

The Impact of Climate Change on Air-Water Exchange of Toxaphene in Lake Superior

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Michelle Knabb

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Dedication

This thesis is dedicated to my parents, Bob and Maureen Knabb. Two scientists who have indulged my curiosity and instilled in me a passion for science. I am forever grateful.

Abstract

This study examined how toxaphene dynamics in Lake Superior have changed since 1995. A model developed by Swackhamer et al. (1999) was updated using measurements taken by the National Data Buoy Center to represent conditions from 1995 to 2012. Buoy trends observed on Lake Superior from 1979-2012 were projected out to 2035 to predict conditions resulting from climate change. The model was compared to sampling measurements taken in Lake Superior during the summer of 2006 and was within the 95% confidence interval of vapor-phase and dissolved-phase toxaphene concentrations. Moreover, the model predicts that climate change will decrease concentrations of toxaphene in the lake faster than if conditions remained the same, however the effect is small. In 2035, the dissolved concentration is predicted to be 20.6% less when the model includes climate change. With climate change, volatilization dominates year-round across the air-water interface, making Lake Superior an indirect source of toxaphene to the atmosphere.

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Introduction

Toxaphene is a broad-spectrum pesticide developed by the Hercules Company in 1947 (Hercules Company 1951). Produced through chlorination of pine stump derivatives, toxaphene encompasses approximately two hundred compounds, primarily hexa- to decachlorinated camphenes and bornanes (de Geus et al. 1999, Hainzl et al. 1994). With the high degree of chlorination, toxaphene is semi-volatile, lipophilic, and persistent in the environment. It was predominantly applied on cotton crops in the southern United States during the 1960s and 1970s, however it was first used as a piscicide in the Great Lakes (Sergeant and Onuska 1989, Miskimmin and Schindler 1994). Once DDT was banned, its use was encouraged as a replacement and was more widespread (Gianessi 1992). It is estimated that a total of 10^9 kg of toxaphene were used in the southern United States. The U.S. Environmental Protection Agency banned toxaphene in 1982 due to its potential to cause ecological and human health problems (de Geus et al. 1999). Toxaphene has been detected in a wide range of aquatic species and is responsible for 12% of fish consumption advisories in Lake Superior (Muir et al. 2004, Ontario Ministry of the Environment 2013). In toxicological studies, toxaphene has been shown to be toxic to the kidneys, nervous system, and liver (de Geus et al. 1999). Despite the lack of studies on human health effects of toxaphene exposure, it is designated a human carcinogen as a result of studies in rats and mice (de Geus et al. 1999). Toxaphene is currently regulated by the Safe Drinking Water Act and has a Maximum Contaminant Level (MCL) of 3 parts per billion (U.S. EPA 2012).

Dynamics of toxaphene in the environment are dependent on climatic factors.

While it was used in the Great Lakes basin, most of burden of toxaphene is attributed to the southern United States due to the relative proportion of toxaphene use in each region, and the potential for long-range transport (James and Hites 2002). Given its general structure and high degree of chlorination, toxaphene volatilizes and is transported through the atmosphere and deposits over the Great Lakes. Because each Great Lake has different physical properties, the concentration of toxaphene varies considerably. Lake Superior has the highest burden of toxaphene due to its larger size, colder temperature, and longer hydraulic residence time compared to the other lakes (Swackhamer et al. 1999). The Great Lakes are not a permanent sink for toxaphene and it continues to cycle through compartments of the environment. In the mid 1990s, net transport of toxaphene from air-water exchange is to the atmosphere, indicating that Lake Superior has become a source (Swackhamer et al. 1999).

Air-water exchange is particularly important for toxaphene transport and is dependent on climatic factors such as wind speed and temperature. Anthropogenic climate change is leading to distinct transformations of the physical characteristics of Lake Superior. Reduced ice cover in the winter lessens the albedo effect and results in more energy transfer to the lake. This in turn, leads to earlier summer stratification and an overall trend of the water warming faster than the surrounding air. Moreover, as the water temperature increases faster than the air, the atmospheric boundary layer is reduced, thus increasing wind speed (Austin and Coleman 2007). As humans continue to utilize fossil fuels and alter the global climate, ice cover in Lake Superior will become less likely and

the physical characteristics of the lake will continue to change. Since air-water exchange of toxaphene is based on the physical characteristics of the environment, climate change will alter the fate and distribution of toxaphene.

However, it is unknown how toxaphene will behave in Lake Superior as climate continues to change. Therefore, the purpose of this study was to determine how toxaphene dynamics have changed in the twenty-first century and to provide predictions as to how they will continue to change in the future. This was investigated through two main pathways: 1) air and water sampling of toxaphene in Lake Superior 2) update of a model developed by Swackhamer et al. 1999 to incorporate climate change.

Materials and Methods

Sampling

All water and air samples were collected aboard the USEPA's *R/V Lake Guardian* during spring and summer cruises of 2006. Site locations are a mixture of open-lake and nearshore stations depicted in Figure 1. Open lake sites are meant to characterize pollutant levels in the main basins of the Lake, where the water is well-mixed. These sites serve as "background" sites. Pollutant levels can vary more in nearshore areas, which are more likely to reflect impacts of activities on land. Nearshore stations were selected near major urban areas.

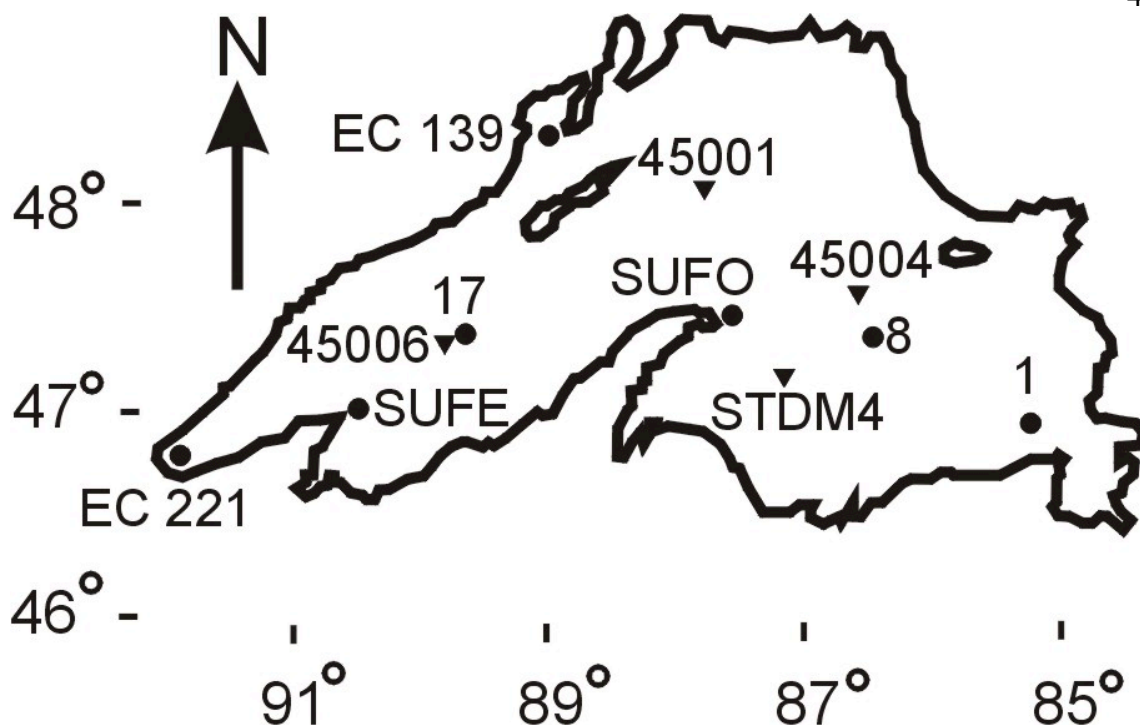


Figure 1. Map of Lake Superior showing sampling locations and buoy and CMAN stations. Circles represent sampling locations and triangles represent buoy (45001, 45004, 45006) or CMAN (STD M4) stations.

Water was sampled from the water column of Lake Superior using a submersible pump at a depth of 3m below the surface. The water was pumped through a glass fiber filter (GFF) and a glass column containing XAD-2 polymeric resin to collect the particle associated and dissolved phases, respectively. GFF's were combusted at 450 °C overnight and placed in combusted aluminum foil prior to sampling. The XAD-2 resin was cleaned by successive Soxhlet extractions, twice for 24 hours each in dichloromethane, then 24 hours in methanol. The XAD was then rinsed several times with MilliQ water and stored in fresh MilliQ water. The glass columns were water packed with the XAD-2 resin and kept refrigerated until sampling. Sample volumes varied, but were generally around 800L (see appendix).

Air was sampled by high volume air samplers deployed on a boom over the bow of the research vessel to prevent contamination from the ship itself. Air was pulled for 12 consecutive hours through two 8 by 10 inch glass fiber series F filter (GFF) and then a stainless steel cartridge containing cleaned XAD-2 resin. Flow through the air sampler will be determined using a Roots meter on one air sampler. GFF and XAD-2 was cleaned in the same manner as for the water samples.

After sampling GFFs were folded in fourths and returned to their combusted aluminum foil envelopes and placed in a zip closure bag. Water XAD-2 columns were emptied into cleaned glass jars and placed in zip closure bags. Air XAD-2 cartridges were replaced in their combusted aluminum foil, steel tins, sealed with PTFE (Teflon) tape and electrical tape, and placed in a zip closure bag. All samples were stored at 4°C (water GFF and XAD-2) or frozen at -20°C (air GFF and XAD-2) until extraction.

Extraction and Analysis

XAD and GFF samples were placed in a Soxhlet extractor, and washed with 5 aliquots of 20 mL of methanol into a separatory funnel. Methanol (300 mL) was then added to the Soxhlet with a 500 mL round-bottom flask. A set of samples consisted of four water samples, one field blank and a laboratory procedural blank. Laboratory procedural blanks consisted of all reagents used in the volumes required for the analyses carried through the entire analytical procedure in the same manner as a sample. The sample was extracted for 4 hours. The methanol was quantitatively removed to the separatory funnel, and the Soxhlet charged with 300 mL dichloromethane (DCM). The sample was extracted for an additional 16-24 hrs. To the separatory funnel 100 mL of

Barnstead Nanopure water, 50 mL saturated NaCl solution and 50 mL of hexane was added. The separatory funnel was shaken for 3 minutes, venting funnel often. Water was drained to a large bottle, and hexane is drained to a round bottom flask via a glass funnel containing 150 g Na₂SO₄. The separatory funnel was then rinsed with approximately 2x15 mL hexane and poured over the Na₂SO₄. Water from bottle was poured back into its corresponding separatory funnel with a rinse of the bottle with 50 mL hexane. This procedure is repeated twice more. Methanol extracts were reduced by rotary evaporation (approximately 10-15 mL) and DCM extracts added, volume reduced and solvent switched to hexane.

Interfering organic compounds must be removed from extracts to accurately detect and quantify the analytes of interest. Interfering compound removal was accomplished on a glass column (1 x 30 cm) containing 3 g ashed sodium sulfate, 4.5 g 0% deactivated silica, 1 g ashed sodium sulfate, and 6 g 2% deactivated alumina and 1 g ashed sodium sulfate. The column was eluted with 175 mL 15% DCM/hexane and collected in a 250 mL round bottom. This was labeled the F1 fraction. The column was eluted again with 50 mL 40% DCM in hexane and collected in 50 mL amber bottle. This was labeled the F2 fraction. F1 was solvent exchanged to hexane and reduced to a volume of approximately 1 mL. At this time the extract was stored in a vial with teflon-lined cap and stored in a freezer. Prior to instrumental analysis, the extract was reduced to a few hundred microliters by gentle nitrogen gas stream, and the internal standard was added (PCB #204) to Fraction 1.

After PCB analysis, Fractions 1 and 2 were recombined and toxaphene analysis performed. Toxaphene, was analyzed by gas chromatography mass spectrometry – electron capture negative ionization (GCMS-ECNI). This technique is as sensitive as GC-ECD, but is far more accurate because it affords a means of eliminating interferences and providing confirmation from the resulting mass spectra. The method is similar to that described in Swackhamer et al. (1999), but in general the mass spectrometer was a Hewlett-Packard 5973 coupled to a 5890A gas chromatograph. The carrier gas was helium, and the reagent gas was methane. The column was a 60 m 0.25 mm DB-5MS (J&W Scientific) with 0.25 mm coating thickness. The temperature program was as follows: 80-210 °C at 10 °C/min; 210-250 °C at 0.8 °C/min; 250-290 °C at 10 °C/min. The transfer line and injection port were kept at 270 °C, the source temperature was 100 °C, and the source pressure was 1.0 Torr.

Toxaphene is a complex mixture of hundreds of compounds, and requires a separate analysis. Because of the similarities in mass spectra, cis- and trans-chlordane and cis- and trans-nonachlor were also analyzed in the same run. The method quantifies total toxaphene, and the contributions of each of its homologs (hexa-, hepta-, octa-, nona-, and deca-chlorinated bornanes and bornenes), and was originally developed by Dr. Swackhamer, (Swackhamer et al. 1987) and subsequently modified by Glassmeyer (1999). The method includes strict confirmation criteria to exclude non-toxaphene interferences. The method monitors selected ions for each of the bornane and bornene homologs, as well as for known interferences so that they can be accounted for.

Please note that sampling, extraction and analysis were conducted prior to my work on this project, however this was how these procedures were conducted.

Model development

The model developed in this study was a continuation of the model described in Swackhamer et al. (1999) for toxaphene mass balance in Lake Superior using STELLA Modeling & Simulation Software (Lebanon, New Hampshire). That study provides a more detailed description of model design and inputs. In general, equation 1 demonstrates how the net air-water exchange flux of toxaphene was calculated:

$$\text{Flux} = k_a (C_{w,d}(H/RT) - C_{a,v}) \quad (1)$$

Where k_a represents the air-side mass transfer coefficient (m/s), $C_{a,v}$ describes concentration in the air vapor (ng/m^3), $C_{w,d}$ is concentration in the water that is dissolved (ng/m^3), H is the Henry's law constant ($\text{Pa m}^3/\text{mol}$), R is the ideal gas law constant ($8.3145 \text{ Pa m}^3/\text{mol K}$), and T is the temperature in Kelvin. In this case, a positive value indicates net transport to the atmosphere and negative value indicates net transport to the water, in units of $\text{ng}/\text{m}^2 \text{ s}$.

