Understanding Geochemical Recovery in Anthropogenically Disturbed Landscapes

By

Ryan Glenn Vannier

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ABSTRACT

UNDERSTANDING GEOCHEMICAL RECOVERY IN ANTHROPOGENICALLY DISTURBED LANDSCAPES

By

Ryan Glenn Vannier

Environmental regulations have greatly reduced the output of anthropogenic chemicals to the environment from the mid 1970's to the present. However, lake sediment cores collected in Michigan show temporal concentration profiles of chemicals considered toxic to humans and wildlife to decrease at variable rates during the decades following the 1970s. This disparity may be due factors affecting recovery such as watershed or regional land use, population, and chemical production/consumption trends. For this study, sediment chemical chronologies collected from inland lakes across Michigan were compared to determine temporal and spatial trends of two organic chemicals: PCBs and DDT. These chemicals were selected for study as they both represent banned chemicals with different utilization and dispersion patterns, as well as, different chemical characteristics. Surface water chemistry was also studied in the Saginaw Bay Watershed attempting to relate differences in the dissolved constituent make-up with land use as a means of determining changes to the chemical pathways through the changing seasons.

Results for DDT show US production and usage to be the overriding determinants of the general sediment profiles. However, results show significant variation amongst the individual lakes in terms of temporal peak values and recovery since the ban of these chemicals. This is thought to be the result of both independent watershed-scale and regional sources of DDT recorded in the lake sediment. Some correlation to watershed %urban land-use is apparent but land-use characteristics overall were poorly correlated to DDT concentrations, peak and onset dates. DDT and its metabolites found in recent sediment (top 4 cm), as well as, sediment

accumulation rates of these chemicals in each sediment core are well correlated to latitudes of Michigan with higher populations, even if the lake watershed itself wasn't especially populace. This suggests a significant regional component to DDT both historically and since its ban.

PCBs were elevated in the Lower Peninsula compared to the Upper Peninsula and locations of high PCB inventories near urban areas were found. However, concentration and accumulation peak dates increased with latitude of the lake possibly due to secondary mobility and deposition away from sources. During high PCB production years, congener clusters show clear localized patterns, but more recently, congener distributions suggest a more regional signal. However, state-wide regional patterns appear to serve as a component to both recent and historical data, despite the prominence of local and sub-regional trends during the peak PCB production/consumption years.

The SBW study documented strong local fluctuations of solutes attributed primarily to local proximity of urban centers and agricultural land use. However, the geochemical fingerprint of a given land use varied in intensity throughout the year: agricultural land use on surface water chemistry was most evident during a summer low flow event and a spring high flow event, which may be a reflection of seasonal variations in the intensity of agricultural practices. Urban land use exhibited its strongest fingerprint during winter high flow, likely due to road deicing salt application.

Overall, we conclude that studies attempting to link chemical concentrations to a particular land use should give consideration to coordinating surface water analytes to the hydrologic regime and time of year the sample collection is to be undertaken. Further, the regional component of banned chemicals continues to be represented in modern sediment, despite several decades since cessation of production.

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CHAPTER 1. INTRODUCTION

Since the 1800's, humans have altered ecosystems in North America more rapidly and extensively than in any prior period of time in human history, largely to meet rapidly growing demands for food, fresh water, timber, fiber, and energy (Fleischner, 1994; McNeill, 2000). These demands have stressed ecosystems through activities such as caused by deforestation, industrialization, urbanization, and other forms of both intentional and unintentional land use change (Latimer, 2003). These activities have also led to environmental contamination affecting surface water bodies through nutrient addition, sediment runoff, and the addition of air and water-borne chemicals, all of which occur simultaneously and during a period of global climate change (Cohen, 2004).

Efforts are being made to restore perturbed environments to a pre disturbance target or time from of 'minimal human impact' as an established predetermined target (Vile et al., 2000). Environmental managers are increasingly bound by legal requirements to define restoration targets (Battarbee et al., 2005, Stoddard et al, 2006). Therefore there to define these targets there is a need to understand the degree of disturbance and conditions prior to disturbance e.g., "reference" conditions (Stoddard et al., 2006).

One method for reconstruction of historical surface water quality and watershed histories is in the analysis of lake sediment cores. It has been demonstrated that lacustrine sediments function as one of the best preserved timelines of both watershed and regional environmental disturbances available in a terrestrial setting (Last, 2001). These sedimentary records contain chemical records or "signals" of changes in the environment during this time period both from climate fluctuation, natural watershed-scale and regional processes and anthropogenic impacts. Using these sediment cores provides a means of understanding both anthropogenic change to the landscape and failure to recover to geochemical reference values despite over 30 years of environmental legislation (Long, 2010). Such information is critical for land-use planning and to better understand the effects of land use change on our aquatic environments (Schindler, 2008)

Historically, analysis of lake sediments has served to infer changes in vegetation or assess the success of environmental laws or management. Lake sediments have also been successfully employed for analysis of changes in trophic status (Heathwaite, 1994; Brezonik and Engstrom, 1998), lake redox condition by examination of the Fe and Mn sediment profiles (Mackereth, 1966; Davison, 1993) and anthropogenically induced pollution (Norton et al., 1992; and Engstrom et al., 2007). However, the distribution of anthropogenic chemicals remains poorly understood and some aspects relating land use and surface water impacts remains elusive (Boyle, 1998). Due to the poorly understood biogeochemistry and toxic nature often associated with them, trace metals and synthetic chemicals released to the environment remain a source of concern for environmental managers.

The State of Michigan occupies a large geographic footprint in the Great Lakes region. The landscape is characterized by a diversity of land use and land cover types. It is a glaciated terrain and as such contains many inland lakes that hold sediment records from their birth at the end of the Ice Age (approximately 10,000 years ago) to the present. The combination of the diversity of land use and lakes affords an opportunity to study and assess environmental disturbance and recovery from disturbance. Preliminary observations of data collected from selected inland lakes sediment in Michigan have shown some lakes to recover fully from large anthropogenic perturbation, some to establish a new geochemical stable state different from its initial state, and some to remain in a state of temporal change (Long, 2010). Questions that can be asked are: can several decades since the cessation in chemical production of toxic chemicals provide time enough for landscape recovery of these compounds, if not, can we forecast a time when these chemicals will not be present?

Overarching Research Hypothesis and Approach

Given environmental legislation, erosion control measures, and the variety of measures undertaken to keep surface water bodies in Michigan pristine, pollution recovery should be observed in those surface water bodies. This study attempts to provide some elucidation both on the degree of recovery of these chemicals since their historical peaks in consumption and usage, and the association of land use to recovery (or lack thereof). The overarching hypothesis for this research then is: the recovery of surface water systems from environmental contaminants is driven not only by the production and consumption of the contaminant chemicals but the physical relationship to land use. To test this hypothesis, three methodologies will be employed:

1.) Develop temporal patterns of anthropogenic chemicals in relationship to both their production and consumption peaks and the years associated with their ban.

2.) Perform degradation half-life calculations when capable.

3.) Determine the statistical correlation of these chemicals to historical and modern land use.

These steps are described in more detail in the following sections.

General Methodology

Fifty eight sediment cores have been collected from 47 individual inland lakes distributed throughout Michigan since 1999 as part of the Michigan Department of Environmental Quality (MDEQ) Michigan Inland Lakes Trends project (http://www.michigan.gov/deq/0,4561,7-135-3313_3686_3728-32365--,00.html ; Figure 1, below). Lakes were selected in collaboration with MDEQ and chosen to cover a large spatial distribution, different land uses and population densities within the watershed. Collection of sediments was conducted from the deepest portion of each lake using an MC-400 Lake/Shelf Multi-corer deployed from the Monitoring Vessel Nibi. The M/V Nibi was designed and has successfully provided access to both major and remote inland lakes throughout Michigan. The MC-400 is designed to collect four simultaneous cores from a single location. Collected sediment cores were described and examined for color, texture, and signs of zoobenthos. Cores were then extruded and sectioned at 0.5 cm intervals for the top 8 cm, and at 1 cm intervals for the remainder of the core.

Upon collection, sediments were frozen, freeze-dried and digested by nitric acid in a CEM-MDS-81D microwave (Hewitt and Renyolds, 1990). Standard reference material (NIST RM 8704 Buffalo River Sediment) and procedural blanks were processed to test for accuracy and contamination. The concentrated-acid digests were filtered through an acid-washed, e-pure (Barnstead) rinsed 0.40 μm polycarbonate filter. Samples were then analyzed using a either a Micromass Platform inductively coupled, plasma, mass spectrometer with hexapole technology (ICP-MS-HEX)(all analyses prior to September 2013) or, the more recently implemented Thermo-Fisher ICP-Q (all analyses after September 2013). Sediments were analyzed for a suite of metals and metalloids that typically included Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Cd, Ba, Pb, and U. Data was gathered from as many elements as possible during the ICP-MS analysis but are confined to the specific capabilities of the instrument used and the available elemental standards at the time of analysis. Other elements such as Li, Be, B, Na, Se, Ag, Sb, Cs, Tl, and Bi were occasionally able to be quantified with the ICP-Q instrument and data from these elements is made available when possible.

Any freeze-dried sediment remaining from the microwave digestion procedure was potentially subject to Total Kjeldahl nitrogen (TKN) analysis or Loss-on-Ignition (LOI) analysis. TKN is designed to test the sediment for the sum of organic nitrogen, ammonia (NH_3), and ammonium (NH_4) in the sediment. LOI analysis approximates the organic carbon content of the sediment. Both analyses could only be performed if enough material was left from the above described acid digestion procedures as the sediment used for LOI and TKN was taken from the same core. As such, lakes with this data available vary.

^{210}Pb was measured on one sub-core from each lake to determine porosity, accumulated dry mass, sedimentation rates, sediment ages and focusing factors (Freshwater Institute in Winnipeg, Manitoba, Canada). Several models exist to determine sediment ages from ^{210}Pb activities, and sediments were dated using the constant flux: constant sedimentation rate model (CF:CS) (Golden *et al.*, 1993), segmented CF:CS (SCF:CS) (Heyvaert *et al.*, 2000), rapid steady state mixing model (RSSM) (Robbins, 1982), and the constant rate of supply model (CRS) (Sanchez-Cabeza *et al.*, 2000). The CF:CS model assumes a constant sedimentation rate throughout the core. The RSSM model also assumes a constant sedimentation rate, but also allows for a mixed zone. The SCF:CS model allows for more than one sedimentation rate, and accounts for a mixed zone. The CRS model determines a different sedimentation rate for each sample based on the inventory of excess-^{210}Pb. Dating models were verified using ^{137}Cs, stable Pb peak and presence of excess ^{210}Pb.

Sedimentation rates in each lake were determined using all models possible for that lake, and then the models were evaluated to ascertain which was the most appropriate for determining sediment ages. There is no consensus as to which model is more appropriate in all cases (Oldfield and Appleby, 1984), and several factors were considered when choosing a model. Visual examination of the ^{210}Pb profile gave some insight into the most appropriate model to be used. The RSSM or CRS models are more appropriate for lakes with large mixing zones, and the SCF:CS or CRS models are more appropriate for lakes with clear changes in sedimentation. Additionally, this study uses two other indicators to determine the most appropriate model to use: profiles of ^{137}Cs activity and stable lead concentration profiles. ^{137}Cs is an artificial radionuclide that was produced by atmospheric testing of nuclear weapons in the late-1950s and early-1960s. The peak level of fallout occurred in 1963, and therefore the peak activity in the sediment should occur in the early 1960s (Walling and Qingping, 1992). The second indicator is the stable lead peak. Stable lead has an historical pattern of deposition that is very consistent among lakes, with lead concentrations increasing from the mid-1800s to the early to mid-1970s, and decreasing to the present. The peak in lead concentrations in the mid-1970s is consistent enough to use for dating verification (Alfaro-De la Torre and Tessier, 2002, Callender and vanMetre, 1997). Excess-^{210}Pb should not be present in sediment slices older than ca. 1850, therefore, dating models that place sediment slices, containing excess ^{210}Pb, older than ca. 1850 are suspect. The dating model with the most appropriate date for both the ^{137}Cs peak (1963-64), stable lead peak (early to mid-1970s), and assigned appropriate dates to the presence of excess 210Pb is chosen.

Focusing factors were also determined from ^{210}Pb analysis. Sediment focusing occurs when fine-grained sediments in a lake are eroded from higher energy erosional zones near the shore of the lake, transported through transitional zones (where deposition and erosion occur episodically) and deposited in depositional zones (Downing and Rath, 1988, Hakanson, 1977). This process of focusing occurs to different extents among lakes, and must be accounted for by using the focusing factor before comparing inventories and accumulation rates among lakes.

Another sub-core was sectioned and submitted to Michigan State Universities Aquatic Toxicology Laboratory for analysis of organic contaminants. Unlike the metals and ^{210}Pb sub-cores, the organics core was sectioned at 1 cm increments for the entire core length. There was insufficient material for analysis in the topmost sediments, so the first two sections were combined, and the third and fourth sections were combined. The combined samples represent 2 cm intervals through the entire core. The samples were analyzed for PCBs, PAHs, and pesticides (Khim et al., 1999a, Khim et al., 1999b). A portion of the sediment was dried at 100ºC to determine moisture content.

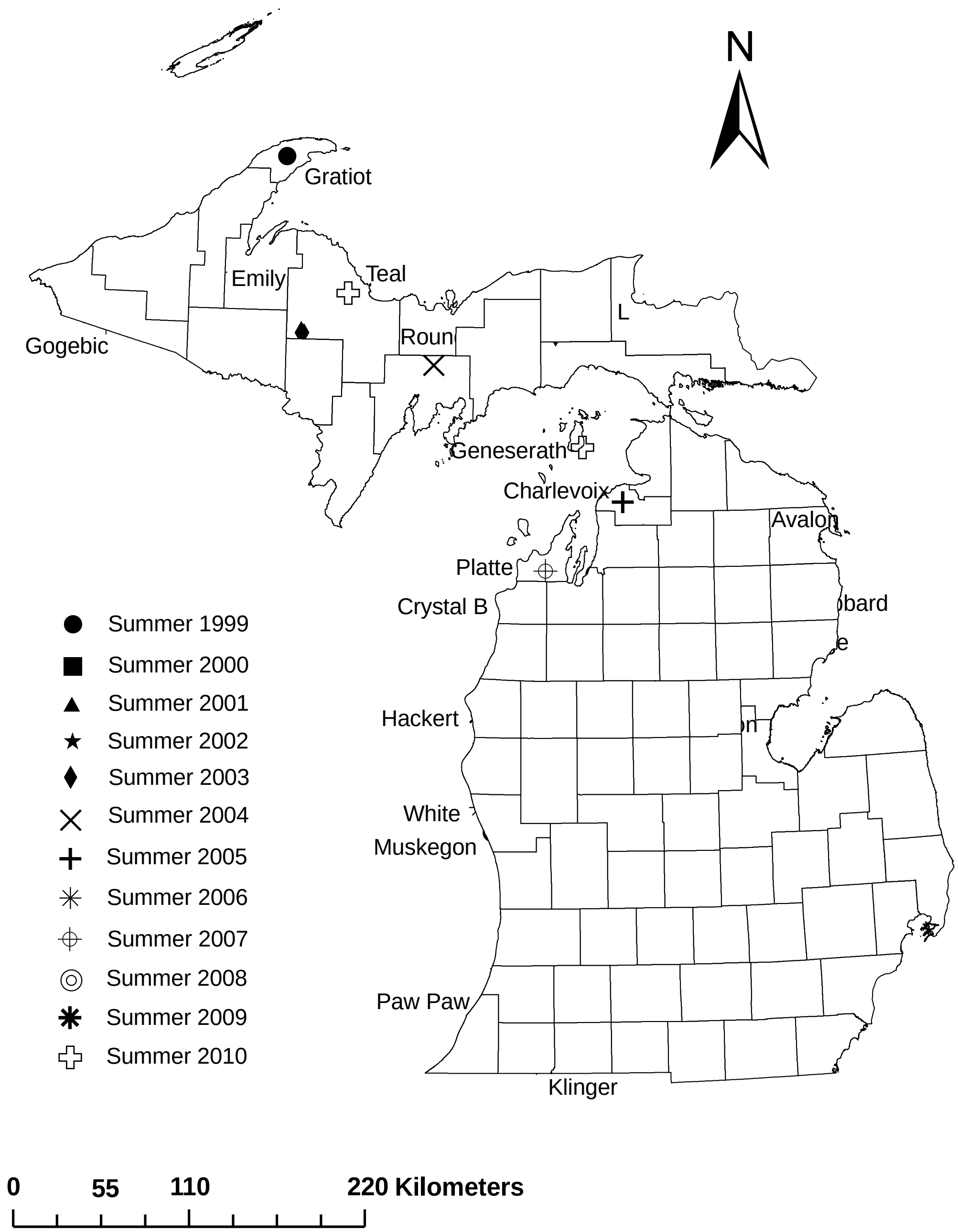

Figure 1.1: Project Lakes 1999 to 2010

To investigate the relationship of water quality to present day land use, water chemistry from selected rivers in the Saginaw Bay Watershed of Michigan were compared to land use. The comparisons were done synoptically for five flow events that ranging from high flow to low flow conditions. Comparisons were made using factor analysis.

The results of this research are summarized in the following three chapters of this dissertation. These chapters are:

- Chapter 2: Historical Distribution and Recovery of DDT as Interpreted from Michigan Inland Sediments
- Chapter 3: Landscape Recovery from Historical PCB Loadings Using Sediment Chemical Chronologies
- Chapter 4: Seasonal Influence on Land Use Biogeochemical Fingerprints in Surface Water Bodies

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CHAPTER 2

TEMPORAL AND SPATIAL PATTERNS OF DDT LOADINGS IN A LARGE GEOGRAPHIC REGION OF THE GREAT LAKES WATERSHEDT

Abstract

Concentrations of DDT, DDD, and DDE were measured in sediment cores collected from 39 inland lakes in Michigan for examination of spatial and temporal trends in accumulation and degradation. It was hypothesized that the trends of DDT observed in the sediment cores would reflect the US production and consumption trends with an increase to peak consumption and use in the late-1950s and early 1960s followed by a decrease of DDT to the present. While it is clear that US production and usage are the overriding determinants of the general DDT profiles, results show significant variation amongst the individual lakes in terms of temporal peak values and recovery since the ban of these chemicals. This is thought to be the result of both independent watershed-scale and regional sources of DDT recorded in the lake sediment. Some correlation to watershed %urban land-use is apparent but land-use characteristics overall were poorly correlated to DDT concentrations, peak and onset dates. However, DDT and its metabolites found in recent sediment (top 4 cm), as well as, sediment accumulation rates of these chemicals in each sediment core are well correlated to latitudes of Michigan with higher populations, even if the lake watershed itself wasn't especially populace. This suggests a significant regional component to DDT both historically and since its ban. However, ratios of DDT to its breakdown products suggest some lakes maintained watershed-scale sources in the

years after the DDT ban. Degradation half-life calculations of DDT in Michigan lakes were determined to average approximately 20 years, similar to reported DDT half-lives of others.

Introduction

Dichlorodiphenyltrichloroethane (DDT) is one of the most well-known and widely distributed synthetic pesticides. The persistent nature of DDT has prevented complete elimination from the food web even though production of this chemical has ceased in the US for decades. In fact, DDT was detected in almost all human blood samples tested by the Center for Disease Control in 2005 (Eskenazi et al., 2009) and the Food and Drug Administration continue to detect DDT in routine food tests (USDA, 2006). As the fate of many of these chemicals is to wash to surface water bodies in the regions in which they are applied, continued work needs to be completed to ascertain the chemicals availability for absorption by aquatic organisms. Here we use inland lake sediment cores to provide some elucidation to DDTs continued presence in sediment dated throughout the chemicals use history in Michigan.

Although first synthesized in 1874 by Othmar Zeidler at the University of Strassburg, Germany (Zimmerman and Lavine, 1946), it was not until the 1930s that scientists discovered its insecticidal properties (WHO, 1979). During the 1930's potent pesticides were sought after for malaria and crop-pest control. In the autumn of 1939, Paul Muller, working in the laboratories of Johann Rudolph Geigy in Basle, Switzerland synthesized the same compound was originally developed by Othmar Zeidler years before (Zimmerman and Lavine, 1946; West and Campbell, 1952; Brooks, 1974). In 1942, the Geigy Company in New York received its first shipment of DDT from Geigy, Switzerland and then submitted DDT to the United States Department of Agriculture for testing. DDT was used extensively during the Second World War among allied troops and proved effective in controlling diseases such as malaria and typhus (ATSDR, 2002). By 1943, DDT was in commercial production at the Cincinnati Chemical Works, and in early 1944, DuPont, Merck, and Hercules Powder Company also went into commercial production of

DDT (Zimmerman and Lavine, 1946). Aside from its effectiveness in controlling biting insect populations that spread disease, DDT was also widely used as a form of agricultural pest control. From 1945 until it was banned, DDT was one of the most widely used pesticides for the control of insects on agricultural crops (ATSDR, 2002).

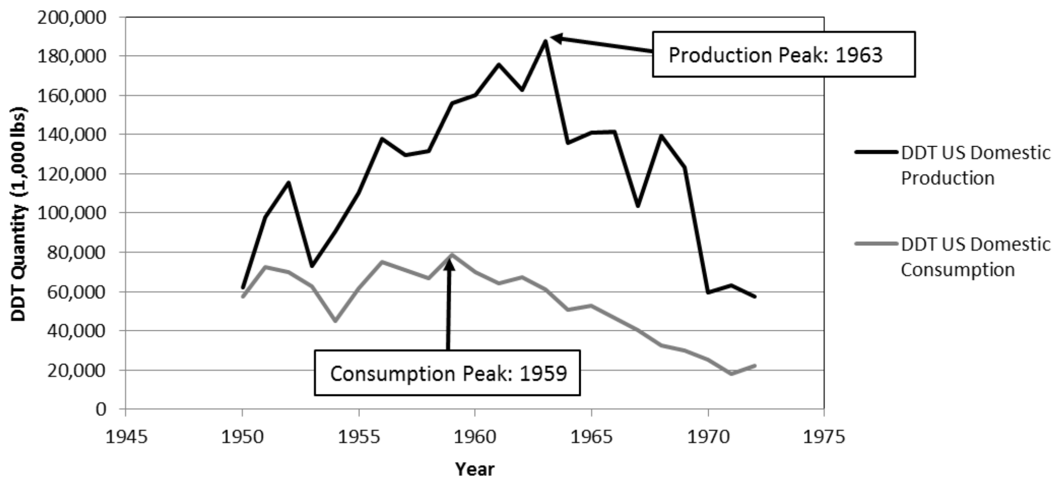

Figure 2.1: Domestic Production and Consumption of DDT in the United States, 1950-1972. The 1975 EPA report entitled *DDT, A Review of Scientific and Economic Aspects of the Decision To Ban Its Use as a Pesticide* analyzed domestic production and consumption data which showed peak production and consumption of DDT to be in 1963 and 1959 respectively. Source: EPA-540/1-75-022, p. 140

By 1959, the US use of DDT peaked with approximately 35,771 tons being used annually after which use began to decline until its ban in 1972 (USEPA, 1975; WHO, 1989)(Figure 1). The decline following the peak use in 1959 was the consequence of growing knowledge amongst users of its human toxicity (first reported in 1946) and by the growing number of ecological studies of its effects on the populations of fish and birds of prey (USEPA, 1975; WHO, 1979). In the United States, the actual ban of DDT was initiated in 1962 with the publication of Rachel Carson's book *Silent Spring*. The book cataloged the environmental impacts of environmental DDT distribution and warning of unforeseen affects to ecological and human health as a result. This led to increased environmental awareness of persistent chemicals and, in combination with the growing scientific evidence of DDT persistence and harmful traits, resulted in political responses banning its use in the Great Lakes basin. As of January 1, 1973, all uses of DDT in the United States were largely suspended with the exception of emergency public health uses (Meister and Sine, 1999; ATSDR, 2002). Although DDT was produced by companies in Mexico and China well into the 2000's, no companies in the United States manufacture DDT for use in other countries (Meister and Sine, 1999). Amongst other countries using the chemical, the actual date of the ban of DDT varies substantially, with some countries continuing production into the 21st century. As of this writing, it believed that India is the only country still manufacturing DDT and is also its largest consumer (Van Den Berg, 2009; Stockholm Convention, 2010).

Since the ban of DDT, scientists have measured the declining environmental concentrations in studies regarding the Great Lakes in the tissues of birds and fish, as well as lake sediment. These studies have shown that the concentration of DDT observed in the environment follow closely the production and use history (Bierman and Swain, 1982; Oliver et al., 1989). Once in the environment, breakdown of DDT occurs slowly as it was formulated to be highly stable. Literature review of DDT half-life of in soil is exceptionally broad, with early research reporting half-lives on the order of 3-5 years with loses caused by metabolism to DDE and DDD, vaporization or erosion (Bierman and Swain, 1982; Matsumara et al., 1971; Hiltbold, 1974; Voerman and Besemer, 1975). Later research showed that DDT remains in soil and sediment much longer than initially reported and are lost on the order of several decades through metabolism and vaporization (Oliver et al., 1989; Dimond and Owen, 1996; Harris et al., 2000).

In surface water bodies, degradation and loss of DDT includes sedimentation, volatilization, photolysis, and both aerobic and anaerobic biodegradation (ATSDR, 1994). The environmental stability of DDT stems from its strong carbon-chlorine covalent bonds which is resistant to enzymatic breakdown by microorganisms. Persistence is further perpetuated by the fact that DDT has low aqueous solubilities (Fiedler and Lau, 1998). As DDT has a strong tendency to adsorb to surfaces, it often enters aquatic systems already attached to soil or organic matter particles (Corolla, 1945). It has been observed that particulate settling to be responsible for 61-95% of the DDT loss rate in the Great Lakes (Bierman and Swain, 1982) and it is assumed that particulate settling to play a large role in loss of DDT from inland lake water column as well. This allows study of lake sediment to reflect changes in use of many pesticides and act as a chemical tape recorder of its presence or use in a given watershed.

Common breakdown products of DDT include include dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD), which are also highly persistent and have similar chemical, physical, and toxicological properties (WHO, 1989). DDE has no commercial use but DDD has been used as an insecticide for contact control of leaf rollers and other insects on vegetables and tobacco and is no longer produced commercially. DDE is the result of dehydrochlorination of DDT. This oxidative process is considered the primary aerobic pathway for dehalogenation of DDT (Mohn and Tiedje, 1992). Aerobic dehydrochlorination of DDT simultaneously removes the hydrogen and chlorine from the aliphatic portion of the molecule. A number of studies conducted in the 1960's and 1970's have found that DDE was the major degradation product of DDT in such aerobic mediums as ocean water (Patil et al., 1972) and aerobic soils (Guenzi and Beard, 1968). Under reducing conditions, reductive dehalogenation is the major mechanism for the conversion of DDT to DDD (Fries et al., 1969). This is considered the primary degredation pathway of DDT under anaerobic conditions such as in lake or ocean sediments (Jensen et al, 1972; Zoro et al. 1974). Reductive dehalogenation effectively dechlorinates the DDT compound by the removal of a chlorine atom directly from the biphenyl ring and adds a hydrogen atom in its place. In anaerobic sediments, such as the application here, this process is usually limited by the availability of electron acceptors. The process may slow upon depletion of the more common natural electron acceptors (e.g. NO_3^-, SO_4^{2-}).

As with many pesticides, these processes of transformation of DDT to a less chlorinated product also results in a reduction in toxicity of the chemical (Mohn and Tiedje, 1992) and this is reflected in the sediment quality guidelines and threshold effect levels published by many agencies for these chemicals (Burton, 2002). However, given the toxicological nature and the environmental persistence, DDD and DDE are still widely considered toxic compounds, and, as such, the conversion of DDT to either DDE or DDD in sediments cannot be considered as a detoxification step (ATSDR, 2002). For these reasons and their known continued presence, both DDD and DDE were measured along with DDT for this project.

Hypothesis and Test

In general, the importance of this study lies in the persistence of organochlorine contaminants in the environment and in understanding their fate since regulations controlling them have developed. This is particularly important with DDT with which its hydrophobicity and solubility in lipids allow it to accumulate to harmful concentrations in biota. This study seeks to answer questions related to an on-going legacy with DDT in the environment: is the chemical still present in measurable amounts? If so, can we project the trends to a date when it will not be present? It is hypothesized that the sediment profiles of DDT observed in the inland lake sediment would reflect the U.S. consumption and production of these chemicals. Peak dates of production/consumption of DDT were 1962 and 1959, respectively (Figure 1). These peaks should be mimicked by the temporal concentration and accumulation rate profiles of the sediment cores, with increasing values in the years prior to these peaks and progressively lower values after these peaks.

To test this hypothesis, sediment cores from 39 inland lakes were collected from across the State of Michigan representing lakes within various types of land use, watershed characteristics, and trophic status. Once collected the sediment cores were taken ashore where they were divided into 2 cm segments, stored on ice for transportation to the laboratory, and concentrations of DDT, DDD and DDE were then measured. Additional sediment cores were processed similarly and used for radiometric dating via ^{210}Pb and metals analysis. DDT, DDE, and DDD concentrations, total inventories, and, with the addition of ^{210}Pb results, accumulation rates of PCBs were then calculated for all lakes sampled.

If the hypothesis proves true: 1) temporal DDT, DDD and DDE concentration and accumulation rate profiles would peak close to the production/consumption timeframe described in the 1975 USEPA report, 2.) increasing trends should be observed in sediment dated from the 1940's time period to the production/consumption peak, and 3.) a decreasing trend in DDT should be observed in the years following the production/consumption time frame, both as the chemical itself is phased out of use and the watersheds in which it is applied hydraulically remove the chemical.

Methodology

Study Setting:

The State of Michigan covers 58,528 sq miles of which land takes up 56,954 sq miles and inland water approximately 1,573 square miles. Sediment cores were collected from 39 lakes throughout the State of Michigan from 2000 to 2010 (Figure 2) as part of the Michigan Department of Environmental Quality's (MDEQ) Inland Lakes Sediment Trend Monitoring program. The number of inland lakes in Michigan exceeds 10,000 (MDNR, 2013) but lakes were chosen for sediment sampling based on a set of criteria including: available boat access to the lake, sufficient depth to preclude significant bioturbation of sediment (generally lakes >25 feet depth), avoidance of lakes potentially mined for marl, and maximizing spatial range of the project.

To maximize the geographic extent of the project, sediment core collection ranged from inland lakes located along its southern border (e.g. Klinger Lake, Latitude: 41.80) to lakes located at its northern extent (e.g. Gratiot Lake, Latitude: 47.36) (Figure 2). This wide geographic distribution of lakes sampled represents a variety of watershed land use types ranging from largely urban near major cities (e.g. Cass Lake, Oakland County) to those that are remote with watersheds almost completely forested (e.g. Emily Lake, Houghton County). Further, lakes were sampled to represent a large range of physical characteristics. These include but are not limited to: physical size (depth, area), watershed size, proximity to Great Lakes, and trophic status. Table1 is included at the end of this report detailing a list of the lakes sampled and some physical characteristics for this research.

