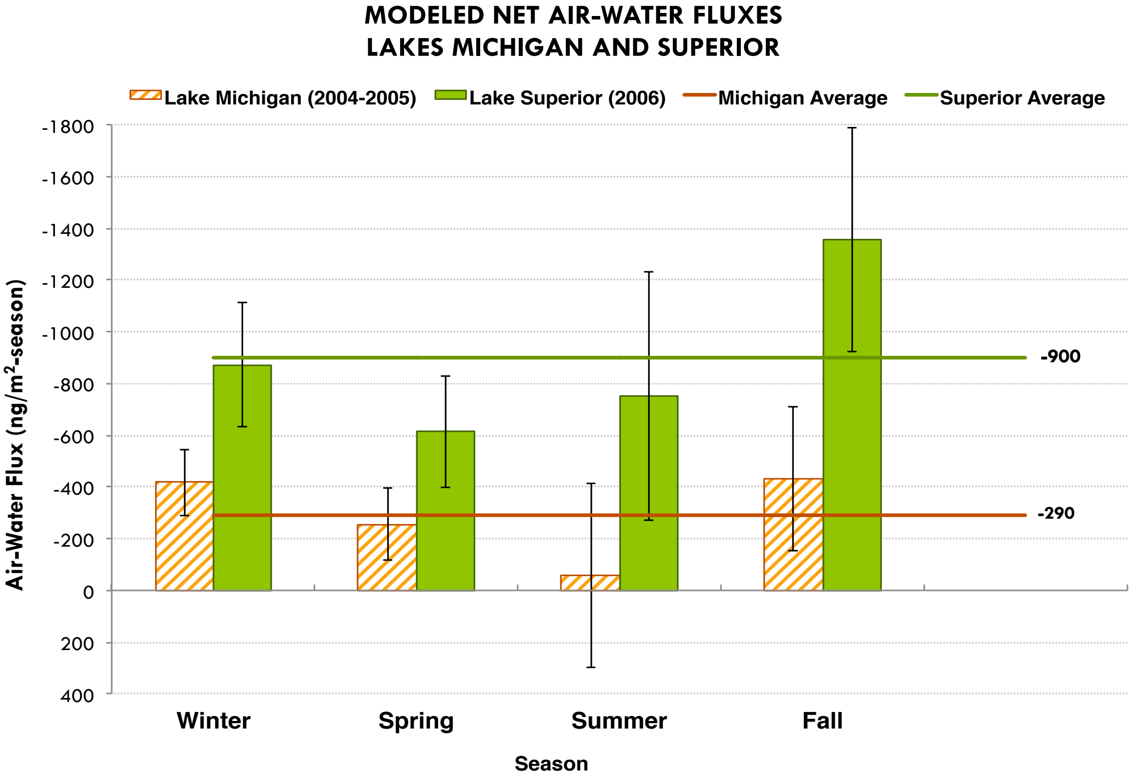

Figure 3.11. Modeled seasonal air-water toxaphene fluxes in Lake Michigan (2004-2005) and Lake Superior (2006). Details listed in Table C.12.

By combining calculated annual air-water fluxes with estimated mass loadings from connecting channels, sedimentation, and wet and dry deposition, toxaphene mass budgets for each lake were created and are shown in Figures 3.12 and 3.13. Input and output equations were based on those used in the mass budget model of Swackhamer *et al.* (1999) and are summarized in Appendix F. The calculated net export of toxaphene from each lake was 81 ±30 kg/yr for Lake Michigan and 365 ±64 kg/yr for Lake Superior.

While volatilization was the dominant loss mechanism in both lakes, sedimentation and connecting channels played a much bigger role in Lake

Michigan's mass budget representing 20% and 18% of the lake's total output respectively. In contrast, sedimentation only represented 15% and connecting channels 11% of Lake Superior's total output. The greater inputs seen in Lake Superior's mass budget were a result of and in proportion to its surface area being approximately 1.4 times larger than Lake Michigan's. In comparison to each lake's total toxaphene inventory, calculated annual net exports for each lake amounted to about a 4% loss of inventory.