The Swackhamer et al. (1999) study modeled toxaphene dynamics from 1950-1995, whereas we were concerned with what has happened beyond that time period. Therefore, we extended the model out from 1995 using the National Oceanic and Atmospheric Administration's National Data Buoy Center and obtained data on the physical characteristics of Lake Superior from 1979-2012. Three buoys (45001, 45004, and 45006) were chosen along with one Coastal Marine Automated Network (CMAN) station (STD4) for their central locations in Lake Superior (Figure 1). Buoys are

situated on the lake from approximately April through November, while CMAN stations collect data year-round. In particular, we utilized measurements of air temperature, water temperature, and wind speed and created seasonal averages as our model functioned on a quarterly basis. Because the model simplifies Lake Superior to a unified system, buoy seasonal averages were averaged in order to develop a summary value for the whole lake for each season. Additionally, we were interested in how toxaphene dynamics might change in the future, so we utilized trends projected from buoy data from 1979-2012 for wind speed and water temperature. The model was extended out to 2035 using these trends.

Results

Model and Measurement Comparison

In order to ensure that our model was functioning properly, we compared our modeled toxaphene gas-phase and dissolved-phase concentrations to the measurements taken. In our model, the gas-phase concentration of toxaphene is specified because most of the toxaphene in Lake Superior originated through atmospheric transport from the southern United States. With data from Swackhamer et al. (1999), an exponential decay for each season was used to extend gas-phase concentration beyond 1995 (see appendix). These modeled values were compared to measurements from our study as well as other studies (Figure 2). Our model is within the range of measurements reported by James et al. (2001) and Glassmeyer et al. (1999). However, it is generally higher than the bulk of measurements taken by Glassmeyer et al (1999). Additionally, when comparing our average summer gas-phase concentration measurements to the model, our average

concentration (37 pg/m^3) was very similar to that predicted for the summer of 2006 (38 pg/m^3). While the 95% confidence interval for summer gas-phase concentration was relatively high, we can be confident that our model is reflecting what is happening during the summer. During the spring, the average measured concentration (12 pg/m^3) is somewhat higher than what was predicted by the model (6 pg/m^3), however the modeled concentration falls within the 95% confidence interval. This may suggest that the concentration of toxaphene in the gas-phase is not dropping as rapidly as the model predicted. Given that the measured concentrations are in range with the predicted concentration, it appears this model parameter is a sufficient representation of Lake Superior.

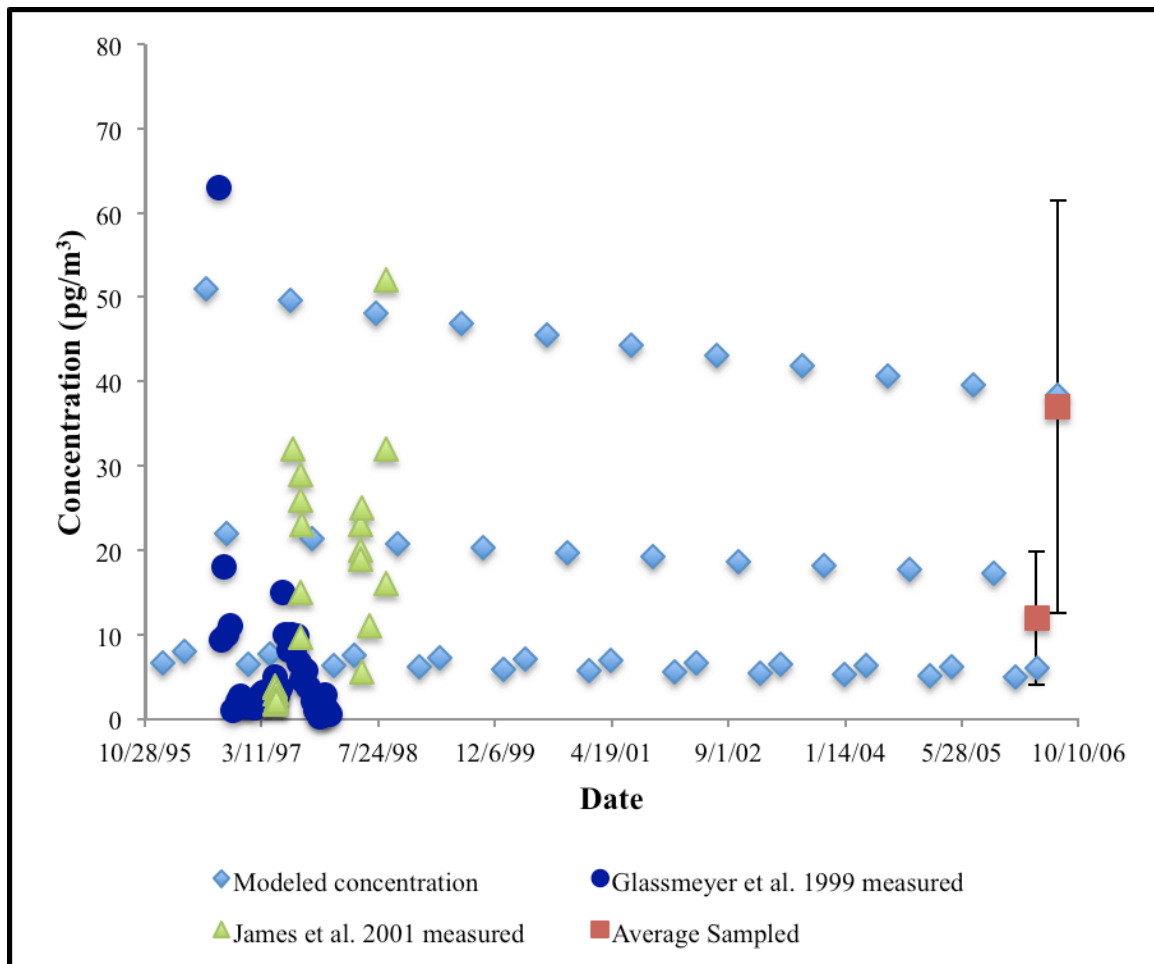


Figure 2. Comparison of modeled gas-phase concentration to measurements taken by Glassmeyer et al. (1999), James et al. (2001), and an average of measurements from our study. Error bars represent 95% confidence intervals for the average sampled concentration.

A comparison between measurements of dissolved concentration and modeled dissolved concentration was also conducted (Figure 3). This comparison actually examines the validity of our model design because toxaphene water concentration is an output of the model. Previously, Swackhamer et al. (1999) validated the model with samples from 1996, however it was important to determine if the model was still a good approximation in the twenty-first century with the use of buoy data. There is clear agreement between the average measured dissolved concentration of the lake and the

concentration predicted by the model (Figure 3). While the measured concentrations are higher than the predicted, the predicted falls within the 95% confidence interval of the measurements. This suggests that the model is still a good estimate of toxaphene dynamics within Lake Superior.

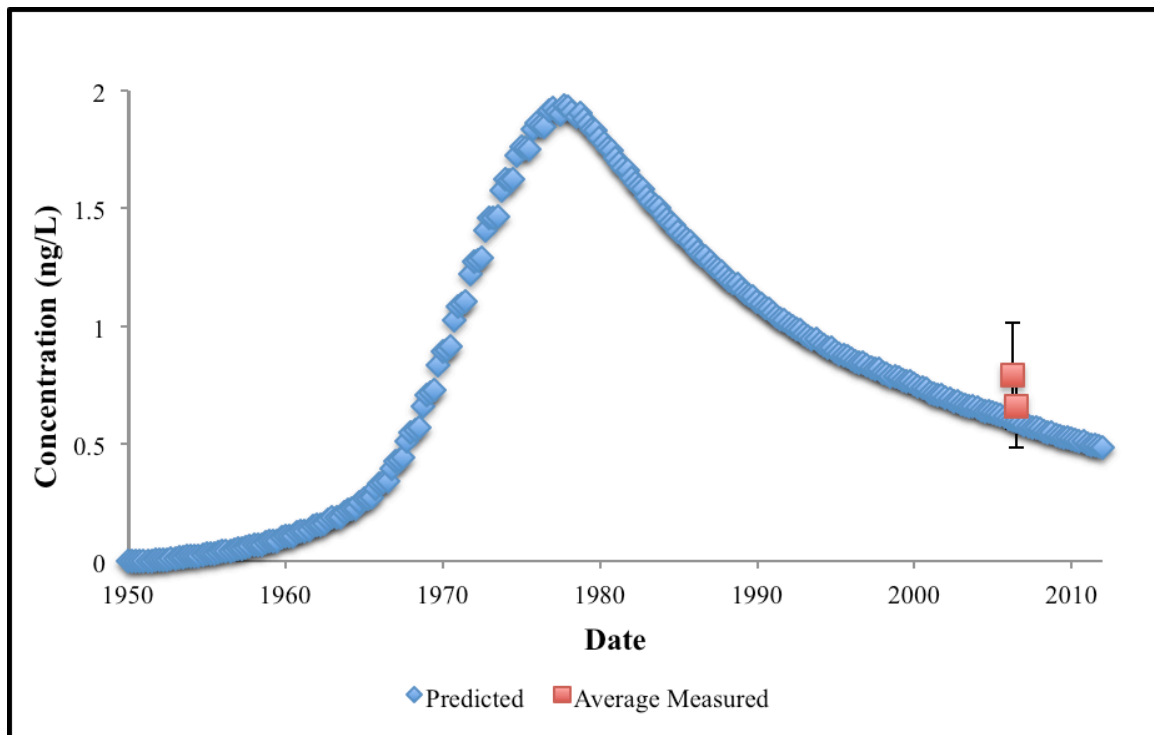
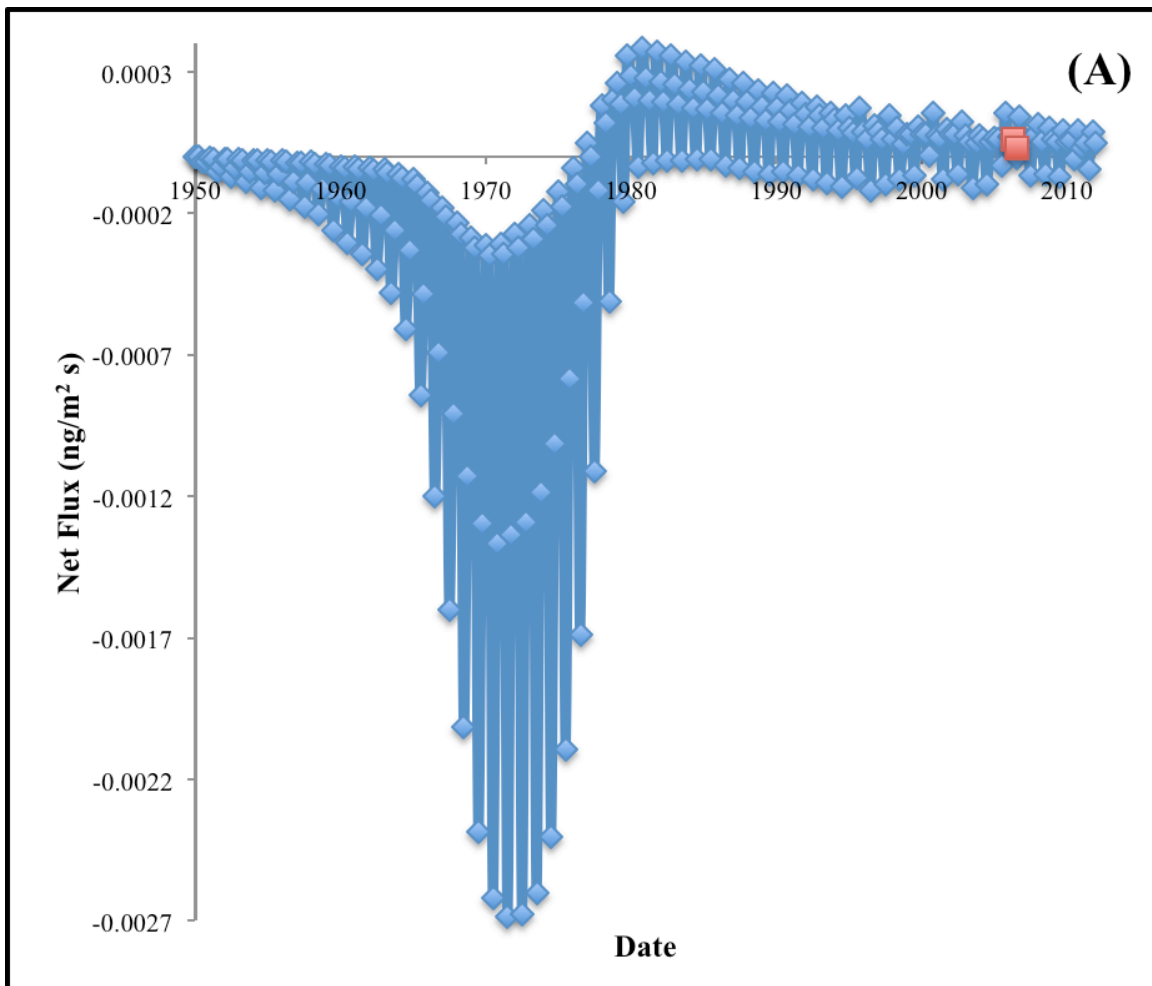


Figure 3. Predicted toxaphene concentration in Lake Superior water in comparison to average measured concentration. Error bars indicate 95% confidence intervals of average measurements.

Additionally, the net flux was calculated for both the samples and the model and compared (Figure 4a and b). During the spring of 2006, the model predicts net flux as $6.19 \times 10^{-5} \text{ ng/m}^2 \text{ s}$, whereas the average sampled net flux was calculated as $6.21 \times 10^{-5} \text{ ng/m}^2 \text{ s}$, indicating that net volatilization is occurring (Figure 4b). In the summer of 2006, the model predicts net flux as $-5.03 \times 10^{-6} \text{ ng/m}^2 \text{ s}$, but the average sampled net flux is

$3.13 \times 10^{-5} \text{ ng/m}^2 \text{ s}$ (Figure 4b). In this case, the model suggests a small amount of absorption and the samples suggest volatilization. This discrepancy it can be attributed to the heterogeneity of across Lake Superior and the limited number of sampling sites. While the inconsistency does occur, we are still confident about the ability of the model to generally reflect dynamics of toxaphene in the lake.