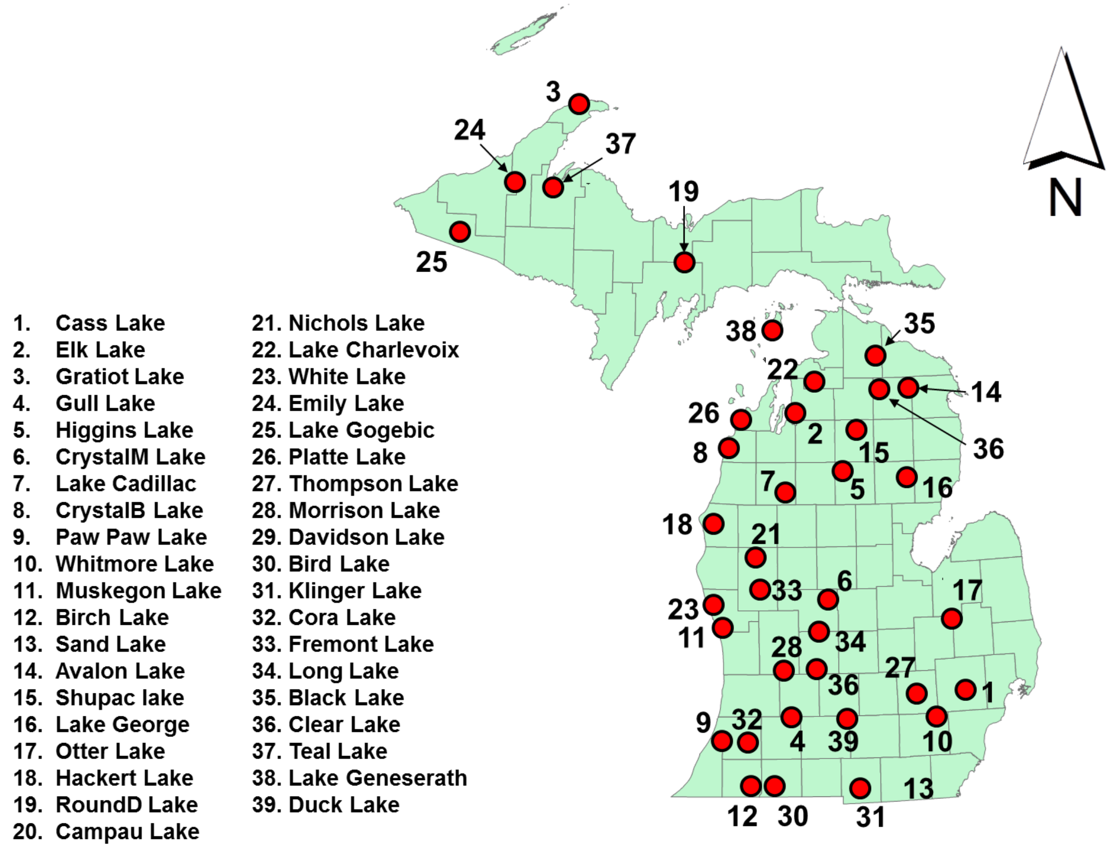

Figure 2.2: Locations of study lakes sampled from 1999 to 2010.

Sample Collection:

Four replicate sediment cores from 40 to 59 cm in length were collected from the deepest portion of each lake using a MC-400 Lake/Shelf Multi-corer deployed from either the EPA Research Vessel *Mudpuppy* or the MDEQ Monitoring Vessel *Nibi*. One entire core was dedicated to analysis of a suite of organic compounds including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and a suite of pesticides which included DDT, DDD, and DDE. In the field, each core was extruded and sectioned into two centimeter intervals through the entire core. Once sectioned, the samples were placed on ice until submittal to Aquatic Toxicology Laboratory at the Department of Animal Science at Michigan State University. Samples were stored at -20°C until analysis. Analytical methods are described in

Khim et al., 1999. A separate core from each lake was sectioned and submitted to the Freshwater Institute in Winnipeg, Manitoba, Canada, for measurement of ^{210}Pb to determine sedimentation rates, sediment ages, and focusing factors. The use of ^{210}Pb dating for these cores in discussed in detail elsewhere (Yohn et al., 2004).

Chemical Analysis:

Analytical methods for DDT and other organic contaminants have been described elsewhere (Khim et al., 1999). Briefly, 40 g sediment (wet) was homogenized with ≈160 g of anhydrous sodium sulfate and extracted with methylene chloride and hexane (3:1, 400 mL) in a Soxhlet apparatus for 16 h. Sulfur was removed by treating the extracts with activated copper granules. Extracts were then concentrated and passed through a glass column packed with activated Florisil (10 g). First fraction, eluted with 100mL hexane contained *p,p'*-DDE . Second fraction eluted with 100 mL of 20% methylene chloride in hexane contained *p,p'*-DDD and *p,p'*-DDT. TCMX and PCB 30 were spiked as internal standards to check for recoveries of analytical procedure. Pesticides were quantified on a Hewlett-Packard 5890 series II gas chromatograph equipped with a 5972 series mass spectrometric detector. The MS was operated in selected ion monitoring mode by use of the molecular ions selective for the individual compounds. Other QA/QC procedures include matrix spikes and analytical blanks. DDT could not be quantified in Black, Clear, Whitmore07 Lakes due to excessive interferences (likely sulfate) and DDT samples collected from White and Muskegon Lakes were not able to meet adequate QA/QC recovery.

Age Dating:

The ^{210}Pb profiles for these sediment cores varied greatly lake to lake. This variation can be attributed to the land use changes altering the rates in which erosive material is washed to the lakes and nutrient-driven trophic changes. In general, lakes exhibited a relatively stable background prior to the mid-1800's when deforestation began to impact erosion within the watershed, significantly increasing the sedimentation rates of the lake. The specific timing and scale of the increase in sedimentation rate is addressed on an individual lake basis with a best fit model. Each model applied to a ^{210}Pb profile was evaluated as to its appropriate fit with ^{137}Cs and mass spectrometer determined stable lead peak as independent age markers. The ^{210}Pb - determined average sedimentation rate is offered with other lake characteristics in Table 1. The oldest (deepest) dated sediment within the cores varied from A.D. 890 (Lake Geneserath) to 1972 (Morrison Lake). Despite the wide range of sedimentation rates, most sediment cores were able to reach sediments dated to the early 1800's. It should be noted that sediment deeper than the presence of excess- ^{210}Pb cannot be directly dated and dates older than this were determined via extrapolation using the assumption that sedimentation rates remain constant below this depth.

As mentioned, this study uses two other indicators to assist in determining the most appropriate model to apply to the ^{210}Pb data. These indicators include profiles of ^{137}Cs activity and stable lead concentration profiles (^{208}Pb) of which the peak dates are known and ubiquitous amongst lakes in this region. ^{137}Cs is an artificial radionuclide that was produced by atmospheric testing of nuclear weapons in the late 1950s and early 1960s. The peak level of fallout occurred in 1963, and therefore the peak activity in the sediment should occur in the early 1960s (Walling and Qingping, 1992). The second indicator is from mass spectrometry analytical results for stable lead (^{208}Pb). This stable lead isotope has an historical pattern of deposition that is very consistent among lakes, with lead concentrations increasing from the mid-1800s to the early to mid-1970s, and decreasing to the present. The peak in lead concentrations in the mid-1970s is consistent enough to use for dating verification (Alfaro-De la Torre and Tessier, 2002, Callender and VanMetre, 1997). Excess-^{210}Pb should not be present in sediment slices older than ca. 1850, therefore, dating models that place sediment slices, containing excess ^{210}Pb, older than ca. 1850 are suspect. The dating model with the most appropriate date for both the ^{137}Cs peak (1963-64), stable lead peak (early to mid-1970s), and assigned appropriate dates to the presence of excess ^{210}Pb is chosen.

Results and Discussion

Spatial DDT/DDD/DDE Concentrations, Inventories, and Accumulation Rates:

DDT or it breakdown products (DDD and DDE) is detected in all 39 study lakes. While sample concentrations vary considerably, nearly all elevated values are noted in lower portion of Michigan (Figure 2). Whitmore, Paw Paw, Otter, Davidson, Cass, and Cora Lakes contain the highest peak concentrations close to 1960 for each lake except Davidson, which has a peak concentration in 1974 (Figure 3). Overall, the highest concentrations of any individual sample analyzed for DDT, DDD, and DDE is observed in Lake Cora with values of 366, 1456 and 1064 ng/g dry weight (respectively) occurring in sediment dated to 1966. Lowest concentrations amongst the individual study lakes are those of Lake Gogebic (Upper Peninsula) with only DDE detected at its highest value of 1.19 ng/g dry weight in sediment dated to 1983.

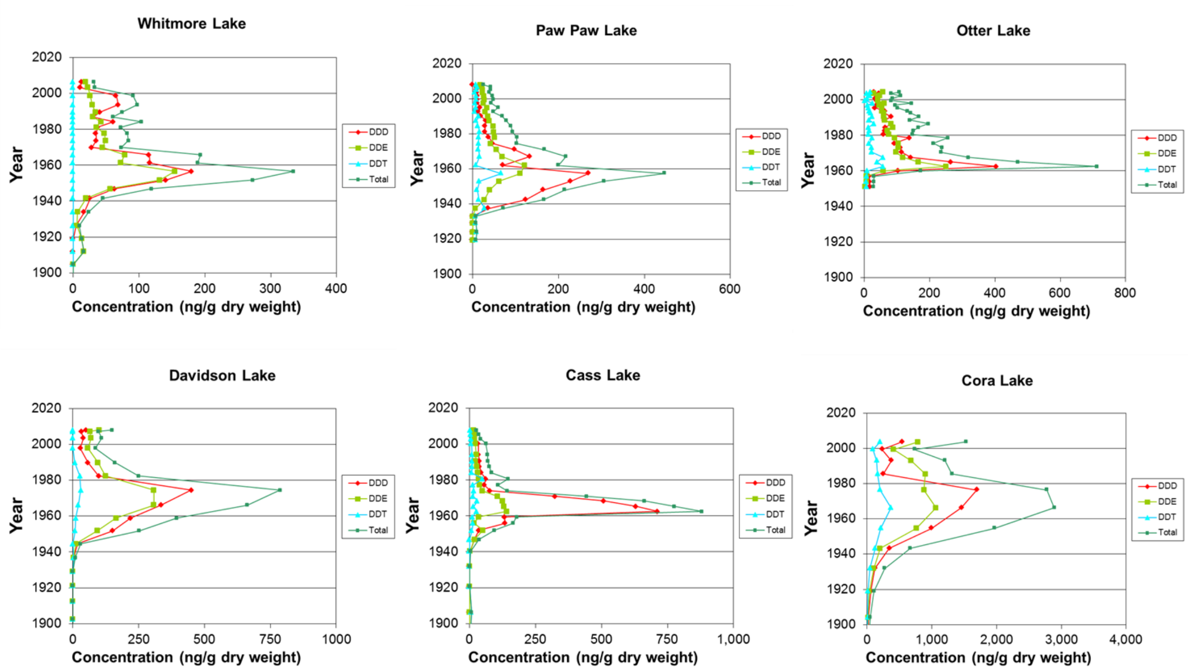

Figure 2.3: Temporal concentration profiles for six study lakes with highest peak total DDT in order by peak concentration value.

Concentrations of DDD, DDE, and DDT were summed in the top two samples collected from each core (Figure 3). These measurements are of particular concern as concentrations from the top sample intervals most directly affect benthic organisms. The concentrations are shown in a south to north distribution by latitude of the coring sites in Figure 4. Most populous latitudes (as determined by U.S. Census Bureau 2000 Census Data) are shown in the grey portion of the graph. Visual inspection of the graph shows relatively low values of DDT and breakdown products in the four southernmost lakes, followed by elevated values in the more populous lower-middle and middle latitudes of Michigan. The upper latitudes of the Lower Peninsula of Michigan and the Upper Peninsula generally show reduced values relative to the populace centers of the State located in the lower and middle latitudes.

The relatively reduced concentrations of DDT or its products in the northern Lower Peninsula lakes could be a function of the ultra-oligotrophic nature of these lakes. The reduced water column nutrient concentrations in these lakes results in reduced productivity (e.g. phytoplankton growth) which drives a portion of the sedimentation rate. With a reduced flux of this organic material that these chemicals are often sorbed to, it is expected that DDT is more likely to avoid sedimentation in these lakes (e.g. Elk, Crystal).

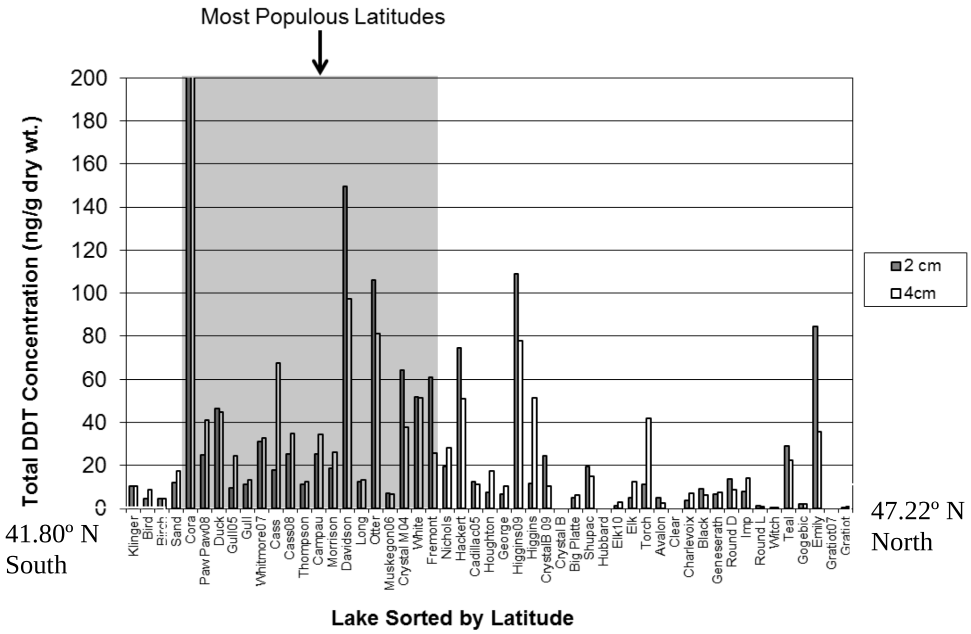

Figure 2.4: Summed concentrations of DDT and its breakdown products (DDD and DDE) in the 0-2 cm and 2-4 cm sediment depth intervals for Michigan inland lakes arranged by latitude.

Many of the lakes with elevated surficial DDT results (Cora, Davidson, Otter, Hackert, Higgins and Emily) also show an increase from the 2-4 cm interval to the 0-2 cm interval. Overall, this increasing trend in sediment concentration between the two samples is observed in 21 of the 39 lakes studied. However, interpretations regarding concentrations can be misleading without accounting for changes in sedimentation rate and the differences in the physical characteristics of the sediment both temporally through the core and between individual study lakes (e.g. quantity of organic material versus clastic material). Because of these differences, DDT concentration chronologies are difficult to compare between cores. For example, if over time there is an overall increase in total sedimentation rate, but the flux of DDT to the sediment remains the same, the concentration patterns in the sediment core will appear to be reduced. Thus, supplemental to temporal DDT chronologies based solely on concentration data, the sources and pathways of these chemicals to lake sediment are supported with inspection of the spatial trends of DDT accumulation rates, which accounts for the changes in sedimentation rate, and inventories, which is the total mass of DDT in the core per unit area. Accumulation rates of DDT and its breakdown products are calculation made based on the measured concentration of the pesticide in a given sample with the ^{210}Pb-determined mass sedimentation rate. Accumulation rates of DDT and its breakdown products were calculated as follows:

$$Accum(ng/cm^2/yr) = C_{sed}(ng/g) \times W(g/cm^2/yr)$$

Where *Accum* = Pesticide accumulation rate (ng/cm^2/yr);

C_{sed}= concentration of pesticides in surficial sediment (ng/g dry wt);

and W= mass sedimentation rate (ng/cm^2/yr) based on ^{210}Pb dating.

The accumulation rates are then focus-corrected (calculated as accumulation rate divided by a ^{210}Pb-determined focusing factor) (Golden et al., 1993). Sediment focusing of fine sediment and associated chemicals is a process of redistribution laterally from non-depositional zones to depositional zones via wave or wind energy (Golden et al., 1993). Sediment focusing occurs in different intensities largely based on lake morphology. This prevents easy comparison of the chemical trends between lakes. To accommodate this, the focusing factor is calculated as the ratio of the integrated ^{210}Pb inventory measured in the sediment to the expected inventory from ^{210}Pb deposition from the atmosphere (15.5 pCi/cm^2 ; from Golden et al., 1993).

The accumulation rates of the DDT summed with DDE and DDD for the top two samples from each lake is shown as Figure 5, the average accumulation rate for Total DDT in the whole core is shown in Figure 6, and the spatial distribution of average accumulation rates is shown state-wide as Figure 7. Overall, the south to north pattern of average accumulation rates both in the top samples and the whole core is similar in distribution to the average surficial concentration data shown in Figure 5. Again, it appears that the populace middle and lower-middle portions of the State harbor the most elevated values.

Lake Geneserath accumulation data shows elevated accumulation rates of total DDT in the top two samples of this lake relative to lakes of similar latitude (Figure 5). This lake is located on Beaver Island approximately 30 miles northwest of mainland Michigan and has a small watershed with low population. Because of its location and watershed size, this lake is expected to very low atmospheric inputs of DDT. However, this lake contains anomalously high accumulation rates in surficial sediment with an apparent increasing trend to the surface. Examination of the remaining portions of the core reveals that Lake Geneserath has an anomalously low sedimentation rate in the deeper portions of the core. Thus the top samples represent most of the environmental history of the lake and its watershed. As a result, analysis of the top samples from this lake is misleading when comparing to other lakes. The difference is reflected in the whole core average accumulation rate (Figure 6), where the difference between this lake and others of similar latitude are not as profound.

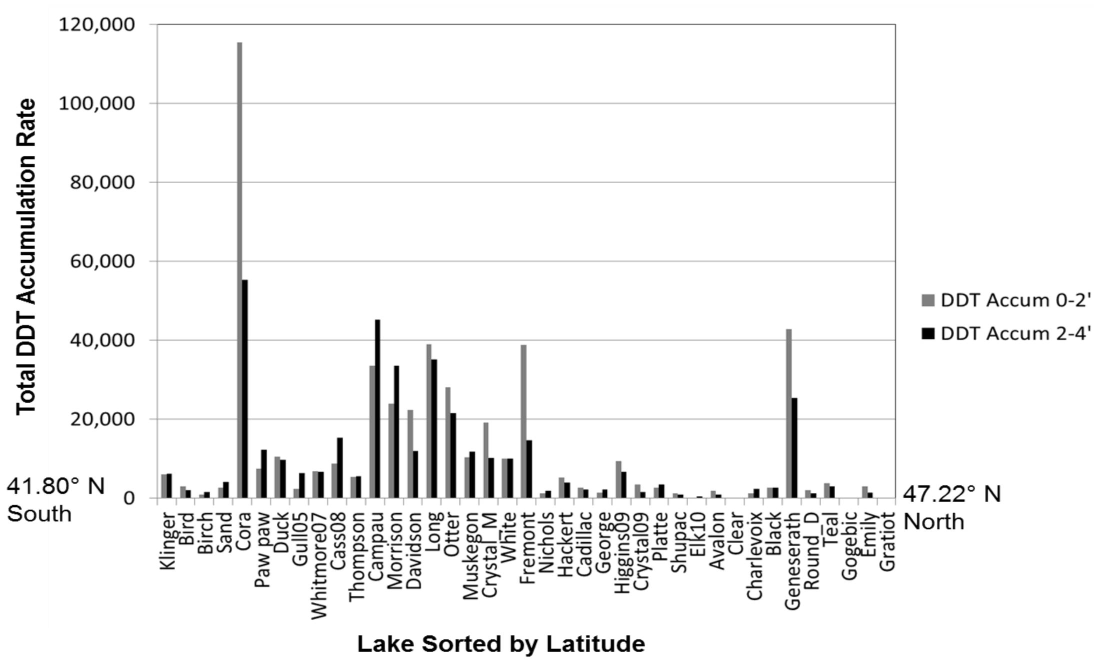

Figure 2.5: Summed focus-corrected accumulation rates of DDT and its breakdown products (DDD and DDE) in the 0-2 cm and 2-4 cm sediment depth intervals for Michigan inland lakes arranged by latitude.

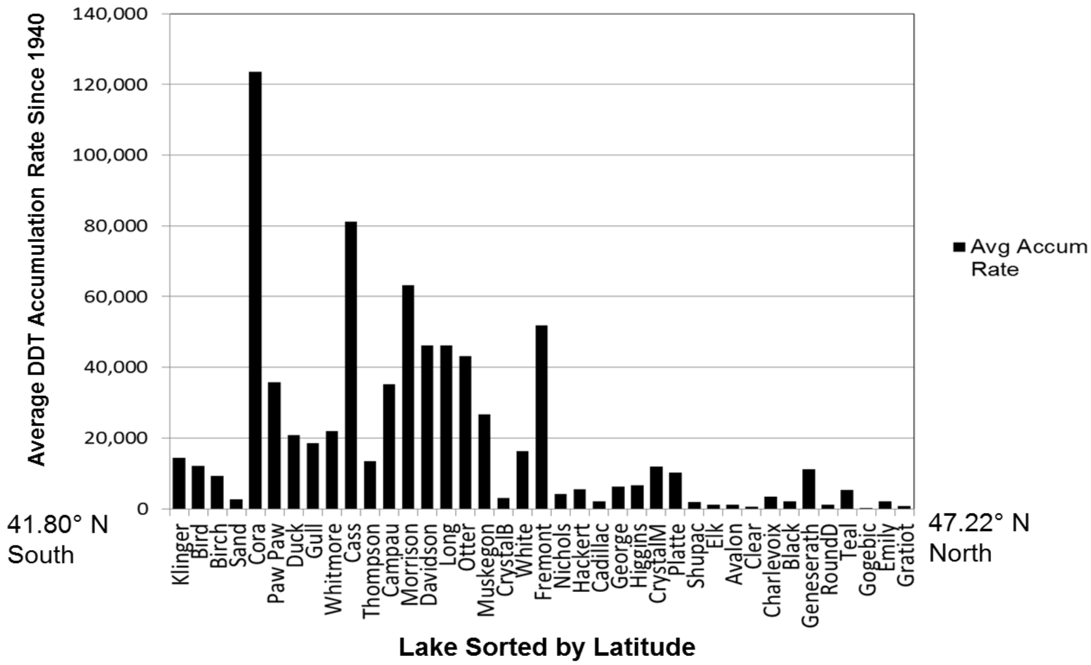

Figure 2.6: Average focus-corrected accumulation rates of DDT and its breakdown products (DDD and DDE) since 1940 for Michigan inland lakes arranged by latitude.

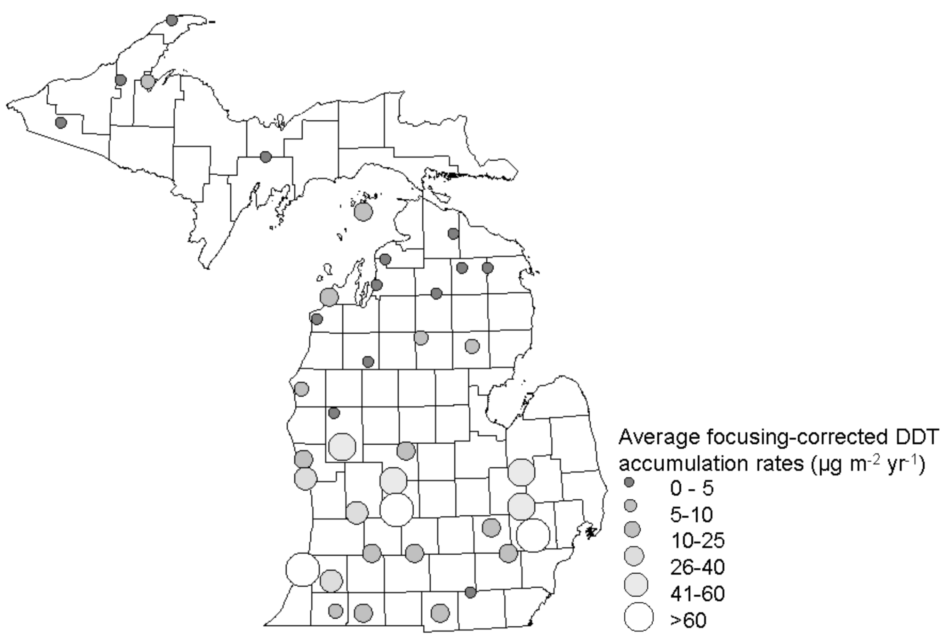

Figure 2.7: Spatial distribution of average focus-corrected accumulation rates of DDT and its breakdown products (DDD and DDE) since 1940 for Michigan inland lakes arranged by latitude.

To further examine the spatial distribution of DDT loadings, focusing-corrected inventories are calculated for each study lake and compared. DDT inventories represent the mass sum of the chemical per unit area through its entire environmental history as represented in the sediment core and are considered independent of individual lake trophic status and sedimentation rates. The utility of determining DDT inventories is to ascertain the degree at which atmospheric deposition of these compounds play a role in their distribution. If local sources alone drive the DDT flux to the surface water bodies, DDT inventories would be expected to have significant inventory differences in watersheds located close to one another. If atmospheric deposition plays a large role in DDT distribution, regional scale inventory gradients should dominate the spatial distribution.

Inventories of DDT and its breakdown products in sediment cores are calculated as:

$$Inv(ng/cm^2) = \sum_i [C_{sed}(ng/g) \times (1-\varphi) \times \rho(g/cm^3) \times d(cm)]$$

Where *Inv*= total chemical dry mass in a core (ng/cm^2);

C_{sed} = sediment concentration;

φ= porosity;

ρ = bulk density;

d = thickness of sediment increment.

The spatial distribution shown in Figure 8 appears to reflect a signal generated by local sources overprinted by a component of regional atmospheric inputs. Like the concentration and accumulation rate data, the study lake inventory appears to generally correlate with population within Michigan. Lakes along the Indiana/Ohio border show relatively low inventories compared to those in the more populace latitudes but not as low as some of the lakes in the UP or in northern lower Michigan. This could be interpreted as indication of extra-watershed inputs from upwind sources such as the areas near Chicago, Kalamazoo, and Lansing. Supporting this interpretation is other remote lakes with measurable DDT inventories such as Lake Geneserath and Emily Lake which, without atmospheric inputs, would not likely contain any measurable DDT within their sediments. Finally, Teal Lake (Figure 2) is noted as representing an anomalously high inventory for the Upper Peninsula of Michigan. However, the Teal Lake watershed contains the city of Ishpeming and is generally much more populace than the other lakes studied in the Upper Peninsula.

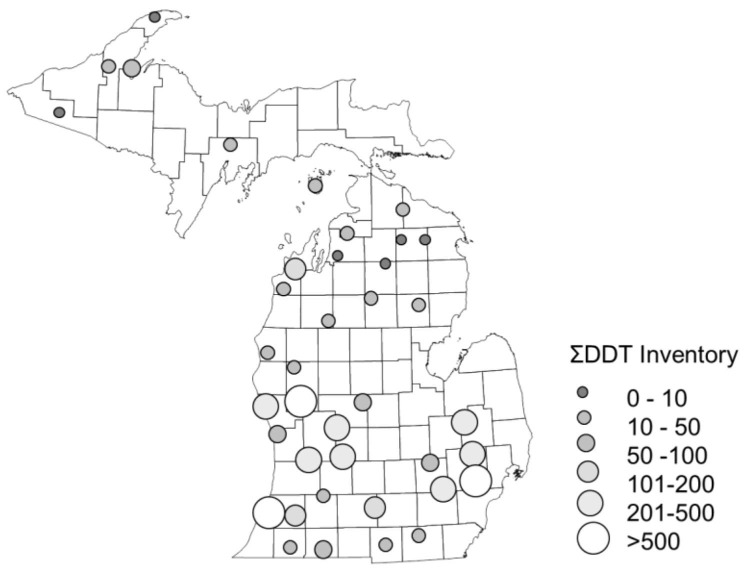

Figure 2.8: Spatial distribution of focus-corrected DDT inventories for Michigan inland lakes arranged by latitude.

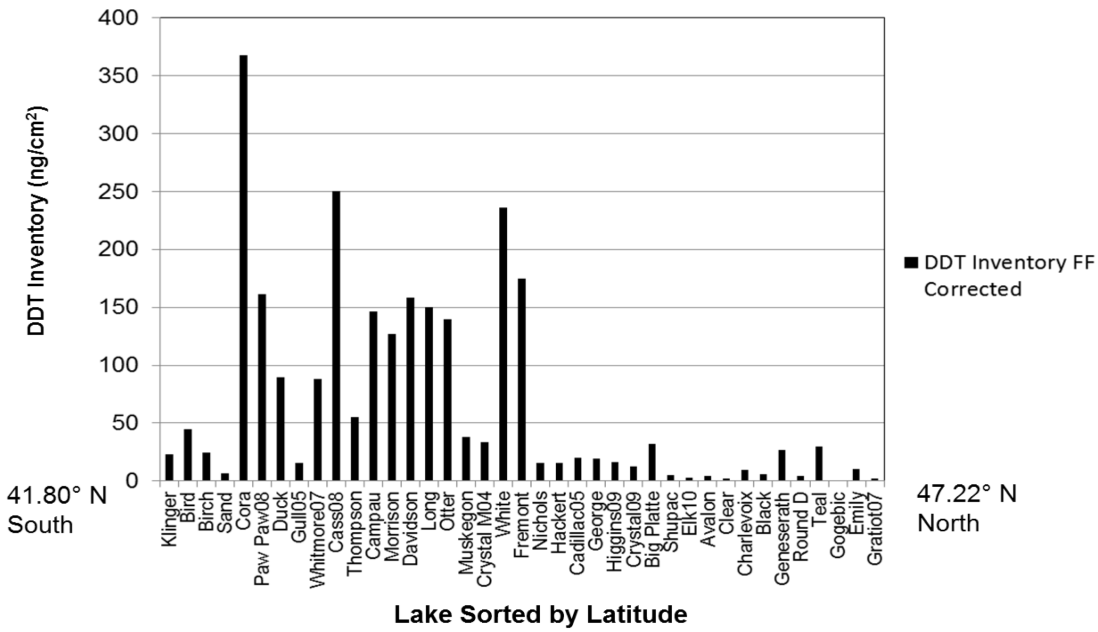

Figure 2.9: Focus-corrected DDT inventories for Michigan inland lakes arranged by latitude.

Temporal DDT/DDD/DDE Trends

On average, temporal changes in concentration of DDT, DDD, and DDE follows the hypothesized trend of an increase to peak production/consumption followed by a decrease in the decades following. Figure 2.10 and 2.11 illustrate the decadal averages of DDT concentrations state-wide with a noted increase in the 2000's decade sediment relative to that of the 1990's. Given that some of the most impacted lakes with regard to DDT exhibit this increase (e.g. Cora Lake), the data is normalized to peak value for comparison in Figure 2.11. Here a continued decrease is observed, however slight, in the 1990s and 2000s decadal concentrations (normalized values of 0.41 and 0.37, respectively). The 1990s and 2000s decadal average concentrations represent a large reduction in the rate of recovery. Possible reasons for this include bioturbation, atmospheric transport of DDT, diffusion, and benthic recycling. These processes are discussed in *Temporal DDT/DDD/DDE Trends* below.