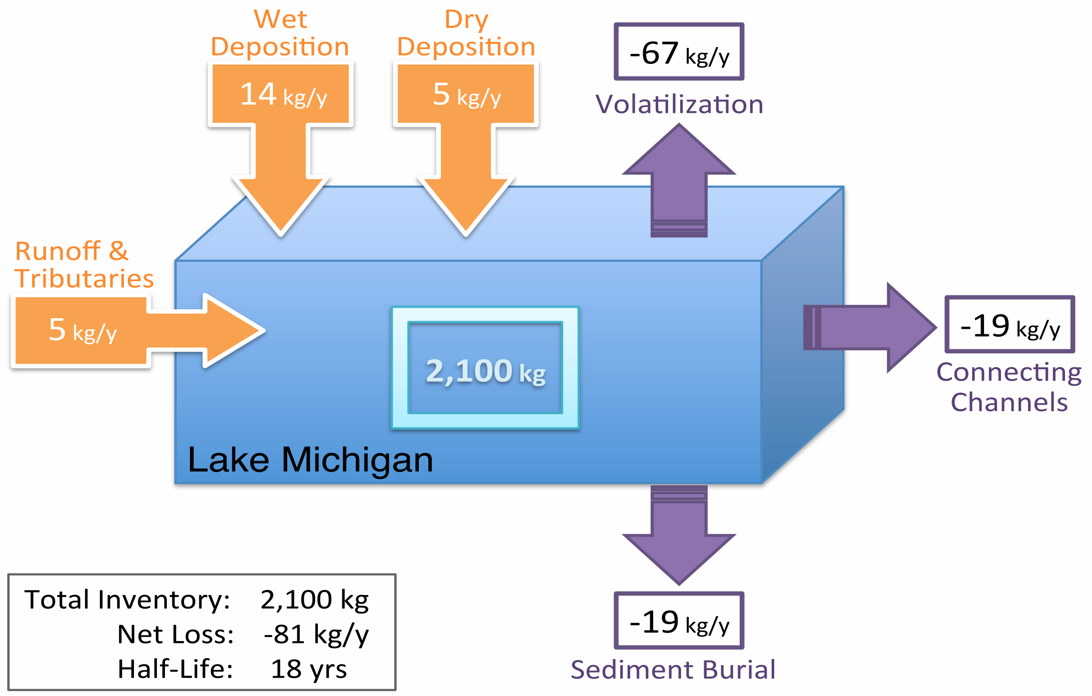

Figure 3.12. Toxaphene mass budget for Lake Michigan, 2004-05. Details listed in Table 3.4.

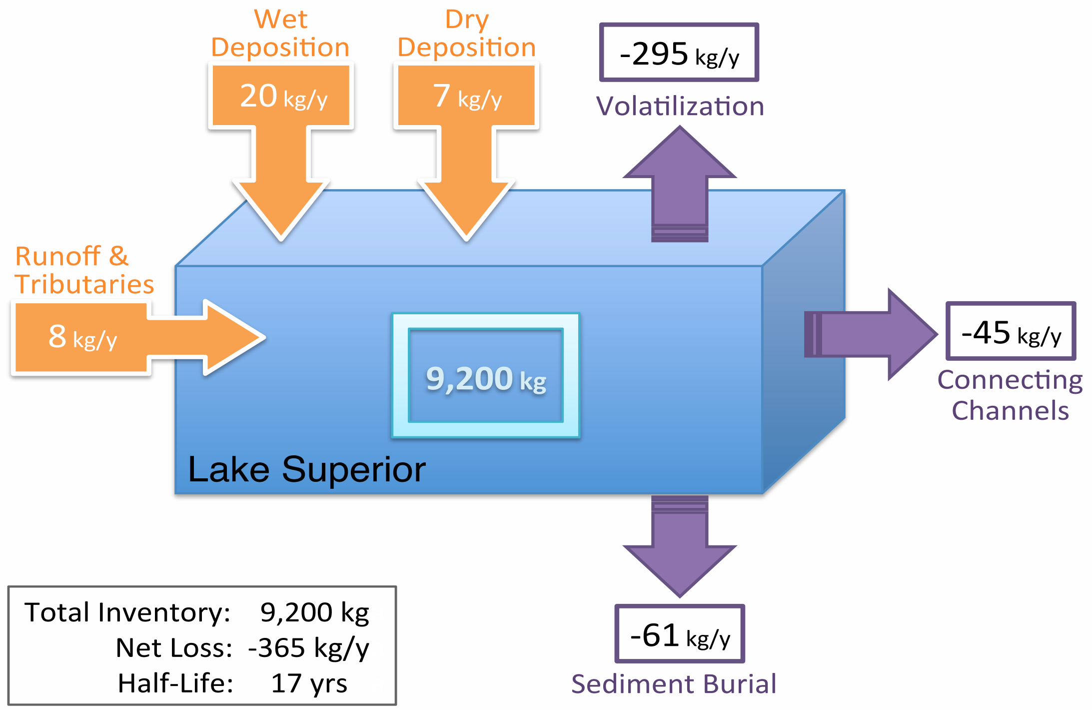

Figure 3.13. Toxaphene mass budget for Lake Superior, 2006. Details listed in Table 3.4.

The 1990's mass budget by Swackhamer *et al.* (1999) is shown in Table 3.3. The individual outputs in Lake Superior's 2006 and mid-1990s mass budget represent relatively the same proportion of the total. This is not the case for Lake Michigan. For one, the mid-1990s mass budget shows sedimentation as the maximum loss mechanism making up 94% of its total output. Additionally, gas-exchange reversed directions switching from contributing 80% of the total input in the mid-1990s to contributing 18% of the output in 2005. This was in part due to the difference in water temperatures used in calculating fluxes in the two mass budgets. The average temperature used for the 2004-2005 flux was 9.7 °C, while the mid-1990s model used an average of 7.1 °C. Due to the sensitivity of toxaphene's Henry's law constant to temperature, a 3 °C difference is capable of reversing the direction of air-water exchange.

Based on the calculated 3.9% and 4.0% removal rates, toxaphene has a half-life of 17.9 and 17.5 years in Lake Michigan and Lake Superior, respectively. Considering the 17.2-year half-life estimated for Lake Superior from the historic water concentrations in Figure 3.6, this study's observations suggest that the lake was removing toxaphene in 2006 at nearly the same rate as in 1993. Contrarily, the removal rate of 3.9% observed in Lake Michigan was in sharp contrast to the 12% seen in the mid-1990's mass budget. Lake Michigan's decline in net exports supports the observation that the lake is nearing a steady state with regards to toxaphene.