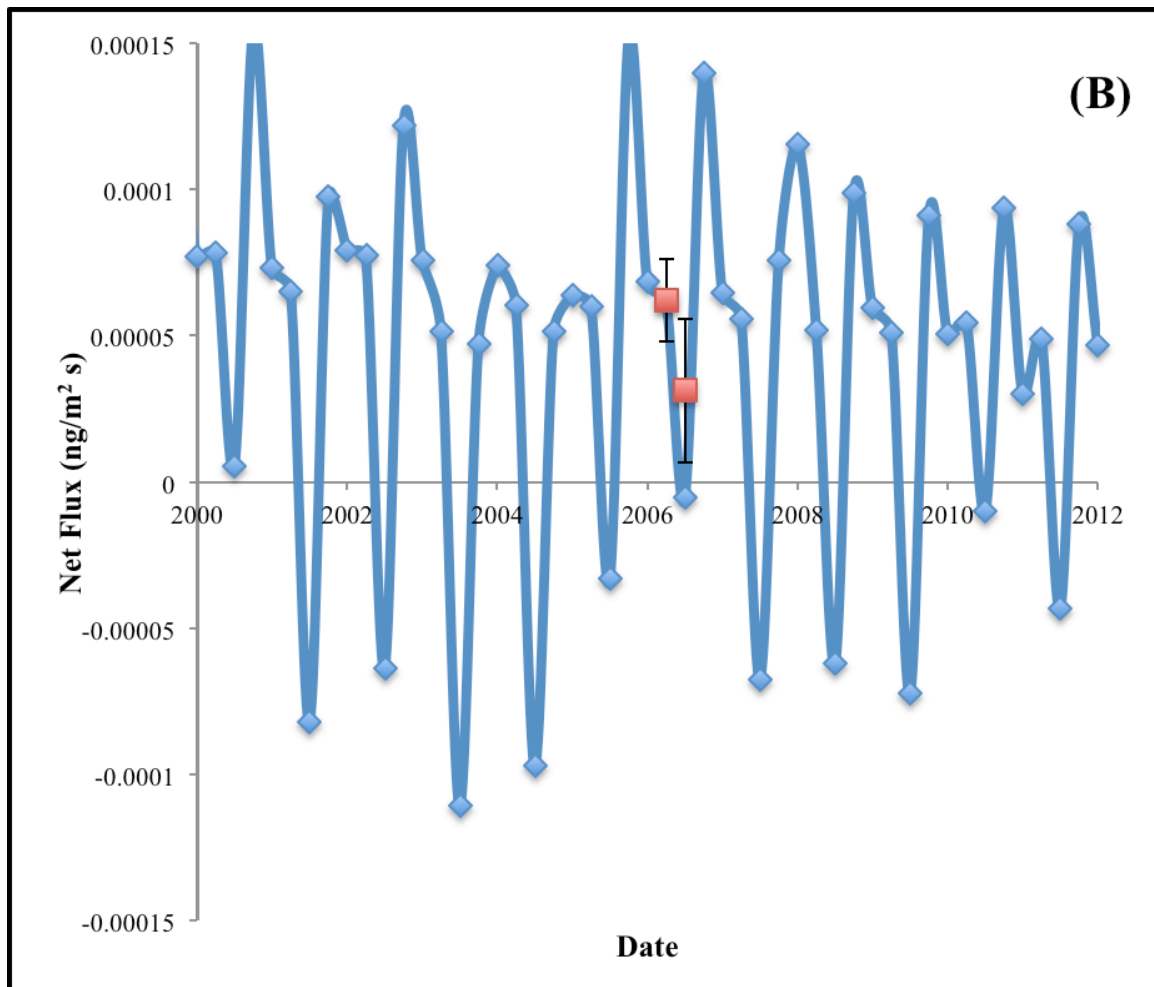


Figure 4. Comparison of net air-water exchange flux for model vs. average measured. Figure A) includes entire time span of the model, whereas B) shows a more localized comparison. Positive values indicate net volatilization and negative values indicate net absorption. Diamonds represent modeled values and squares represent average values calculated from measurements (error bars showing error propagated through calculations of net flux).

Trends in Physical Characteristics of Lake Superior

Accurate trends in the physical characteristics of Lake Superior were crucial to developing the model because they in turn affect the dynamics of toxaphene. There was a discrepancy between the months classified as summer in the Swackhamer et al. (1999) model compared to those described by Austin and Colman (2007). In the previous model,

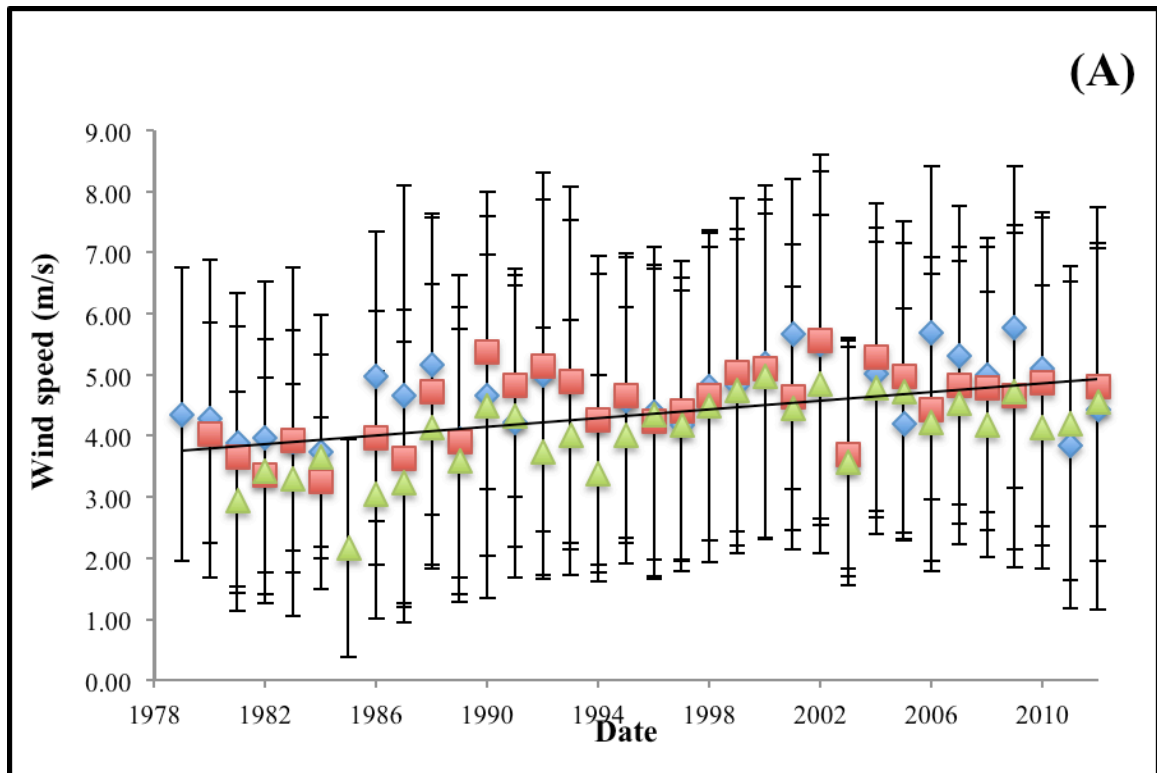
summer was classified as June through August, whereas Austin and Colman (2007) described summer as July through September, thus shifting the classifications of the other seasons. While this may seem like a minor difference, it results in different estimates of the physical properties of the lake environment. When summer is defined as July through September, it more accurately represents the stratified months on Lake Superior, which is representative of summer conditions. Therefore, when the climate change model was developed for this study, seasonal averages were shifted to reflect the stratified season and aligned with Austin and Colman (2007). The impact of this alteration had minor effects on the water concentration and net air-water exchange flux in 2011 (Table 1).

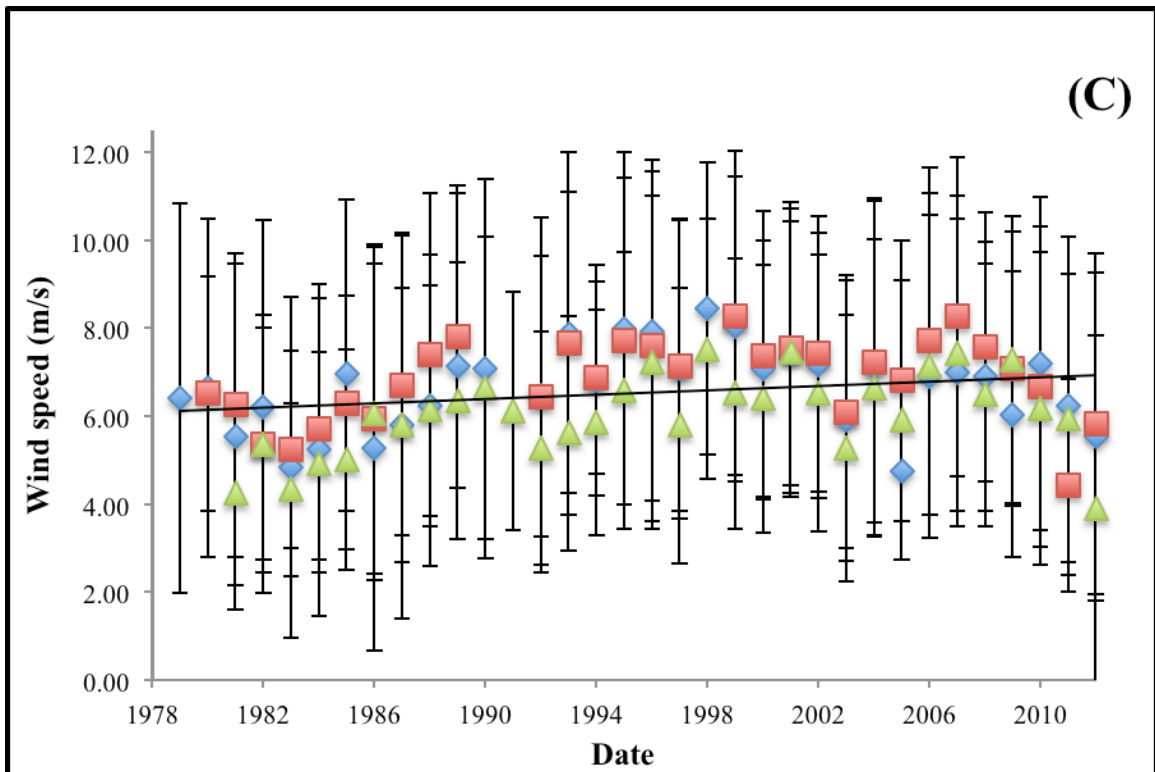
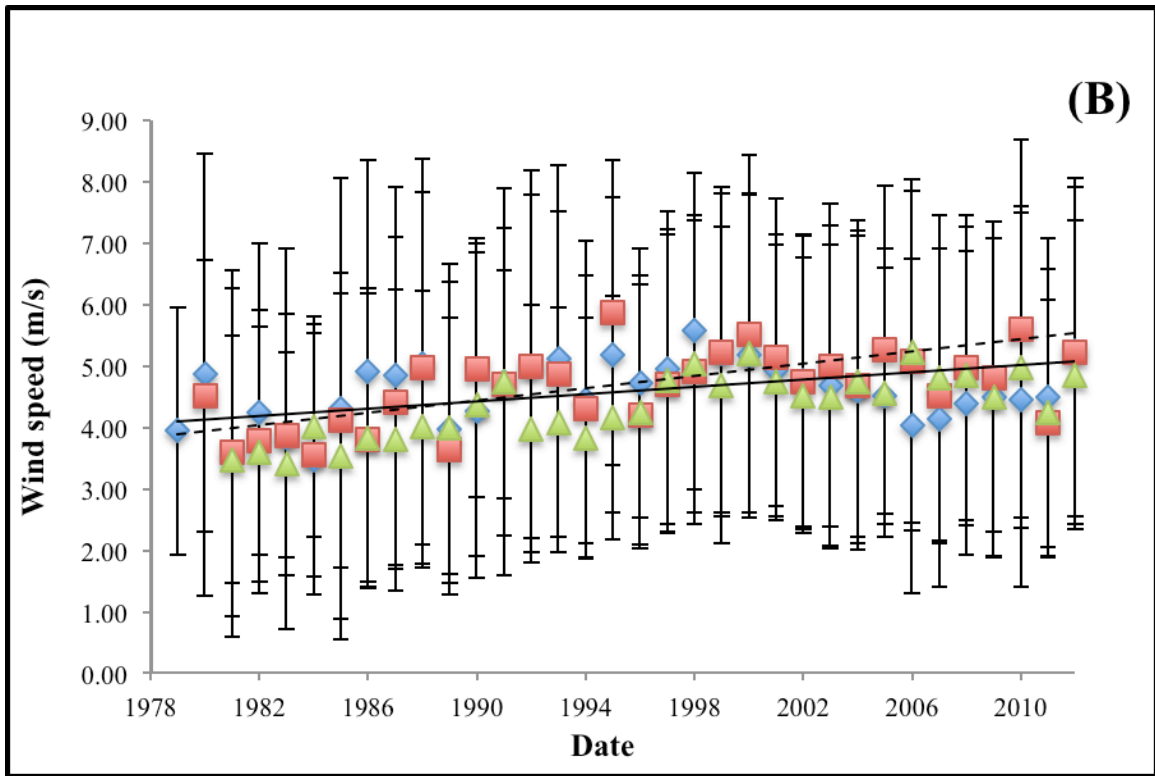
Year	Model	Dissolved Toxaphene Concentration (ng/L)	Summer Net Flux (ng/m² s)
2011	Original Season	0.493	-4.32x10 ⁻⁵
	Stratified Season	0.482	-1.46x10 ⁻⁵
2035	Constant Parameter	0.228	-4.19x10 ⁻⁵
	Climate Change	0.181	1.95x10 ⁻⁵

Table 1. Summary of dissolved toxaphene concentration and summer net flux compared across different models. Negative net flux values indicate net absorption, whereas positive values indicate net volatilization. All values are taken from summer.