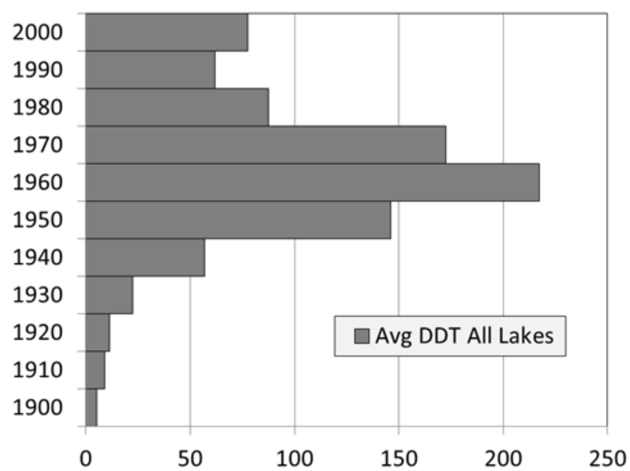

Figure 2.10: Decadal averages of Total DDT concentrations of 39 lakes in Michigan.

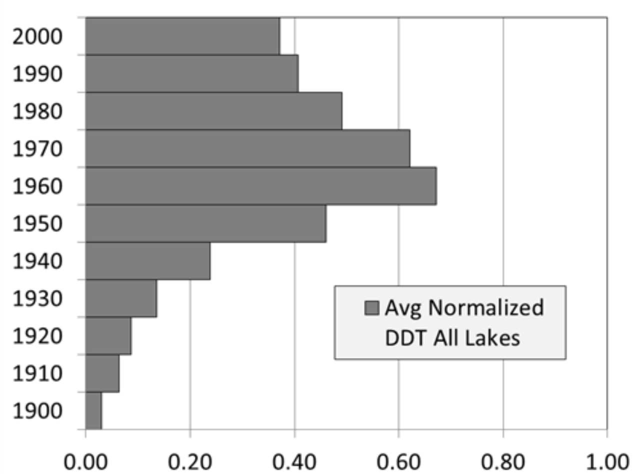

Figure 2.11: Normalized decadal averages of Total DDT concentrations of 39 lakes in Michigan.

Wong et al., 1995 and Eisenreich et al., 1989 conducted studies in which sediment cores were collected from within Lake Ontario. A DDT trend similar to findings in this study was found in these cores with peak value reflecting peak production/consumption and recent sediment maintaining measurable concentrations to the present. However, on an individual lake basis in this study, some variation in the DDT profiles is noted. Many lakes did not exhibit some aspect of the hypothesized temporal trend or those observed by Wong or Eisenreich. The differences between those lakes exhibiting an excursion from the hypothesized trend and studies conducted in the Great Lakes lies in the difference in scales. The Great Lakes watershed occupies a massive area of the US Midwest and Ontario, Canada, with mixing that prevents any single DDT release event from manifesting itself within the sediment record. A normalized average of DDT concentrations in all the study lakes across Michigan provides a signal similar in many respects to that reported by both Wong and Eisenreich because it's integrating DDT concentrations across a large area, similar in size to a Great Lake watershed. As the individual study lakes here occupy watersheds much smaller than those of the Great Lakes, these systems are much more prone to recording local inputs of DDT. As a result, section will describe the discrepancies from the hypothesized trends in three parts: DDT onset trends, DDT trend peak, and recent DDT trends.

DDT Onset Trends:

It is expected that lake sediment dated to time before significant use of DDT in the United States (mid-1940's) to contain no detectable concentrations of DDT. However, 16 of the 39 lakes studied show low but detectable concentrations of DDT in the 1930s dated sediment or earlier. This could possibly be attributed to the smearing effect occurring upon corer insertion into the benthic sediments. However, measures are taken to remove sediment in direct contact with the coring tube and the coring tube assembly is cleaned between lakes. The field methodology designed to prevent this makes these early detections seem improbable.

Post-depositional diffusion of the pesticides offers another potential pathway for this phenomenon. Based on calculations made by Wu and Gschwend (1988), the effective porous media diffusivity for compounds such as DDT controls their flux in lake sediments. Eisenreich et al. (1989) used calculations developed by Thomann and Di Toro (1983) and from Geankoplis (1972) to calculate diffusion fluxes in chlorinated hydrocarbons in Lake Ontario sediment.

Diffusion rates of 2.3 x 10^{-9} cm^2/s were calculated for DDT (approx. 0.06 cm^2/yr). These values match those calculated here using the equation put forth by Thomann and Di Toro (1983). Based on calculations made by Wu and Gschwend (1988), the effective porous media diffusivity for compounds such as DDT controls their flux in lake sediments. Eisenreich et al. (1989) used calculations developed by Thomann and Di Toro (1983) and from Geankoplis (1972) to calculate diffusion fluxes in chlorinated hydrocarbons in Lake Ontario sediment. Diffusion rates of 2.3 x 10^{-9} cm^2/s were calculated for DDT (approx. 0.06 cm^2/yr). These calculation match calculations here using the equation put for by Thomann and Di Toro (1983).

$D_{eff} = (D_{mol}\,\varphi^2) / (1 + K_p\,\rho_b / \varphi)$

where D_{mol} = is the aqueous solution molecular diffusivity (cm^2/sec);

φ is sediment porosity;

φ^2 is a measure of the tortuous path of solute migration in a porous medium;

K_p is the solid-solution partition coefficient (cm^3/g); and

ρ_b is the sediment bulk density (g_{solid}/cm^3_{water}).

Assuming D_{mol} is approximately 32 cm^2/yr; as calculated from the Wilke-Chang and Othmer-Thaker equations (Geankoplis, 1972)

ρ_b is averaged from all lakes 0.3 g/cm^3;

φ is averaged from all lakes to 0.93; and

K_p is estimated at 2.3 x 10^3 cm^3/g after Eisenriech et al., 1989.

then D_{eff} is approximately 0.04 cm^2/yr

This calculation results in approximately 2.1 cm of potential movement from the onset of DDT downward to older sediment.

Another calculation proposed by Edgington et al., 1991 shows similar results. Penetration depth (z) is calculated here from the equation:

$z = (4 \times D_c \times t)^{1/2}$

where D_c = effective diffusion coefficient in pore water (cm^2/year); and *t*, time (46 years, average time between sample collection date and the maximum production year of 1959).

Using the above calculated diffusion coefficients for DDT-related compounds of 1.3×10^{-9} cm^2/s (0.04 cm^2/year) these calculations account for approximately 2.7 cm of downward movement of DDT in the sediment cores. This calculation can account for several of the early detections of DDT and related compounds but is too small a distance to account for all.

Other possible influences on the early detection of DDT is in the mixing of sediments caused by feeding of oligochaete worms on sediment particles on which the DDT compounds are sorbed. These worms have been shown to play an important role in the mobilization of contaminants (Karckhoff and Morriss, 1985). Biological disruption such as oligochaete worms have the potential to rapidly distribute contaminants (mm/day as opposed to mm/month for diffusion) if a significant worm population is present. Oligochaete worms and other benthic organisms serve to smear the sediment record of DDT with a similar effect as diffusion: a reduced peak value but earlier onset dates and later recovery dates. Some correlation is observed between lakes displaying a significant mixing zone and early detections of DDT (Figure 12, Table 2). It is also noted that early detections of DDT occur exclusively in mesotrophic and eutrophic lakes (e.g. Cadillac, Campau, Emily, Klinger Hackert, Paw Paw, Teal, Thompson, and Long Lakes) and not observed in those lakes classified as oligotrophic (e.g. Black, Clear, CrystalB, Elk, Shupac) (See Fuller and Minnerick, 2008 for trophic classification) lending some credibility to the argument that early detections are a function of an biological-sourced smearing effect.

DDT Peak Values, Spatial and Temporal Relationship

The average total DDT concentration in lake sediments nearly tripled in value from the 1940s average total DDT concentration of 57 ng/g to an average value of 146 ng/g in sediment dated to the 1950s. This is expected as DDT saw its first significant widespread use during this time period and these decades overall saw the largest increases in total DDT concentrations. Another increase is then observed to the peak decade (1960s) reflecting the period of peak production and consumption of the chemical in the United States (Figure 13). Specifically, the dates of the peak concentration of total DDT from the 39 lakes is 1966 with an average peak total DDT value of 229 ng/g (Table 3). This is followed by a decrease in the years following the peak production/ consumption to a reduced set of values to the present. On average, the concentrations detected in the study lakes confirm the hypothesis that the sediment core records should reflect the historic usage patterns of these chemicals.

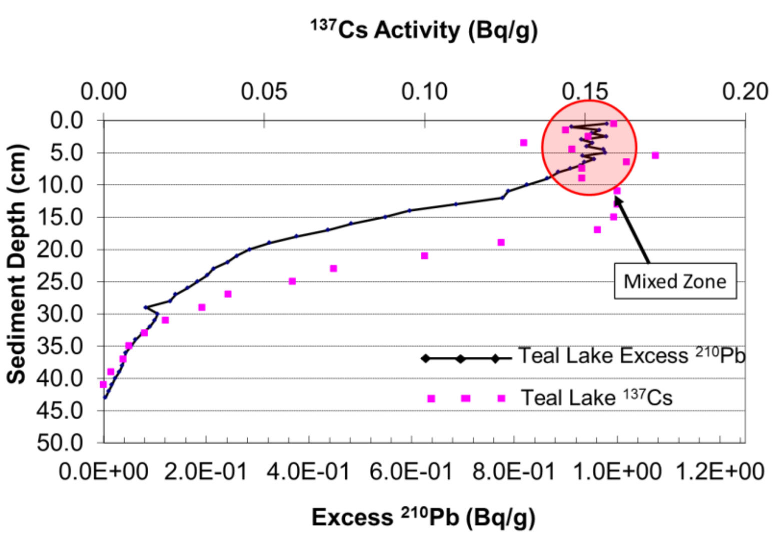

Figure 2.12: Excess ^{210}Pb activity and ^{137}Cs activity versus depth in Teal Lake, Michigan.

On an individual basis, nearly all the lakes studied elicited a definitive peak value in the trends of DDT, DDD, and DDE amongst the sectioned samples of the sediment core. No clear latitudinal trends are recognized from the peak date data. However, there appears to be a delay in the peak values for those several lakes located at higher latitudes (Figure 13). It is possible that the delayed peak values for nearly all lakes studied represents the lag time in the erosion of soil and organic particles the DDT is bound to from its location on the watershed to the lake sediment. This seems unlikely as half-life results in soil studies are typically shorter than those of lake sediment (Varca et al., 1994; Gustafson, 1989; Andrea et al., 1994).

An alternative explanation may lie in post-depositional processes of DDT and its association with organic material susceptible to decay. If an association exists between organic material and DDT (or its congeners), it's possible that these compounds have a post-depositional surface enrichment similar to the findings in regard to trace metals in El Bilali, 2002. Here and in other works (Gobeil et al, 1999) it was described that many trace metals are subject to a mechanism where they are released from the Fe and Mn oxides or organic material they are sorbed to upon burial as a consequence of two processes: organic matter decay and oxide dissolution. These metals can be subject to rerelease into the water column where they are resorbed to other settling materials or released to porewater where, upon continuing sedimentation, compaction causes upward migration. Either recycling mechanism resulted in apparent surficial enrichment of the metals in the sediment, not increased loadings. It seems possible that a similar process could be affecting DDT. Since any additional loading of the chemical after its ban in the early-1970s is highly unlikely, it is plausible that this "recycling" process in surficial sediments may cause these apparent late peaks in concentrations.

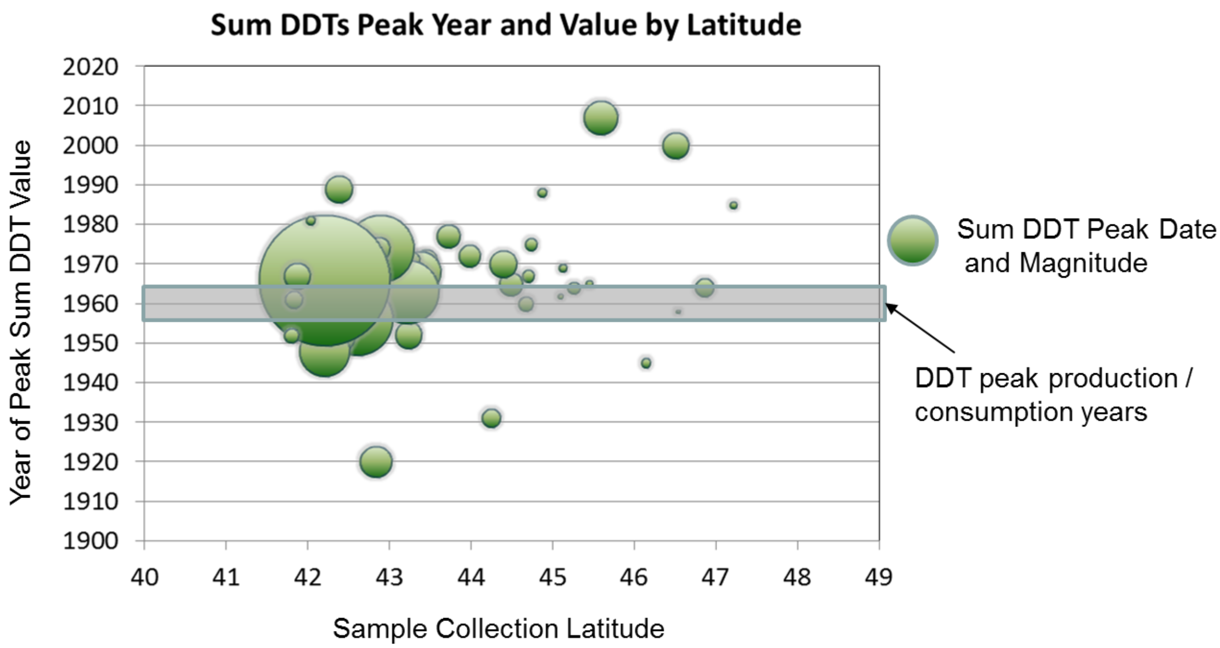

Figure 2.13: Year of peak concentration for DDT in inland lakes of Michigan.

DDT Trends in Recent Sediment

An increase in DDT concentrations in recent (2000s dated sediment) relative to the 1990s dated sediment is noted in 14 of the 39 lakes studied. Several other lakes are noted as having equivalent or only marginal decreases between the 1990s sediment and the 2000s dated sediment (Table 2). It is known that, despite a worldwide ban on DDT for any use but disease vector control, continued use is described in India, North Korea, and possibly elsewhere (Imphal Free Press, 2008; van den Berg, 2009). Since DDT has been banned in North America and considering the magnitude of present fluxes to Michigan surface water bodies, these residues could be attributed to the result of atmospheric transboundary transport. However, it seems unlikely that small usage of these chemicals from areas of great distance from Michigan could generate the atmospheric deposition to produce such a significant increase in concentration in recent sediments. Other research has shown benthic recycling (Baker et al., 1991) and past impacted sites such as Michigan fruit orchards (Hermanson et al., 2007) to continue to be significant sources of DDT into the recent.

Sediment DDT Degradation and Half-Life Calculations:

The large reduction in the recovery rates observed in many of the lakes provide cause for an investigation of the relationship between existing quantities DDT in the sediment with the quantities of it breakdown products, DDD and DDE. Rapaport et al. (1985) made measurements of DDT in rain and snow in eastern North America and reported DDT inputs of atmospheric transboundary transport from neighboring countries where DDT was not banned until a much later date. An attempt to quantify the amount of this "new" DDT that has entered Michigan surface water bodies is made by examination of the DDT/DDE+DDD ratio trends through time. Similar methods has been used by others (Harner et al., 2004; Gingrich et al., 2001) to determine proximity to source and relative age of organochlorine pesticide deposition. In Harner et al., 2004, low values of DDT/DDE were interpreted as an aged DDT source such as previously treated agricultural soil. Others have shown the relatively low ratios of DDT to its breakdown products (generally < 1.0) to be prevalent in areas likely to receive inputs of these chemicals by long range atmospheric transport such as at Integrated Atmospheric Deposition Network sites (Cortes et al, 1998, Audette et al., 2008) and the Canadian Arctic (Halsall et al., 1998). In comparison, elevated ratios (generally >1.0) have been reported in regions in which DDT has recently been applied such as Belize, Central America (Alegria et al., 2000).

For this study, results of these calculations are generally consistent with the manner expected since applications of this chemical have been illegal for many decades. The proportions of DDT to DDE + DDD decrease with time in nearly all lakes studied, and the smallest ratios (reduced DDT concentrations in relation to elevated DDE+DDD concentrations) occurred most often close to the sediment-water interface (younger sediment). The temporal changes in the ratio of DDT to DDE+DDD for selected lakes are shown in Figure 14. Duck Lake in Figure 14a displays the trend indicative of most lakes studied with an overall decreasing ratio of DDT to its breakdown products from older to recent sediments. However, several lakes showed a reversal of the trend at periods of time after the ban of these chemicals. Examples of this are shown in the profiles of DDT to its breakdown products in 1990s dated sediment of Morrison Lake and Cass Lake (Figure 14b and 14c, respectively), where a brief event occurred in the watershed history causing a “peak” in the DDT/product ratios. This may be indicative of a new source of DDT to the watershed or possibly the disturbance of watershed features (e.g. soils) containing DDT that is then hydraulically transported to the lake. Since lakes exhibiting this trend do not lie adjacent to one another these trend reversals in the DDT/product ratios is interpreted to be sourced at a watershed (local) scale. Interpretation of peaks in the DDT ratio trends is difficult due to the coarse resolution of the sampling intervals but it appears at least three other lakes exhibit this trend: Davidson, Bird, and Thompson Lakes (Figures 14d, 14e, 14f, respectively).

A third trend observed in the DDT/product ratio analysis of this study is gradual increase to recent from the older portions of the core to the recent. This is exhibited most obviously in Paw Paw08 Lake, Fremont Lake and Lake Cadillac05 (Figure 10g, 10h, 10i, respectively). Several other lakes show evidence of this trend as well, including CrystalM Lake, Lake Geneserath, Gull Lake, and Higgins Lake. With this observation in at least 6 of the lakes studied, most notably Lake Geneserath, a remote lake on Beaver Island in northern Lake

Michigan, suggests the potential for an atmospherically derived component of new DDT to Michigan.

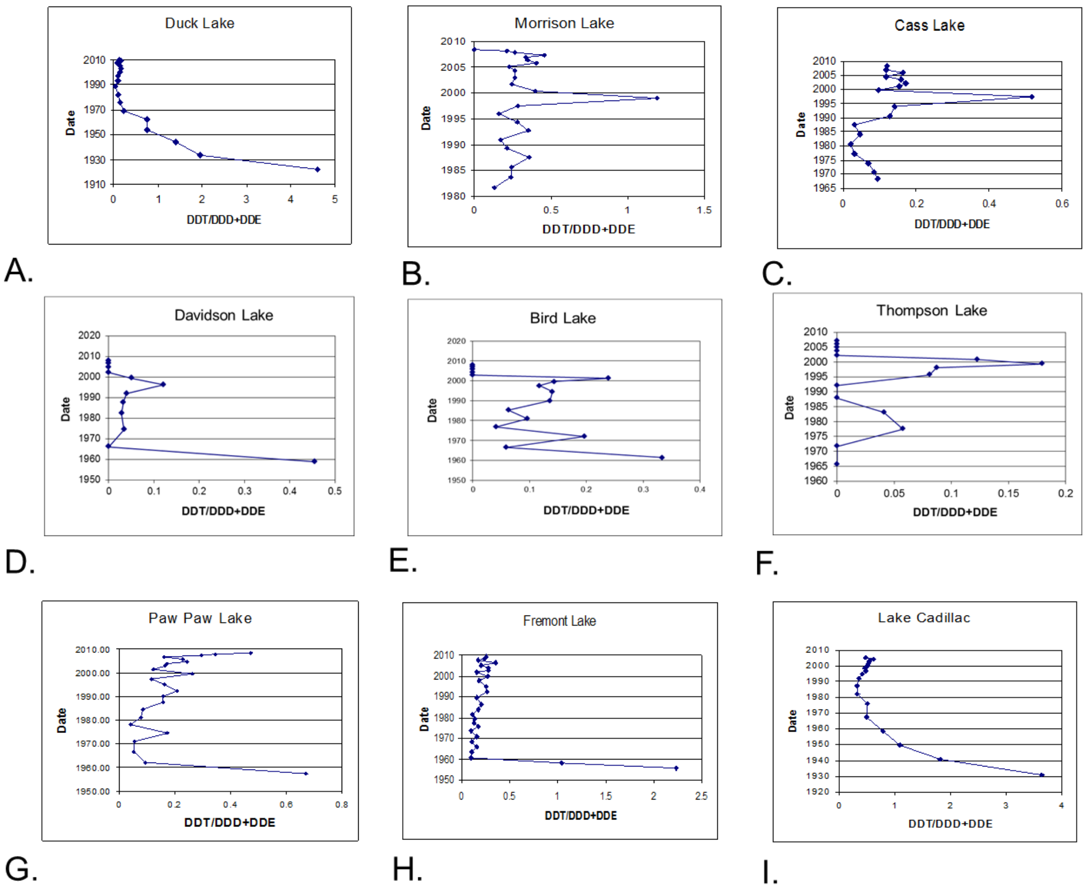

Figure 2.14: Ratios of DDT / (DDD+DDE) as a function of time in selected Michigan inland lake sediments.

Sediment DDT Concentrations and Porewater Trace Metal Profiles

All study lakes were subject to pore water extraction from a replicate sediment core and subject to pore water trace metal analysis via ICP-MS. The sediment pore water is defined as the interstitial water between sediment grains often used for analysis of the redox stratification in lake sediment (Berner, 1980; Davison, 1993; Urban et al., 1997, Koretsky et al., 2006). Iron can be used as a surrogate for sediment oxygen concentrations as Fe (III) form oxides in the presence of oxygen but reductively dissolve to produce the more soluble Fe (II). Thus, it is expected that dissolved Fe to be low near the oxygen-rich surface sediments relative to the suboxic deeper sediments, expected to be enriched in dissolved Fe.

While many of the lake pore water samples are in the process of analysis or interpretation at the time of this writing, preliminary results from Gull Lake pore water show concentrations of iron to be elevated in deeper sediments (> 10 cm depth) and the sediment at these depths do not contain detectable concentrations of DDT or its break down products (Figure 15). In sediment above approximately 10 cm, ratios of DDT to its metabolites undergo an increase to the surface. This suggests that, once buried, reductive dechlorination is the primary pathway for DDT loss from the sediment in this lake. It can be hypothesized that the observed surficial increase of DDT noted in many study lakes is attributed to the absence of reductive dechlorination in surficial sediment as oxygen penetration into the sediment prevents a sufficient microbial community from performing the necessary dechlorinating breakdown.

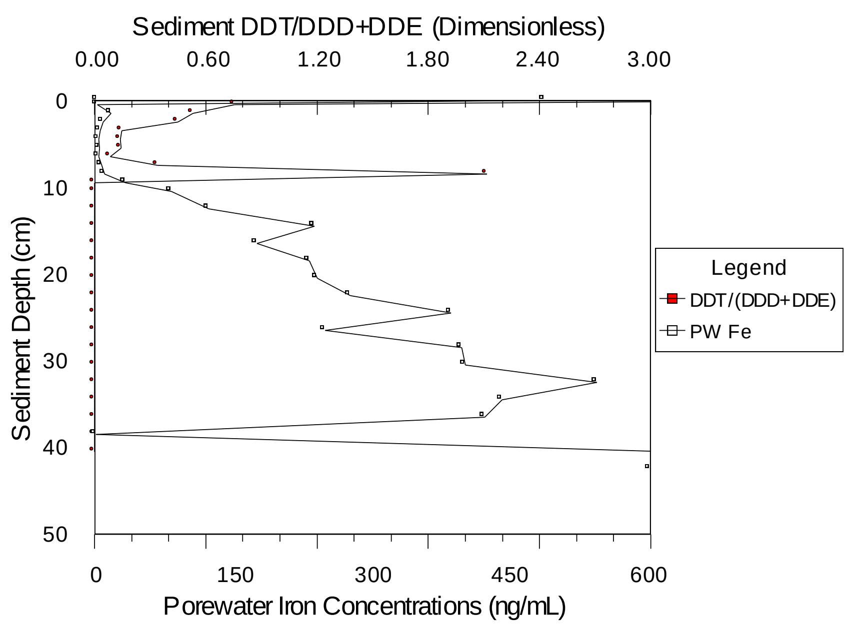

Figure 2.15: DDT/(DDD+DDE) ratio and porewater iron concentrations plotted as a function of depth in Gull Lake.

DDT Half-Life Calculations:

As described above, DDT is highly persistent in the environment. Degradation of DDT in soil occurs by photolysis or biologically-mediated degradation (either aerobic or anaerobic). Other environmental losses of DDT occur by runoff and volatilization (ATSDR, 2002). A review of the literature reveals a substantial variation in the calculated half-lives for DDT in soils. This is likely dependent upon soil-specific conditions such as organic matter content, percent fine clastic material, oxidation-reduction regimes, etc. Some reported half-life calculations for DDT are as short as 3-5 years (Bierman and Swain, 1982; Matsumara et al., 1971). Others report longer half-lives of up to 15 years (USEPA, 1989; Augustijin-Beckers et al., 1994). Still others estimate longer half-lives of approximately 20 years (Martijn et al., 1993).

Upon entering a surface water body, the DDT half-life is expected to be considerably shorter with reported values of 56 days in lake water and 28 dates in river water (USEPA, 1989). Aside from degradation, primary loss pathways include volatilization, photolysis, and sedimentation (ATSDR, 2002). If DDT avoids breakdown in the water column of a lake and becomes sedimented, the half-life expands as the compound is readily stored by adsorption to the organic and clay particles or in the tissues of benthic organisms. Field and laboratory studies in the UK demonstrate very little breakdown of DDT in sediment after a 46 day study was concluded (WHO, 1989). Typical half-life calculations of DDT in sediment range from 8 to 20 years and has been shown to follow a first-order conversion (Wolfe et al., 1977; Oliver et al., 1989).

An estimate of DDT half-life can be performed using the measured concentrations of DDT and its breakdown products (Oliver et al., 1989). Plotting ln [DDT / (DDT + DDD + DDE)] versus time is used because of the changing amount of total DDT in the various core segments. As the presence of both DDT and its breakdown products is required for the calculation, the half-life of DDT in lake sediment is able to be performed for 15 of the 39 lakes studied. Other lakes only contained detectable breakdown products in its sediment (Elk, Clear, Black, Klinger, Gogebic, Platte, Whitmore, Gratiot, Muskegon, White, Nichols, Avalon, George, Sand) or were increasing values of ln [DDT / (DDT + DDD + DDE)] with time (Campau, Birch, CrystalM, Hackert, RoundD) preventing the calculation from being performed. A representative example of the half-life calculation plot is shown as Figure 2.16. The half-life calculation for the 15 lakes averaged 20.31 years (Average R^2 = 0.69). It is not clear why the DDT half-life calculations reflect a longer environmental persistence on average than other studies. It appears that the lakes where half-life calculations tend to be longer (>40 yrs) are correlated to lakes of elevated sedimentation rates. This suggests the possibility that sedimentation of DDT is enhanced in more eutrophic lakes by the increased flux to the sediment of organic material potentially harboring these chemicals.

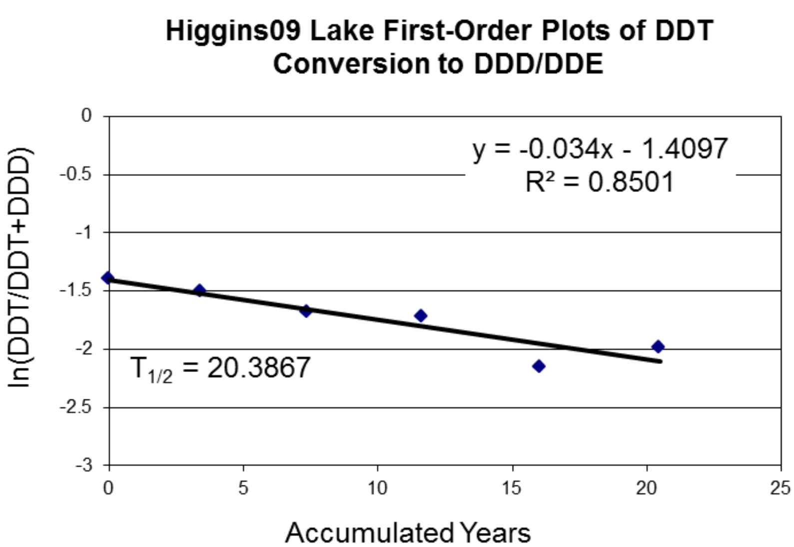

Figure 2.16: Half-life calculation plot for Higgins Lake.

DDT and Land Use:

Based on prior research (Harner et al., 2004; Hermanson, et al., 2007; Wong et al., 2009), it was expected that DDT concentrations in lake sediment to be correlated to anthropogenic land use types (%urban and %agriculture) or watershed population. However, the data showed only weak correlations to any type of land use and the strongest correlation to watershed population density in the 1970s ($R^2 = 0.32$) (Figure 2.17). This generally agrees with Wong et al, 2009 which showed highest DDT concentrations to be located at urban sites in the 1970s. However, the correlation is weak possibly due to the mixed use DDT both in an agricultural setting to control a wide range of insect crop pests but also in range lands and urban settings to control mosquito populations.

It is also possible that the summed core trends reflect the remains of the regional signal of DDT application. The latitudes exhibiting elevated summed core concentrations are also those lying along the more populace belt from the Chicago, IL region east to Detroit, MI. This region of the Michigan hosts many of the larger cities in the state including Jackson, Lansing, Grand Rapids and Kalamazoo. Given the relatively weak correlations between DDT and specific watershed land-use, it's possible that significant extra-watershed sources along the lower-central latitudes could provide supplemental inputs of DDT.

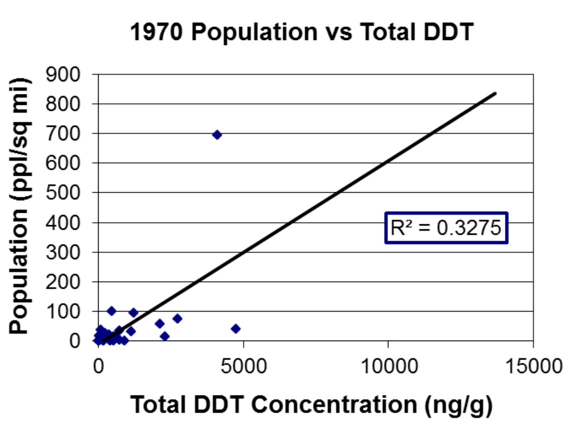

Figure 2.17: 1970s Total DDT versus study lake watershed population.

Conclusion

Concentrations of DDT, DDD, and DDE are measured in sediment cores collected from 39 inland lakes in Michigan for examination of spatial and temporal trends in accumulation and degradation. It is hypothesized that the temporal trends of DDT in the sediment cores would coincide with the reported U.S. production and use trends of the chemical. Peak use and production of DDT occurred in the U.S. in the late 1950's and early 1960's, respectively (Woodwell, 1971) and DDT values should peak in this timeframe as well with reduced values in older and more recent sediment.