Table 3.3. Mid-1990's toxaphene mass budget for Lake Michigan and Lake Superior (Swackhamer et al. 1999).*

Net Load	**Michigan (kg/yr)**	**Superior (kg/yr)**
Wet deposition	9	13
Dry deposition	4	6
Gas absorption	50	0
Connecting channels	0	0
Total inputs	**63**	**19**
Sedimentation	-290	-90
Gas volatilization	0	-390
Connecting channels	-18	-77
Total outputs	**-308**	**-557**
Overall Net Load	**-245**	**-538**
Lake Inventory (kg)	2,010	14,100
Net Load / Inventory	-12.2%	-3.8%

* A negative value indicates a net export of toxaphene out of the lake.

Table 3.4. Toxaphene mass budgets for Lake Michigan (2004-2005) and Lake Superior (2006).*

	Michigan, 2004-'05		**Superior, 2006**	
Net Load	**(kg/yr)**	**Δ**	**(kg/yr)**	**Δ**
Wet deposition	14	*4*	20	*6*
Dry deposition	5	*1*	7	*1*
Gas absorption	0	--	0	--
Runoff & Tributaries	5	*2*	8	*2*
Total inputs	**24**	***5***	**35**	***6***
Sedimentation	-19	*6*	-61	*21*
Gas volatilization	-67	*29*	-295	*60*
Connecting channels	-19	*2*	-45	*5*
Total outputs	**-105**	***30***	**-400**	***64***
Overall Net Load	**-81**	***30***	**-365**	***64***
Lake Inventory (kg)	1,960	*390*	9,200	*1,840*
Net Load / Inventory	-4.1%	*1.7%*	-4.0%	*1.1%*

* A negative value indicates a net export of toxaphene out of the lake. Data for precipitation, runoff, connecting channels, and diversions obtained from NOAA's GLERL database.

Chapter 4. Discussion and Conclusion

4.1. Fish Consumption

As a consequence of elevated water concentrations, toxaphene levels in fish have consistently been the highest in Lake Superior compared to the other Great Lakes (Xia 2012). Concentrations in lake trout collected in 2006 from Lake Superior averaged 430 ng/g wet weight, and indicated that toxaphene levels still warranted consumption guidelines (Xia 2012). According to the Ontario Ministry of the Environment, consumption of fish should be restricted when tissue concentrations reach above 235 ng/g wet weight (OME 2001). When cancer endpoints are included in the risk assessment, the EPA suggests limiting consumption at fish concentrations as low as 2.7 ng/g wet weight (EPA 1999). Lake Superior's lake trout in 2006 averaged 430 ng/g wet weight, a concentration well above the established health standards and posing a health risk to those consuming fish on a monthly basis. Assuming an average fish concentration of 430 ng/g and a cancer slope factor of 1.1 $(\text{mg/kg}\bullet\text{day})^{-1}$, as in (ATSDR 2010), people who eat 1 serving of fish per week over the course of their lifetime would increase their risk of cancer by 1 in 1,000 (see Appendix E for the complete calculation).

Toxaphene has an estimated bioaccumulation factor (BAF) of 1 million in lake trout (Muir 2004). Based on this value, water concentrations would need to drop below 75 ng/m^3 before lake trout would be expected to meet EPA's minimum non-cancer safety guideline of 75 ng/g wet weight. Given Lake Superior's average water concentration of 730 ng/m^3 in 2006, a 90% decrease is necessary to reach 75 ng/m^3. Achieving a concentration drop of this magnitude would take over 50 years based on the rate of loss seen in Lake Superior's 2006 mass budget. As a consequence, fish concentrations in Lake Superior lake trout will likely pose a health risk to frequent consumers beyond the year 2060.

4.2. Global Transport

This study supports previous literature showing that the upper Great Lakes are current exporters of toxaphene to the atmosphere. The mass budgets shown in Tables 3.12 and 3.13, estimate a net atmospheric release of 67 kg for Lake Michigan in 2005 and 295 kg for Lake Superior in 2006. While this would have little ecological significance if it were uniformly dispersed around the world, studies have shown that toxaphene released into the atmosphere preferentially accumulates in colder regions such as the Arctic in a process known as cold distillation (Bidleman 1989).

The Arctic is home to over 4 million people, covering an enormous region that spans one sixth of the planet’s landmass across parts of Canada, Greenland, Europe, and Russia (Young 2008). A 1995 study in Greenland found that blood concentrations in residents increased along with age up to about age 40. This trend suggests that toxaphene began to bioaccumulate in children living in the Arctic around the 1950s (Bjerregaard 2001).

Further comparisons of toxaphene concentrations in blood serum and breast milk have found levels in populations living in the Arctic to be among the highest in the world, a result attributable to the Arctic diet consisting more heavily of fish and piscivores such as seals, walruses, and whales (Bjerregaard 2001). In addition, large predators in the Arctic have shown much higher levels of toxaphene in comparison to similar species at lower latitudes (Muir 1999). Concentrations in large marine mammals were as high as 14,500 ng/g (fresh wt.) in beluga whales off the coast of Baffin Island and as high as 3,500 ng/g (fresh wt.) in walruses from Hudson Bay (Muir 1999). Under current conditions, toxaphene's slow degradation and ongoing transport from lower latitudes will continue to place a disproportional health burden on Arctic communities.