Wind speed trends from 1979 to 2012 were similar to those observed by Austin and Colman (2007) (Figure 5). With the addition of data from 2007-2012, there is still an increase in wind speed during the summer (Figure 5b). There is a slight leveling off of wind speed from 2007-2012, making the trend for all buoys slightly reduced. Austin and Colman (2007) did not report data for trends in spring, fall, and winter, however they too showed positive trends in wind speed from 1979-2012 (Figure 5a, 5c, and 5d respectively). Since buoys are removed during the winter, the only data available for that season is from the CMAN station, STD4. This site was not used for wind speed trends

for spring, summer, and fall because when data was transformed to wind speeds at 10 m elevation, they were consistently higher. However, it was used for winter as it provided the only available data. Overall, Figure 5 suggests that wind speed is still increasing with increasing lake temperatures due to climate change.





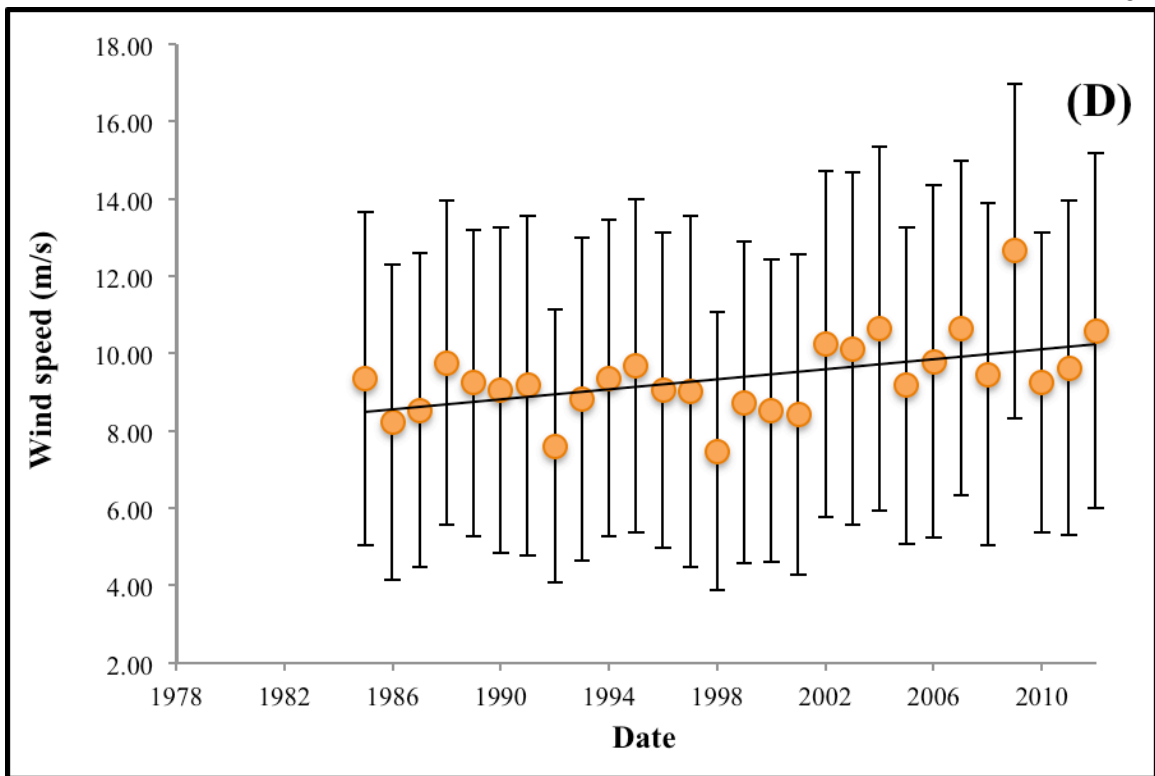
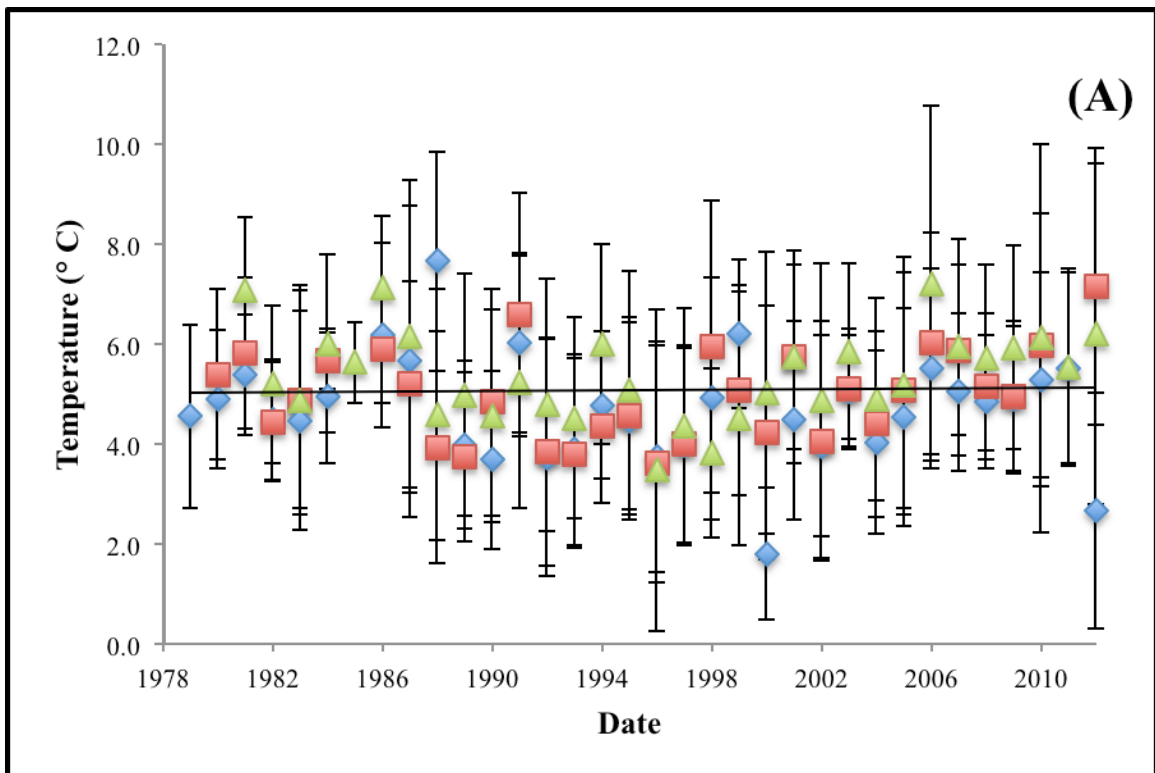
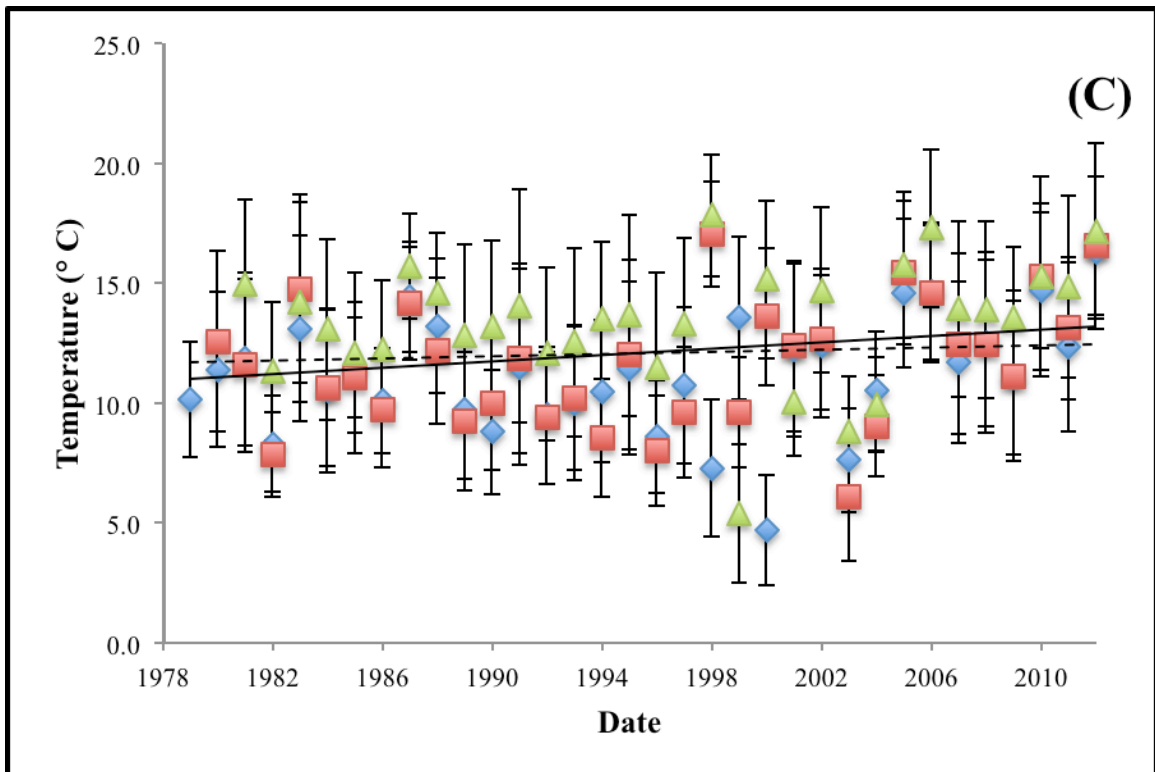
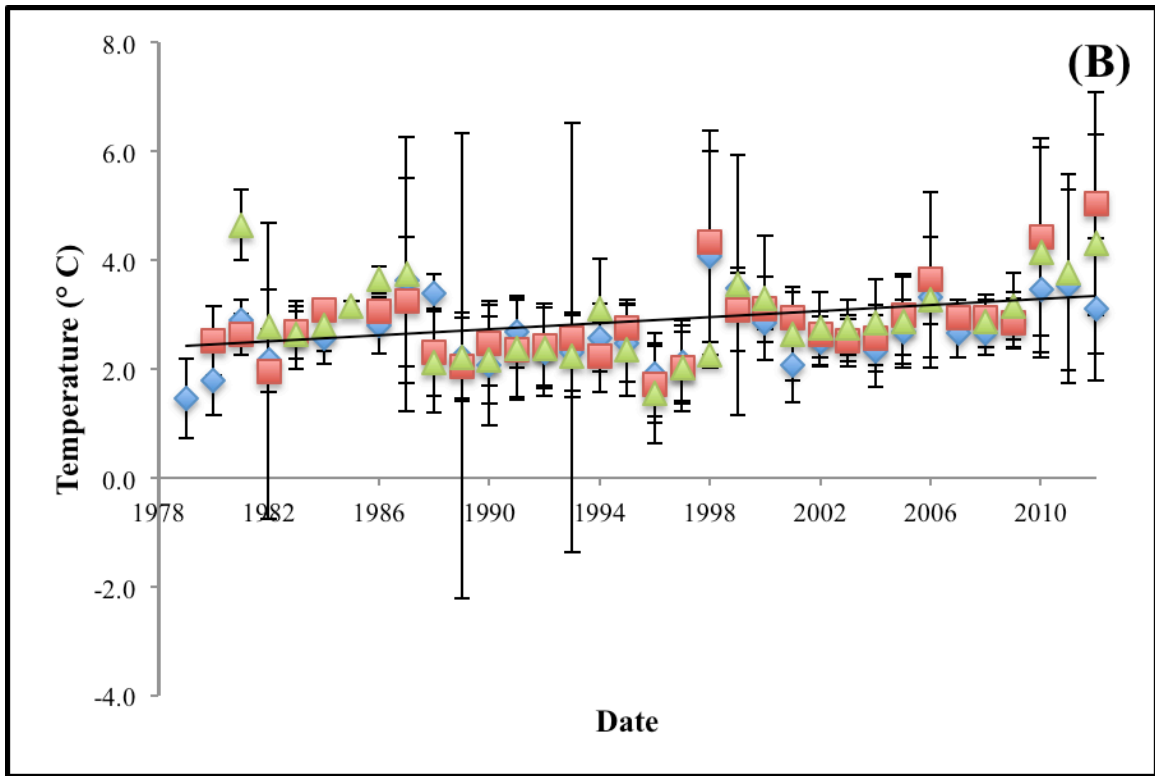