Overall, temporal profiles of DDT in the lake sediment typically reflect the peak production/consumption timeframe of the compound, validating the hypothesis. However, a significant portion of the lake sediment data show DDT results to peak outside of the production/consumption peak time frame illustrating the independence of the historical use of DDT at the watershed scale. Many lakes exhibit concentration data of both DDT and its breakdown products in ^{210}Pb dated sediment prior to its known use in the United States. Potential explanation include bioturbation of the sediment or molecular diffusion of the chemicals but neither explanation seems sufficient given the depth of the cores and the distance over which the chemicals have traveled in some lakes. Also, many lakes show recent increasing trends in both DDT and its break down products.

While it is clear that US production and usage are the overriding determinants of the general DDT profiles, results show significant variation of peak concentrations and dates of the peaks amongst the individual lakes. Concentrations appear to be related to historic population trends on a regional scale, with the most elevated concentrations, accumulation rates and inventories of DDT in the southern, more populous, portion of the State. However, specific watershed land use or population did not exhibit exceptionally strong relationships. The prevalence of "new" DDT in sediment dated to time after the chemicals ban is suggestive of some remaining local or watershed scale sources supplementing the larger regional signal amongst the lakes.

Degradation half-life calculations of DDT in Michigan lakes were determined to average approximately 20 yrs, which is similar to those reported by others. Preliminary pore water results point to anaerobic dehalogenation as the primary means for breakdown of these chemicals. This occurs at varying depths in the sediment profile dependent upon the site specific enrichment of oxygen at the benthic boundary.

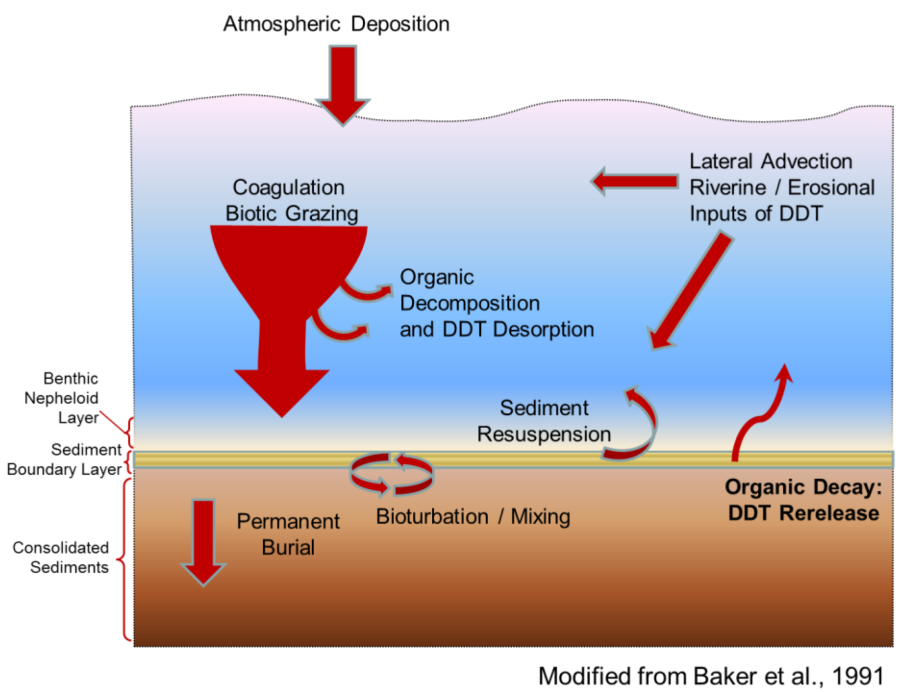

Figure 2.18: Sources and water column cycling of DDT associated with suspended and settling solids

It is proposed that cycling of the DDT compounds associated with decaying organic material both in the water column and recently deposited in the sediment serves as a potential cause for this phenomenon. It is possible that extra-watershed sources continue to play a role in the cycle of these chemicals (Harmonson, et al., 2007; Giesz, et al., 2008), however, they are not likely to prevent the full recovery in such a significant portion of the lakes studied. Rather, a combination of small quantities of extra-watershed sources, continued volatilization from historically impacted sites within a given watershed (Monosmith and Hermanson 1996), and the continued cycling of DDT in the water column and recent sediment all interact to produce the observed signal (Figure 2.18). Similar studies in the Great Lakes have shown organic contaminants to have a residence time of the 2-3 times the particulate residence time due to the effects of resuspension and mixing of surficial sediments by aquatic organisms (Eisenreich, 1989).

APPENDIX

Table 2.1: Physical characteristics of study lakes.

Lake	Sampling year	Counties of watershed	Lake area (km^2)	Sampling depth (m)	Oldest section	Surficial Sedimentation rate (g/m2/yr)	Watershed area (km^2)
Avalon	2003	Montmorency	1.5	21.3	1790	296	3.1
Birch	2003	Cass	1.2	29.6	1824	540	2.7
Bird	2008	Hillsdale	4.2	19.5	1916	759	4.2
Black	2009	Cheboygan, Montmorency, Otsego, Presque Isle	41.0	14.0	1627	550	1382.5
Cadillac	2005	Wexford, Missaukee	4.7	8.2	1825	396	47.6
Campau	2005	Kent	0.5	16.2	1848	2100	4.7
Cass M	2008	Oakland	5.2	36.6	1856	965	46.8
Charlevoix	2005	Antrim, Charlevoix, Ottawa, Emmitt	69.8	33.5	1653	707	765.1
Clear	2009	Montmorency	0.5	27.1	1809	294	4.4
Cora	2008	Van Buren	0.9	18.9	1733	369	6.3
CrystalB	2009	Benzie	39.3	49.7	1657	555	106.2
CrystalM	2004	Montcalm	2.9	16.8	1804	559	12.1
Davidson	2008	Oakland, Lapeer	0.2	21.6	1675	232	1.9
Duck	2010	Calhoun	2.4	15.6	1792	453	7.9
Elk	2010	Grand Traverse, Antrim, Kalkaska	31.3	58.8	1398	442	130.9
Emily	2007	Houghton	0.2	27.9	1800	104	0.8
Fremont	2009	Newaygo	3.2	26.5	1941	2054	40.5
Geneserath	2010	Charlevoix	1.9	15.5	795	273	23.5
George	2004	Ogemaw	0.8	26.2	1932	417	5.1
Gogebic	2007	Gogebic	51.8	7.62	1611	337	454.1
Gratiot	2007	Keweenaw	5.8	23.8	1837	444	27.0
Gull	2005	Kalamazoo, Barry	8.2	33.5	1674	423	61.7
Hackert	2004	Mason	0.5	15.5	1840	451	1.5
Klinger	2008	St. Joseph	3.3	21.9	1800	464	48.8
Long	2009	Ionia, Montcalm	1.4	18.0	1892	367	22.3
Morrison	2008	Ionia	1.3	10.3	1973	2590	27.8
Mullett	2001	Cheboygan, Otsego	70.3	35.7	1708	801	718.0
Muskegon	2006	Muskegon, Newaygo	16.8	14.5	1965	1607	885.0
Nichols	2005	Newaygo	0.64	19.1	1972	193	1.0
Otter	2004	Genesee, Lapeer, Tuscola	0.3	36.9	1945	933	3.4
Paw Paw	2008	Berrien, Van Buren	3.7	27.7	1923	828	30.0
Platte Lake	2007	Benzie County	10.2	28.8	1910	1885	374.6
RoundD	2004	Delta	1.8	16.0	1852	270	2.0
Sand	2003	Lenawee	1.8	17.3	1864	441	24.5
Shupac	2003	Crawford	0.4	30.4	1829	261	2.2
Teal	2010	Marquette	2.0	10.8	1816	323	5.5
Thompson	2007	Livingston	0.61	17.0	1698	815	55.5
Whitmore	2007	Washtenaw, Livingston	2.7	20.8	1876	534	5.6
White*	2006	Muskegon	10.4	21.6	1873	977	

* A watershed was not delineated for White Lake.

Table 2.2: Decadal average DDT concentration of all study lakes.

	Avalon	Birch	Bird	Black	Cadillac05	Campau	Cass08	Charlevoix	Clear	Cora
2000	**4.8**	4.6	**4.8**	**7.8**	**11.7**	32.5	40.8	3.7	2.7	**1526.4**
1990	3.4	8.5	4.5	6.0	9.4	39.0	68.0	7.1	11.9	967.2
1980	4.3	36.3	11.2	6.7	11.1	73.4	113.7	12.0	0.0	1311.9
1970	5.9	62.7	18.4	10.7	12.8	73.4	230.2	23.0	0.0	2773.5
1960	6.5	92.5	44.2	9.2	14.5	166.6	772.1	31.7	0.0	2888.1
1950	6.9	11.5	24.3	4.2	20.9	180.0	145.3	4.8	0.0	1965.5
1940	5.1	0.2	8.1	1.2	39.4	67.8	19.5	16.8	0.0	668.0
1930	**4.7**	0.0	**0.6**	0.0	**66.2**	**55.7**	0.0	**10.3**	0.0	**268.7**
1920	**4.4**	0.0	0.0	0.0	**63.9**	**55.8**	0.0	0.0	0.0	**106.5**
1910	**2.8**	0.0	0.0	0.0	**32.6**	**87.5**	**6.5**	0.0	0.0	**47.2**
1900	**0.9**	**0.6**	0.0	0.0	**16.6**	**68.7**	0.0	0.0	0.0	**24.1**

	Crystal B09	Crystal M04	Davidson	Duck	Elk10	Emily	Fremont	Geneserath	George	Gogebic
2000	17.6	**64.0**	**118.7**	50.7	2.0	**84.3**	**38.4**	**210.2**	8.7	**2.1**
1990	26.4	38.4	85.6	92.0	12.7	35.5	33.1	124.6	9.9	1.9
1980	18.8	37.7	204.4	116.9	17.5	25.9	59.1	84.2	19.8	2.8
1970	0.0	58.6	787.0	49.4	1.3	39.1	78.1	10.8	59.7	3.8
1960	0.0	45.5	662.6	15.5	0.0	68.1	52.0	0.0	78.0	4.4
1950	0.0	21.6	323.3	9.0	0.0	55.7	60.5	0.0	17.9	2.3
1940	0.0	10.3	29.0	7.9	0.0	34.3	2.7	0.0	1.3	0.0
1930	0.0	**5.8**	**9.3**	**6.9**	0.0	**15.1**	**0.8**	**4.5**	0.0	0.0
1920	0.0	**3.4**	0.0	**7.4**	0.0	**2.8**		0.0		0.0
1910	0.0	**2.5**	0.0	**3.7**	0.0	**29.4**		0.0		0.0
1900	0.0	**2.6**	0.0		0.0	**2.8**		0.0		0.0

	Gratiot07	Gull05	Hackert	Higgins09	Klinger	Long	Morrison	Muskegon	Nichols	Otter
2000	0.0	9.4	**62.8**	**109.0**	10.3	13.8	29.6	13.2	23.8	95.8
1990	0.0	24.3	41.4	77.8	10.5	35.7	45.0	12.4	44.6	122.9
1980	11.8	32.3	54.2	102.9	14.0	50.8	62.6	18.7	62.2	159.2
1970	10.7	57.5	93.2	85.4	40.9	64.9	93.0	30.8	99.5	234.6
1960	10.4	143.0	87.2	102.0	44.9	50.8		76.8	74.1	417.8
1950	9.1	162.7	15.4	42.6	24.7	10.3		115.3	59.2	28.4
1940	8.0	138.3	1.5	14.5	32.5	4.2			21.4	
1930	0.0	**59.9**	**1.1**	**7.1**	**12.9**	**4.5**			0.0	
1920	0.0	**26.1**	**1.0**	0.0	**4.7**	**0.8**			0.0	
1910	0.0	0.0	**1.2**	0.0	0.0	**0.5**			0.0	
1900	0.0	0.0	**1.6**	0.0	0.0	**0.3**			0.0	

	PawPaw08	Platte	RoundD	Sand	Shupac	Teal	Thompson	White	Whitmore07
2000	38.2	7.5	11.1	14.7	**19.3**	35.1	12.7	37.9	32.0
1990	52.9	15.2	12.4	16.6	15.1	58.8	16.9	42.9	94.1
1980	86.4	33.0	12.2	18.2	21.6	23.3	28.8	55.6	77.4
1970	123.7	47.3	8.6	18.5	31.3	36.0	53.8	150.3	82.9
1960	207.8	5.3	11.2	18.8	27.9	20.3	77.6	302.2	151.6
1950	375.6		9.9	15.9	16.1	10.5	240.4	248.8	303.5
1940	189.6		20.6	5.6	1.3	8.7	46.9	184.7	81.8
1930	38.8		19.2	3.7	1.2	12.4	3.5	43.4	23.3
1920	8.1		12.6	2.1	0.1	12.4	0.0	0.0	9.4
1910	7.1		5.7	2.0	0.0	9.4	3.4	0.0	12.9
1900			2.8	0.5	0.1	4.8	2.5	0.0	15.9

Notes: Concentrations below the detection limit are treated as a concentration of 0.0
Due to high sedimentation rates, some lake cores did not acquire sediment dated to early 20th century.
Concentrations in bold represent detected values prior to significant world-wide use of DDT.

Table 2.3. DDT Concentration Peak Date, Peak DDT Concentration, Total Sediment Core DDT Concentration, Calculated DDT Half-Life, and R2 for Half-Life.

Lake	Latitude	Peak Date	Peak Conc	Surficial sedimentation rate ($g\ m^{-2}\ yr^{-1}$)	Average focus-corrected DDT accum. rate since 1940's ($\mu g\ m^{-2}\ yr^{-1}$)	DDT Inventory (ng cm-2)	$t_{1/2}$	R^2
Gratiot	47.22	1985	11.78	444	0.8	2.61		
Emily	46.86	1964	68.01	104	2.2	27.56[a]		
Gogebic	46.54	1958	4.36	337	0.1	0.31		
Teal	46.51	2000	127.33	323	5.3	56.99[a]		
RoundD	46.15	1945	20.57	270	1.1	10.17		
Geneserath	45.60	2007	210.19	273	11.2	42.99[a]		
Black	45.45	1965	10.73	550	2.0	10.52		
Charlevoix	45.26	1964	31.69	707	3.5	19.52		
Clear	45.13	1969	16.23	294	0.5	4.82		
Avalon	45.10	1962	7.34	296	1.2	6.26		
Elk	44.87	1988	17.52	442	1.2	7.41		
Shupac	44.73	1975	31.34	261	1.9	9.48		
Platte	44.70	1967	33.38	1885	10.2	110.72		
CrystalB	44.67	1960	43.72	555	3.1	42.84	13.9	0.51
Higgins	44.49	1965	101.96	214	6.6	41.35	20.4	0.85
George	44.40	1970	135.38	417	6.3	40.68		
Cadillac	44.24	1931	66.23	396	2.1	35.59[a]	44.1	0.87
Hackert	43.98	1972	93.17	451	5.4	29.80	10.4	0.71
Nichols	43.73	1977	102.51	193	4.2	36.01		
Fremont	43.45	1971	84.07	2054	51.9	594.09[a]	49.9	0.63
White	43.38	1968	302.16	977	16.2	354.65[a]		
CrystalM	43.26	1971	58.53	554	12.0	52.40	6.5	0.96
Muskegon	43.23	1952	133.87	1607	26.7[b]	88.85[a]		
Otter	43.22	1963	711.45	933	43.2	475.54[a]	45.9	0.11
Long	43.11	1973	69.71	367	46.2	348.50[a]	10.2	0.64
Davidson	42.89	1974	787.01	232	46.1	232.21	14.3	0.57
Morrison	42.87	1974	102.09	2590	63.2[b]	258.22[a]	29.2	0.51
Campau	42.83	1920	179.99	2100	35.2	232.76		
Thompson	42.61	1956	274.65	815	13.4	82.83		
Cass	42.60	1956	879.43	965	81.1	800.52	9.6	0.71
Whitmore	42.44	1957	334.68	534	22.0	205.32		
Gull05	42.40	1952	162.73	423	18.5	26.70	10.3	0.95
Duck	42.39	1989	137.08	453	20.8	165.64[a]	18.4	0.6
Paw Paw	42.21	1948	446.24	828	35.8	398.42[a]	16.3	0.81
Cora	42.20	1966	2888.14	369	123.5	730.01		
Sand	42.03	1981	19.02	441	2.7	12.19		
Birch	41.87	1967	132.74	540	9.2	41.26		
Bird	41.83	1961	63.57	759	12.2	66.89	5.3	0.76
Klinger	41.80	1952	44.88	464	14.4	41.11		
Average		**1966**	**229.37**	**1364.15**	**18.2**	**107.3**	**20.3**	**0.68**

[a] = Indicates Total DDT concentrations were detected above 1 ng/g to the bottom of the sediment core. DDT concentrations may exist below the depth of the core taken and the DDT Inventory calculations may be under represented.
[b] = Sediment core dating showed deepest sediment to age younger than 1940s, thus average DDT accumulation rate may be subject to some error.

Table 2.4. Select data from ^{210}Pb analysis, including the model used for dating, mixed depth, surficial sedimentation rate, focusing factor (FF) and the age of the oldest section in the sediment core.

Lake	Model	Approximate mixed depth (cm)	Surficial Sedimentation rate ($g/m^2/yr$)	FF	Oldest section
Avalon	CRS	4	296	1.5	1790[a]
Birch	CRS	3	540	1.7	1824[a]
Bird	CRS	1.5	759	1.7	1916[a]
Black	SCF:CS	0	550	1.7	1627[a]
Cadillac	CRS	17	396	1.8	1825[a]
Campau	SCF:CS	4.5	2100	1.6	1848[a]
Cass	CRS	0	965	3.2	1856
Charlevoix	CRS	1.5	707	2.0	1653[a]
Clear	CF:CS	2.5	294	2.4	1809[a]
Cora	SCF:CS	3.5	369	2.1	1733[a]
CrystalB	SCF:CS	4	555	3.5	1657[a]
CrystalM	CRS	0	559	1.6	1804
Davidson	CRS	4	232	3.5	1675[a]
Duck	CRS	2.5	453	1.8	1792[a]
Elk	CF:CS	0.5	442	2.1	1398[a]
Emily	CRS	0	104	2.7	1800[a]
Fremont	CRS	3.5	2054	4.1	1941
Geneserath	CRS	3	273	1.7	795
George	CF:CS	9	417	2.1	1932
Gogebic	CF:CS	4	337	1.3	1611[a]
Gratiot07	CF:CS	4	444	1.5	1837[a]
Gull05	CRS	0	423	1.7	1674[a]
Hackert	CRS	0	451	1.9	1840
Higgins	CRS	1.5	214	2.5	1663[a]
Houghton	SCF:CS	8	165	1.2	1715[a]
Imp	CRS	3	119	1.5	1745[a]
Klinger	SCF:CF	1.5	464	2.4	1900
Long	SCF:CS	1.0	367	2.5	1892
Morrison	CF:CS	3.5	2590	2.0	1973
Muskegon	CF:CS	3	1607	2.9[c]	1965
Nichols	CRS[d]	0	193	2.3[c]	1972[d]
Otter	CF:CS	8	933	3.5	1945
Paw Paw	CF:CS	3	828	2.7[c]	1923
Platte	CF:CS	6	1885	3.4	1910
RoundL	CRS	7	317	2.3	1851
RoundD	CRS	9	270	2.4	1852
Sand	CRS	0	441	1.8	1864
Shupac	CRS	1	261	2.0	1829[a]
Teal	CF:CS	5.5	323	2.4	1816[a]
Thompson	CRS	8	815	1.5	1698[a]
Torch	CRS	0	365	2.4	1493[a]
Whitmore	SCF:CS	3	534	2.3	1876
White	SCF:CS	3	977	1.5[c]	1873
Witch	CRS	6	269	1.7	1767[a]

a = Estimated dates based on extrapolation
b = focusing factor could not be calculated for Littlefield Lake, so the average focusing factor of all lakes sampled previously (except Cass Lake) was used
c = Estimated focusing factor based on extrapolation
d = An extrapolation of the ^{210}Pb integral was used

Table 2.5: GIS-determined 1970s watershed land-use percentages for all Michigan study lakes organized by latitude.

Lake	Urban %	Agriculture %	Forest %	Range %	Wetland %
Avalon	2.9	70.0	25.7	1.2	0.1
Birch	2.2	33.0	42.2	19.9	2.8
Bird	10.6	66.6	19.8	2.6	0.1
Black	1.1	5.5	80.1	8.6	3.8
Cadillac	19.9	41.1	24.6	10.3	4.2
Campau	17.8	28.1	22.2	27.2	1.9
Cass	62.0	2.5	8.8	14.3	12.5
Charlevoix	4.0	20.5	57.0	15.7	2.0
Clear	20.6	0.0	76.6	1.5	0.0
Cora	19.4	48.1	23.3	4.9	4.0
Crystal B	12.4	13.0	52.1	21.3	1.2
Crystal M	11.1	58.6	17.0	5.0	8.3
Davison	14.1	17.2	26.8	38.6	2.7
Duck	6.2	43.1	30.2	11.4	7.7
Elk	6.4	28.2	41.4	20.0	4.0
Emily	0.0	0.0	93.2	0.0	5.5
Fremont	20.5	58.2	13.2	3.1	3.7
Geneserath	0.3	0.0	84.3	0.4	8.0
George	9.7	23.1	40.0	24.3	2.8
Gogebic	1.2	0.0	92.1	0.5	5.0
Gratiot	0.9	0.0	98.5	0.0	0.6
Gull	10.0	61.1	14.6	8.2	6.0
Hackert	21.5	31.9	28.5	16.0	2.1
Higgins	15.0	0.5	77.6	3.5	3.4
Houghton	7.2	1.6	75.8	5.4	10.0
Imp	7.1	0.0	88.1	0.0	4.8
Klinger	6.8	57.0	21.5	5.4	5.9
Littlefield	1.9	9.4	70.5	14.0	4.3
Long	5.7	39.5	42.0	4.6	7.5
Morrison	6.0	74.4	13.9	1.9	3.7
Mullett	3.0	7.4	71.4	15.3	2.9
Muskegon	11.4	71.0	4.1	13.2	0.3
Nichols	7.3	0.0	84.2	0.0	1.6
Otter	9.3	8.3	50.3	17.3	14.8
Paw Paw	17.8	30.8	35.8	13.5	2.1
Platte	2.3	9.9	63.5	22.0	1.2
Round	4.8	13.9	68.9	11.5	1.0
Round_D	9.9	0.0	89.1	0.0	1.0
Sand	20.5	11.8	50.2	15.2	2.3
Shupac	0.9	0.5	83.6	13.9	1.1
Teal	27.0	0.0	59.7	6.2	2.6
Thompson	22.9	25.7	17.4	29.8	3.8
Torch	7.4	23.6	45.1	22.0	1.9
White	3.3	24.2	58.9	9.5	2.8
Whitmore	22.4	23.9	24.1	20.8	8.8
Witch	1.8	3.0	81.8	6.8	6.6

Table 2.6: GIS-determined 1970s watershed land-use percentages for all Michigan study lakes organized by latitude.

Lake	Urban %	Agriculture %	Upland %	Forest %	Wetland %	Barren %
Avalon	8.8	0.0	12.2	71.2	1.2	0.2
Birch	6.4	48.3	7.8	27.8	4.4	0.1
Bird	8.3	52.8	8.4	23.2	6.5	0.0
Black	1.4	3.0	16.2	69.9	8.3	0.1
Cadillac	10.7	26.6	18.8	35.1	5.7	1.7
Campau	10.4	31.9	13.7	32.7	9.2	0.0
Cass	24.8	0.5	18.9	37.5	11.0	0.1
Charlevoix	3.4	17.3	14.8	61.0	2.3	0.3
Clear	3.3	0.0	11.4	82.2	1.1	0.1
Cora	7.2	49.7	9.0	31.0	2.3	0.1
Crystal B	5.5	9.4	22.3	60.0	0.9	0.3
Crystal M	20.0	56.7	3.5	13.7	3.3	0.1
Davison	3.5	21.0	13.1	50.7	11.2	0.0
Duck	17.0	49.8	6.9	21.4	4.6	0.0
Elk	4.2	20.4	18.6	53.6	1.8	0.2
Emily	1.8	0.0	0.6	89.5	2.1	0.0
Fremont	9.9	47.8	12.7	22.8	4.2	0.8
Geneserath	0.1	0.0	6.7	74.2	18.2	0.0
George	5.0	6.3	17.4	59.9	9.4	0.2
Gogebic	1.2	0.0	1.8	86.6	8.4	0.2
Gratiot	0.9	0.0	6.2	89.3	3.0	0.1
Gull	5.6	59.8	6.1	21.0	4.9	0.1
Hackert	5.9	33.8	10.2	42.3	4.3	0.2
Higgins	6.9	0.2	15.8	72.2	3.7	0.2
Houghton	3.7	0.8	14.6	62.2	16.4	0.2
Imp	3.5	0.0	0.6	89.2	0.5	0.3
Klinger	5.8	53.4	5.3	27.1	5.5	0.2
Littlefield	2.9	2.3	12.6	75.6	4.6	0.1
Long	4.8	30.6	9.0	31.1	23.4	0.1
Morrison	6.4	72.2	4.5	11.9	4.7	0.2
Mullett	2.8	7.2	17.7	68.1	3.2	0.2
Muskegon	7.0	17.2	18.0	47.4	7.0	0.4
Nichols	0.9	0.0	2.0	86.4	5.4	0.2
Otter	8.3	4.8	16.7	49.6	17.9	0.0
Paw Paw	9.2	38.6	13.2	31.6	6.4	0.0
Platte	2.6	8.7	19.6	66.7	1.3	0.2
Round	0.4	7.2	9.2	72.9	9.3	0.3
Sand	8.5	6.9	13.4	62.6	7.0	0.0
Shupac	2.8	0.0	18.5	74.8	2.8	0.0
Teal	20.0	0.0	5.5	69.8	1.3	0.1
Thompson	17.4	26.3	15.7	32.0	0.4	0.3
Torch	4.2	18.6	19.4	54.3	1.5	0.2
White	3.0	17.4	16.2	58.1	0.3	4.1
Whitmore	7.6	35.9	12.5	32.7	10.4	0.0
Witch	3.0	0.0	2.8	87.2	0.0	2.1

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CHAPTER 3

LANDSCAPE RECOVERY FROM HISTORICAL PCB LOADINGS USING SEDIMENT-CHEMICAL CHRONOLOGIES

Abstract

Previous studies have shown atmospheric transport to be a dominant pathway for PCB loadings to the environment and that urban areas typically serve as major sources of these chemicals. A significant segment of the existing research to date in the Great Lakes region mainly involves the Great Lakes themselves. These water bodies occupy an enormous footprint on the North American continent and results on PCB studies here are more reflective of a coarse regional signal of PCB distribution than local inputs. More detailed understanding of loading patterns is needed for a more complete understanding of sources of PCBs and the current state of environmental recovery. In this study, sediment records were studied from 44 inland lakes across the State of Michigan representing a variety of watershed land use and trophic characteristics to better understand the spatial distribution and changes over time of PCB loadings. ^{210}Pb dated PCB concentrations, accumulation rates and inventories from each lake were compared to GIS-determined watershed land-use characteristics. Overall, sediment PCBs were elevated in the Lower Peninsula compared to the Upper Peninsula and locations of high PCB inventories near urban areas were found. However, concentration and accumulation peak dates increased with latitude of the lake possibly due to secondary mobility and deposition away from sources. Individual PCB congener concentrations were subject to cluster analysis via Jump 5.0 software. During high PCB production years, congener clusters show clear localized

patterns, but more recently, congener distributions suggest a more regional signal. However, state-wide regional patterns appear to serve as a component to both recent and historical data, despite the prominence of local and sub-regional trends during the peak PCB production/consumption years.

Introduction

Polychlorinated biphenyls (PCBs) have been studied for decades as the hazards associated with exposure of these chemicals to human and ecosystem health has been described (Carpenter, 2006; Mozaffarian et al., 2006; Longnecker et al., 1997; Cordle et al., 1978; Nisbet and Sarofim, 1972). Results from these studies show that, although manufacture and use of PCBs has been banned for over 30 years, they still remain present in significant quantities in the environment. A common fate of many environmentally-persistent chemicals in freshwater systems is ultimately to become deposited to areas of low energy such as a lake bottom. Contaminated sediments can directly impact bottom-dwelling organisms and represent a continuing source for toxic substances in the aquatic food wed. This affects wildlife and humans through food or water consumption. Therefore, an understanding of the trends of these toxic chemicals accumulation in the environment is necessary to assess the current state and potential future problems of surface water quality. Here we use chemical analysis of inland lake sediment cores to provide some elucidation to PCBs continued environmental presence dated throughout the chemicals use history in Michigan.

PCBs are a group of synthetic chemical compounds characterized by a pair of benzene rings with between 2 and 10 attached with chlorine atoms of various configurations (Pohanish, 2008; USEPA, 2003; ATSDR, 2000). Historically, PCBs were first synthesized in 1881 but not manufactured commercially until 1929. The chemistry of these compounds provides for excellent heat conduction, low flammability, chemical stability and inertness. As such, PCBs saw widespread use as coolants and lubricants in electrical equipment such as transformers and capacitors (USEPA, 1013; Callahan, et al., 1983). In addition, PCBs were also used as coatings on electrical wiring and components, pesticide extenders, cutting oils, flame retardants, and hydraulic fluid providing the potential for many anthropogenic sources. Additional complications arise in PCB dispersal when considering different congeners of PCBs were used at different times and for different applications. For example, Aroclor 1260 and 1254 were predominately used in the U.S. prior to 1950, Aroclor 1242 was the primary mixture used in the 1950s and 1960s, and Aroclor 1016 has been the most widely used since the 1970s (UNEP, 1997). Overall, annual U.S. production peaked in 1970 with a volume on the order of 1.5 million tons (Voogt and Brinkman, 1989). Thereafter, PCB manufacture was ended in 1979 in the United States as evidence of its causing cancer in animals and humans (Tanabe, 1988).

All 130 of the commercially-used chlorine-biphenyl arrangements of PCBs share a generalized set of similar physical properties. They are odorless, tasteless and typically clear to slightly yellow and viscous. All PCBs share the characteristic of having very low water solubilities and low vapor pressures at room temperature, and have high solubilities in solvents, oils, and fats. This lipophilicity property of PCBs is attributed to the significant bioaccumulation in the food chain. Significant differences amongst the PCB congeners are usually attributed to the degree of chlorination of the biphenyls. Physically, the more chlorinated the congener of PCB, the more viscous and yellow-colored it becomes. Chemical differences as chlorination increases amongst congeners of PCBs include increasing melting point and lipophilicity and decreasing vapor pressure and water solubility decrease. As a result of the differential chlorination, lighter PCB congeners are much more apt to volatilize to the atmosphere than the heavier congeners. These properties provide for some confounding environmental behavior for scientists attempting to generalize PCBs as a whole. Despite the differences amongst individual PCB chemistries, their general presence can still be measured globally in various environmental media even though production and use of PCBs has been banned in many countries decades ago

(Muir et al., 2000; Xing et al., 2005; Macgregor et al., 2010). The transport, distribution, environmental behavior, and global fate of PCBs, is therefore of continuing concern.