4.3. Conclusion

Results from this study supported earlier findings showing air-water exchange dominating toxaphene's mass budget in Lake Michigan and Lake Superior and both lakes showing annual net volatilization (Swackhamer 1999, James 2001). However, contrary to previous mass budgets for Lake Michigan, this study found sedimentation to play a secondary role to volatilization in the lake's total mass output. Furthermore, the total burial of toxaphene in Lake Superior was nearly triple that of Lake Michigan. This suggests that Lake Superior's elimination of organochlorides such as toxaphene is less limited by its productivity and sedimentation than previously suspected. Despite this, Lake Superior's colder water temperature and longer residence time will guarantee that toxaphene concentrations in its water and fish remain the highest relative to the rest of the other Great Lakes.

Bibliography

Achman, D. R., Hornbuckle, K. C., & Eisenreich, S. J. (1993). Volatilization of polychlorinated biphenyls from Green Bay, Lake Michigan. *Environmental science & technology, 27*(1), 75-87.

ATSDR. (2010). Toxicological profile for Toxaphene (Vol. 2013). Atlanta, GA: Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Public Health Service.

Austin, J. A., & Colman, S. M. (2007). Lake Superior summer water temperatures are increasing more rapidly than regional air temperatures: A positive ice-albedo feedback. *Geophysical Research Letters, 34*(6), L06604.

Bidleman, T. F., Patton, G. W., Walla, M. D., Hargrave, B. T., Vass, W. P., Erickson, P., . . . Gregor, D. J. (1989). Toxaphene and other organochlorines in Arctic Ocean fauna: evidence for atmospheric delivery. *Arctic*, 307-313.

Bjerregaard, P., Dewailly, E., Ayotte, P., Pars, T., Ferron, L., & Mulvad, G. (2001). Exposure of Inuit in Greenland to organochlorines through the marine diet. *Journal of toxicology and environmental health. Part A, 62*(2), 69-81.

Buntln, G. A. (1951). U.S. Patent No. US2565471 A. U. S. P. a. T. Office.

Cotner, J. B., Biddanda, B. A., Makino, W., & Stets, E. (2004). Organic carbon biogeochemistry of Lake Superior. *Aquatic Ecosystem Health & Management, 7*(4), 451-464.

de Boer, J., & Wester, P. G. (1993). Determination of toxaphene in human milk from Nicaragua and in fish and marine mammals from the northeastern Atlantic and the North Sea. *Chemosphere, 27*(10), 1879-1890.

de Geus, H.-J., Besselink, H., Brouwer, A., Klungsøyr, J., McHugh, B., Nixon, E., . . . de Boer, J. (1999). Environmental occurrence, analysis, and toxicology of toxaphene compounds. *Environmental health perspectives, 107*(Suppl 1), 115.

Dean, W. E., & Gorham, E. (1998). Magnitude and significance of carbon burial in lakes, reservoirs, and peatlands. *Geology, 26*(6), 535-538.

Eadie, B. J., Chambers, R. L., Gardner, W. S., & Bell, G. L. (1984). Sediment trap studies in Lake Michigan: Resuspension and chemical fluxes in the southern basin. *Journal of Great Lakes Research, 10*(3), 307-321.

EPA, U. S. (1999). Fact Sheet: Toxaphene update: impact on fish advisories (pp. 1-6). Washington, D.C.: Office of Water.

EPA, U.S. (2004) Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual. OSWER 9285.7-02EP.

EPA, U.S. (2009) National primary drinking water regulations. Washington, DC: U.S. Environmental Protection Agency. Office of Ground Water and

Drinking Water. EPA816F09004.

Falk, C., Hanrahan, L., Anderson, H. A., Kanarek, M. S., Draheim, L., Needham, L., & Patterson Jr, D. (1999). Body burden levels of dioxin, furans, and..., *Environmental research, 80*(2), S19-S25.

Fuller, E. N., Schettler, P. D., & Giddings, J. C. (1966). New method for prediction of binary gas-phase diffusion coefficients. *Industrial & Engineering Chemistry, 58*(5), 18-27.

Gianessi, L. P. (1992). U.S. Pesticide Trends: 1966-1989. In U. S. E. O. o. P. Analysis (Ed.), (pp. 22). Washington, DC: Resources for the Future, Quality of the Environment Division.

Glassmeyer, S. T., Brice, K. A., & Hites, R. A. (1999). Atmospheric Concentrations of Toxaphene on the Coast of Lake Superior. *Journal of Great Lakes Research, 25*(3), 492-499. doi: http://dx.doi.org/10.1016/S0380-1330(99)70757-4

Glassmeyer, S. T., De Vault, D. S., & Hites, R. A. (2000). Rates at which toxaphene concentrations decrease in lake trout from the Great Lakes. *Environmental science & technology, 34*(9), 1851-1855.

Glassmeyer, S. T., De Vault, D. S., Myers, T. R., & Hites, R. A. (1996). Toxaphene in Great Lakes fish: A temporal, spatial, and trophic study. *Environmental science & technology, 31*(1), 84-88.

Hanrahan, L. P., Falk, C., Anderson, H. A., Draheim, L., Kanarek, M. S., & Olson, J. (1999). Serum PCB and DDE levels of frequent Great Lakes sport fish consumers—a first look. *Environmental research, 80*(2), S26-S37.

Hites, R. A., & Eisenreich, S. J. (1987). Sources and fates of aquatic pollutants: American Chemical Society, Washington, DC.

Hoff, R. M., Bidleman, T. F., & Eisenreich, S. J. (1993). Estimation of PCC loadings from the atmosphere to the Great Lakes. *Chemosphere, 27*(10), 2047-2055.