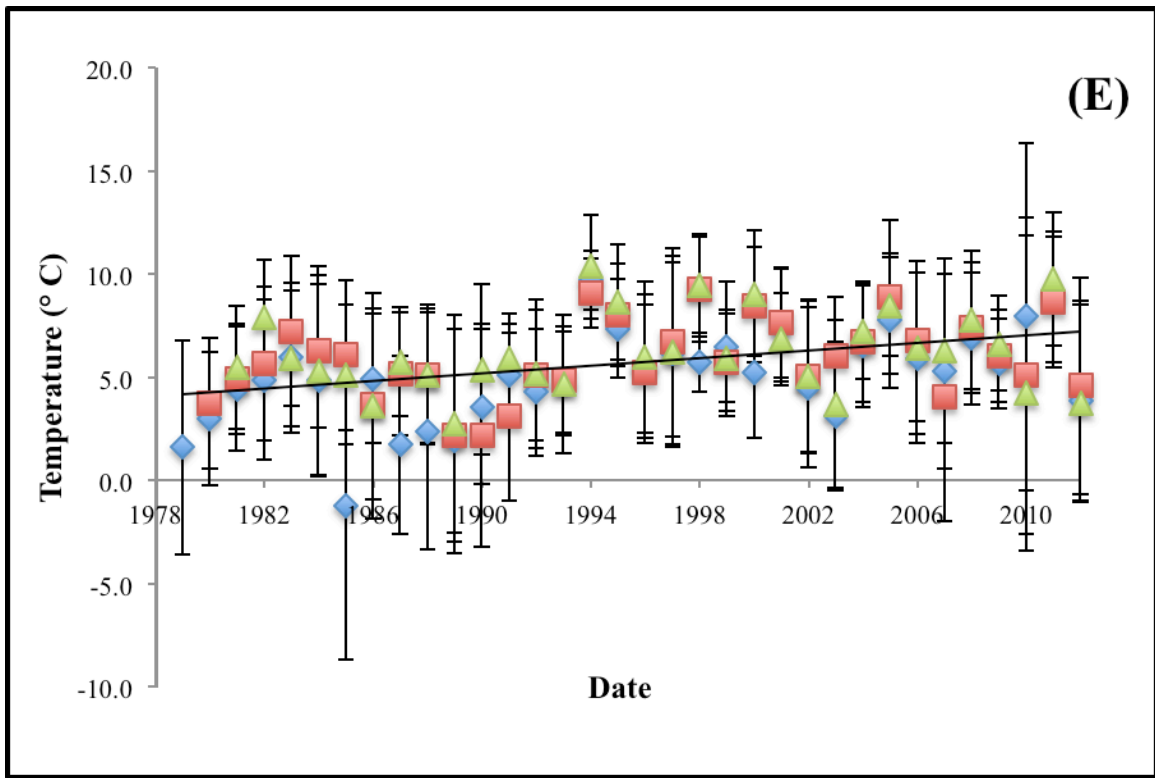
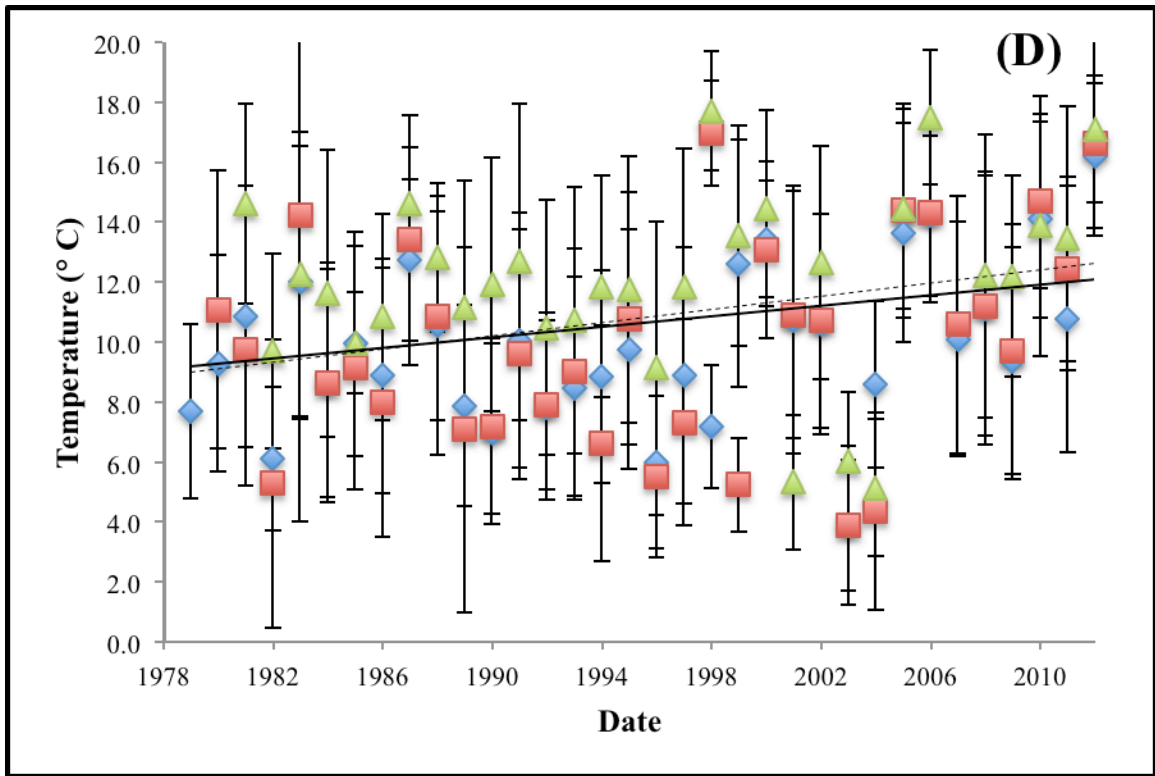
Figure 5. Wind speed trends over Lake Superior by season. Values shown are from elevation where they were recorded, buoy stations at 5m and STD4 at 35.2 m. Diamond: buoy 45001, square: 45004, triangle: 45006, circles STD4. A) Spring, B) Summer, C) Fall, and D) Winter. Note: dotted line in (B) represents trend shown by Austin and Colman (2007), whereas solid lines indicate trends shown from our data.

Air and water temperature trends were also inspected both for development of the model and to determine whether these characteristics have changed (Figure 6). In general, air and water temperatures have increased from 1979 through 2012. Austin and Colman (2007) showed water temperature increased 0.11 ± 0.06 °C per year, whereas our data showed 0.089 ± 0.069 °C per year, which is within the range. Additionally, in the study conducted by Austin and Colman (2007), air temperature increased 0.059 ± 0.021 °C per year, with our trend of $0.068 \pm .048$ °C per year, again within the range (IPCC 2007). Overall, the positive trends in buoy observations suggest that climate change is evident in

the air over and water in Lake Superior. From 1979-2012, most of the air temperature trends are not statistically significant at the 5% level, however most of the water temperature trends are significant. Additionally, the water temperature increases more rapidly than the air temperature during the spring and summer, which is consistent with the results from Austin and Colman (2007).







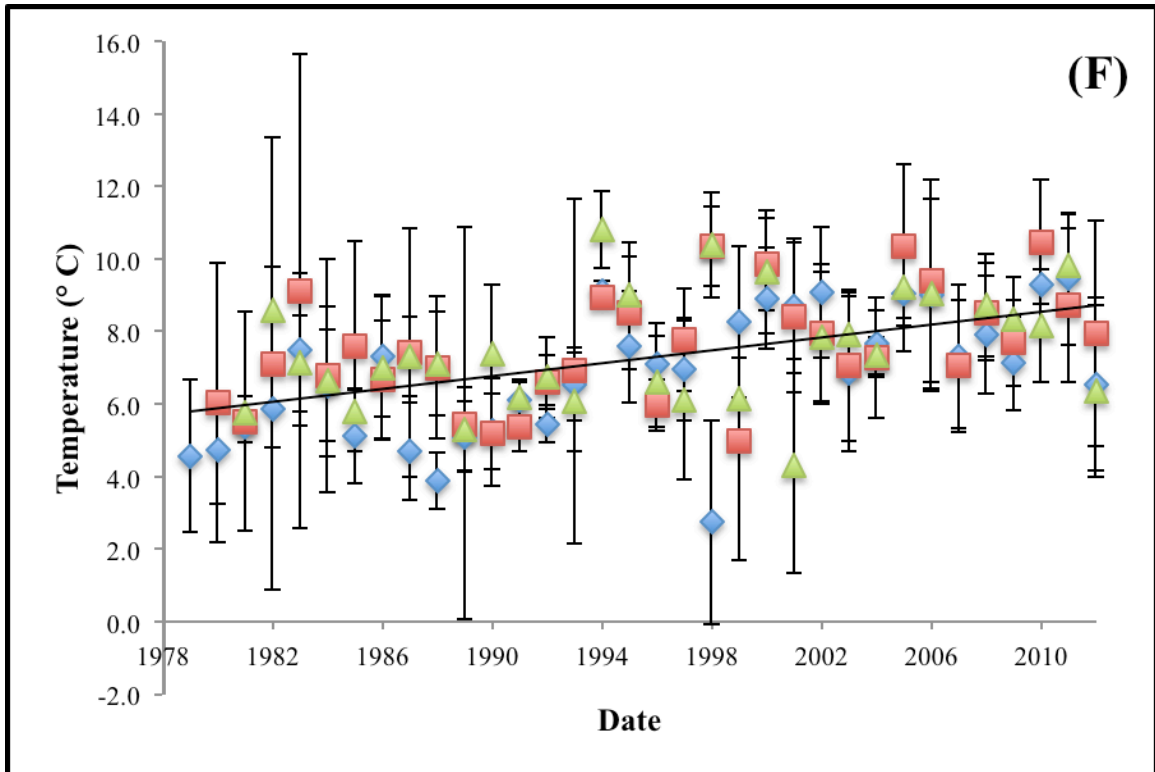


Figure 6. Air and water temperature trends from 1979 to 2012 from 3 buoys in Lake Superior. Symbols defined as: diamonds: buoy 45001, squares: buoy 45004, triangles: buoy 45006. A) Average air measurements in spring, B) Average water measurements in spring, C) Average air measurements in summer, D) Average water measurements in summer E) Average air measurements in fall, F) Average water measurements in fall. Note: dotted line in (C) and (D) represent trend lines from Austin and Colman (2007).

Sensitivity Analysis

A sensitivity analysis was conducted to determine which parameters had the greatest impact on model output. More specifically, average wind speed and water temperature values for each season from 1995-2012 were increased and decreased by 25% and the model was run with each manipulation, while holding other values constant. These alterations, in turn, affected the air-side mass transfer coefficient and Henry's Law constant as they are functions of wind speed and temperature, respectively (see

appendix). Figure 7 demonstrates how the dissolved concentration of toxaphene varied across these manipulations. As temperature and wind speed are increased, the concentration of toxaphene decreases faster, and the converse is true when temperature and wind speed are lowered. Additionally, when temperature is altered by 25%, it results in a greater change in the dissolved concentration of toxaphene in comparison to when wind speed is altered by 25%. Table 2 demonstrates how the final dissolved concentration of toxaphene for the baseline compares to each parameter manipulation. This table shows that when wind speed and temperature are altered to the same degree, the changes in temperature result in approximately twice the percent difference in toxaphene concentration by 2012. Together, Figure 7 and Table 2 suggest that the dissolved concentration is more dependent on the temperature of the water than the wind speed across the lake.

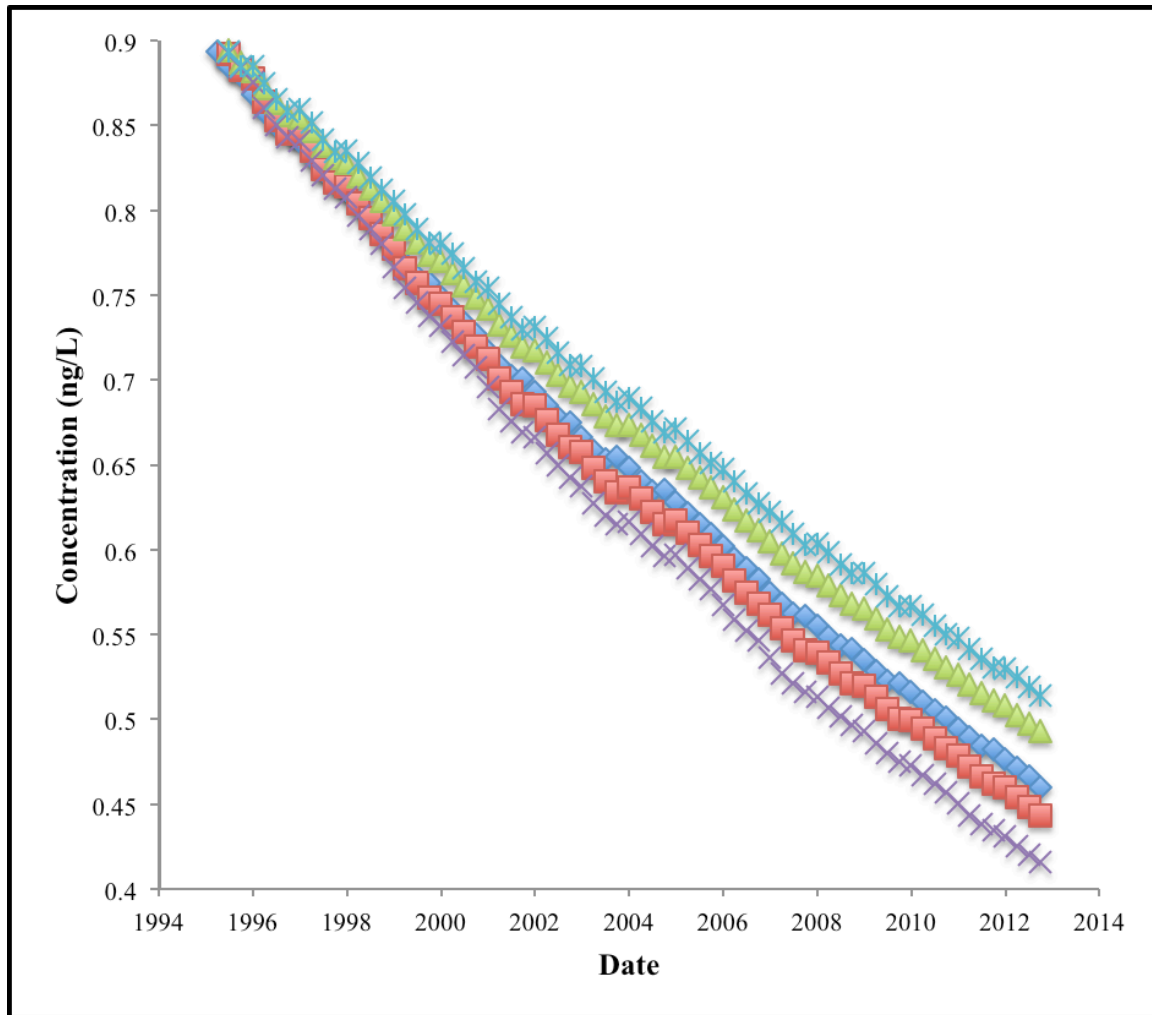


Figure 7. Sensitivity analysis of wind speed and temperature manipulation on dissolved concentration of toxaphene in Lake Superior. Diamonds represent the baseline model, squares represent high wind speed model, triangles represent low wind speed, x's represent high temperature, and asterisks' indicate low temperature.

Dissolved Toxaphene Concentration Percent Difference from Baseline		
Parameter Altered	Wind Speed	Temperature
High	-4.93%	-11.67%
Low	5.82%	10.59%

Table 2. Comparison of dissolved toxaphene concentration in fall 2012 to when wind speed or temperature are increased/decreased by 25%.

Projections out to 2035

The model was projected out to 2035 using trends in wind speed, temperature, and air concentration. It was extrapolated to 2035 because it was estimated that Lake Superior would be ice free most winters after that date (Austin and Colman 2007). Therefore, we assumed trends would continue as they have up until that point. Wind speed values were altered to represent wind speed at 10 m elevation and these trends were projected out for the model. This meant that wind speed was increased by 0.057 m/s per year in winter, 0.038 m/s per year in spring, 0.032 m/s per year in summer, and 0.026 m/s per year in fall. Additionally, there were clear trends in water temperature that could be applied to the 2013-2035 time frame. Trends for spring and fall were taken from the trend lines for data from 1979-2012 and showed a 0.028 K and 0.088 K increase per year, respectively. Austin and Colman (2007) found a 0.11 K increase in water temperature per year in the summer and our data indicated a 0.089 K increase per year, the latter being used for our model. Since we did not have consistent data for water temperature in the winter, it was assumed that water temperature would not change. Finally, toxaphene gas-phase concentration was projected out in the same way it had been to 2012, using an exponential decay (see appendix).