As described above, PCBs can be linked to many aspects of anthropogenic presence. Since the start if its commercial manufacture, PCBs have entered into the environment from accidental spills during transport and handling, leaks from electrical transformers or other equipment utilizing PCBs as a coolant, or by incineration of wastes containing PCBs (Voogt et al., 1989; Rachdawong and Christensen, 1997). Also, redistribution of PCBs already in the environment has been shown to be a contributing source (ATSDR, 2000). Even though the production and use of PCBs has been discontinued in the United States, PCBs are still released during some industrial processes. It is known that PCBs may be formed whenever a carbon source and chlorine are combusted together, such as during municipal and hazardous waste incineration (Bergman et al., 1984; Brown and Ganey, 1995; Alcock et al., 1999). Accidental production is estimated to account for over 50 tons of PCBs released into the environment annually. The USEPA has identified 80 chemicals which have a production means prone to producing PCBs as a byproduct (Callahan et al., 1983).

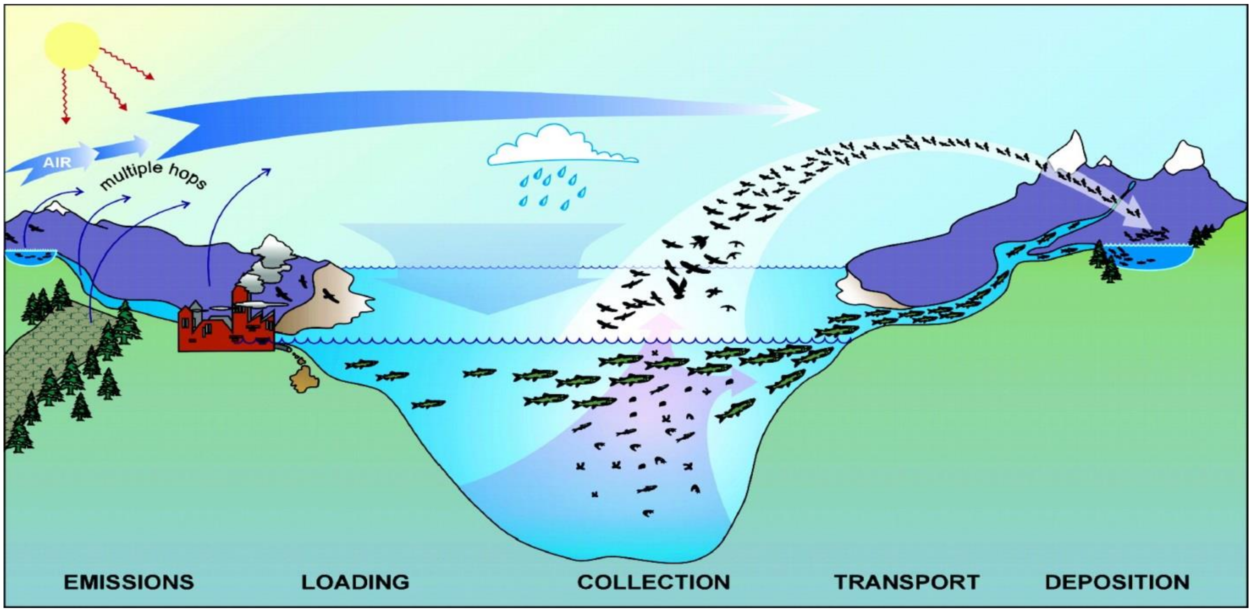


Figure 3.1: A schematic of the biologically mediated transport of PCBs to the inland lake ecosystem. Initially, PCBs are emitted into the environment from industrial, municipal, or agricultural regions into the atmosphere or directly to surface water bodies. Much of the PCBs in Michigan are transported by air to the Great Lakes where they can become widely distributed around the entire Great Lakes Region. Biota in the higher trophic levels of the Great Lakes ecosystem (including piscivorous birds and fish) bioaccumulate the PCBs primarily in fatty tissues. The wildlife then travels to inland where the PCBs are then deposited inland by delivery of fecal matter, molting, or mortality of the organism. From Blais et al., 2007.

Once released into the environment, the compositions of commercial PCB mixtures are altered through processes such as volatilization and other kinds of partitioning, chemical or biological transformation, and preferential bioaccumulation (Figure 1). The degree to which these processes occur is highly dependent upon the degree of chlorination of the biphenyl molecule. Generally, the lower chlorinated congeners of PCBs are more apt to volatilize to the atmosphere and are generally present in elevated concentrations relative to the higher chlorinated congeners, especially in northern latitudes (Halsall et al., 1999; Harner et al., 1998; Ockenden et al,. 1998). The more highly chlorinated congeners tend to adsorb more strongly to sediment and soil (Smith et al., 1990; Oliver and Niimi 1988). All PCBs rely upon the high bond strength of the carbon-chlorine covalent bond for its environmental stability and long half-life (8 to 10 years) (Hillery et al., 1997), particularly if buried in soil or sediment (Sinkkonen and Paasivirta, 2000). The most critical step in the decomposition of PCBs is the cleavage of this carbon-chlorine covalent bond. In lake sediments, this dechlorination usually occurs through hydrolysis or through reductive dechlorination of the compound.

In addition to the aforementioned carcinogenity, compounds in the PCB group share a structural similarity to, and toxic mode of action as, dioxin, with health effects such as endocrine disruption and neurotoxicity. Health concerns have served as the impetus for development in the understanding the sources, fate and transport of PCBs and has been the goal of many bodies of research since the 1970s accordingly (Schuster et al., 2011; Schuster et al., 2010; Wong et al., 1995; Hillery et al., 1997; Muir et al., 1996; Eisenreich et al., 1989; Murphy and Rzeszutko, 1977; Nisbet and Sarofim, 1972). PCBs history as an environmental contaminant begins in its first documented detection of fish in Swedish lakes (Jensen, 1966). Since this time, findings in the UK show that local urban sources cause PCB concentrations to be amplified 5-10 times compared to rural regions (Schuster et al., 2010; Sun et al., 2007; Totten et al, 2004). Other studies link environmental PCB concentrations specifically to more populace areas of the U.S. and decrease away from these locations (Shen et al., 2006; Golden et al., 1993). The same trend was also found in the European atmosphere with a general spatial trend showing a decline in concentration from high population density in the United Kingdom to low population density in Norway (Schuster et al., 2010).

In the Great Lakes region of the United States, research has shown that urban areas such as Chicago, Illinois and Milwaukee, Wisconsin serve as major sources of PCBs to the Great Lakes (Sun et al., 2007; Hafner and Hites, 2003; Buehler and Hites, 2002; Strandberg et al., 2001; Eisenreich et al., 1981). Also, most PCB inputs are shown to be locally sourced and atmospheric appears to be the dominant pathway for the transfer of PCBs from land to natural waters (Offenberg et al. 2005, Hoff et al, 1996; Sweet et al, 1993; Swackhamer et al, 1988;

Eisenreich et al. 1979, 1981). It was estimated that 55-90% of the PCBs entering Lake Superior, Huron, and Michigan and 7-13% of the PCBs entering Lakes Erie and Ontario come from atmospheric inputs (Hoff et al, 1996; Strachan et al., 1979, Strachan and Eisenreich, 1990; Eisenreich et al, 1979, 1981). PCB emissions in the Chicago atmosphere lead to dramatically increased atmospheric concentrations and deposition to southern Lake Michigan compared to the regional signal (Offenberg et al., 2005). This indicates that near urban areas, localized, urban sources are relatively more dominant than long-range atmospheric transport.

Due to the high degree of PCB emissions, the Great Lakes region of the United States has been closely monitored. From 1991 to 1997, studies have shown the change in atmospheric PCB concentration at the city of Chicago and Lakes Superior, Michigan, and Erie (Simcik et al. 1999). Gas-phase concentrations were found to have decreased in Chicago and near Lake Michigan and Erie, but remained fairly constant near Lake Superior. Inputs of PCBs to the Great Lakes region are influenced heavily by atmospheric transport and deposition (Franz et al. 1998, Jeremiason et al. 1998). A strong correlation between sediment accumulation of PCBs and dry deposition to Lake Michigan has also been observed and suggests that dry deposition may account for most of the particulate PCBs accumulating in the sediments of Lake Michigan (Franz et al. 1998).

In most research, PCBs appear in the sediment record around 1930 in the Great Lakes region, at the time they were first produced, and remain at very high levels between 1960 and 1980 (Helm et al., 2011; Hu et al., 2011; Golden et al, 1993; Eisenreich et al., 1989; Oliver et al., 1989; Rapaport and Eisenreich, 1988). This peak is followed by a decrease after 1980 when they were banned by the US government. Concentrations in soils and sediments have followed a downward trend over time and appear to have reached a steady state concentration in several locations (Bopp et al. 1998; Van Metre et al. 1998; Lead et al. 1997). Review of past water monitoring studies indicate that detectable concentrations of PCBs are widely found in surface waters but their low solubility generally prevents them from reaching high concentrations, especially in groundwater (USEPA, 1980). PCB concentrations have also been shown to be decreasing in surface water bodies since the late 1970s due to the cessation of production and manufacturing (Anderson et al., 1999; Jeremiason et al., 1998).

Lake sediment acts as strong sinks for chemicals like PCBs because of their persistence and hydrophobicity (Blais and Muir, 2001). As described above, lake sediment records the historical PCB concentration as the particles that they are absorbed to settle out and are deposited at the bottom of a lake and, therefore, provide an excellent means of determining a chronological sequence of deposition. However, these sediments also record both atmospheric inputs and inputs from the surrounding watershed and differentiating between these two inputs remain an issue. Much of the existing research includes collected and dated sediment cores with measured *total* PCB concentrations at different depths of the cores to construct temporal profiles of PCBs (Muir et al, 1996; Golden et al, 1993; Eisenreich et al, 1989). Studies of total PCB temporal profiles do adequately reflect the production and usage history of PCBs (Helm et al, 2011; Hu et al 2010; Golden et al, 1993; Eisenreich et al, 1989; Oliver et al, 1989; Rapaport et al, 1988) but in some cases fail to account for the differences in chemistry amongst the congeners.

The concentration differences through time among different lakes can utilize temporal profiles to include a spatial component to these studies. Around 1970, total PCBs concentration in Lake Superior sediment peaks at 15 ng/g while in Lake Ontario it peaks at 800 ng/g. The concentrations had then decreased to about 7 and 200 ng/g respectively in lake sediment dated approximately to 1990 (Golden et al., 1993). It has also been shown that the percentage of lower chlorinated congeners (tri to penta) decreased with depth, while hexachlorobiphenyls remained fairly constant throughout and the concentration of highly chlorinated congeners increased with depth (Oliver et al., 1989). It was determined that the deposition rate of PCBs from the atmosphere to the Great Lakes is approximately equal to the amount evaporating from the lakes to the atmosphere. This suggests PCB cycling in the Great Lakes ecosphere may have reached a steady state (Simcik et al., 2000). These studies of PCB sediment records in the Great Lakes have provided much in the way of understanding large-scale regional trends of these chemicals.

Studying inland lake sediment cores has the benefit of providing insight into the PCB inputs on a smaller scale, when observed on the individual lake basis. Also, data from a number of smaller lakes across a region can provide regional signals in the same vain as the Great Lakes studies when results from several lakes in proximity to one another are compared. This strategy has provided understanding in the behavior of many anthropogenically sourced trace metals (Parsons et al., 2007; Yohn et al., 2002). However, few studies have examined the spatial and temporal trends of PCBs using many inland lakes across a large region (Golden et al., 1993). The ability to examine the results of distinct PCB congeners on a large scale can provide insight into the composition of the emissions, which may be quite variable on a local scale (Wania and Su, 2004). Applications of such studies provide insight into global fractionation, which results in changes in the composition of persistent organic pollutant mixtures with latitude (von Waldow et al., 2010; Wania and Mackay, 1993) and PCB dechlorination, where more highly chlorinated congeners dechlorinate to lower chlorinated congener through time (Magar et al, 2005).

Hypothesis and Test

The hypothesis driving this research is that during the time of high PCB production (1970s) the influence of population centers on loadings will cause a localized spatial pattern in PCB distribution with elevated concentrations in watersheds occupied primarily by urban land use. With the prohibition of manufacture and use of these chemicals and with the direct evidence of a steady air concentrations of PCBs persisting in the Great Lake region to the present (Strandberg et al., 2001), it follows that recent trends should exhibit PCB loadings more reflective of a regional signal, with larger distribution gradients between available sources of the chemicals independent of watershed boundaries. Ancillary to this hypothesis is that congener data should provide a gradient across the State of Michigan with the heavier PCB congeners located more closely to primary sources in the southern, more populace end of the state, and the light PCB congeners primarily located in the northern portion of the state (Upper Peninsula).

To test these hypotheses, sediment cores from 44 inland lakes were collected from across the State of Michigan representing lakes within various land use, watershed characteristics, and trophic status. The sediment-chemical chronologies were studied in these cores. If the hypotheses is true, then: 1) total PCB inventories in Michigan inland lakes would show a south to north decreasing pattern due to larger population and more industries in the south, and would show a relatively higher PCB concentrations in the urban/industry area, 2) temporal PCB concentration profiles would show significant differences during high PCB production years among different lakes, with higher concentration near urban areas and lower concentration in the remote areas but the difference among lakes would become smaller in recent years, and 3) the relative abundances of the PCB congeners in sediment samples during the period of high production should show a characteristic change from south to north. This change would be evident during the high production period then in more recently deposited sediment, when loading and atmospheric mixing would work to reduce the intensity of the change.

Methodology

Sampling Methodology

The number of inland lakes in Michigan exceeds 11,000 (MIDNR, 2013) and lakes chosen amongst these for sediment sampling were based on a set of criteria including but not limited to: availability of boat access to the lake, sufficient depth to preclude significant bioturbation of sediment (generally lakes >25 feet depth), avoidance of lakes potentially mined for marl or had other significant sediment disturbances, and maximizing spatial range of the project. Sediment core collection was conducted using an MC-400 Multi-corer modified for inland lake use. This instrument was deployed from the M/V *Nibi* built to house the multi-corer and designed for access to shallow water entry and exit.

Once collected, cores intended for ^{210}Pb and metals analyses were extruded and sectioned at 0.5 cm intervals for the top 8 cm, and at 1 cm intervals for the remainder of the core. The ^{210}Pb analyses were conducted by Freshwater Institute in Winnipeg, Manitoba, Canada and determined porosity, accumulated dry mass, sedimentation rates, sediment ages and focusing factors. Dating models were verified using ^{137}Cs, the temporal peak of the stable ^{208}Pb concentrations and presence/absence of excess ^{210}Pb.

Another sub-core was sectioned and used for analysis of a suite of trace persistent organic pollutants (POPs) that included PCBs. Unlike the ^{210}Pb sub-core, it was sectioned at 2 cm increments for the entire core length to provide sufficient sediment mass for the required analyses. Several lakes sampled prior to 2003 were sampled again in subsequent years both in order to recover the POP analysis not described earlier and to provide a measure of quality assurance for other analytes (^{210}Pb, trace metals, and others). Lakes sampled twice include Lake Cadillac, Cass Lake, Crystal Lake (Montcalm County), Crystal Lake (Benzie County), Elk Lake, Gratiot Lake, Gull Lake, Higgins Lake, Muskegon Lake, Paw Paw Lake, and Whitmore Lake. For clarity, lakes with similar names will include an abbreviation of the county in which it is located (e.g., Round D, D for Delta County). Lakes that have been revisited will include the year of resampling (e.g. Gratiot07 is Gratiot Lake in Keweenaw County sampled in 2007).

Analytical methods for PCBs have been described elsewhere (Khim et al, 1999). Since a 2 cm sediment increment provided inadequate mass, equal amount of sediment from each sample were pooled in the laboratory to obtain adequate material representing each layer. A total of 40 g of wet sediment was then weighed and extracted for analysis. Moisture content was determined by drying 5 g of wet sediment overnight at 100°C. The sediment was homogenized with 120 g of anhydrous sodium sulfate and extracted with dichloromethane and hexane (3:1, 400 mL) in a Soxhlet apparatus for 16 hours. Extracts were then concentrated to 1 mL. The sample cleanup was done using an SPE cartridge packed with Florisil (Waters, Sep-Pak Florisil 6 mL). The cartridge was eluted with 10% acetone in hexane (9 mL). The eluent was concentrated to 1 mL and placed in gas chromatograph vial for analysis of PCBs. Di through Deca polychlorinated biphenyls were added as internal standards. PCBs were quantified using bracketed calibration generated by averaging two calibration curves that were run before and after each set of 10 samples to better adjust to changes in instruments during analytical runs.

Study Setting

Sediment cores were collected from 44 individual inland lakes from 1999 to 2010 (Figure 1) as part of the Michigan Department of Environmental Quality's (MDEQ) Inland Lakes Sediment Trend Monitoring program. As described above, 11 lakes were sampled twice which totals 58 separate sample events throughout the State of Michigan. Several lakes early in the project were not analyzed for POPs such as PCBs. The total usable sediment cores for this research then totaled 44 (Figure 2).

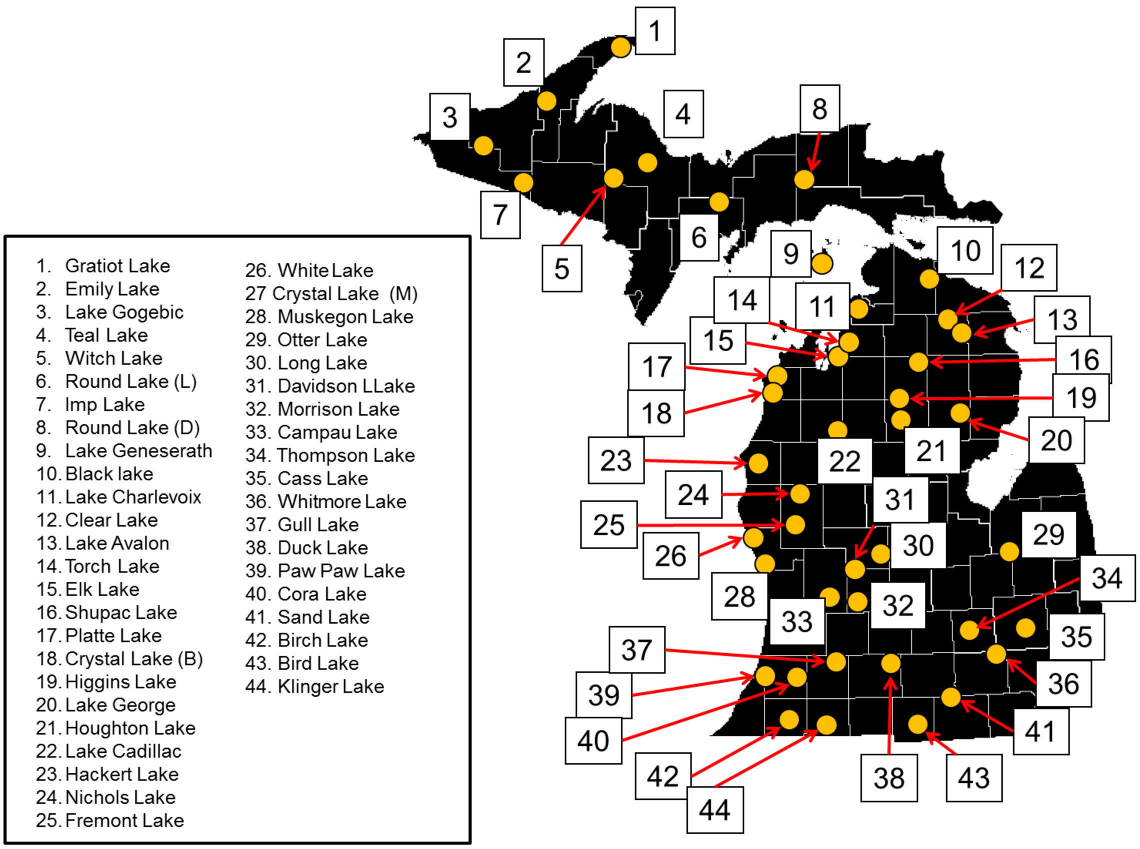


Figure 3.2: 44 lakes studied with full core subject to PCB analysis. Note that this is a subset of the 47 individual lakes cored total, 3 of which only top 4 cm were analyzed for PCBs.

Michigan covers 58,528 sq miles of which land takes up 56,954 sq. miles and inland water approximately 1,573 square miles. Sediment core collection ranged from lakes located along its southern border (e.g. Klinger Lake, Latitude: 41.80) to lakes located at its northern extent (e.g. Gratiot Lake, Latitude: 47.37). This wide geographic distribution of lakes sampled represents a variety of watershed land use types (Figure 2) ranging from largely urban near major cities (e.g. Cass Lake, Oakland County) to those that are remote with watersheds almost completely forested (e.g. Emily Lake, Houghton County). Further, lakes were sampled to represent a large range of physical characteristics. These include but are not limited to: physical size (depth, area), watershed size, proximity to Great Lakes, and trophic status. Table 1 (below) is included detailing a list of the lakes sampled and some physical characteristics for this research.

Land use data were obtained from the 2001 IFMAP/GAP Lower and Upper Peninsula data sets (MDNR, 2003) for the watershed of each study lake. Land use was classified using the upper-most level Anderson classification and resulted in 7 fundamental land use types: Urban, Agriculture, Forest, Barren, Upland, Water, and Wetland. Watersheds were delineated from the National Elevation Dataset (NED) 1 arc second digital elevation models (DEM), available from the USGS seamless website (USGS, 2008), using the watershed command in ESRI ArcGIS (ESRI, 2011).

Age Dating

The radioactive isotope ^{210}Pb was used to date sediments from each lake. Several models exist to determine sediment ages from ^{210}Pb activities, and sediments were dated using the constant flux: constant sedimentation rate model (CF:CS) (Golden et al., 1993), segmented CF:CS (SCF:CS) (Heyvaert et al., 2000), rapid steady state mixing model (RSSM) (Robbins, 1982), and the constant rate of supply model (CRS) (Sanchez-Cabeza et al., 2000). For all models, only sediment layers containing excess-^{210}Pb could be dated. The ages of sediment slices not containing excess-^{210}Pb were estimated by extrapolation using the assumption that sedimentation rates remain constant below the existence of excess ^{210}Pb.

Sedimentation rates in each lake were determined using all models possible for that lake, and then the models were evaluated to ascertain which was the most appropriate for determining sediment ages. Profiles of ^{137}Cs activity and stable lead concentration profiles were used as indicators to determine the most appropriate model (Robbins, 1978). Focusing factors were also determined from ^{210}Pb analysis. Sediment focusing occurs when fine-grained sediments in a lake are eroded from higher energy erosional zones near the shore of the lake, transported through transitional zones (where deposition and erosion occur episodically) and deposited in depositional zones (Downing and Rath, 1988; Hakanson, 1977). This process of focusing occurs to different extents among lakes, and must be accounted for by using the focusing factor before comparing inventories and accumulation rates among lakes. Focusing factors (FF) were estimated at each site from the ratio of unsupported ^{210}Pb inventory measured in the core to the ^{210}Pb inventory expected from atmospheric deposition (Muir et al., 1996; Golden et al., 1993).

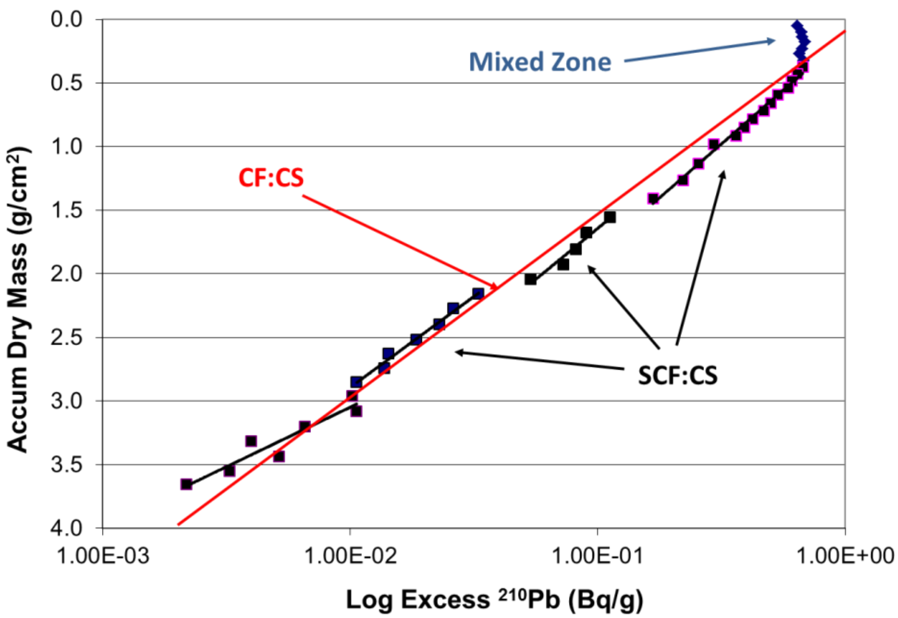


Figure 3.3. Log ^{210}Pb activity (Bq/g) versus accumulated dry mass (g/cm2) in Lake Gogebic. Regression lines for the CF:CS (constant flux-constant sedimentation) model and the SCF:CS (segmented constant flux-constant sedimentation) model are shown.

In addition to information regarding sediment age, rates of sedimentation and general quality of the sediment core can be determined from ^{210}Pb analysis. Results from lakes used for this study show no indication of significant disturbance in the sediment cores. However, results do indicate some sediment mixing near the surface of the core. The surficial sediment mixing is likely influenced by benthic organisms (bioturbation). This mixing zone is determined by plotting accumulated dry mass versus log activity of ^{210}Pb, where the slope is related to sedimentation rates. The non-linear portion near the surface is considered the mixing zone (Figure 3). The estimated mixed depth is listed in Table 1.

Results and Discussion

PCB Temporal Concentration Analysis

Due to the scale and scope of the Michigan Inland Lake Sediment Trends Project, lakes were considered in three groups based on Albert, et al. (1986, 1995) regional classification of Michigan (Figure 4). These lakes were grouped based on the relative homogeneity of climate and physiography identified in the landscape ecosystems. In their work, Albert, et al. (1995) had the Upper Peninsula separated into two distinct zones. However, since the amount of lakes meeting the depth and accessibility criteria needed to be utilized in this study were much less than those in the lower portions of Michigan, the Upper Peninsula here will be considered as a whole.

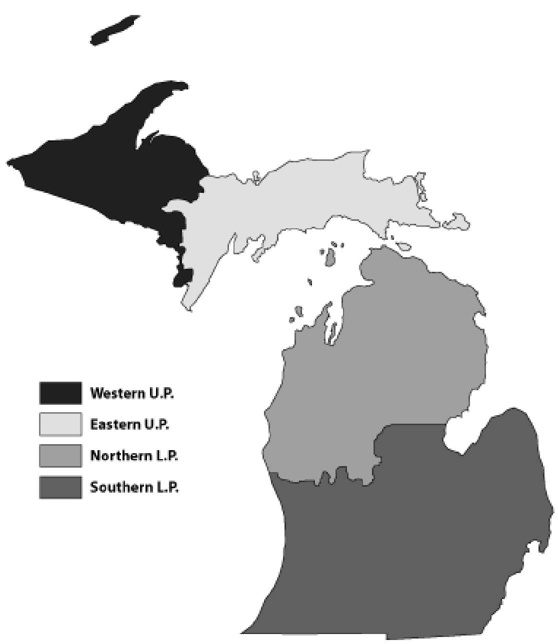


Figure 3.4: Terrestrial ecoregions framework as defined by Albert (1995). The separate Upper Peninsula ecoregions were considered together for this study due to the lack of suitable lakes meeting the criteria needed to qualify them for this project.

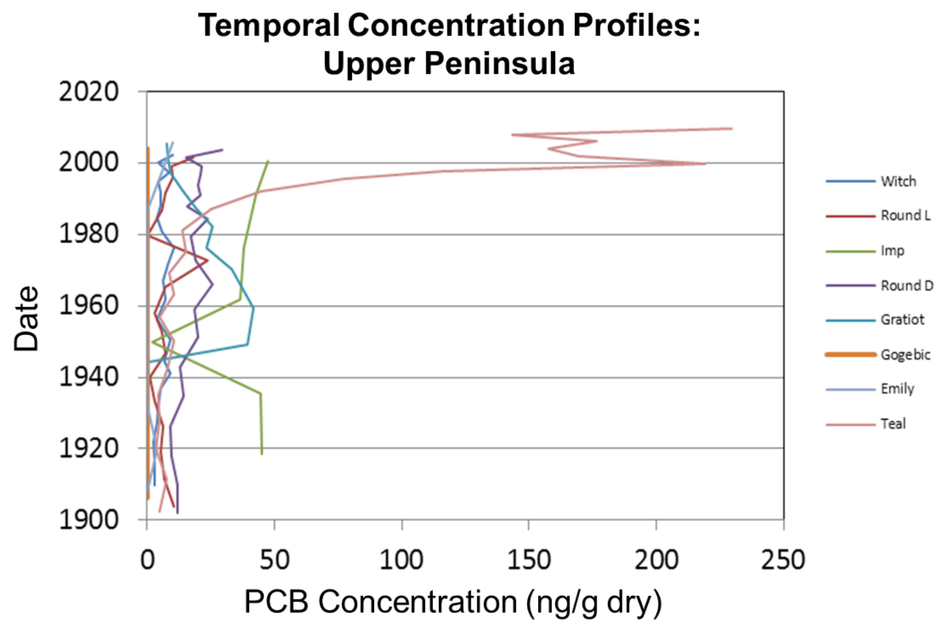


Figure 3.5a: Temporal Concentration Profiles of lakes in the Upper Peninsula of Michigan since the year 1900.

Lakes in the Upper Peninsula elicited PCB concentrations generally with temporal concentrations below 50 ng/g dry wt. The only exception is Teal, which has its highest value in the most recent sediment slice at 229.42 ng/g (Figure 5a). There appears to be no clear historical trend found in these lakes such as an increase to the time frame of peak production of PCBs followed by a decrease to recent sediments. Due to the remote locations of U.P. lakes, the sediment concentrations are assumed to be representative of uncontaminated ecosystems dominated by atmospheric deposition with the noted exception of Teal Lake, which has much more urban land use within its watershed than any other U.P. lakes studied. Land use for Teal was 27.01% and 20.01% urban in the 1970s and 1990s MiGDL data layers (respectively). The next largest watershed percent urban was Imp Lake with 7.14% 1970s and 3.46% 1990s.

Overall, the average concentrations of PCBs in U.P lakes are relatively low compared to lakes in the southern areas of the State and the most important decade for PCB deposition here is the 2000s (Table 2). Both the spatial remoteness of these lakes from significant sources and the number of years since the peak production and ban of PCBs points to atmospheric deposition is as being a significant source of PCBs in this region.