Imm, P., Knobeloch, L., & Anderson, H. A. (2005). Fish consumption and advisory awareness in the Great Lakes Basin. *Environmental health perspectives, 113*(10), 1325.

James, R. R., McDonald, J. G., Symonik, D. M., Swackhamer, D. L., & Hites, R. A. (2001). Volatilization of toxaphene from Lakes Michigan and Superior. *Environmental science & technology, 35*(18), 3653-3660.

Jantunen, L. M. M., & Bidleman, T. F. (2000). Temperature dependent Henry's law constant for technical toxaphene. *Chemosphere-Global Change Science, 2*(2), 225-231.

Jantunen, L. M. M., Bidleman, T. F., Harner, T., & Parkhurst, W. J. (2000). Toxaphene, chlordane, and other organochlorine pesticides in Alabama air. *Environmental science & technology, 34*(24), 5097-5105.

Li, Y. F., Bidleman, T. F., & Barrie, L. A. (2001). Toxaphene in the United States: 2. Emissions and residues. *Journal of Geophysical Research: Atmospheres*, *106*(D16), 17929-17938.

MacLeod, M., Woodfine, D., Brimacombe, J., Toose, L., & Mackay, D. (2002). A dynamic mass budget for toxaphene in North America. *Environmental Toxicology and Chemistry, 21*(8), 1628-1637.

Muir, D., Braune, B., DeMarch, B., Norstrom, R., Wagemann, R., Lockhart, L., . . . Payne, J. (1999). Spatial and temporal trends and effects of contaminants in the Canadian Arctic marine ecosystem: a review. *Science of the total Environment, 230*(1), 83-144.

Muir, D. C. G., Michael Whittle, D., De Vault, D. S., Bronte, C. R., Karlsson, H., Backus, S., & Teixeira, C. (2004). Bioaccumulation of toxaphene congeners in the Lake Superior food web. *Journal of Great Lakes Research, 30*(2), 316-340.

Muir, D. C. G., Swackhamer, D. L., Bidleman, T. F., & Jantunen, L. M. (2006). Toxaphene in the Great Lakes *Persistent Organic Pollutants in the Great Lakes* (pp. 201-265): Springer.

OME. (2001). Guide to Eating Ontario Sport Fish (21 ed., pp. 14-15). Toronto: Ontario Ministry of the Environment.

Pearson, R. F., Swackhamer, D. L., Eisenreich, S. J., & Long, D. T. (1997). Concentrations, accumulations, and inventories of toxaphene in sediments of the Great Lakes. *Environmental science & technology, 31*(12), 3523-3529.

Quinn, F. H. (1992). Hydraulic residence times for the Laurentian Great Lakes. *Journal of Great Lakes Research, 18*(1), 22-28.

Rice, C. P., & Evans, M. S. (1984). Toxaphene in the Great Lakes. *Toxic contaminants in the Great Lakes, 14*, 163-194.

Schwab, D. J., Leshkevich, G. A., & Muhr, G. C. (1999). Automated Mapping of Surface Water Temperature in the Great Lakes. *Journal of Great Lakes Research, 25*(3), 468-481. doi: http://dx.doi.org/10.1016/S0380-1330(99)70755-0

Schwarzenbach, R. P., Gschwend, P. M., & Imboden, D. M. (1992). *Environmental Organic Chemistry*. New York: Wiley Interscience.

Smith, J. H., Bomberger, D. C., & Haynes, D. L. (1980). Prediction of the volatilization rates of high-volatility chemicals from natural water bodies. *Environmental science & technology, 14*(11), 1332-1337.

Swackhamer, D. L., Pearson, R. F., & Schottler, S. P. (1998). Toxaphene in the great lakes. *Chemosphere, 37*(9), 2545-2561.

Swackhamer, D. L., Schottler, S., & Pearson, R. F. (1999). Air-water exchange and mass balance of toxaphene in the Great Lakes. *Environmental science & technology, 33*(21), 3864-3872.

Swain, W. R. (1978). Chlorinated organic residues in fish, water, and precipitation from the vicinity of Isle Royale, Lake Superior. *Journal of Great Lakes Research, 4*(3), 398-407.

Voldner, E. C., & Li, Y. F. (1993). Global Usage of Toxaphene. *Chemosphere, 27*(10), 2073-2078.

Voldner, E. C., & Li, Y. F. (1995). Global usage of selected persistent organochlorines. *Science of the total Environment, 160*, 201-210.

Von Rumker, R., Lawless, E. W., & Meiners, A. F. (1974). Production, Distribution, Use, and Environmental Impact Potential of Selected Pesticides. Washington, D.C.: Office of Pesticide Programs, Office of Water and Hazardous Materials, Environmental Protection Agency.

Whitman, W. G. (1923). The two-film theory of gas absorption. *Chemical and Metallurgical Engineering., 29*(1), 146-148.

Xia, X., Hopke, P. K., Crimmins, B. S., Pagano, J. J., Milligan, M. S., & Holsen, T. M. (2012). Toxaphene trends in the Great Lakes fish. *Journal of Great Lakes Research, 38*(1), 31-38.

Young, T. K., & Bjerregaard, P. (Eds.). (2008). *Health transitions in Arctic populations*. University of Toronto Press.

Appendix A. Site Coordinates

Table A.1. Site coordinates for sampling sites on Lake Michigan.