The results of the model can be used to determine net flux of toxaphene in Lake Superior, which describes the overall transport of toxaphene across the air-water interface. This is important because it describes the dynamics of toxaphene in a succinct manner. There are some distinct trends in toxaphene net flux in the time frame beyond 1995 (Figure 8). The net flux is most erratic from the period of 1995 through 2012, which

makes sense because it is based on actual measurements, so there is more variability in the model inputs. During that time, absorption dominates in the summer and volatilization dominates in the spring, fall, and winter. From 2013 to 2035, the dynamics are much more consistent due to smoothed temperature and wind speed data. Toxaphene is approaching equilibrium in Lake Superior, as demonstrated by the decrease in deviation from zero in Figure 8. Additionally, once trends are projected, the lake volatilizes toxaphene year-round. This is occurring as a result of decreasing burden of toxaphene in Lake Superior as well as increased temperature and wind speed.

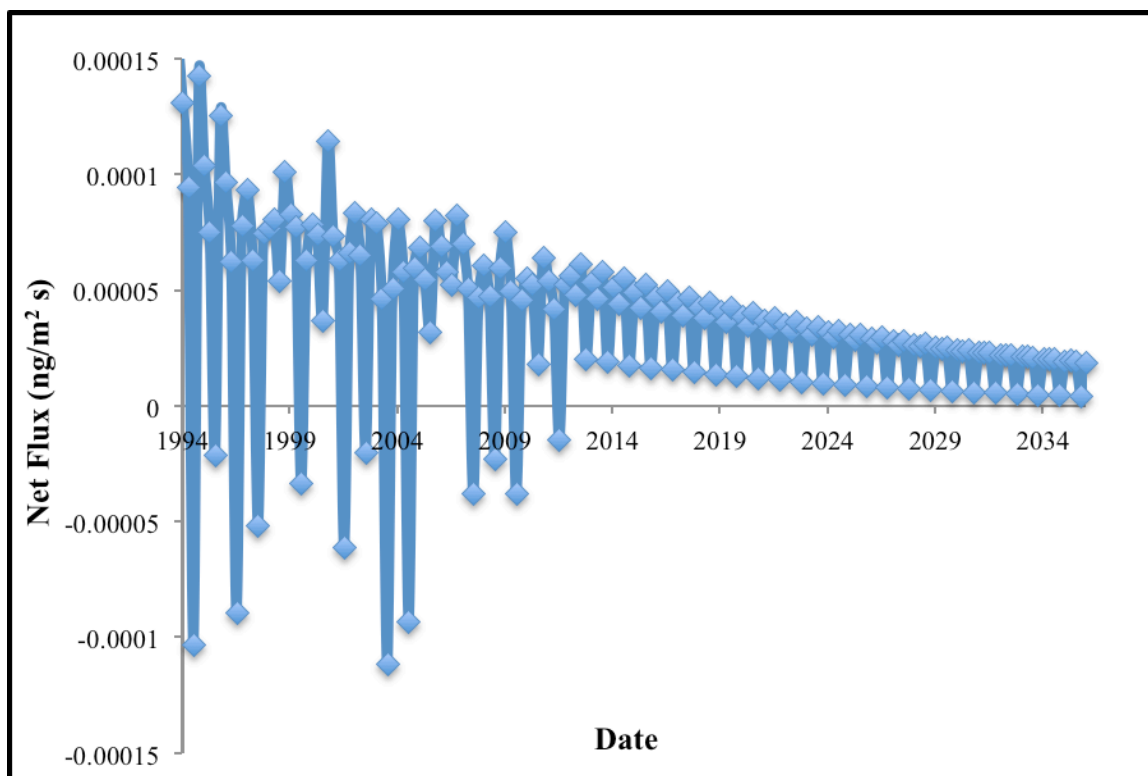
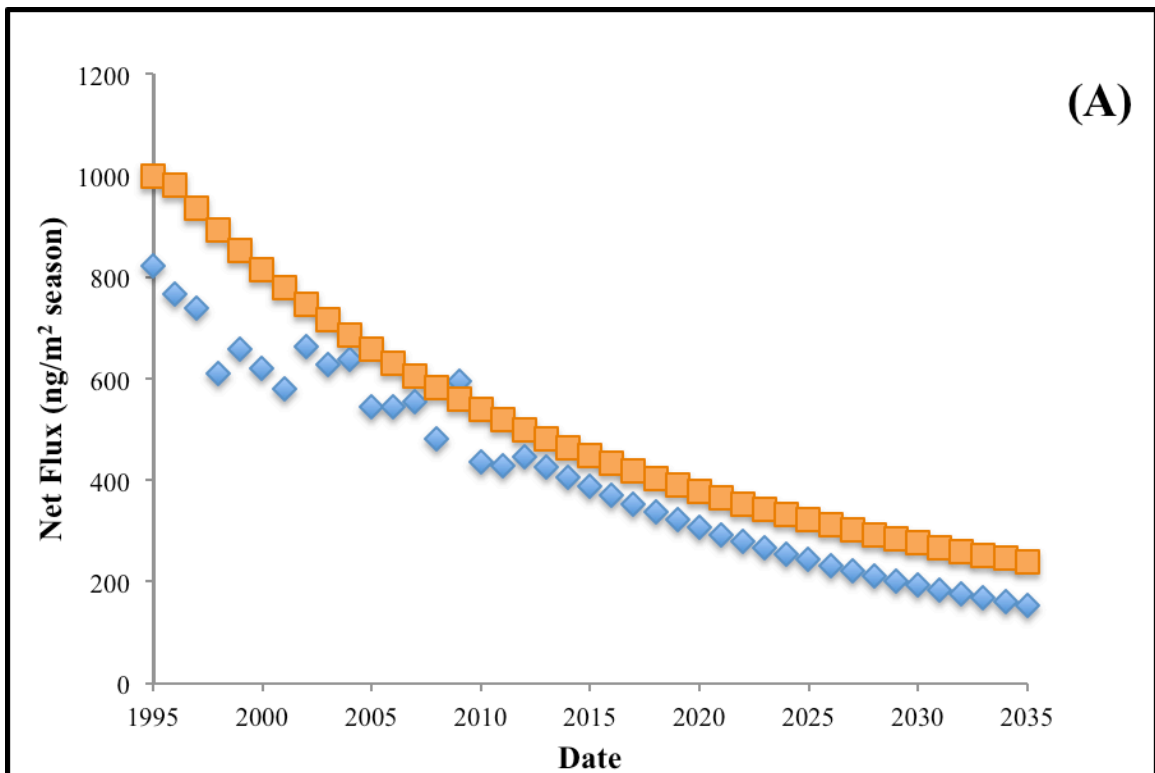


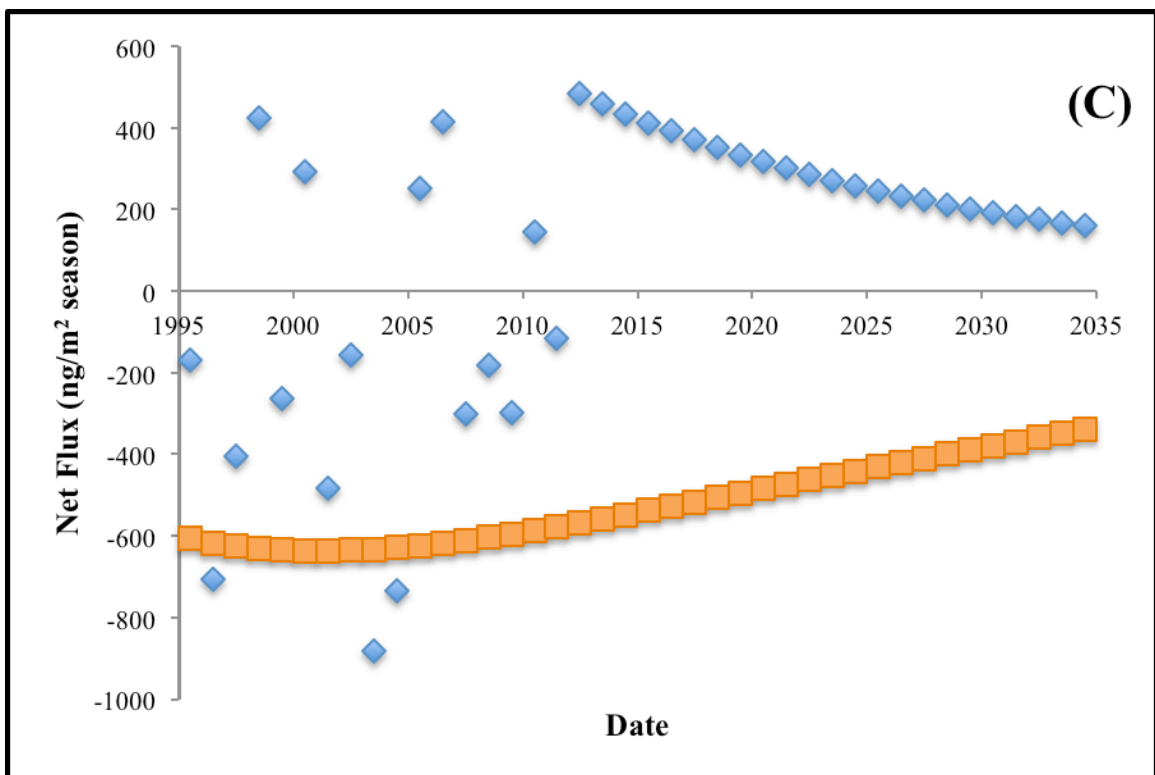
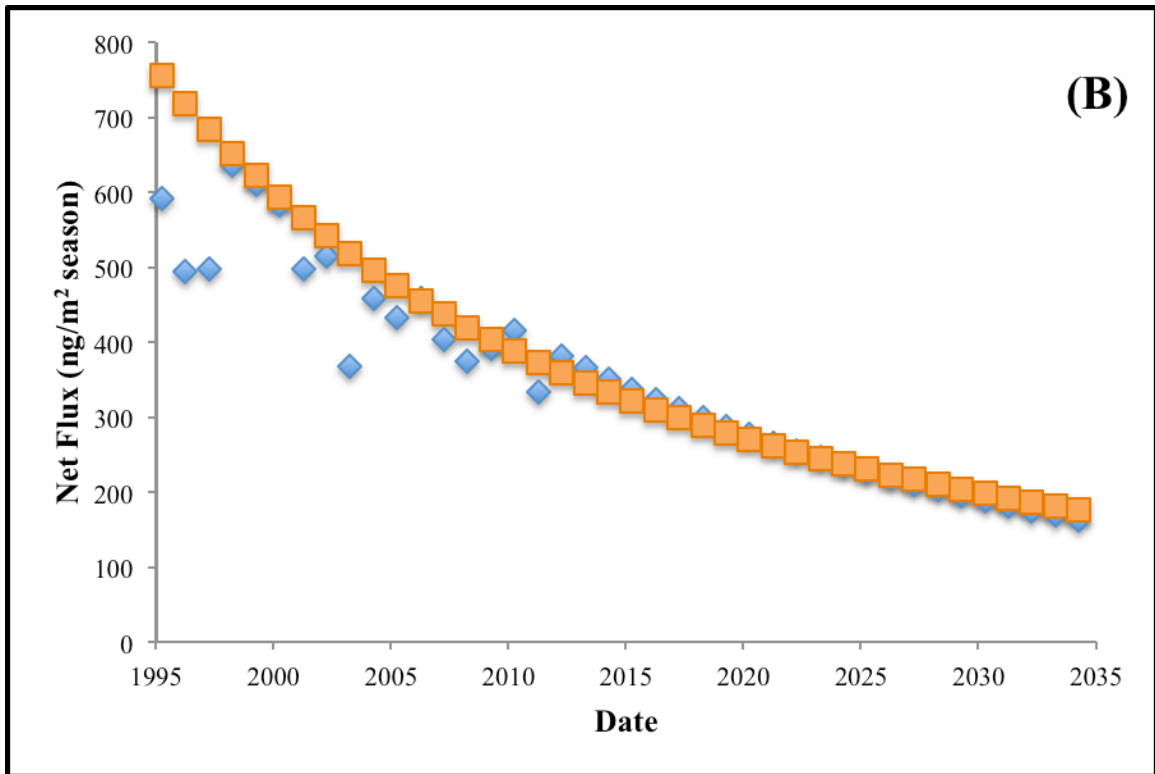
Figure 8. Modeled net air-water exchange flux of toxaphene in Lake Superior. Negative values indicate net flux into the lake, whereas positive values indicate net flux into the atmosphere.

Comparison to Constant Parameter Model

The model projected out to 2035 can be compared to a constant parameter model to determine the influence of climate change. More specifically, the constant parameter model was created by maintaining parameters from the original model while projecting gas-phase concentration out through 2035. Since the climate change model was not altered until 1995, there are no differences between the two models prior to that time. Beyond that time, each season responds differently to climate change incorporation (Figure 9). The climate change model predicts that net flux from Lake Superior will be lower than the constant temperature model in winter (Figure 9A). There is a distinct difference in magnitude between the two models. In contrast, the net flux for the climate change and constant parameter model are very similar in the spring (Figure 9B). There is variation between the two from 1995 to 2012, which is based on buoy sampling measurements. The net flux trends are the most distinctly different during the summer (Figure 9C). There is a significant amount of variation in net seasonal flux from 1995 to 2012 in the climate change model and most of those flux values are higher than that predicted by the constant model. Once the climate change model is projected out beyond 2012, it predicts net volatilization during summer out through 2035. During that time period, the constant parameter model is still absorbing toxaphene. These differences help to explain why the dissolved phase concentration in Lake Superior is lower in the climate change model than in the constant parameter model in 2035 (Table 1, Figure 10). Finally, there are differences between the climate change model and constant parameter model in the fall (Figure 9D). From 1995 through 2035, net volatilization from Lake Superior is

generally lower. During the fall, the climate change model is significantly closer to equilibrium than the constant model. From an annual perspective, the constant parameter model shows net annual flux to be lower than the climate change model (see appendix). Overall, it is apparent that by changing the physical characteristics, such as water temperature and wind speed of Lake Superior, the net flux is altered.