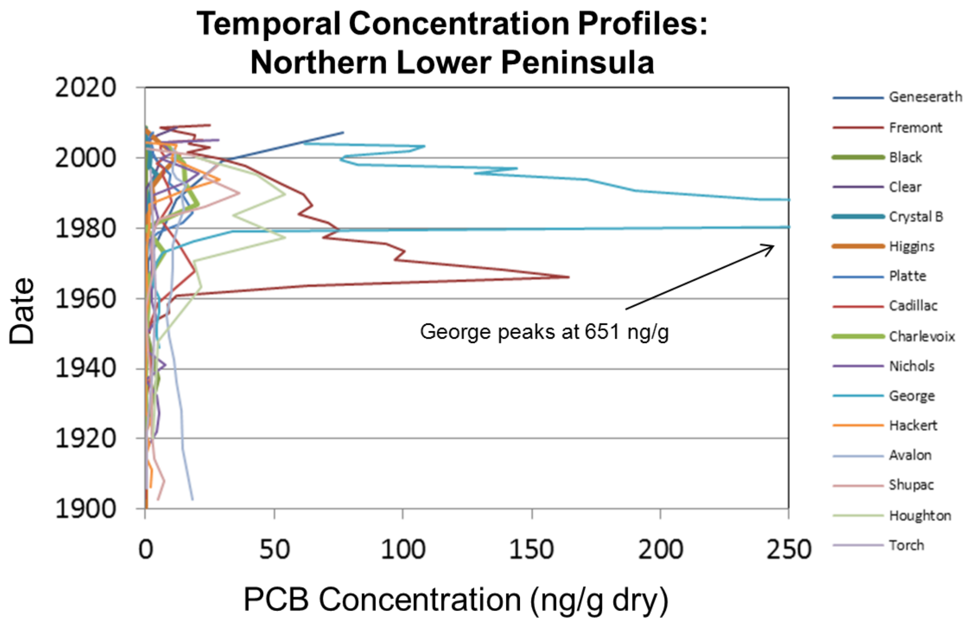


Figure 3.5b: Temporal Concentration Profiles of lakes in the northern portion of the Lower Peninsula since the year 1900. The peak of Lake George was not included for clarity of the lower concentration lakes.

In the northern portion of the Lower Peninsula, the temporal profiles vary significantly from lake to lake (Figure 5b). Like the Upper Peninsula, lakes here generally maintained values below 50 ng/g with the exception of George, Cadillac and Houghton. These lakes did have the presence of relatively elevated % urban watershed land use compared some many of the other lakes in this region (9.66%, 19.93%, 7.23% urban 1970s, respectively). However, many other lakes in this region with significant % urban such as Hackert (21.53%), Higgins (15.02%), and Fremont (20.46%) did not exhibit concentration peaks as large. Also, lakes in this region of Michigan appear to exhibit earlier peak trends relative to study lakes in the U.P. These trends are interpreted as being the result from closer proximity to source than the more remote lakes in the U.P.

It appears, in this region of Michigan, land use is either not one of the fundamental drivers of PCB loadings or one of several other contributing watershed or regional features serving as sources of PCBs to these lakes. Table 3 shows the lake sediment of lakes in this region to be, on average, lower than those lakes in the Upper Peninsula despite the proximity of larger urban centers (e.g. Traverse City, Alpena, etc.). It is believed that trophic status of the lakes in this region to play an important role in the sediment contaminant record. Lakes studied in this region such as Torch, Crystal (Benzie County), Clear, Higgins, Black, Elk and Charlevoix are all known to be oligotrophic (low water nutrient concentrations) (Fuller and Minnerick, 2008). Thus, the sediment is lacking much of the organic material PCBs would normally be adsorbed to. It is possible that this reduces the flux of PCBs to the sediment. The decadal block most important to deliver of PCBs to the sediment in this region is the 1980s. Since this is the decade after PCBs were prohibited, it is possible that the PCB signal in this portion of Michigan is derived from a combination of atmospheric deposition from sources further south and west along with point sources of PCBs in the individual watersheds.

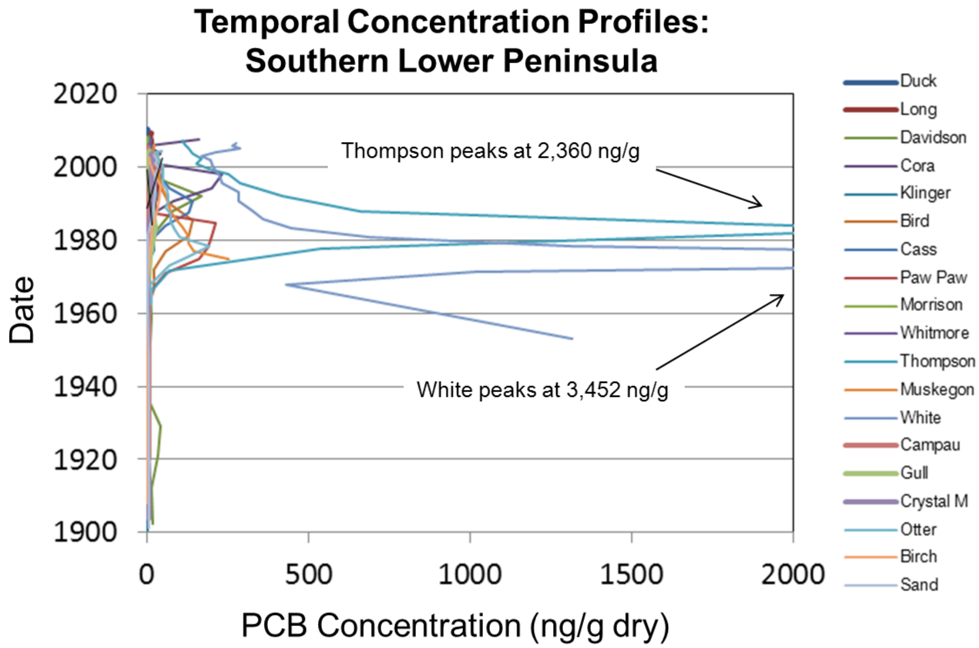


Figure 3.5c: Temporal Concentration Profiles of lakes in the southern portion of the Lower Peninsula since the year 1900. The peak of lakes Thompson and White were not included for clarity. Note the change in PCB Concentration scale of the X-axis relative to those of the Figures 3.5a and 3.5b.

The Southern Lower Peninsula region is characterized by significantly higher concentrations of PCBs than the lakes described above (Table 2). Much like the Northern Lower Peninsula region, these temporal trends do not appear to closely follow watershed land use as anticipated. For example, the two lakes with the highest concentration peaks, Thompson and White, at much different land use characteristics. Thompson had 1970s % urban calculated at 22.90% and White had the same land use calculated at 3.33%. If should be noted that White Lake has historically been an EPA Area of Concern and remediation steps have been taken to rid the lake of many contaminants contained in the sediment, including PCBs (MDNR, 2013; USEPA, 2013). Thus, it appears that PCB concentrations detected in lake sediment are more closely tied to particular industries that utilize the chemical than they are a particular land use.

Table 3.1: PCB concentrations of all study lakes averaged by decade and concentrations averaged by decade for each of the three regional zones. UP = Upper Peninsula, LP North = Northern Lower Peninsula, LP South = Southern Lower Peninsula. Values are normalized to peak concentration of the individual lakes for the table on the right.

Average Decadal Lake Concentrations (ng/g)

	All Lakes	UP	LP North	LP South
2000s	26.87	33.49	18.34	29.87
1990s	39.47	24.80	21.12	59.84
1980s	79.39	9.93	41.71	138.39
1970s	83.11	13.50	6.39	172.60
1960s	24.45	10.79	4.35	48.62
1950s	40.04	9.98	1.87	83.71
1940s	2.85	6.14	1.97	1.40
1930s	3.12	7.96	2.09	0.56

Decadal Lake Concentrations Normalized to Peak

	All Lakes	UP	LP North	LP South
2000s	0.31	0.60	0.36	0.14
1990s	0.41	0.47	0.46	0.35
1980s	0.37	0.30	0.40	0.37
1970s	0.26	0.38	0.17	0.27
1960s	0.23	0.31	0.27	0.16
1950s	0.11	0.32	0.07	0.04
1940s	0.10	0.22	0.10	0.01
1930s	0.11	0.21	0.17	0.01

Table 3.2: Focus-Corrected Accumulation Rates (ug/m2/yr) of all study lakes averaged by decade and concentrations averaged by decade for each of the three regional zones. The highest value in each category is colored grey. UP = Upper Peninsula, LP North = Northern Lower Peninsula, LP South = Southern Lower Peninsula.

	AVERAGE	UP	LP North	LP South
2000s	0.64	0.84	0.32	0.82
1990s	0.63	0.70	0.33	0.87
1980s	0.93	0.89	0.55	1.29
1970s	1.39	0.43	1.06	2.07
1960s	1.41	0.25	0.51	2.82
1950s	1.09	0.12	0.59	1.90
1940s	0.45	0.14	0.08	1.10
1930s	0.09	0.22	0.04	0.04

Table 3.3: Focus-Corrected PCB Inventories (ug/cm2) of all study lakes averaged by decade and concentrations averaged by decade for each of the three regional zones. Highest value in each category in grey. UP = Upper Peninsula, LP North = Northern Lower Peninsula, LP South = Southern Lower Peninsula.

	All Lakes	UP	LP North	LP South
2000s	4.47	8.24	2.10	4.88
1990s	6.33	6.51	3.30	8.80
1980s	8.72	7.47	5.46	11.99
1970s	14.05	2.78	11.25	21.15
1960s	15.37	2.83	4.46	30.66
1950s	12.18	1.12	5.26	23.90
1940s	10.67	1.47	0.63	25.30
1930s	1.36	2.43	0.44	1.72

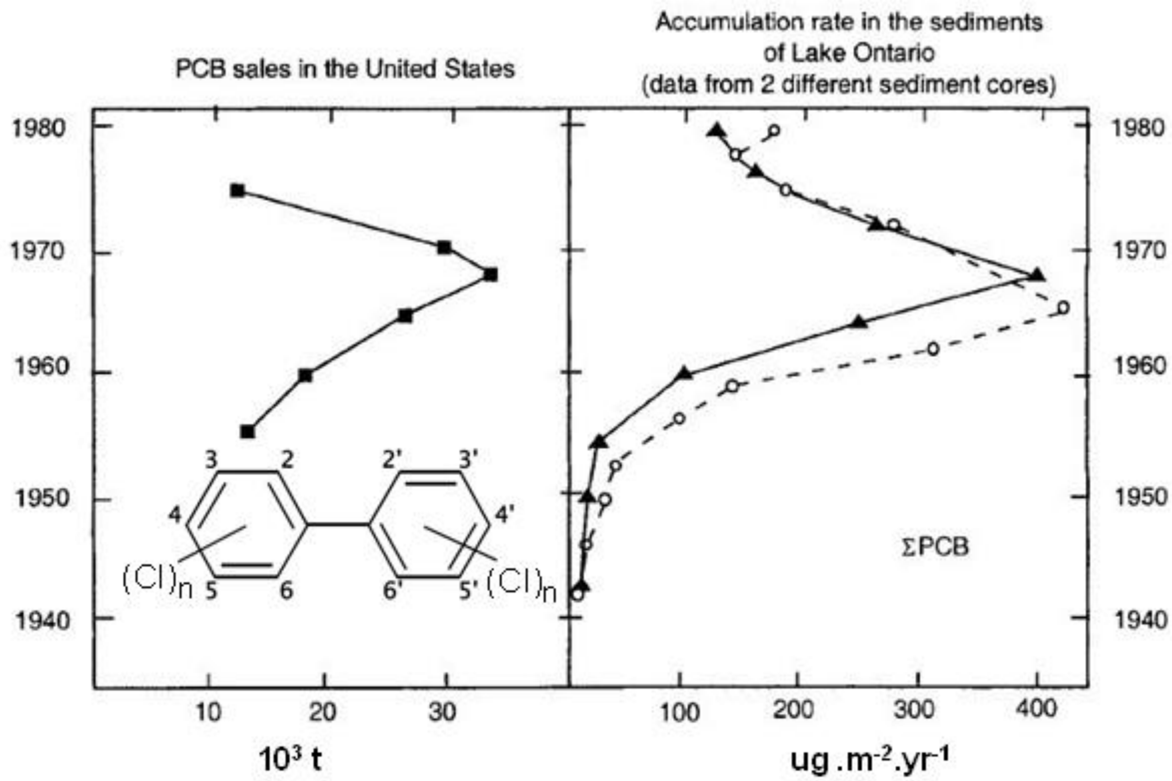


Figure 3.6: Historical records of the sales/production volumes of PCBs and the similarity of these time-varying trends to the accumulation rates of these chemicals in the sediments of Lake Ontario (from Eisenreich et al., 1989)

The decadal averages of these lakes exhibit average concentrations to be greatest in 1970s, closest to the peak U.S. sales of these chemicals as described by Eisenreich et al, 1989 (Figure 6). This is probably due to the fact that the lake watersheds of the Southern Lower Peninsula region are generally more populace and closer to the sources of PCBs for both point sources and regional atmospheric deposition. However, on an individual basis, Michigan inland lakes only occasionally appear to have recorded a clear signal of U.S. sales of PCBs as seen by Eisenreich et al., 1989 in the Great Lakes.

Care should be taken when comparing concentrations of organic contaminants among lakes. Due to the low amount of sediment in the top-most sections of the core, the top two slices were combined, and slices 3 and 4 were combined, to create two samples. As a result of combination and variable sedimentation rates among lakes, each sample represents a range of deposition years. For example, Lake Geneserath (sampled in 2010), had an extremely low sedimentation rate for much of the described core. Thus, the surficial sediments represented a larger range of sediment ages and might be expected to have higher concentrations of PCB contamination than Cass Lake, which had a much higher sedimentation rate (sampled in 1999).

As Michigan hosts inland lakes with a wide range of trophic status, watershed sizes, and morphologies, sedimentation rates are quite variable. Many of the nutrient-poor, oligotrophic lakes reflect low sedimentation rates such as Clear Lake with a sedimentation rate of 294 g/m^2/yr. Conversely, other lakes, typically eutrophic in nature, exhibited elevated sedimentation rates such as Morrison Lake with a sedimentation rate of 2,590 g/m^2/yr. (See Fuller and Minnerick, 2008 for Michigan lake trophic classifications).

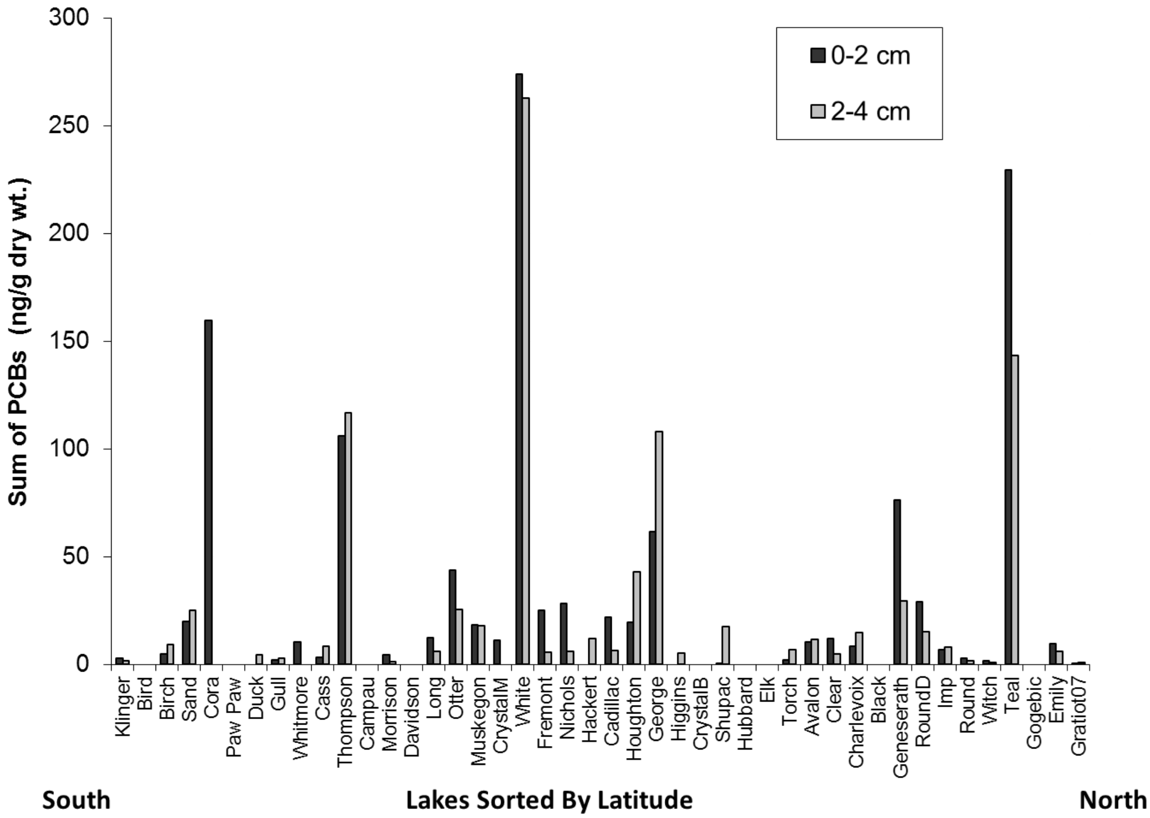


Figure 3.7: Sum of PCB congener concentration (ng/g dry wt) in surficial sediments of inland lakes across Michigan organized by latitude.

Due to the wide range of sediment accumulation within these lakes, it is difficult to draw conclusions simply from examination of surficial sediments.   As expected, PCB totals measured in the top 4 cm allowing for graphical comparison of all 44 sample events show a wide range of PCB total concentrations (Figure 7). This is reflective of the rate at which the lakes are accumulating both sediment and the actual contaminant under study. A more adequate assessment of PCB impacts to a surface water body may be in its accumulation rate or total inventory of the PCB quantity. PCB accumulation rate accounts for the sedimentation rates and sediment focusing while PCB inventories measure the total quantity of PCBs per unit area. These measurements and how they are calculated are described further in the *PCB Accumulation Rate Analysis* and *PCB Inventory Analysis* below.

PCB concentrations in the top portion of sediment are of special concern as they provide an estimation of the amount of PCBs potentially available for redistribution (i.e., are not permanently buried) into the water column by sediment-water exchange (as described by Wong et al, 1995). Surficial sediments are of also much more directly accessible to benthic biota, and thus, the remainder of the aquatic food web. The PCB surficial concentrations appear quite variable across Michigan with elevated quantities found as far south as Cora Lake (latitude 42.20) and as far north as Teal Lake (latitude 46.51). There does not appear to be a significant latitudinal trend associated with the distribution of elevated PCB concentrations and lakes exhibiting high surficial concentrations maybe receiving continued inputs from watershed sources. Comparing the 0-2 cm core slice and the 2-4 cm core slice in most of the impacted lakes (such as Cora, Teal, and White Lakes) show increasing trends of PCB concentrations to the surface sediments.

White Lake in particular is anticipated having elevated values of PCBs throughout its core as it has been listed as an EPA Area of Concern since 1985 (EPA, 2013[4]). The Occidental (Hooker) Chemical Company and the Whitehall Leather Company were the primary sources of contamination and measures were taken to remove sediments associated with the two contaminant "hot spots" in 2002. A variety of organic chemicals has historically been discharged to White Lake including PCBs.

Examination of PCB concentrations to the maximum depth of the cores (approximately 40 to 60 cm) usually provides the entire PCB temporal history of the given lake. The only exceptions of are those lakes with high sedimentation rates. High sedimentation rates prevent the recovered sediment from the coring device from reaching the lakes "background" values (i.e. prior to anthropogenic disturbance) and a longer (deeper) core is needed. The "Oldest Section" column of Table 1 illustrates this by noting the ^{210}Pb determined date of the deepest recovered sample in the given lake.

Averaging decadal concentrations for the entire database reveals that the most significant increases occur in lakes from 1940s to 1950s and from 1960s to 1970s. The historic peak is then observed, on average, to occur in the 1970s as expected with a significant average concentration following into the next decade. This could be representative of the lag time of soil and waterborne PCB inputs into the environment during the 1970s (again, PCBs were banned in 1979), continued input of PCB containing equipment and unlined landfills, and continued atmospheric rainout of extra-watershed PCBs. This is followed by recovery to the present possibly due to the removal of most sources and the continued breakdown released PCBs. Finally, it is noted that trace concentrations of PCBs appear to exist in the years prior to its starting use. This could possibly be attributed to the smearing effect occurring upon corer insertion into the benthic sediments. However, measures are taken during field sampling to remove sediment in direct contact with the coring tube and the coring tube assembly is cleaned between lakes. The field methodology designed to prevent this makes these early detections seem improbable. Post-depositional mobility of the PCB compounds offers another possibility for their early detections. The PCB concentrations found in sediment dated to earlier than 1930 were comprised primarily of the less chlorinated or “lighter” and thus more mobile, fraction of the PCB congeners.

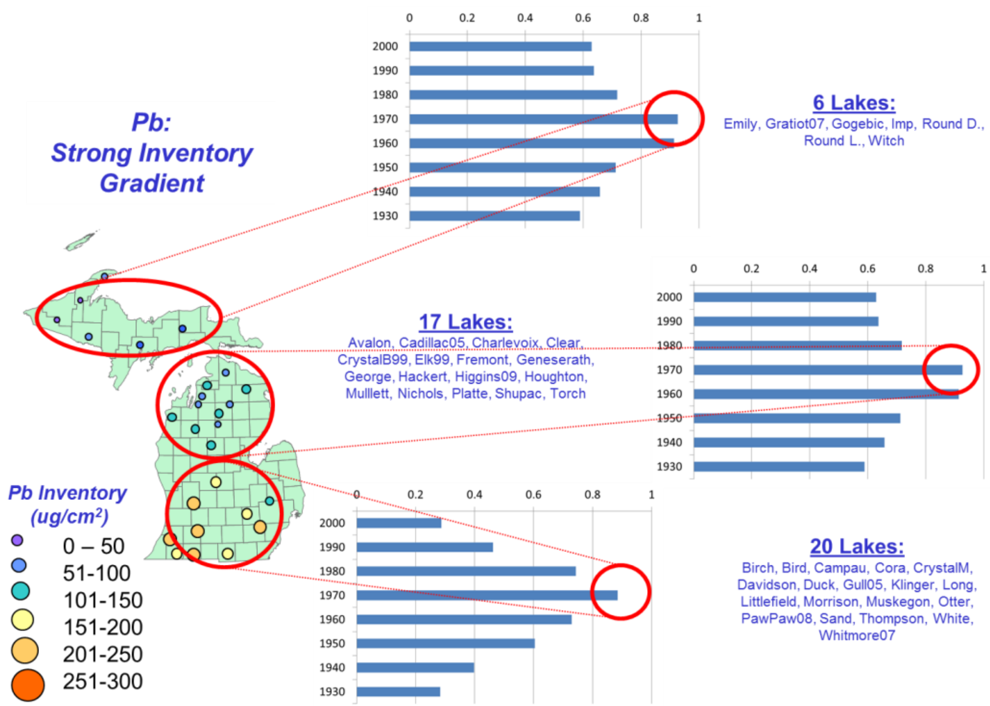


Figure 3.8: Comparison of averaged ^{210}Pb dated decadal block of normalized Pb concentrations from 1930s to present in three physiographic zones described by Albert et al., 1995. Note: not all lakes were available for Pb inventory analysis as it requires recognizable background (reference) trends of Pb which are not recognized in several cores.

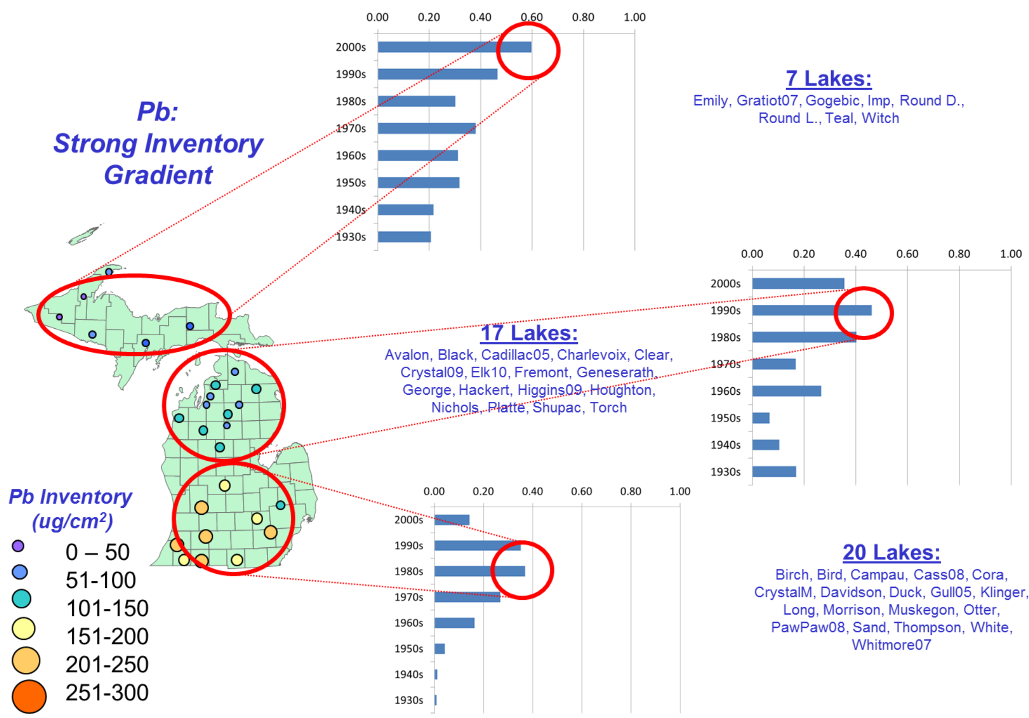


Figure 3.9: Comparison of averaged ^{210}Pb dated decadal block of normalized PCB concentrations from 1930s to present in three physiographic zones described by Albert et al., 1995.

PCB spatial trends are compared to lead (Pb) inventories to examine correlations in their spatial distribution. Pb inventories are calculated by combining the total sediment abundance of Pb per unit area (i.e. by considering vertically integrated sediment inventories). Corrections are applied to the Pb inventories to account for the watershed erosional inputs and sediment focusing (Discussed in *PCB Inventory Analysis* below). This allows for conclusions to be drawn about the anthropogenic-specific quantity of Pb atmospherically deposited to each lake. Work on trace metals distribution and histories in Michigan lakes show that lead (Pb) inventories across Michigan can be roughly divided into three separate zones (Vannier et al., 2013). These zones coincide with the three climate and physiographic zones as described by Albert et al., 1995 (Figure 4). Given the known sources of Pb to the environment, anthropogenic inputs to Michigan surface water bodies are more likely related population densities. The southern-Lower Peninsula zone is the most populous area of the State and contains the most elevated Pb inventories, the Upper Peninsula the lowest, and the northern half of the Lower Peninsula has Pb inventories generally between these two (Vannier et al., unpublished data).

As shown in Figure 8, despite relative latitude or Pb inventory, Pb concentrations peak in the 1970s. This is attributed to the effectiveness of environmental legislation (e.g. Clean Air Act, Clean Water Act) as this period coincides with the time these major legislative bodies were enacted. However, comparing inventories to the peak PCB concentration dates in these lakes reveals a gradient from south to north, with the normalized average PCB concentration in each zone tending to peak earlier in the south than in the northern extents of the State (Figure 3.8).

If the PCB distribution is driven by direct atmospheric deposition to the northern latitude lakes, the profiles of these lakes should follow the PCB sales history with an observable peak in the late 1960s. However, lakes in the northern extents of the State have a tendency to peak in the most recent decade and could be interpreted as evidence for secondary deposition of PCBs from its primary source locations (near populace areas) to more remote locations (e.g. Upper Peninsula, Michigan). This was hypothesized by others (Wania and Dugani, 2003; Wania and Mackay, 1995, 1996) that a gradual movement of PCBs northward, caused by temperature-dependent partitioning results in elevated PCB concentrations in relatively recent surficial sediments (dated to 1980s and early 1990s). Hassanin et al., 2005 also observed decreasing percentages of lighter congeners with increasing latitude while the opposite is true for heavier congeners. Such observations have been explained by the global fractionation theory (Wania and Mackay, 1995).

In general, spatial and temporal total PCB concentration results correspond well with previous reports (Hu et al., 2010; Golden et al., 1993; Eisenreich et al., 1989; Rapaport et al., 1988). The low PCB concentrations in Lake Superior which is close to the Upper Peninsula reflect atmospheric inputs and the higher concentrations in Lake Michigan and Ontario reflect regional and localized atmospheric deposition (Golden et al., 1993).

PCB Accumulation Rate Analysis

Accumulation rate of PCBs in the sediment cores were calculated as follows:

$$Accum(ng/cm^2/yr) = C_{sed}(ng/g) \times W(g/cm^2/yr)$$

Where *Accum* = PCB accumulation rate (ng/cm^2/yr),
C_{sed}= concentration of PCB in surficial sediment (ng/g dry wt), and
W= mass sedimentation rate (ng/cm^2/yr) based on ^{210}Pb dating results.

Accumulation rates of PCBs were then corrected for sediment focusing which is calculated as raw accumulation rate / ^{210}Pb determined focusing factor. Focusing factor is the calculated ratio of the unsupported, or atmospherically derived, ^{210}Pb inventory to the expected 210Pb inventory (Eisenreich et al., 1989; Simcik et al., 1996). It is a positive, unitless ratio accounting for the tendency of lake sediment to become redistributed from shallow portions of the lake (via wind or water movement energy) to the deeper portions of the lake (after Golden et al., 1993). Simcik et al. (1996) selected 15.5 picocuries cm^{-2} as the expected value for the entire region. This concept was used in studies of eastern Lake Ontario sediments (Eisenreich et al., 1989) and Lake Superior sediments (Jeremiason et al., 1994). In this work, the value selected by Simcik et al. (1996) is used to retain uniformity in all lakes studied. As sediment focusing at the point of maximum depth where the samples are collected always results in a net gain of material and, when the correction is applied, the concentration is less than raw value.

Figure 10 and 11 illustrates the general reduction in the rate at which inland lakes in Michigan are accumulating PCBs since the 1970s: the averaged focusing corrected accumulation rates for sediment in the 1970s vary from approximately 0 to 9 ng/cm^2/yr (average 1.33 ng/cm^2/yr). In the 2000s, these values have been reduced to 0 to 5 ng/cm^2/yr (average 0.63

ng/cm^2/yr). This reduction is expected as the 1970s accumulation rates encompassed the production peak year (around 1970). It appears from these figures that atmospheric fallout is the primary pathway of PCBs to most lakes in the northern extents of the State. This is concluded due to the relatively low watershed populations, the general remoteness of the lakes (e.g. low % urban), and the similarities between lake accumulation rates as one would expect from a mixed atmospheric signal. This is considerably less than those lakes located along the more populace latitudes to the south giving indication of point-source or sub-regional PCB pollution providing a significant quantity PCB to these lakes, both historically and in the present. It also appears that atmospheric fallout of PCBs hasn't decreased substantially in many lakes as lakes in the extreme southern and northern extents of Michigan are receiving nearly as much (in some cases more) PCB inputs currently than they have been in the 1970s.