Lake Michigan sample site	Latitude	Longitude
LM47	45°10.7400 N	086°22.5002 W
GB17	44°53.8101 N	087°30.1403 W
LM110	44°40.8500 N	087°20.4401 W
LM27	43°36.000 N	086°54.2000 W
Milwaukee	43°00.8501 N	087°50.2100 W
LM18	42°43.9601 N	086°59.9803 W
LM310	42°42.0801 N	086°13.9003 W
Chicago	41°47.4600 N	087°30.2403 W

[a] Sites listed from north to south.

Table A.2. Site coordinates for sampling sites on Lake Superior.

Lake Superior sample site	Latitude	Longitude
Duluth	46°46.8500 N	092°03.2501 W
Apostles	46°54.9901 N	090°24.9802 W
SU17	47°09.8701 N	089°39.7001 W
Thunder Bay	48°17.8302 N	089°10.8601 W
Keweenaw	47°24.8502 N	087°35.4203 W
SU08	47°36.3601 N	086°49.0600 W
SU01	46°59.5900 N	085°09.6701 W

[a] Sites listed from west to east.

Appendix B. Sample Volumes

Table B.1. Water sample volumes collected from Lake Superior, 2006.

Lake Superior sample site	May-06 (Liters)	July-06 (Liters)
Duluth	854	805
Duluth (Duplicate)	854	--
Apostles	804	--
SU-17	804	1503
Thunder Bay	1210	799
Thunder Bay (Duplicate)	--	805
Keweenaw	806	--
SU-08	794	821
SU-08 (Duplicate)	825	--
SU-01	802	754
Average	861	915

-- Sample not collected.

Appendix C. Data Tables

Table C.1. Gas-phase ($C_{a,g}$) toxaphene concentrations over Lake Michigan, May 2005.

Lake Michigan sample site[a]	**May-05 (pg/m^3)**
LM-47	6.3
GB-17	7.9
Milwaukee	5.4
LM-18	15.7
Chicago	13.0
Chicago (Duplicate)	7.9
Average	9.4
SD	4.1
Relative Error	30%

[a] Sites listed from north to south.

Table C.2. Gas-phase ($C_{a,g}$) toxaphene concentrations over Lake Superior, 2006.

Lake Superior sample site[a]	**May-06 (pg/m^3)**	**July-06 (pg/m^3)**
Duluth	4.7	--
SU-17	9.0	35.5
Thunder Bay	9.1	10.9
Thunder Bay (Duplicate)	--	9.6
SU-08	27.2	69.7
SU-01	12.0	30.9
Average	12.4	31.3
SD	8.7	24.4
Relative Error	30%	30%

[a] Sites listed from west to east. -- Sample not collected.

Table C.3. Summary of gas-phase ($C_{a,g}$) toxaphene concentrations over Lake Superior, 1993-2006 (pg/m^3).

Lake Superior	Spring		Summer	
Year	Mean	SD	Mean	SD
1993[a]	10	--	60	--
1996[b]	--	--	28	10
1997[b]	12	5	--	--
1997[c]	7	6	9	1
1997[d]	3	1	22	9
1998[d]	19	8	36	18
2006[e]	12	9	31	24
Average	10	5	31	17

-- Sample not collected. [a] Hoff *et al.* (1993). [b] Jantunen *et al.* (2003). [c] Glassmeyer *et al.* (1999). [d] James *et al*. (2001). [e] This study.

Table C.4. Dissolved water ($C_{w,d}$) toxaphene concentrations in Lake Michigan, 2004-2005.

Lake Michigan sample site[a]	July-04 (ng/m^3)	May-05 (ng/m^3)
LM-47	460	--
LM-110	--	700
LM-27	240	--
LM-18	240	270
LM-310	--	250
Chicago	--	490
Average	320	430
SD	130	210
Relative Error	20%	20%

[a] Sites listed from north to south. -- Sample not collected.

Table C.5. Dissolved water ($C_{w,d}$) toxaphene concentrations in Lake Superior, 2006.

Lake Superior sample site[a]	**May-06 (ng/m^3)**	**July-06 (ng/m^3)**
Duluth	760	900
Duluth (Duplicate)	590	--
Apostles	620	--
SU-17	930	420
Thunder Bay	460	710
Thunder Bay (Duplicate)	--	730
Keweenaw	1330	--
SU-08	660	660
SU-08 (Duplicate)	930	--
SU-01	840	580
Average	790	670
SD	260	160
Relative Error	20%	20%

[a] Sites listed from west to east. -- Sample not collected.

Table C.6. Summary of dissolved water ($C_{w,d}$) toxaphene concentrations in Lake Michigan, 1993-2005 (ng/m^3).

Lake Michigan	**Spring**		**Summer**	
Year	**Mean**	**SD**	**Mean**	**SD**
1993[a1]	570*	*180*	570*	*180*
1995[a2]	380*	*120*	380*	*120*
1997[b]	560	*140*	290	*50*
1998[b]	450	*140*	310	*50*
2005[c]	430	*210*	315	*130*

* Average annual concentration. [a1] As modeled by Swackhammer *et al.* (1999).
[a2] Swackhammer *et al.* (1999). [b] James *et al*. (2001). [c] This study.

Table C.7. Summary of dissolved water ($C_{w,d}$) toxaphene concentrations in Lake Superior, 1993-2006 (ng/m^3).