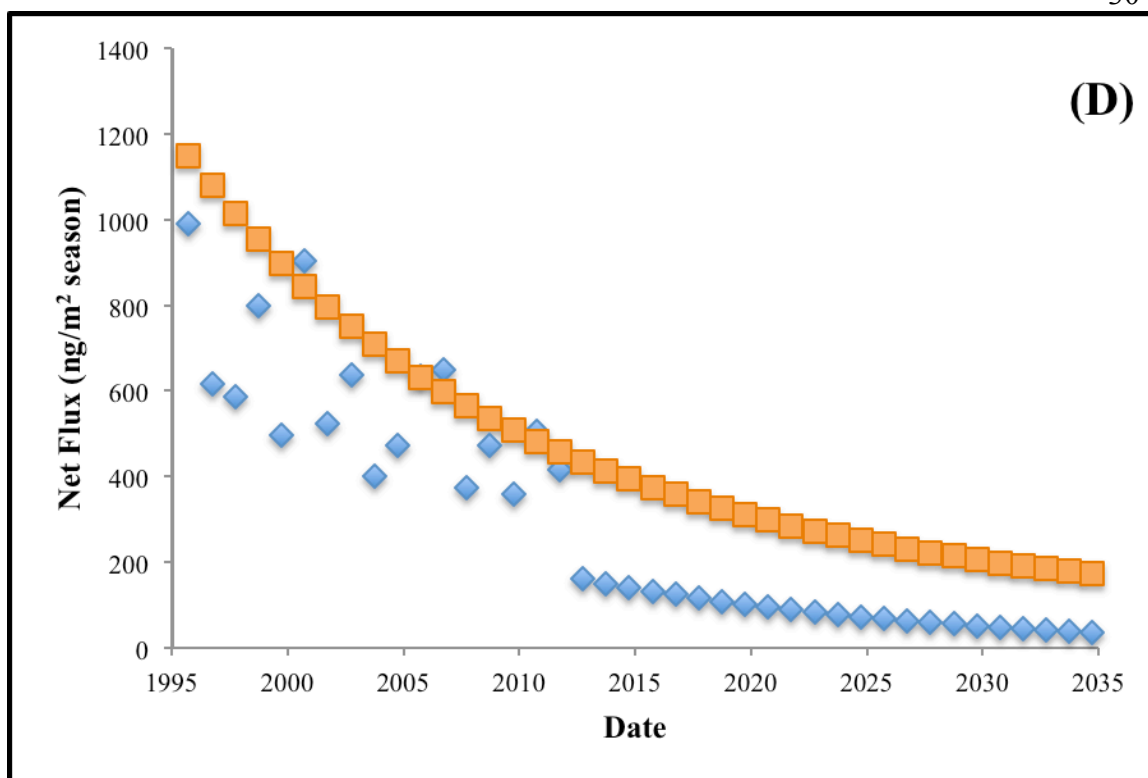


Figure 9. Comparison seasonal net flux for constant parameter and climate change models. Positive values indicate net volatilization whereas negative values indicate net absorption. Squares designate the constant temperature model whereas diamonds represent the climate change model. Figures show net flux in (A) winter, (B) spring, (C) summer, and (D) fall.

Additionally, the dissolved toxaphene concentration in Lake Superior can be compared across the two models (Figure 10). As mentioned previously, comparison is not relevant until 1995 when the climate change model is altered from the constant parameter model. Clearly, the two models show very similar trends in dissolved phase toxaphene concentration. The climate change model shows slightly higher concentrations when buoy data are used to represent lake conditions. Once the physical characteristics of Lake Superior are projected out beyond 2012, the climate change model predicts that the toxaphene dissolved phase concentration will decrease more quickly than the constant

parameter model. In fact, this difference in concentration leads to an added 590 kg of toxaphene to the atmosphere by 2035. This suggests that with increased temperatures and wind speeds, climate change will lead to lower dissolved concentrations of toxaphene in the lake and higher amounts in the atmosphere.

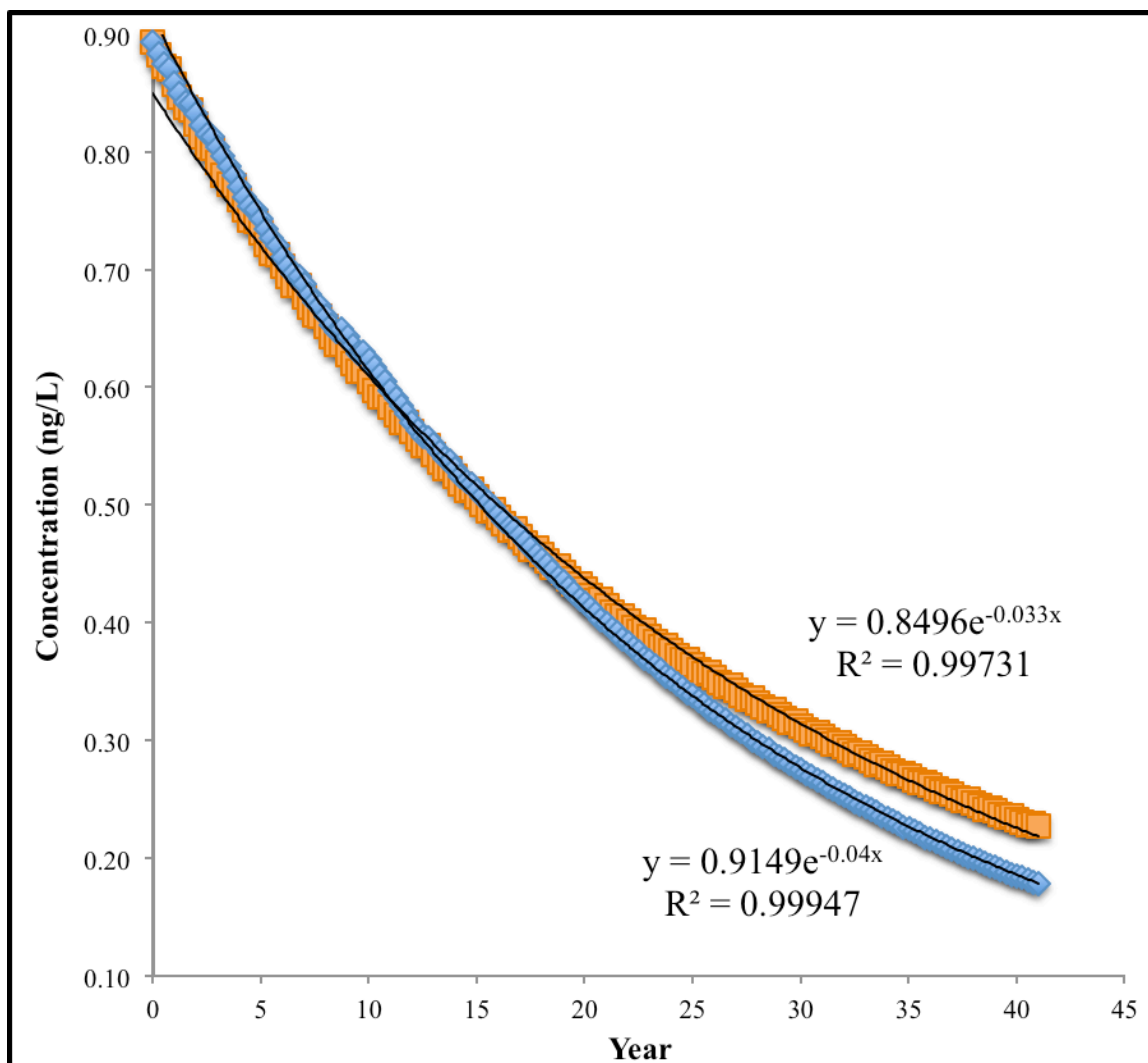


Figure 10. Comparison of modeled dissolved toxaphene concentration. Year 0 represents the year 1995. Diamonds represent climate change model and squares represent constant parameter model.

Moreover, all of these factors influence the aquatic life in Lake Superior because the dissolved concentration of toxaphene will regulate the amount that accumulates in

fish tissue. In turn, this will affect the need for fish consumption advisories for toxaphene contamination. Currently, Ontario's Ministry of the Environment advises limiting consumption at 0.235 parts per million (ppm) toxaphene and complete restriction of consuming fish when levels reach 0.469 ppm for sensitive groups and 1.877 ppm for the general population (Ontario Ministry of the Environment 2013). EPA has suggested consuming no fish above 0.18 ppm toxaphene and only one fish per week at concentrations above 0.011 ppm to reduce the risk of cancer (U.S EPA 1999). We estimated a bioaccumulation factor (BAF) of 1×10^6 for Lake Superior fish using concentration of toxaphene in fish and dissolved phase concentration (Lake Superior Binational Program 2012). Using first order decay (Figure 10), the climate change model estimates that the dissolved concentration will be low enough by 2106 to allow one fish meal per week from Lake Superior without cancer endpoints. In contrast, when the same analysis is performed for the constant parameter model, it suggests dissolved phase toxaphene concentration will not be low enough until 2126. While this difference is not very large, it helps to illustrate the indirect influence of climate change on public health associated with toxaphene in the water.

Discussion

Overall, this model summarizes the dynamics of toxaphene in Lake Superior. By comparing concentrations of toxaphene to measurements taken in the air and water, we were able to reaffirm that it reflects actual values. Of course, as with all models, this one has limitations. First, it simplifies Lake Superior as one uniform system, although physical characteristics vary across the lake, and thus, so will the cycling of toxaphene.

Therefore, we only have a general estimate of what may be happening rather than a thorough understanding. Second, the model relies on the physical characteristics of the lake, however we do not always have consistent data because buoys are removed in the winter. This means that we have fewer observations in winter to work with to make an estimate. Moreover, we generally used measurements from three buoys to represent the entire lake, which has a surface area of $8.21 \times 10^{10} \text{ m}^2$. As would be expected, there is variability among buoys, which impacts the model. Third, our model attempts to provide insight into how toxaphene may behave in the future, but this requires a number of assumptions. For example, we assume that temperature trends observed over a thirty-three-year period will be consistent for another thirty years. However, even with these limitations, the model still is an effective tool for understanding toxaphene behavior in Lake Superior because it allows us to detect the impacts of climate change in a concise manner.

Climate change has both distinct and minor impacts on the dynamics of toxaphene in Lake Superior. Climate change has the potential to influence distinct changes in seasonal net flux, particularly in summer, and alters the lake so that it volatilizes toxaphene year-round. Additionally, climate change results in high amounts of variability in net flux, as shown by the 1995-2012 span of Figure 9c. These changes only have minor impacts on the overall dissolved toxaphene concentration and on fish consumption advisories. In our model, we assumed a ‘business as usual’ scenario because characteristics that have been observed are extrapolated out into the future. Upon manipulation of the model, the dissolved concentration is much more dependent on the

gas-phase concentration than it is on the temperature of the water or wind speed.

However, our climate change scenario does alter the concentration of toxaphene in the lake. With our increased temperatures and wind speeds, the dissolved concentration of toxaphene is lower in 2035 than if the model variables had been held constant (Table 1). Additionally, climate change has been shown to alter the onset of the stratified season, by approximately 0.5 days per year (Austin and Colman 2007). If this trend continues, the lake will exhibit summer conditions longer with time. When this is taken into consideration, the annual net flux of toxaphene from Lake Superior is slightly increased because volatilization is higher in summer than it is in the fall. Based on this information, it is clear that climate change impacts toxaphene dynamics in Lake Superior in complex ways.

While this study focused on toxaphene in Lake Superior, it has a broader relevance to the global toxaphene cycle. Volatilization is a major mechanism of toxaphene removal from the Great Lakes. Once toxaphene is recirculated in the atmosphere, it can be transported and deposited in the Arctic, where it has been detected in air, snow, and aquatic biota (Bidleman et al. 1989). Moreover, volatilization is a major removal mechanism for other organochlorine compounds, such as polychlorinated biphenyls (PCBs) (Jeremiason et al. 1994). These organochlorine compounds bioaccumulate and pose risks to higher trophic level organisms, such as polar bears and humans (Muir et al. 1999). People of the First Nations are particularly at risk to these contaminants because they consume seals and polar bears. This suggests that over time, mid-latitude water bodies, such as the Laurentian Great Lakes, continue to be sources of increased

contamination for the Arctic. Since this is the case, despite banning many organochlorine compounds, the Arctic will continue to receive them from many parts of the world for years to come.