As with the spatial analysis of PCB concentrations, PCB accumulation rates also follow a general trend of peaking temporally later as latitude increases (Table 3.3). This is consistent with the interpretation that the observed trend is a result of distillation of PCBs evaporating and condensing at higher latitudes due to temperature differences. It is also possible that this effect represents the lag time between the deposition of atmospherically derived PCBs to the watershed and the hydraulic washing of the chemicals to the lake sediment. However, watersheds of the lakes studied in the Upper Peninsula average to be much smaller than those of the Lower Peninsula (approximately 170 sq mi versus 54 sq mi), thus, it would be anticipated that the lag time effect would be reduced compared to those lakes in lower Michigan.

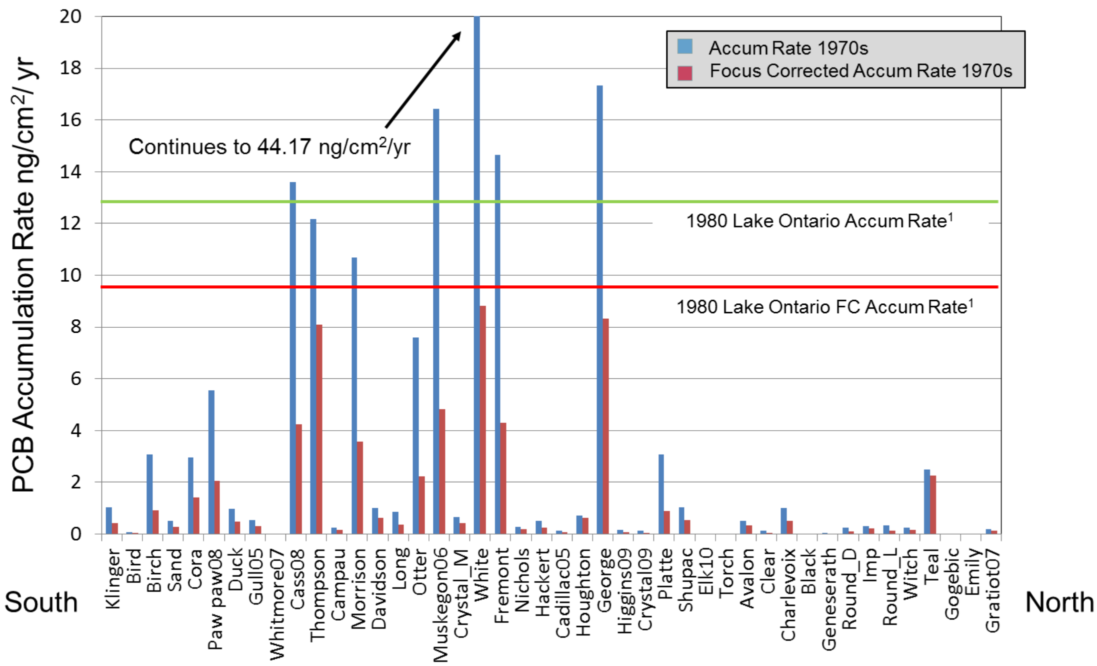


Figure 3.10: 1970s PCB Accumulation Rates for all lakes organized by latitude. White Lake peak removed for clarity.
[1]: From Eisenreich et al., 1989.

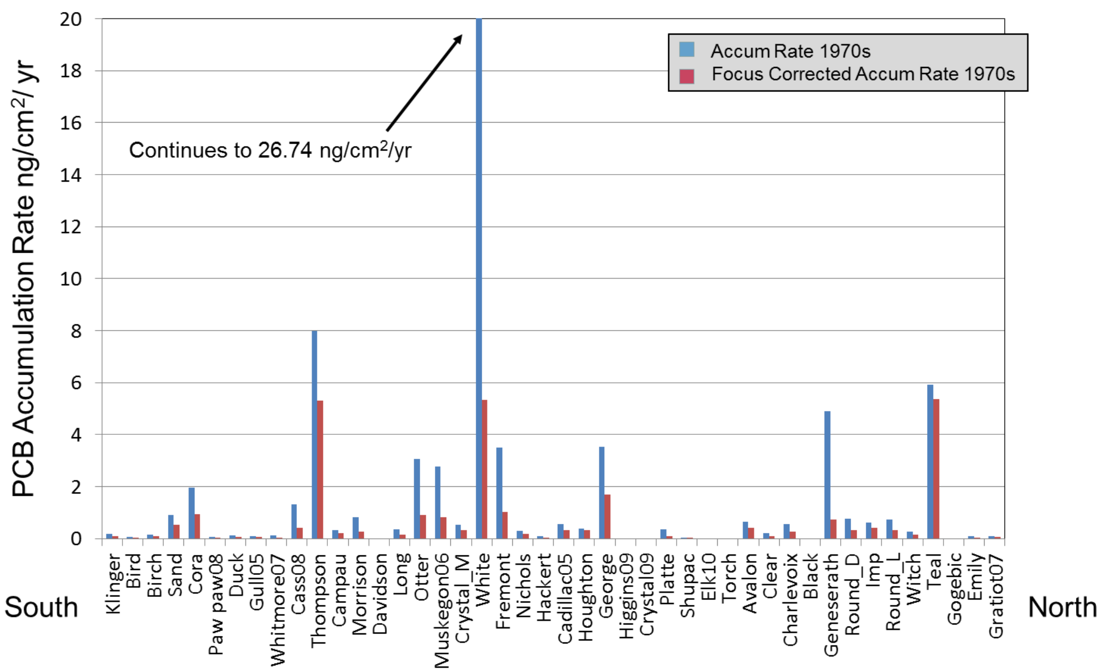


Figure 3.11: 2000s PCB Accumulation Rates for all lakes organized by latitude. White Lake peak removed for clarity.

PCB Inventory Analysis

PCB inventories are calculated by combining the total sediment abundance of PCBs per unit area (i.e. by considering vertically integrated sediment inventories). Similar to both concentrations and accumulation rates of PCBs, the inventories vary significantly amongst the lakes. Inventories of PCBs in sediment cores were calculated as follows:

$$Inv(ng/cm^2) = \sum_i [C_{sed}(ng/g) \times (1-\varphi) \times \rho(g/cm^3) \times d(cm)]$$

Where Inv = total PCB dry mass in a core (ng/cm^2),
C_{sed} = sediment concentration,
ϕ = porosity,
ρ = bulk density,
d = thickness of sediment increment.

Focusing-corrected inventories were calculated as sediment PCB inventories divided by the ^{210}Pb calculated focusing factor. Focusing-corrected PCB inventories represent the historical sum of all PCB loadings to a given lake per unit area. The advantage of utilizing inventories in this study is that, unlike raw concentrations or accumulation rates, inventories integrate the whole core thereby removing the influence of sediment slice thickness and errors in sample dating. However, even with the focusing corrections, the inventories from the southern to the northern extent of Michigan in the lakes studies show results similar to those of the 2000s PCB accumulation rates (Figure 3.11). Peaks are noted in several of the lakes with significant urban land use in the watershed (e.g. Thompson, Teal, and Muskegon). A few lakes are noted as having elevated inventories but very low recent accumulation rates (e.g. Teal) indicating that historical inputs of PCBs to the lake are much greater than current inputs. The reverse is true comparing Cora where inventories of PCBs are relatively low compared to other lakes but accumulation rates are relatively high. This is a result of recent trends in Cora for PCB accumulation rates being elevated but, historically, PCBs do not appear to have impacted the lake significantly.

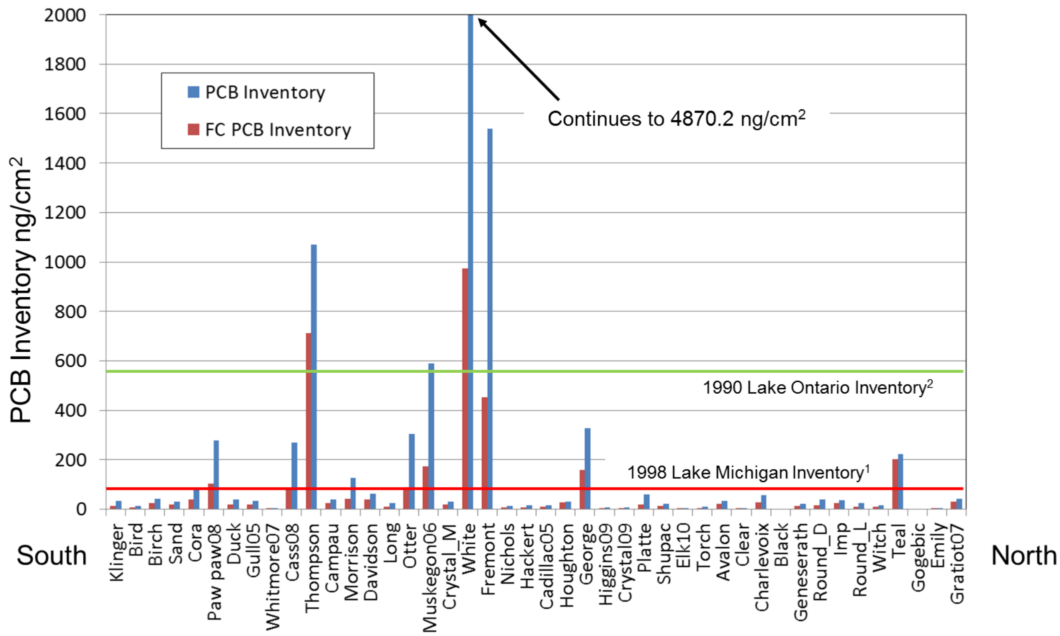


Figure 3.12: PCB Inventories in all lakes organized by latitude. White Lake peak removed for clarity. [1]: From Schneider et al., 2001; [2]: From Pearson et al., 1997.

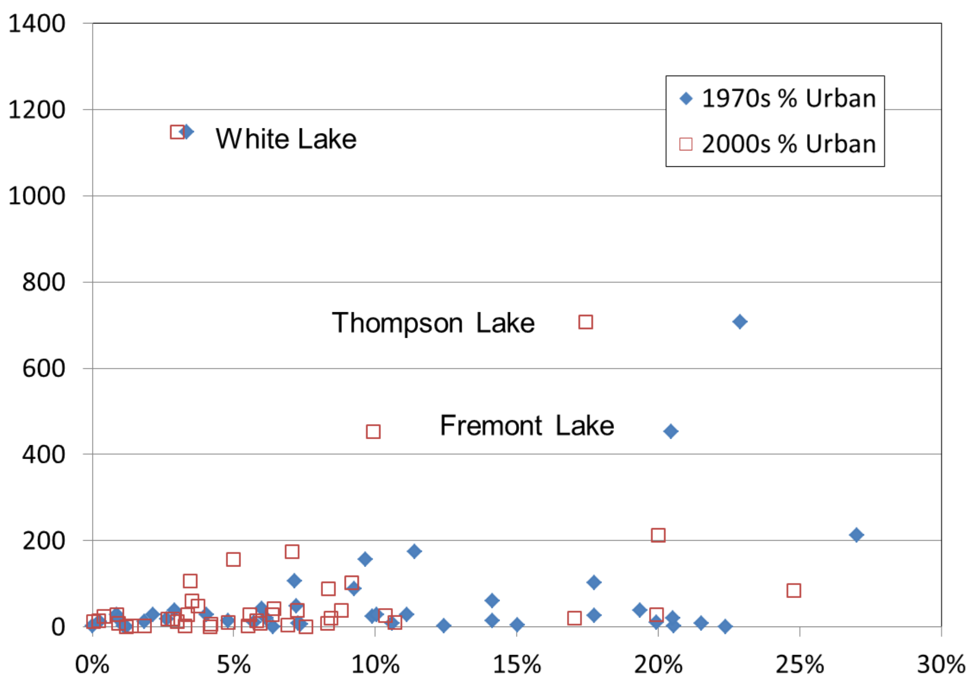


Figure 3.13: Focusing-Corrected PCB Inventories versus watershed % urban in the 1970s and 2000s. The top three study lake PCB inventories are labeled illustrating the PCB inventory independence of % urban.

Residential neighborhoods have been shown to account for more than 70% and 45% of PCB spills from transformers and capacitors (respectively) and industrial areas approximately 14% and 29% (Voogt and Brinkman, 1989). Other studies have linked environmental PCB detections with various anthropogenic activities (Breivik et al., 2002) and atmospheric PCB studies have clearly shown ties to urban land use (e.g. Hafner and Hites., 2003; Harner et al., 2004; Jaward et al., 2004). This study appears to reflect these finding as sedimentary PCB inventories and accumulation rates match of the lake watersheds occupied with high % urban land use exhibited elevated PCB inventories or accumulation rates. Teal Lake, for example, was determined as having approximately 27% urban land use in the 1970s and approximately 20% in the 1990s. This watershed was much more urban and had higher PCBs inventories than any other in the Upper Peninsula of Michigan. The correlation between urban land use and elevated PCB inventories and accumulation rates also appears to carry through with Paw Paw, Cass and Thompson lakes (17.75%, 61.97%, and 22.90% 1970s urban, respectively). However, the correlation weakens between watershed % urban and elevated PCB values weakens in some lakes such as White Lake, the most impacted lake studied but with little 1970s watershed % urban (3.33% 1970s urban). Others lakes with elevated PCB accumulation rates and inventories but relatively low % urban include Otter, Muskegon, and George (9.26%, 11.40%, and 9.66% 1970s urban respectively). Figure 3.13 is shown to illustrate the low correlation between % urban land use and PCBs in the lakes studied both historically (1970s) and recently (2000s).

Clearly, point sources of PCBs continue to play a significant role in the accumulation of PCBs both historically and in the present. For example, White Lake is known to be and Environmental Protection Agency Area of Concern originally due to organic solvent contaminated groundwater migrating to the lake from the Occidental Chemical Site (formerly

Hooker Chemical Company) along with eight other sites affecting the lake with contamination. (MDEQ, 2013; USEPA[3], 2013). On the other hand, atmospheric fallout from extra-watershed sources must play a significant role as well with many lakes containing measurable PCBs in their sediment with relatively low % urban land use (e.g. Morrison Lake, 6.00% 1970s urban land use). Further, focus-corrected PCB inventories of each decadal time block were calculated and presented in Table 3.4. Much like the sediment accumulation rates of PCBs, a temporal stepwise inventory peak proceeds from the southern portions of Michigan (closer to potential source) to the much less populous Upper Peninsula.

PCB Congener Analysis:

The term "polychlorinated biphenyl" is actually a generalization for a class of compounds manufactured in a similar fashion through progressive chlorination of biphenyl. With few exceptions, PCBs were manufactured and sold as mixtures that may contain as many as 70-100 PCB congeners. A PCB congeners is any single, uniquely defined chemical in the PCB category (EPA, 2013[2]). The name of a given congener specifies the total number of chlorine atoms that are attached to the biphenyl rings. For example, dichlorobiphenyl is a congener with two chlorine atoms. There are 209 individual PCB congeners, most of which contain from one to ten chlorine atoms. Total concentration of PCBs is simply the sum of the congeners for each sample. The compositional data of an individual sample is the term used to describe the concentrations of the individual congeners

PCBs were manufactured under the common name "Aroclor" by the Monsanto Corporation, the single largest producer of the chemical in the United States. In general, each PCB is assigned a four digit number detailing the number of carbon atoms in the phenyl rings (first two numbers) followed by the percentage of chlorine by mass in the mixture (last two numbers). For example, Aroclor 1254 is a PCB mixture containing 12 carbon atoms and is 54% chlorine by weight. To simplify, the nomenclature used herein will include the PCB congener chemical name without the position indication of the chlorine atom. For example, 4,4'-Dichlorobiphenyl will simply be noted as 'dichloro' or simply 'di' indicating a biphenyl structure with two chlorine substituents. The importance of identifying individual PCB congeners lies in the differences of their physical/chemical properties. Their varying degree of chlorination effects properties such as solubility, vapor pressure, Henry's law constant, and the tendency to sorb to particles can cause significant differences in environmental behavior between individual congeners (Mackay, 2010; Hites, 1987). PCBs also vary in their susceptibility to dechlorination which has the potential to complicate PCB trend interpretation and source identification. Some long-term studies of contaminated sediments have shown specific bacterial groups to transform particular PCB congeners in a distinctive dechlorination pattern (Brown et al., 1987; Brown et al., 1984). Often, instead of completely deconstructing the PCB molecule, bacterial-mediated dechlorination will work to create less chlorinated congeners from PCBs as chlorines are selectively removed. However, this process depends heavily on site specific conditions and overall chemistry of the individual PCBs present (Bedard and Quensen, 1995), preventing easy generalization of degradation trends.

In general, meta-substituted chlorines are dechlorinated more readily followed by para-substituted chlorines. The presence of chlorines adjacent to one another (i.e., "flanked" meta- and para-substituted chlorine) increases the susceptibility to dechlorination. A double-flanked meta-substituted congener (i.e., with also a chlorine in the adjacent para- and ortho-positions) is particularly susceptible to dechlorination of the chlorine in the meta position (Klasson and Just, 1999; Karcher et al., 2007). The most heavily chlorinated PCB congeners (e.g., hepta-, octa-, nona- and deca-chlorobiphenyls) tend to be less susceptible to dechlorination than the less chlorinated congeners (e.g., tri-, tetra-, penta-, and hexa-chlorobiphenyls) (NAVFAC, 2012).

The relative distribution of the individual PCB congener concentrations in a given sediment sample or suite of samples can be used to develop a PCB “fingerprint“. Applications of fingerprinting PCB composition to reconstruct the original source fingerprint have been successful in the Magar, et al. 2005 work examining PCB contaminated sediements at the Lake Hartwell Superfund Site. However, only the recent sediment resembled that of the known source and deeper sediment was found to be significantly dechlorinated and no longer resembled the known source mixtures. Given the differential rates of dechlorination of individual congeners, the data used for this project could not be used in that capacity, especially given the likelihood of multiple sources of the compounds into the environment.

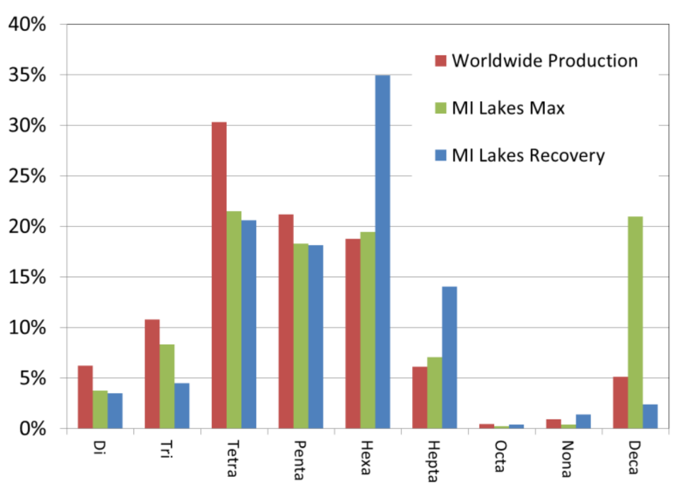
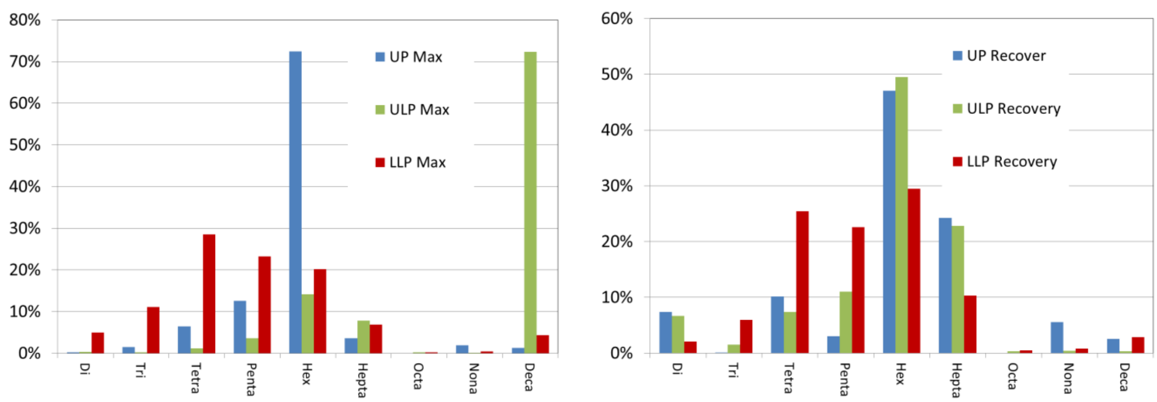


Figure 3.14: Average PCB congener fingerprints for worldwide production (as compiled by Breivik et al., 2002), Michigan study lakes during maximum production, and Michigan study lakes after PCB ban.

Inspection of the spatial and temporal trends of the PCB congeners was undertaken with to provide clarification in the differences of the decadal peaks in concentration and accumulation. The average congener fingerprint of all lakes studied in this research is calculated for the period of peak production and usage of PCBs (1960s to 1980s) and during the timeframe in which the surface water bodies should be recovering (1990s to present). In Figure 3.14, these calculations are compared to the global average PCB congener fingerprint as compiled by Breivik et al., 2002. Neither time period matches perfectly with the global production fingerprint. However, it would be expected that if atmospheric deposition is now driving inputs in all lakes compared to the consumption/use decades of PCBs, atmospheric mixing and secondary deposition would cause the recovery time frame to much more closely match that of worldwide production. The differences must be attributed to continued local inputs of PCBs. Since PCBs with different congener profiles were produced at different times, at different locations, and often for different purposes, the continued presence of PCB sources allow Michigan to maintain a unique fingerprint with regard to PCB pollution fingerprints.



A **B**

Figure 3.15: Average PCB congener fingerprints for Michigan inland lakes divided into subregions: UP = Upper Peninsula, ULP = Upper Lower Peninsula, LLP = Lower Lower Peninsula. Figure 15a shows the average fingerprint for sediment dated to the time period of maximum consumption/use of PCBs. Figure 15b shows the fingerprint for sediment dated to the years since the PCB ban.

When the data specific to Michigan inland lakes is compiled and averaged by sub-region, it becomes apparent that PCBs dispersed to surface water bodies during the maximum consumption use period varied substantially by location (Figure 3.15a). Upper Peninsula lakes exhibited elevated concentrations of hexachloro PCBs while lakes in the Upper Lower Peninsula showed an abundance of decachloro PCBs. Increasing similarities are seen during the recovery time period. This time period was calculated by averaging the fingerprints of PCBs from sediment dated from the 1990s to the present. In order to minimize signal mixture, the year of the PCB ban (1979) was not used to account for potential lag times of PCB inputs into the watershed to be deposited to the lake sediment. This time period shows increased similarities in the average congener signal amongst the PCBs present. This gives some indication that individual sources have become less important than the historical maximum production time period as a more ubiquitous signal is being generated. Comparing Figure 3.15b to the worldwide production calculations in Figure 3.14 still shows significant differences from the worldwide average production signature. Thus, the signal generated by the recovery time period can be considered a regional signal for Michigan and the immediate area only, not a global pattern.

Cluster analysis

To examine differences and similarities in the relative abundances of PCB congeners measured at various locations; cluster analysis was performed on the PCB congener data using JMP 5.0 (JMP, 2005). Cluster analysis refers to a general category of algorithms designed to classify samples into groups of similar characteristics, i.e., the relative abundances of the PCBs. The most common type of cluster analysis is the hierarchical cluster analysis (HCA) which is an exploratory method that, used here, includes calculations describing the similarity amongst the individual congener results of the sediment samples. The most common similarity metrics are based on distances calculated in multivariate space. When the distances are small, it is implied that there is greater similarity between all the present congeners representing two individual samples. Dissimilar samples will be separated by larger distances.

For this study, twenty PCB congeners were measured and analyzed. Examination of the literature has shown there to be a large number of multivariate statistical methods applied to environmental data (Howell, 2007; Skrbic and Durisic-Mladenovic, 2007; Onuska and Davies, 1991). It is suggested that use of log-ratio transformation is useful for describing compositional data (such as those data used here) as it avoids many problems associated with the analysis and interpretation of raw compositional data (Howell, 2007). All congener concentration values were expressed as the proportion of total PCB mass (by weight), where PCB mass total is defined as the sum of congeners. This is termed percentage standardization. These data are often described as "compositional data" as they have the feature that the proportions of pollutants in a sample sum to 1. Compositional data have been shown to have problems with correlation coefficients and standard multivariate techniques which lead to problems with the interpretation of simple summary statistics (Pearson, 1897). Therefore, log-ratio transformation of the compositional data was also used as proposed by Aitchison (1986). The log-ratios are calculated by dividing the compositional data of each PCB congener in each lake by the geometric mean of the twenty PCB congeners of that lake.

$$\textit{Centered Log-ratio} = \log\left(p_{ij} / g(p_j)\right)$$

Where p_{ij} = the proportion of PCB congener i in Lake j,
And $g(p_j) = (p_{1j}p_{2j} \ldots, p_{dj})^{1/20}$

The congener compositional data and log-ratio transformed data of two particular time horizons were calculated and used for the cluster analysis. High PCB emission years from 1950s to the 1980s were both averaged and summed to represent the years with significant quantities of PCBs cycling in the environment. The 1990s and the 2000s were then averaged and summed to represent the years of environmental recovery. Six, eight, ten and twelve clusters were studied for both data sets and similar patterns were found. The ten cluster analysis shows the clearest patterns and only these results are presented. Likewise, as the summed and averaged data provide near-identical clustering results, only the summed (or inventory) data from the respective time horizons are presented.

The analysis itself indicates which lakes are similar in the relative abundance or fingerprint of the congeners. Examining the relationships amongst the clusters assist identify common sources. This approach has been successfully employed by Weiss et al., 1994 to cluster PCB signatures amongst more polluted sites, adjacent sites and background sites. A hierarchical cluster approach was also used in PCB congener analysis of sediment cores collected in Lake Hartwell Superfund site (Pickens County, SC) in the characterization of PCB sources and dechlorination patterns in lieu of direct comparisons of chromatograms (Magar, 2005).

The results of the cluster analysis are shown in Figure 3.16 and 3.17 where similar colors reflect similar fingerprints. In the 1950s to 1980s ^{210}Pb dates sediment, the congener cluster pattern of compositional data shows several major clusters and a number of smaller clusters of two or three lakes (Figure 3.16). The cluster analysis revealed an increased quantity of clusters of smaller groups of lakes appears to be consistent with a combination of atmospherically-derived and local point source pollution. Most of the lakes occupying the smaller clusters are those within significant urban land use watersheds (e.g. Teal Lake in the UP, Cass Lake in the Detroit area). However, interspersed throughout lakes shown in Figure 3.16 are lakes with watersheds that are much less populous all sharing similar congener patterns (Figure 13A inset). These lakes share two prominent clusters in the dendrogram and are interpreted as receiving atmospherically-derived PCB inputs. As the atmosphere mixes the signals from extra-watershed sources, inputs of PCBs into these more remote lakes become much more uniform than those lying close to the source. Both the UP and the LP have a set of lakes sharing clusters in Figure

3.16.

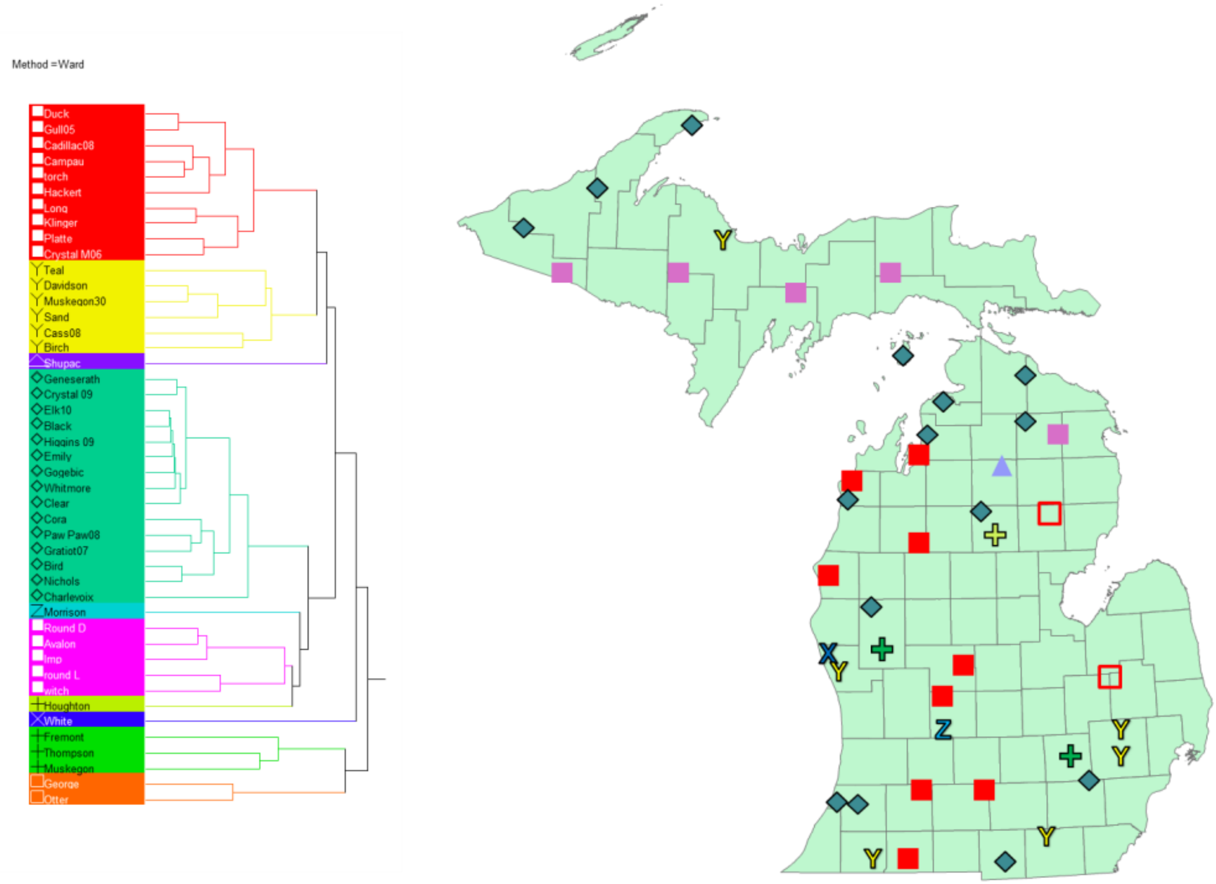


Figure 3.16: Cluster analysis of compositional data: Landscape Peak Inventories (1950s to 1980s)

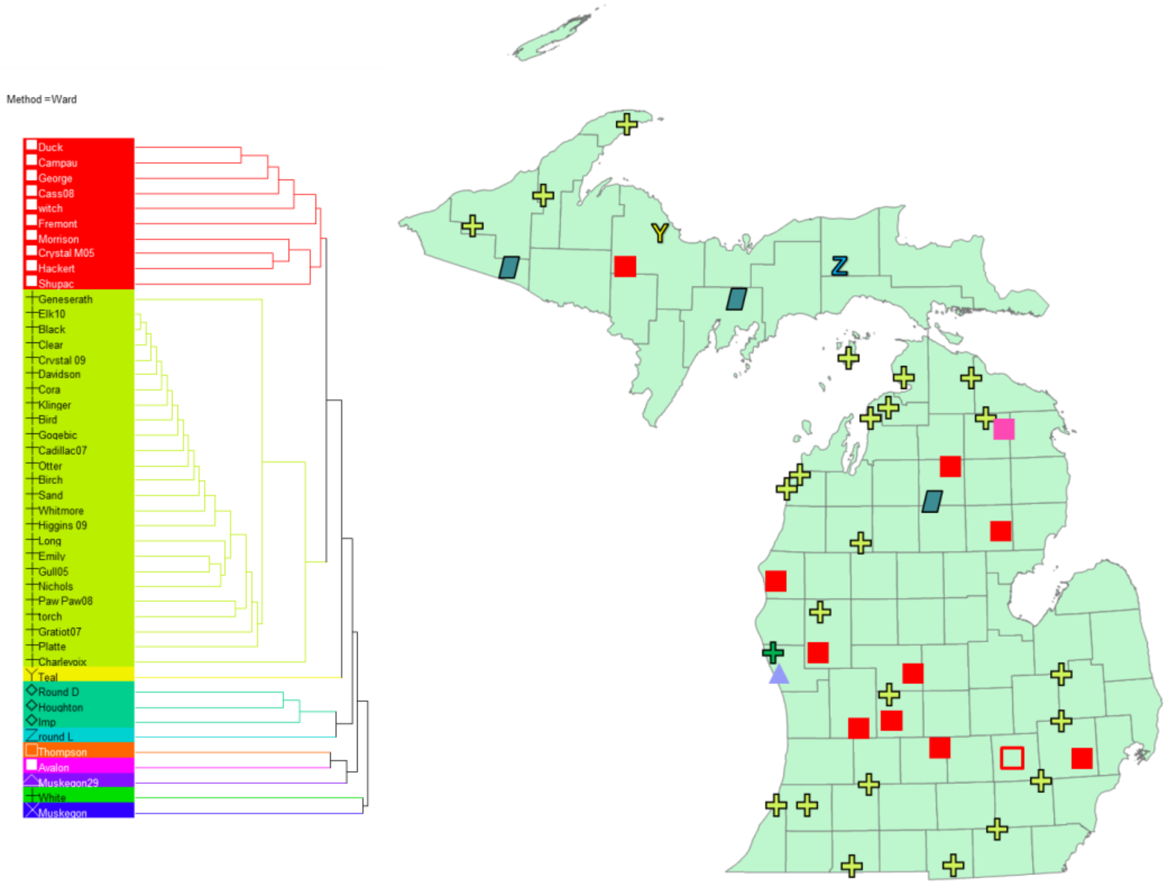


Figure 3.17: Cluster analysis of compositional data: Landscape Recovery Inventories (1990s to present).