Lake Superior	Spring		Summer	
Year	Mean	SD	Mean	SD
1993[a1]	1200*	*190*	1200*	*190*
1996[a2]	1120*	*180*	1120*	*180*
1996[b]	--	--	890	*260*
1997[b]	950	*160*	--	--
1997[c]	1030	*50*	880	*180*
1998[c]	960	*50*	700	*60*
2006[d]	790	*260*	670	*160*

* Average annual concentration. -- Sample not collected. [a1] As modeled by Swackhammer *et al.* (1999). [a2] Swackhammer *et al.* (1999). [b] Jantunen *et al.* (2003). [c] James *et al.* (2001). [d] This study.

Table C.8. Seasonal air-water toxaphene fluxes for Lake Michigan, spring 2005.

Lake Michigan	Spring 2005	
sample site	ng/m²-season*	Δ[a]
LM-18	140	*210*
Chicago	-610	*220*
Lakewide Average[b]	-465	*90*

* A negative flux indicates net volatilization. [a] Absolute uncertainty represents propagation of uncertainty in wind speeds, Henry's law constants, and duplicate gas-pase and dissolved water samples. [b] Lakewide Average calculated from average air and lake concentrations shown in Figures 3.1 and 3.4.

Table C.9. Seasonal air-water toxaphene fluxes for Lake Superior, 2006.

Lake Superior	Spring		Summer	
sample site	ng/m^2-season*	Δ[a]	ng/m^2-season	Δ
Duluth	-1090	*140*	--	--
SU-17	-570	*180*	-510	*400*
Thunder Bay	-460	*150*	-1560	*320*
SU-08	210	*420*	1800	*430*
SU-01	-530	*120*	-710	*380*
Lakewide Average	-630	*70*	-960	*200*

* A negative flux indicates net volatilization. -- Sample not collected. [a] Absolute uncertainty represents propagation of uncertainty in wind speeds, Henry's law constants, and duplicate gas-pase and dissolved water samples. [b] Lakewide Average calculated from average air and lake concentrations shown in Figures 3.2 and 3.5.

Table C.10. Summary of seasonal air-water toxaphene fluxes for Lake Michigan, 1995-2005.

Lake Michigan	Spring		Summer	
Year	Mean*	Δ**	Mean	Δ
1995[a]	41	--	1580	--
1997[b]	-890	*140*	-1380	*355*
1998[b]	-250	*165*	-2550	*355*
2004[c]	--	--	-350[§]	*290*
2005[c]	-312	*110*	--	--

* A negative flux indicates net volatilization. ** Uncertainty represents one standard deviation for 1997 and 1998, and propagated error for 2004 and 2005. -- Sample not collected. [§] Summer flux estimated using the average of summer water concentrations in this study and the calculated air concentration using the Clausius-Clapeyron equation. [a] Swackhammer *et al.* (1999). [b] James *et al.* (2001). [c] This study.

Table C.11. Summary of seasonal air-water toxaphene fluxes for Lake Superior, 1996-2006.

Lake Superior	Spring		Summer	
Year	Mean*	Δ**	Mean	Δ
1996[a]	-990	--	398	--
1996[b]	--	--	-1001	*600*
1997[b]	-380	*220*	--	--
1997[c]	-1720	*150*	-2270	*560*
1998[c]	-780	*200*	-3090	*530*
2006[d]	-512	*90*	-388	*160*

* A negative flux indicates net volatilization. ** Uncertainty represents one standard deviation for 1997 and 1998, and propagated error for 2006. -- Sample not collected. [a] Swackhammer *et al.* (1999). [b] Jantunen *et al.* (2003). [c] James *et al.* (2001). [d] This study.

Table C.12. Modeled seasonal air-water toxaphene fluxes in Lakes Michigan and Superior (ng/m^2-season).

	Winter		Spring		Summer		Fall		Annual	
Lake (Year)	Flux*	Δ[a]	Flux	Δ	Flux	Δ	Flux	Δ	Flux	Δ
Lake Michigan (2004-05)	-417	*128*	-256	*140*	-57	*355*	-433	*279*	-1163	*490*
Lake Superior (2006)	-872	*240*	-613	*214*	-750	*480*	-1357	*434*	-3591	*723*

* A negative flux indicates net volatilization. [a] Absolute uncertainty represents propagation of uncertainty in wind speeds, Henry's law constants, duplicate water samples, and the Clausius-Clapeyron equation from James *et al*. (2001).

Appendix D. Flux Parameters

Table D.1. Parameters used in flux calculations for Lake Superior, May and July 2006.

		Sample Site	Date	u_{10} (m/s)	Lake Temp (K)	H'	D_w	D_{tox}	k_{water} (m/s)	k_{tox} (m/s)	Flux (ng/m^2-sec)
Lake Superior	May	SU-17	5/14/06	3.2	277.3	3.04E-05	0.198	0.044	0.009	0.004	-7.27E-05
		SU-08	5/17/06	7.3	276.9	2.95E-05	0.198	0.044	0.018	0.007	2.66E-05
		Thunder Bay	5/17/06	9.4	278.5	3.41E-05	0.200	0.045	0.022	0.009	-5.86E-05
		Duluth	5/13/06	7.8	278.6	3.44E-05	0.200	0.045	0.019	0.008	-1.38E-04
		SU-01	5/16/06	4.8	277.2	3.03E-05	0.198	0.044	0.013	0.005	-6.75E-05
		Lakewide Average	5/13-5/17	6.4	277.7	3.17E-05	0.199	0.045	0.016	0.006	-8.04E-05
		AVG		**6.5**	**277.7**	**3.17E-05**	**0.199**	**0.044**	**0.016**	**0.007**	**-6.51E-05**
	July	SU-01	7/19/06	5.4	288.3	8.10E-05	0.212	0.048	0.014	0.006	-9.02E-05
		SU-17	7/18/06	3.2	293.4	1.25E-04	0.219	0.049	0.009	0.004	-6.50E-05
		SU-08	7/20/06	8.6	285.3	6.25E-05	0.208	0.047	0.020	0.008	2.29E-04
		Thunder Bay	7/20/06	5.1	286.0	6.64E-05	0.209	0.047	0.013	0.005	-1.99E-04
		Lakewide Average	7/17-7/21	5.5	289.3	8.86E-05	0.213	0.048	0.014	0.006	-1.22E-04
		AVG		**5.6**	**288.5**	**8.47E-05**	**0.212**	**0.048**	**0.014**	**0.006**	**-4.94E-05**