References

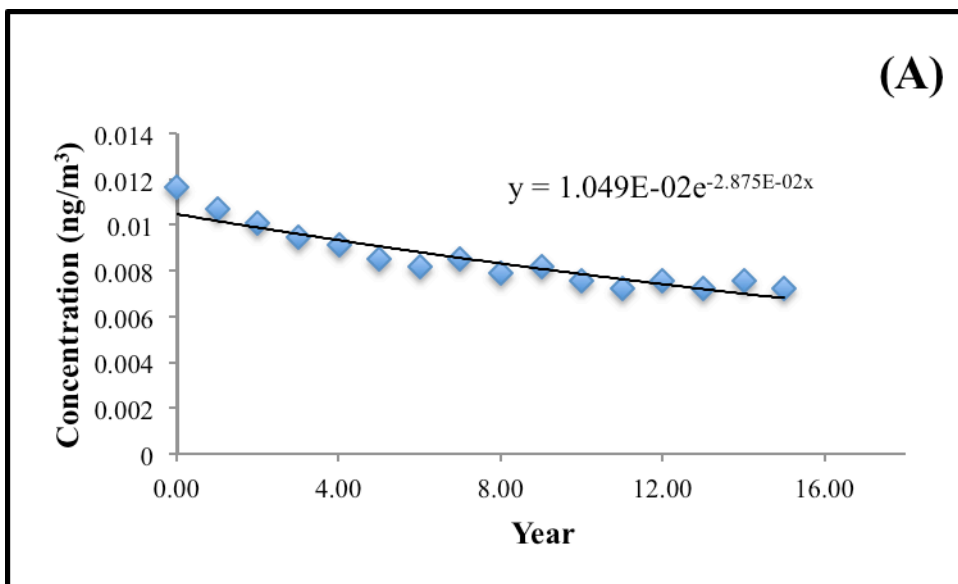
- Austin, J.A.; Colman, S.M. *Geophys. Res. Lett.*, **2007**, *34*(6).
- Bidleman, T.F.; Patton, G.W.; Walla, M.D.; Hargrave, B.T.; Vass, W.P.; Erickson, P.; Fowler, B.; Scott, V.; Gregor, D.J. *Arctic*. **1989**, *42*, 307-313.
- de Geus, H-J.; Besselink, H.; Brouwer, A.; Klungsøyr, J.; McHugh, B.; Nixon, E.; Rimkus, G.G.; Wester, P.G.; de Boer, J. *Environ. Health Persp.*, **1999**, *107*, 115.
- Glassmeyer, S.T.; Brice, K.A.; Hites, R.A. *J. Great Lakes Res.* **1999**, *25*(3), 492-499.
- Gianessi, L.P. *U.S. Pesticide Use Trends: 1966-1989*; U.S. EPA Office of Policy Analysis, National Center for Food and Agricultural Policy: Washington D.C., 1992.
- Hainzl, D.; Burhenne, J.; Parlar, H. *Chemosphere*, **1994**, *28*, 245.
- Hercules Company, Insecticidal Compositions Comprising Chlorinated Camphene, U.S. Patent 2,565,471, 1951.
- IPCC. Fourth Assessment Report, **2007**.
< http://www.ipcc.ch/publications_and_data/ar4/wg1/en/spmsspmp-projections-of.html>.
- James, R.R.; Hites, R.A. *Environ. Sci. Technol.* **2002**, *36*, 3474.
- James, R.R.; McDonald, J.G.; Symonik, D.M.; Swackhamer, D.L.; Hites, R.A. *Environ. Sci. Technol.* **2001**, *35*, 3653-3660.
- Jantunen, L.M.M.; Bidleman, T.F. *Chemosphere: Global Change Sci.* **2000**, *2*, 225-231.
- Jeremiason, J.D.; Hornbuckle, K.C.; Eisenreich, S.J. **1994**, *28*, 903-914.
- Lake Superior Binational Program. **2012**, Lake Superior Lakewide Management Plan: 1990-2010 Critical Chemical Reduction Milestones. Prepared by the Superior Work Group – Chemical Committee. Toronto and Chicago.

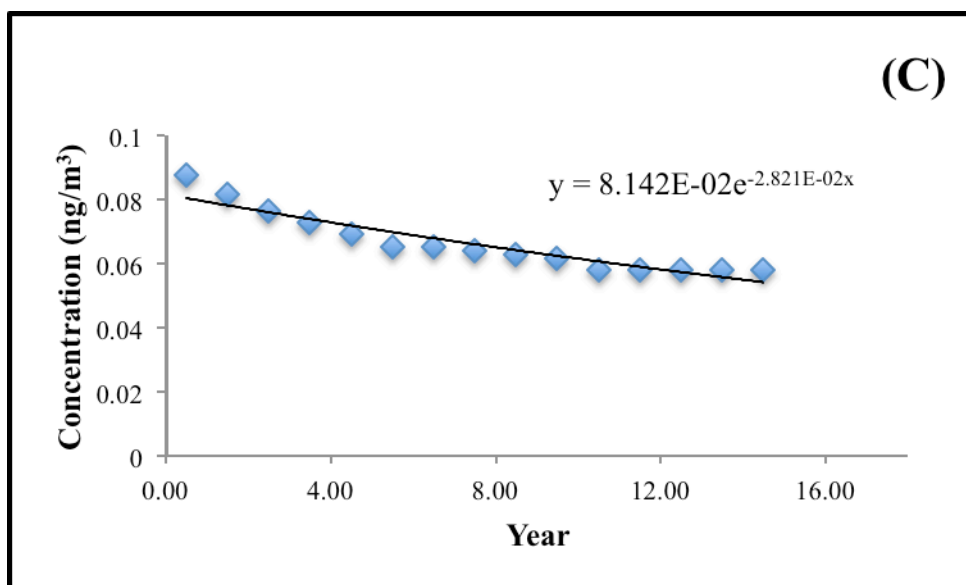
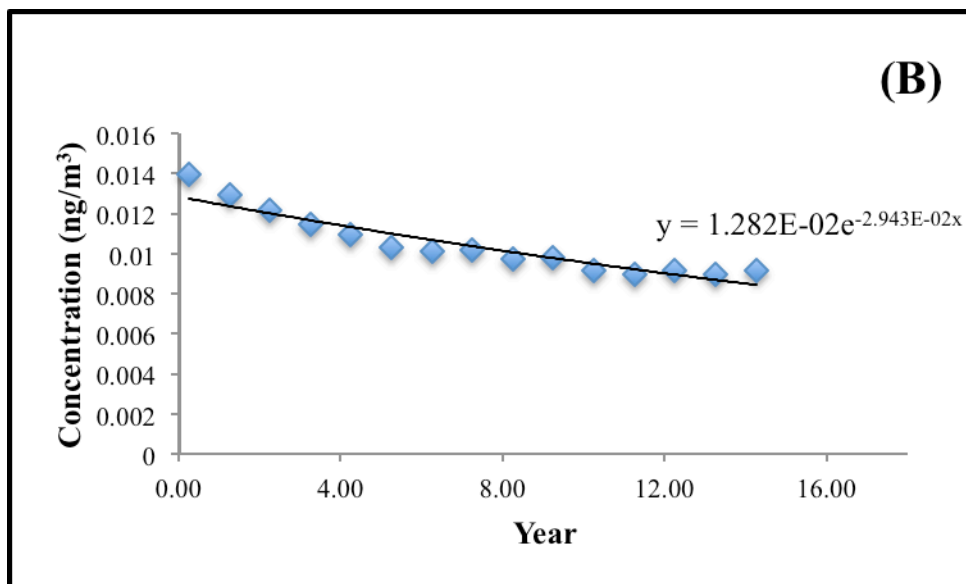
- Miskimmin, B.M.; Schindler, D.W.; *Canad. J. Fish. Aquat. Sci.*, **1994**, *51*, 923.
- Muir, D.C.G.; Whittle, D.M.; De Vault, D.S.; Bronte, C.R.; Karlsson, H.; Backus, S. Teixeira, C. *J. Great Lakes Res.*, **2004**, *30*, 316.
- Muir, D.; Braune, B. DeMarch, B.; Norstrom, R.; Wagemann, R.; Lockhart, L.; Hargrave, B.; Bright, D.; Addison, R.; Payne, J.; Reimer, K. *Sci. Total Environ.* **1999**, *230*, 83-144.
- Ontario Ministry of the Environment. **2013**,
<http://www.ene.gov.on.ca/environment/en/resources/collection/guide_to_eating_ontario_sport_fish/STDPROD_075994.html#1>.
- U.S. EPA. **2012**,
<<http://water.epa.gov/drink/contaminants/basicinformation/toxaphene.cfm>>.
- U.S. EPA. **1999**,
<http://water.epa.gov/scitech/swguidance/fishshellfish/outreach/upload/1999_09_13_fish_toxaph.pdf>.
- Sergeant, D.B.; Onuska, F.I. In *Analysis of Trace Organics in the Aquatic Environment*; Afghan, B.K., Chau, A.S., Eds.; CRC Press: Boca Raton, FL, **1989**, 69-118.
- Swackhamer, D.L.; Schottler, S.; Pearson, R.F. *Environ. Sci. Technol.* **1999**, *33*, 3864.
- Swackhamer, D.L.; Charles, M.J.; Hites, R.A. *Anal. Chem.* **1987**, *59*, 913-917.

Appendix

Site	Date	Volume (L)
EC-221	5/13/06	853.86
EC-221	5/13/06	853.86
17	5/14/06	803.5
SUFE	5/14/06	804.34
SUFO	5/15/06	805.5
1	5/16/06	802.03
8	5/16/06	794.21
8	5/17/06	825.27
EC-139	5/18/06	1210.05
EC-139	5/18/06	1210.05
EC-221	7/17/06	804.5
17	7/18/06	1503.49
1	7/19/06	754.48
8	7/20/06	821.34
EC-139	7/20/06	799.48
EC-139	7/21/06	804.9

Table 2. Water sample volumes from Lake Superior across sampling locations.





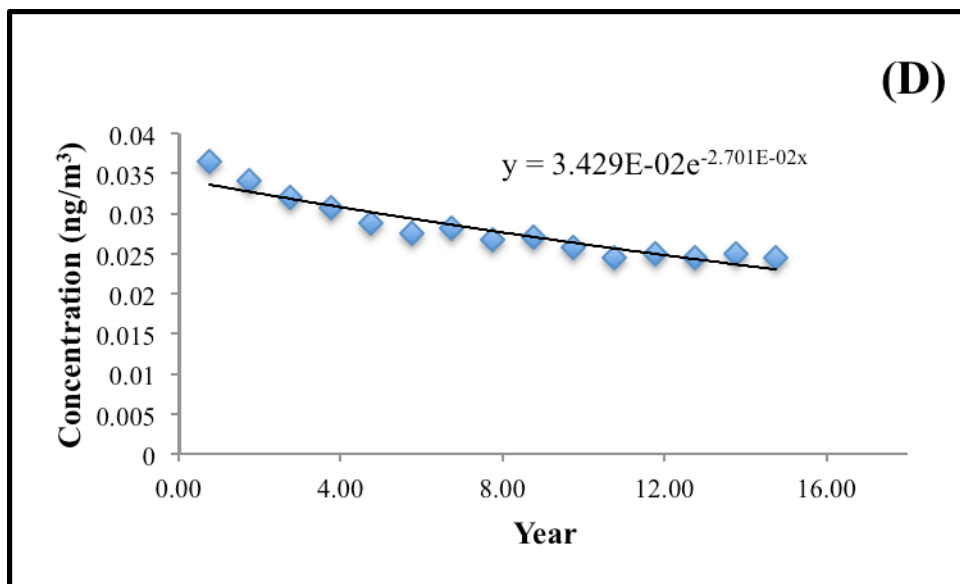


Figure 11. Seasonal exponential fit of air concentration used to project out through 2035. When year is 0, it represents date of 1980. A) Represents winter fit, B) spring, C) summer, and D) fall.

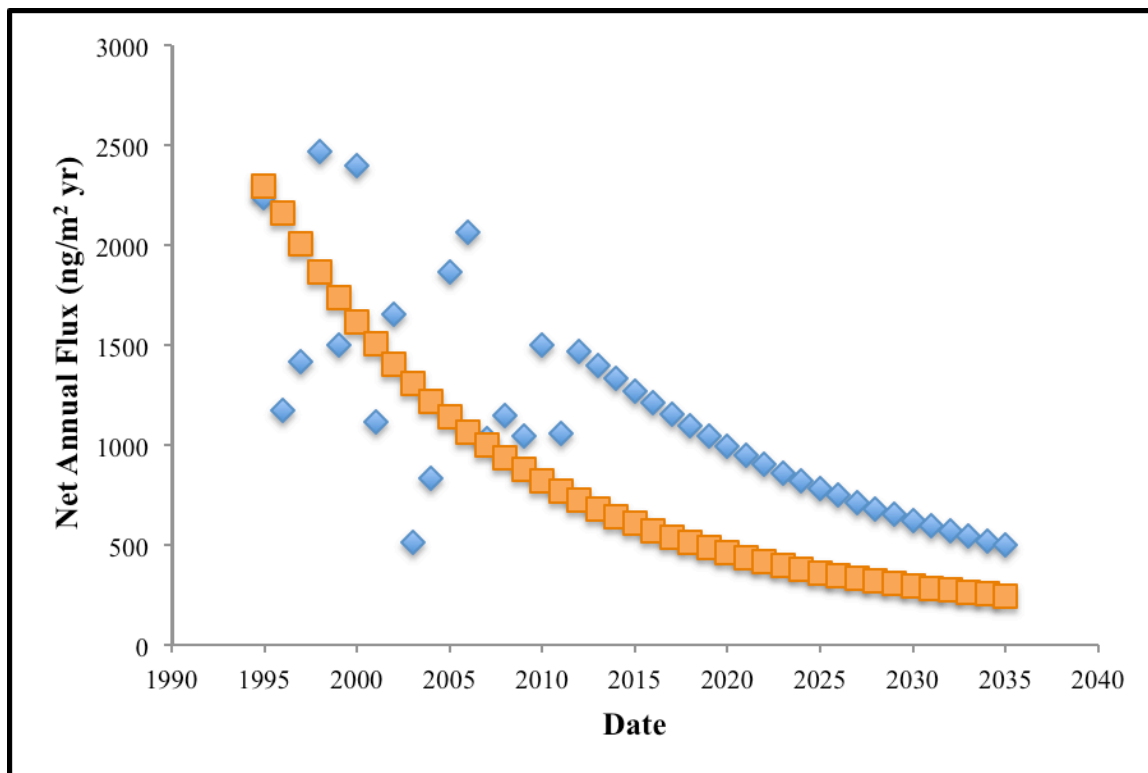


Figure 12. Comparison of net annual flux for climate change and constant parameter model. Diamonds represent climate change model and squares represent constant parameter model.

Additional Equations:

$$H' = (1/RT)10^{10.42-3209/T}$$

R= ideal gas law constant (8.31 Pa m³/mol K)

T=Temperature (K)

(Equation developed by Jantunen and Bidleman 2000).

$$k_{a,tox} = k_{a,H_2O} * (D_{tox} / D_{H_2O})^{0.61}$$

k_a = air side mass transfer coefficient (m/s)

D= diffusivity (cm²/s)

$$k_{a,H_2O} = 0.2u_{10} + 0.3$$

$$u_{10} = 10.4u_z / (\ln(z) + 8.1)$$

u=wind speed (m/s)

Z=height at which wind speed was measured (m)

$$D_a = \frac{10^{-3} T^{1.75} [(1/m_{air}) + (1/m)]^{1/2}}{P[V_{air}^{1/3} + V_a^{1/3}]^2}$$

m=molecular mass (m_{air}=28.97 g/mol)

P=gas phase pressure (atm)

V= molar volume (V_{air} ~22.414 L/mol)

$$V_{tox} = m/\rho_l$$

ρ_l= liquid density (g/cm³)