Table D.2. Parameters used in flux calculations for Lake Michigan, May 2005.

		Sample Site	Date	u_{10} (m/s)	Lake Temp. (K)	H'	Dw	Dtox	k_{water} (m/s)	k_{tox} (m/s)	Flux (ng/m^2-sec)
Lake Michigan	May	LM-18	5/28/05	4.5	281.5	4.46E-05	0.203	0.046	0.012	0.005	1.75E-05
		Chicago	5/29/05	3.1	285.5	6.36E-05	0.208	0.047	0.009	0.004	-7.76E-05
		Lakewide Average	5/28-6/01	4.2	283.3	5.23E-05	0.206	0.046	0.011	0.005	-5.91E-05
		AVG		**3.9**	**283.4**	**5.35E-05**	**0.208**	**0.046**	**0.011**	**0.004**	**-3.97E-05**

Appendix E. Cancer Risk Calculation

Table E.1. Parameters used in cancer risk calculations for Lake Superior lake trout (EPA 2004).

		Age Intervals, *i*			
Parameter	**Units**	**0 - <2**	**2 - <6**	**6 - <16**	**16 - 70**
C_{fish}	mg/g-lipid	4.30E-04	4.30E-04	4.30E-04	4.30E-04
IR	g/day	3.6	7.1	14.3	14.3
BW	kg	15	15	70	70
EF	days	365	365	365	365
ED	years	2	4	10	54
AT	days	25,550	25,550	25,550	25,550
SF_{oral}	$(mg/kg\text{-}day)^{-1}$	1.1	1.1	1.1	1.1
ADAF	unitless	10	3	3	1

For each age interval *i,* cancer risk is computed as in EPA (2004):

$$Risk_i = \frac{C_{fish} \times IR_i \times EF_i \times ED_i \times SF_{oral} \times ADAF_i}{BW_i \times AT} \tag{9}$$

where:

C_{fish} = Concentration of the chemical in the fish (mg/g-lipid).
IR_i = Intake rate of the contaminated fish for age bin *i* (g/day).
BW_i = Body weight of the exposed person for age bin *i* (kg).
EF_i = Exposure frequency for age bin *i* (days/year). This describes how often a person is likely to be exposed to the contaminated medium over the course of a typical year.
ED_i = Exposure duration for age bin *i* (years). This describes how long a person is likely to be exposed to the contaminated medium.
AT = Averaging time (days). For quantifying cancer risk, "lifetime" exposure employs an averaging time of 70 years (i.e., 70 years × 365 days/year).
SF = Cancer slope factor $(mg/kg\text{-}day)^{-1}$
$ADAF_i$ = Age-dependent adjustment factor for age bin *i* (unitless)

Appendix F. Mass Budget Equations

Table F.1. Mass budget parameters and equations from Swackhamer *et al.* (1999).

Parameter	Equation*
Lake Superior Surface Area (SA)	$= 8.21 \times 10^{10}\ (m^2)$
Lake Michigan Surface Area (SA)	$= 5.78 \times 10^{10}\ (m^2)$
Air-water exchange	$= Net\ Annual\ Flux \times SA$
Wet deposition	$= C_J \times J \times SA$
J	$annual\ precip.rate\ (m/yr)$
C_J	$= C_{a,Total} \times W_T$
W_T	$= H'^{-1} \times (1 - \Phi) + W_p \times \Phi$
W_p	$= 10^{4.5}$
Dry deposition	$= C_{a,p} \times V_d \times SA$
V_d	$= 6.31 \times 10^4\ (m/yr)$
$C_{a,p}$	$= C_{a,Total} \times \Phi$
$C_{a,Total}$	$= C_{a,g}\ /(1 - \Phi)$
Φ	$= c \times \theta\ /({P_L}^{\circ} + c \times \theta)$
c	$= 17.2\ (Pa\ cm)$
θ	$= 1.0 \times 10^{-6}\ (cm^2/cm^3)$
$\log {P_L}^{\circ}\ (Pa)$	$= 12.25 - (4{,}487/\ T)$
Inflow	$= C_{in} \times Q_{in}$
Outflow	$= C_{w,d} \times Q_{out}$
Sedimentation	$= C_{oc} \times \omega_{oc}$
ω_{oc}	$org.carbon\ burial\ rate\ (kg/yr)$

* Values for SA, precipitation, runoff, connecting channels, and diversions obtained from NOAA's GLERL database. Equations for Φ and W_p from Hoff *et al.* (1993).