Since the lakes sharing these clusters are spread across a fairly vast geographic area, it could be interpreted that sources for these PCB inputs lie outside the State of Michigan. The distance required for atmospheric mixing and deposition to occur across such an area points to regional sources lying across Lake Michigan (e.g., Green Bay, Milwaukee, and Chicago). As most of Michigan's UP lakes cluster differently, their regional sources are likely separate (e.g. Duluth, Minneapolis) from those in the LP but likely not farther than the American Midwest. Otherwise, the atmosphere would have sufficient time/distance to provide a ubiquitous signal for lakes in both the UP and the LP.

The cluster analysis performed on the Landscape Recovery Inventories shows a much more uniform pattern of PCB congeners across the entire State. One clear cluster pattern appears to dominate (yellow 'plus' signs) followed by a secondary pattern situated primarily in the central portion of the State (red squares). As this change from the Landscape Peak Inventory analysis is to a smaller number of cluster groups over a wider geographical area is consistent with the hypothesis. However, the reasons for the particular clustering patterns remain unknown. For example, it is not immediately clear why the suite of lakes represented by the 'red squares' clustered together throughout the Lower Peninsula, other than the fact that they all represent primarily agricultural watershed land use. As to why these lakes do not correlate with the agriculture dominated southern portion of the State is not clear. It appears that many of the small clusters or clusters represented by an individual lake lie within watersheds of elevated population or urban land use (e.g. Thompson, Muskegon), likely representing inputs at the sub-regional or watershed scale. Others are lakes known to have significant loadings of PCBs to the lake itself by known watershed industrial practices (White). These lakes are interpreted to be still within a recovery phase as the watershed and lake appear to continue cycling through previous PCBs loadings.

Clustering all both the historical and recent PCB inventory data was performed to provide insight into the significance of previously deposited PCBs in modern sediment. Hypothetically, if lakes from the peak depositional years correlate with the same lakes as those in the present, it could be interpreted that the source of the PCBs has not changed since this period. Since PCBs dechlorination occurs at different rates, clustered lakes cannot be the result of previous PCB loadings continuing to cycle in the lakes sediment and water column. Results show lakes correlating in the same clade for both time slices (Peak Inventory and Recovery Inventory) include Teal, Charlevoix, Muskegon, and Avalon lakes. White lake from both time slices occupied the same clade but at a high geometric x distance, probably the result of cleanup efforts of the lakes sediment. Many of the lakes from the more recent time slice correlate to one another, likely an artifact of similarities because of atmospheric mixing as observed in Figure 3.18.

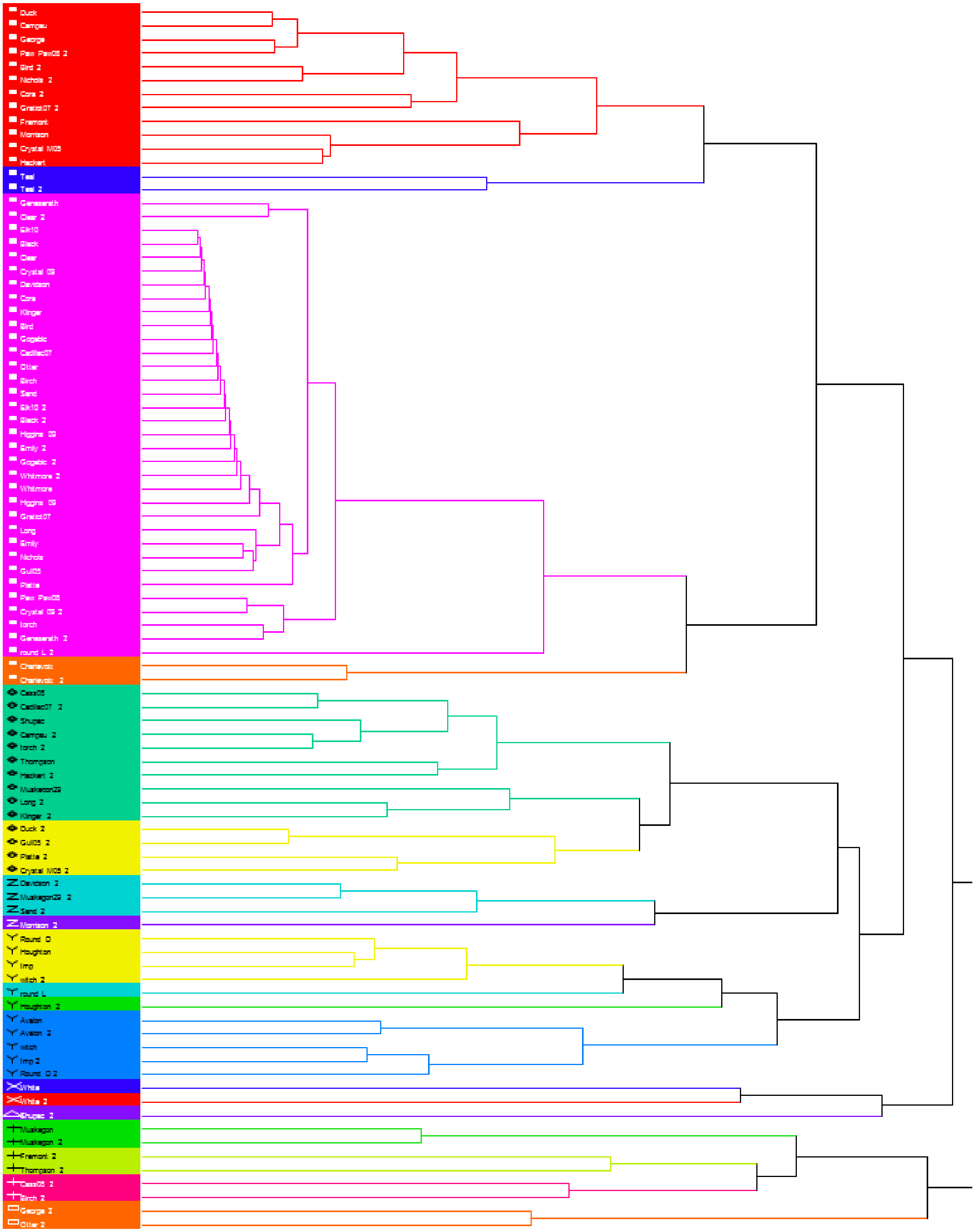


Figure 3.18: Cluster analysis of all compositional data. Original lake names refer to the lake data from the historical peak loadings time slice (1950s to 1980s) and lake names followed by a ‘2’ refer to the lake data from the recent time slice (1990s to present).

Conclusion

Sediment records from 44 inland lakes widely distributed in the State of Michigan were studied to better understand PCB spatial and temporal patterns. The hypothesis driving this study is that the high PCB production years (e.g., 1960s) and the influence of population centers on loadings will cause a localized pattern in PCB loadings compared to recent times (e.g., 2000s), where PCB loadings should be more reflective of a regional signal. The regional signal is expected to dominate more remote lakes and these lakes are anticipated to be largely composed of the lighter, more mobile, fraction of the PCB congeners. To test the hypothesis, total PCB inventories, temporal concentrations and accumulation rates of all the lakes were studied along with the congener makeup of these PCB values. These data were subject to both temporal and spatial evaluation across the State of Michigan in lake sediment dated from the 1930's to present.

It is clear from the data that the State is in a general recovery trajectory in terms of both PCB concentration and accumulation rates in recent lake sediment relative to sediment deposited during the high PCB production/consumption years. PCB values are generally a fraction of these values in the recent compared to what they had been in previous decades with few exceptions, notably lakes in the Upper Peninsula. Temporally, concentration and accumulation rate values appear to reflect consumption data only close to the populous portion of the State, and peaks typically occur later with increased latitude. The exceptions to this observation are likely caused by inputs overwhelmed by local point sources (e.g. White Lake).

The concentration profiles of most lakes exhibit PCB production and usage history, onset after 1940, peak during 1960-1980, and decrease after 1980. During high PCB production years, the total concentrations and accumulation rates among the lakes were significantly different.

Lakes near urban areas have higher PCB concentrations and accumulation rates than lakes in remote areas. In recent years, those differences appear to be smaller. PCB inventories show a regional pattern and a localized pattern, with higher inventories in the Lower Peninsula than in the Upper Peninsula and with higher inventories in urban areas than in rural areas.

Congener cluster analysis was performed on select time horizons of the data set. These time horizons included ^{210}Pb-dated sediment from years that include elevated PCB production and consumption in the United States (sediment dated from 1950s to 1980s) and sediment from years of landscape recovery from the previous period of PCB loading (sediment dated 1990s to 2000s). Results from the congener analysis revealed the period of elevated PCB loadings to cluster into primarily local or sub-regional groups overprinted by a regional signal. As the regional signal was different in the Upper Peninsula relative to the remainder of Michigan, it is possible that this cluster is sourced from industrialized west coast of Lake Michigan. Much of the recent time horizon of sediment clustered into one large, state-wide group with several smaller groups and individual lakes clustering separately. It is not clear what the most important characteristics are of this secondary group. Lakes not clustered with these two groups have a significant % urban component to their watershed (e.g. Thompson) or are formerly highly impacted lakes (e.g. White Lake). This is likely indicative of continued recovery of the watersheds from historical PCB loadings.

Clustering all the data together provides some insight into lakes that continue to carry similar congener signatures in both recent and historical sediment. As inland lake sediment subject to both local and regional inputs of PCBs will likely result in the presence of several Aroclor mixtures that are dechlorinated to some degree, it can be inferred that the same lakes could not cluster together unless they continue to receive PCBs from the same source currently as in the past. This appears to be true for Avalon, Charlevoix, Muskegon, Teal and, to a lesser degree, White Lake.

Overall, the results indicate that during the time of high PCB production, the influence of population centers on loadings caused a spatial gradient in PCB distribution from the more populous areas of the State to the more remote areas. Localized, urban sources have been relatively more dominant than long-range atmospheric transport during this period but an atmospheric component to the PCB loadings is almost certainly present. In recent years; PCB loadings appear to be dominated by a regional signal with long-range atmospheric transport serving as the primary source of PCB loading to many of the lakes in the recent. The data also show both PCB concentrations and accumulation rates in to peak later with increasing latitude. Comparing this to atmospherically derived stable Pb profiles that have a strong tendency to peak during the early to mid-1970s points to the possibility of secondary mobilization and deposition of much of the observed PCBs in the northern extents of the state. Difficulties arise when attempting to correlate specific watershed attributes (e.g. land use, population) to the PCB data. This is probably the result of PCB use being more closely tied to particular industries that utilize the chemical than they are a particular land use. However, utilization of GIS data layers characterizing land use and population appear to have a weak correlation to PCBs because of the ubiquitous use of the chemicals in both residential and industrial practices. The correlation between watershed factors and the PCB data of all the lakes studied remains weak probably due to continued independent local inputs to some lakes overprinted by a regional signal and further complexed by secondary mobilization of the chemicals.

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CHAPTER 4

SEASONAL INFLUENCE ON LAND USE BIOGEOCHEMICAL FINGERPRINTS IN SURFACE WATER BODIES

Abstract

Surface water quality in many areas of the United States has declined over the past several decades due to increases in loads of dissolved chemicals, some of which are approaching toxic thresholds for aquatic biota. Land use characteristics and temporal loading characteristics associated with the sources of the chemicals have yet to be ascertained in many cases. Five synoptic sample events targeting seasonal and hydrologic variation in the Saginaw Bay Watershed (SBW), Michigan were collected during the years 1995-96 to evaluate the associations between land use and dissolved concentrations of major ions, such as calcium, magnesium, sodium, etc. Significant local variations in stream chemistry were documented with change in season and hydrologic regime, but when considering the entire SBW, the concentration ranges for dissolved constituents generally were similar across all sampling events. Stream chemistry data was combined with Geographic Information System (GIS)-derived land use characteristics in a single database for use in an R-mode factor analysis to examine potential relationships between land use and surface water chemistry across the entire SBW. Strong local fluctuations of solutes were documented, attributed primarily to local proximity of urban centers and agricultural land use. The lowest concentrations of solutes were observed in association with forested land use. The fingerprint of agricultural land use on surface water chemistry was most evident during a summer low flow event and a spring high flow event, which may be a

reflection of seasonal variations in the intensity of agricultural practices. Urban land use exhibited its strongest fingerprint during winter high flow, likely due to road deicing salt application. The SBW as a whole did not exhibit strong temporal fluctuation of sodium and bromide concentrations despite considerable application of salt applied as a road-deicer in the winter months. Cl/Br ratios are analyzed as tracers of surface water processes. Overall, we conclude that studies attempting to link chemical concentrations to a particular land use should give consideration to coordinating surface water analytes to the hydrologic regime and time of year the sample collection is to be undertaken.

Introduction

Land use change has been shown to adversely affect the chemistry of aquatic ecosystems (Fitzpatrick, 2007; Lindeman, 2007; Deocampa, 2004, Grimm et al., 2003; Wayland, 2003). Dissolved solids concentrations is one aspect of aquatic chemistry profoundly affected by anthropogenic alterations to land use (e.g., deforestation) (USEPA, 2000). Dissolved solids have been linked to various impacts on surface water integrity such as decreased fish communities (Meador and Goldstein, 2003) and trophic quality of wetland communities (Crosbie and Chow-Frasier, 1999). With dissolved solids concentrations increasing over the last several decades in surface water bodies of the Great Lakes region (Susanna and Chen, 2002; Richards et al., 1993), identifying the sources of the dissolved solids has become increasingly important, especially given the number of other stressors that may collectively contribute to overall degradation of environmental quality and ecosystem integrity within the Great Lakes region (Allan et al., 2013). Many of the increases in dissolved solids are directly attributable to anthropogenic practices such as road salting (Kaushal et al., 2005; D'Itri, 1992) and nutrient addition to agricultural lands (Gordon et al., 2010, Hofmann et al., 2010). Understanding sources and fate of these chemicals is a need important to address, given continued expansion of urban areas, the likely expansion of practices such as road deicing and the fact that these chemicals not flushed out of SBW in near term may recharge shallow groundwater and raise baseflow concentrations.

The SBW in central Michigan is an area susceptible to the adverse effects of the increasing dissolved load in the aquatic ecosystem, given the significant changes in land use from pre-settlement to the current mix of land-use types (Einheuser et al., 2013; Giri et al., 2012). Water quality in the SBW has declined over the last several decades, prompting studies to identify potential pollutant sources and to develop strategies to mitigate or reduce these sources (Science Subgroup of the Great Lakes Regional Working Group, 2013; Selzer, 2008; Public Sector Consultants, Inc., 2002). Although changes in stream chemistry can be attributed to land use (Riseng et al., 2010; Johnson et al., 1997), separating the relative contributions natural sources (e.g., natural landscape erosion), anthropogenically-enhanced natural processes (e.g., accelerated weathering of soils due to agricultural tilling), and direct anthropogenic additions (e.g., dispersal of road deicers) is challenging.

Previous studies of the SBW have evaluated general river water quality but lacked extensive spatial coverage to determine solute sources (e.g., Wood, 1970; Tiffany et al., 1969) or focused primarily on nutrient concentrations (Giri et al., 2013, Dodds and Oakes, 2006; Johnson et al., 1997). As urbanization and agricultural land use in the SBW continues to change, there exists the potential for the increase in chemical fluxes associated with both agricultural and urban land use. Use of agricultural chemicals, septic systems and landfills, and road-deicing agents associated with these land use types have been shown to result in elevated concentrations of dissolved solids in surface water bodies (Barber et al., 2006; Baker, 2005; Allan and Johnson, 1997). Fingerprinting the sources of these dissolved solids for any particular watershed has challenges arising from spatial and temporal variations in the fluxes of chemical from the landscape to the surface water bodies (Hildebrandt et al., 2008). Research in temporal variations has shown conflicting views in the magnitude of the flux of chemicals from the landscape: some studies exhibit highly variable chemical concentrations through time (Clow et al., 1996) and other show water chemistry to be relatively constant (Pionke et al., 1999). Cyclical variations in natural environmental conditions (e.g., air temperature, precipitation form/quantity) might be expected to influence both the individual chemicals that constitute the dissolved load of a surface water body and the total concentration of the dissolved solids. Also, variations in watershed biomass and geology have been shown to complicate the use of cation and anion species for environmental process interpretation (Drever, 1997). Finally, the presence of natural sources of dissolved solids, such as soil or rock-water interactions and basin brines, elevated levels of dissolved solids could be erroneously attributed to anthropogenic inputs. The upward flux of solutes from subsurface brines of this region has been shown to potentially alter the geochemical cycling of chloride or metals (Kolak et al., 1999). Thus, associations of dissolved solids concentrations to land use types in watersheds like the SBW is complicated by these natural variations and conclusions as to a biogeochemical fingerprint of a particular land use type may change throughout the year.

Temporal heterogeneity in the flux of dissolved solids to surface water bodies may be further modified by temporal variations in anthropogenic activities. Significant landscape disturbance variations cycling over a given year in predominately agricultural areas are likely to include soil tilling, fertilizer application and crop harvesting. Urban sources are also expected to contribute a cyclical load of dissolved solids due to road deicer application in the colder months and the tendency for major construction projects to occur in the warmer months.

Spatial challenges in identifying sources of dissolved solids could include the effects of distance traveled by water at the specific sample collection location. Head water/low order streams could be expected to generate a stronger connection to land use than higher order streams, which integrate chemical signatures from a larger area and heterogeneity in land use characteristics. The amount of chemical processing and alteration of water as it is transported through soil or bedrock, prior to discharging to surface water may also vary as the relative contributions of baseflow change. Dissolution, precipitation, biological activity within the root zone, anion sorption, and exchange all potentially affect dissolved solids introduced to the groundwater (Drever, 1997), thereby complicating interpretation of source and biogeochemical fingerprint.

The study reported herein focuses on comparing GIS-calculated land use from 72 sample locations to water-quality data from five synoptic sampling events obtained from July 1995 to May 1996. Interpretation of complex data sets including geospatial components frequently includes the use of multivariate statistical methods. The large number of variables resulting from such studies is difficult and time consuming to thoroughly analyze. Our approach here is to apply factor analysis (also referred to as principal component analysis) on the data set generated by both laboratory results from surface water sampling and the GIS-calculated land use associated with each sample locations. Factor analysis is a statistical method used to describe variability among observed, correlated variables in terms of a potentially lower number of unobserved, uncorrelated variables called factors. Factor analysis returns a quantitative assessment of the strength of a series of factors in explaining the variance of variables in the dataset (Gorsuch, 1974). Thus, a detailed biogeochemical fingerprinting can be developed to identify how the chemical variables behave amongst the different land use characteristics (Wayland et al., 2003). This methodology has been applied been successfully applied in a number of related works (Fitzpatrick, 2007; Wayland et al., 2003; McGuire et al., 2000; Drever, 1997; Long et al., 1992; Long et al., 1988).

This research was driven by the hypothesis that periods of elevated runoff should produce a much clearer biogeochemical signature of respective land use types than periods of low flow. The primary goal of this paper is to provide an optimal time of year for collection of surface water samples used to represent a particular land use with an ancillary goal of discerning the relative contributions of these chemicals by their respective land use types. In this study, we provide an evaluation of spatial and temporal variations of water quality in the SBW along with statistical association (factor analysis) of the chemical results with GIS-calculated land use.

Methodology

Study Site

This study was conducted in the Saginaw Bay Watershed (SBW) in east-central Michigan (Figure 1). The SBW is Michigan's largest watershed (22,556 km^2), includes portions of 22 counties, and contains the United States' largest contiguous freshwater coastal wetland system. The presence of saline fluids in the SBW hydrogeologic system has been documented as far back as 1838 (Houghton, 1838). This phenomenon has created an excellent location for a history of studies regarding ground-water, large-lake interactions (Kolak, 1999; Mandle and Westjohn, 1989; Wahrer et al., 1996). These studies, along with those focused on toxic chemicals (e.g., Kannan et al., 2008) and pollution loadings (e.g., He et al., 2006) have provided a significant literature body describing the hydrologic system of the SBW. Bedrock lithology (e.g., extent of Michigan confining unit) does limit ground-water discharge in the case of the Saginaw Bay itself (Hoaglund et al., 2004), but in the case of SBW, ground-water surface water interaction is likely dominated by the Glaciofluvial aquifer (i.e., a shallow circulating system), and bedrock does not constrain this exchange. It is likely that glacial material (lodgment till, etc.) limits bedrock aquifer contributions to SBW. Wahrer et al. (1996) supports this interpretation: only a small portion of Glaciofluvial aquifer has total dissolved solids (TDS) measurements in excess of 10,000 mg/L. For most of glaciofluvial aquifer underlying SBW, TDS measurements are below 1,000 mg/L. Given this lack of communication between bedrock aquifers (and associated brines/saline ground-water) and surface water bodies in the SBW, brine inputs will not likely affect land use fingerprints, allowing river chemistry to more adequately represent the biogeochemistry of land use.

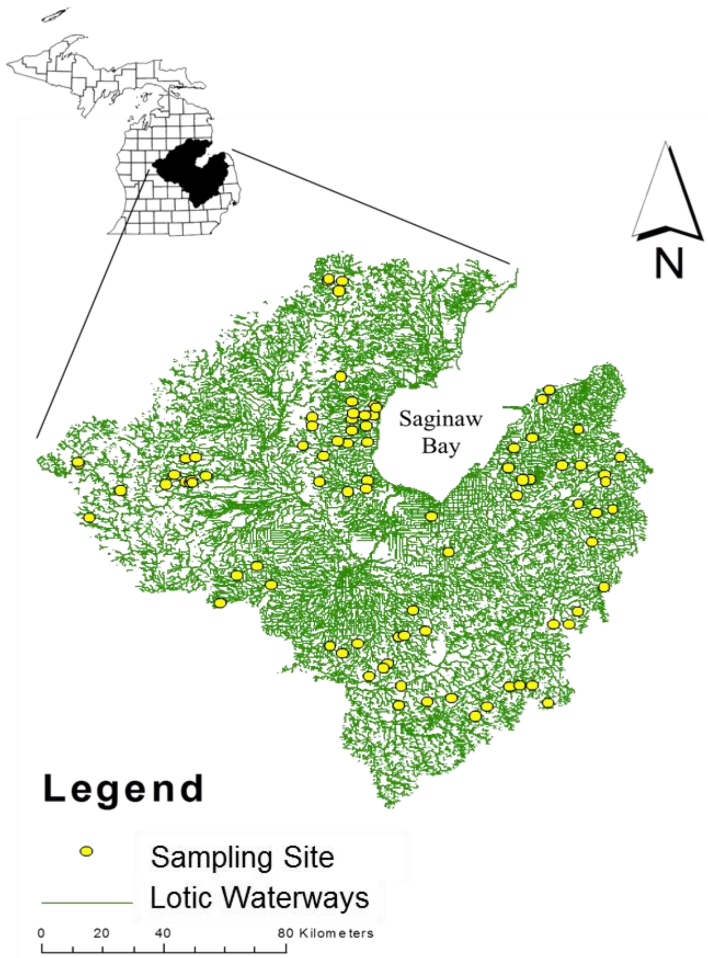


Figure 4.1: Location of Saginaw Bay Watershed, Michigan, and sampling sites.

Sample Plan and Analysis

Biogeochemical data were collected during five sets of synoptic river water sampling events in the SBW from July 1995 to May 1996. Each set of river water samples was collected with the intention of providing a large "snapshot" of stream chemistry by collection of samples from a large number of sample sites in a short period of time (Eyre and Pepperell, 1999; Fetter, 1994). Use of this sampling methodology (provided flow remains relatively constant) eliminates discharge-related chemical variability and allows for the spatial relationships of land use to stream chemistry to be explored (Grayson et al., 1997). Each synoptic sampling event was designed to target different hydrologic flow regimes (i.e. high flow, low flow) to allow evaluation of temporal variations in solute concentrations (Figure 4.2 and 4.3). Sampling events RIV-I and RIV-III were collected during summer, low-flow events. Sample event RIV-II is a summer, high-flow event. RIV-IV is a winter, high-flow event and RIV-V is a spring, high-flow event. Hydrologic flow regimes were monitored prior to each sampling event via U.S. Geological Survey gaging stations located within the watershed. All samples were collected within 3-4 days for each event to minimize potential artifacts from a change in flow regime.

The samples collected in this study were filtered (0.45 μm) and analyzed for major cations (calcium, magnesium, sodium, and potassium), anions (chloride and bromide) and dissolved silica (as SiO_2). Filtered samples for major cations were acidified in the field to pH<2 with ultra-pure nitric acid. All samples were stored on ice during transport to the laboratory, and refrigerated thereafter. During one sampling event (RIV-III), a subset of samples was subjected to further analyses (pH, alkalinity, and T, all measured on site; and sulfate, measured in the laboratory) to support geochemical modeling efforts to delineate mineral-water interactions that might influence river chemistry. Processing of analytes intended for geochemical modeling (pH, alkalinity, and temperature) was conducted immediately in the field. Samples intended for dissolved major cations and anion analysis were field filtered with disposable 0.45 um filters and laboratory analysis was typically initiated within 72 hours following completion of the sampling event. Sample processing and analytical procedures are described in greater detail in Kolak (2000). Stream chemistry data were then combined with GIS-derived land use characteristics in a single database for use in an R-mode factor analysis to examine the relationships between land use and surface water chemistry.

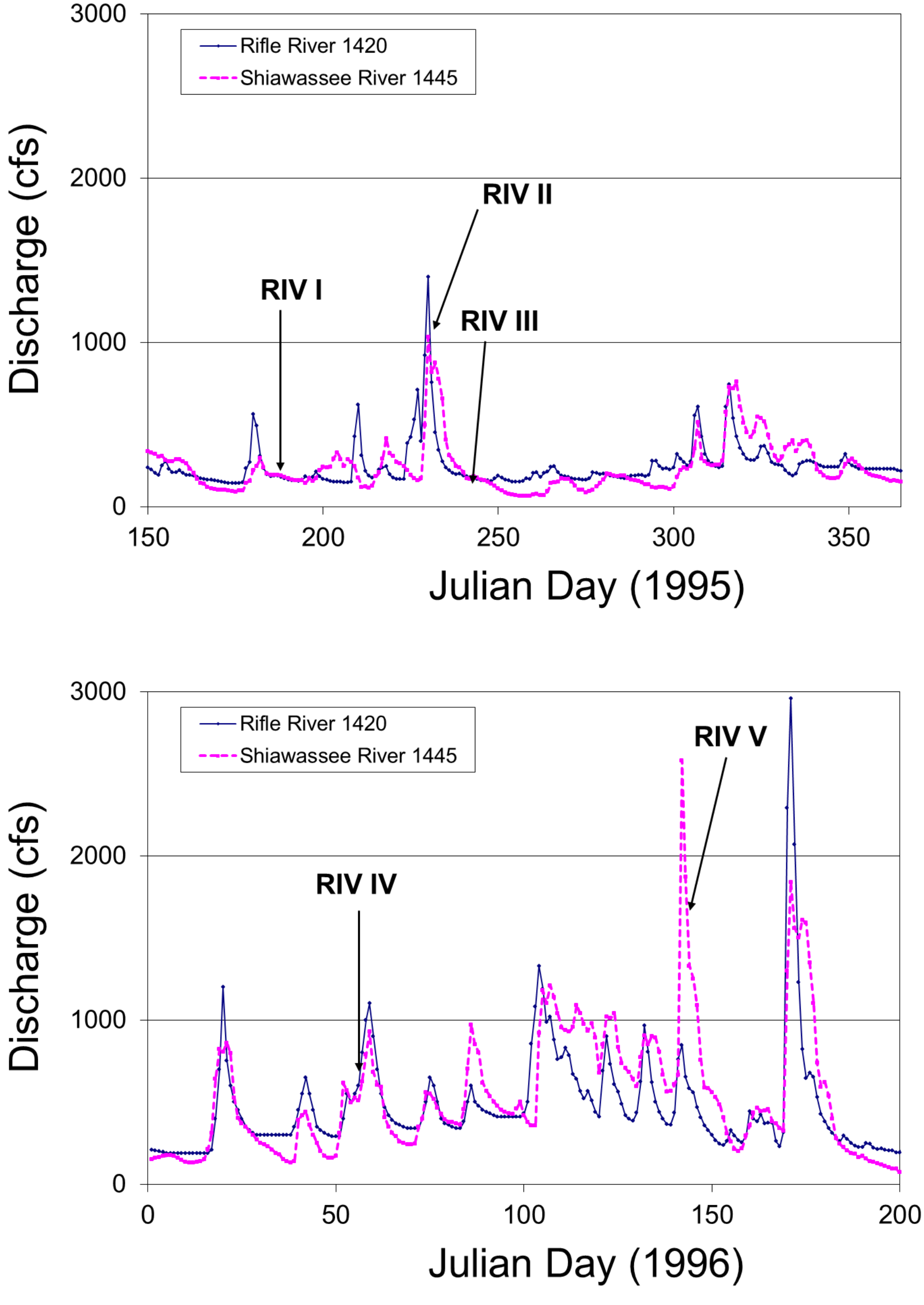
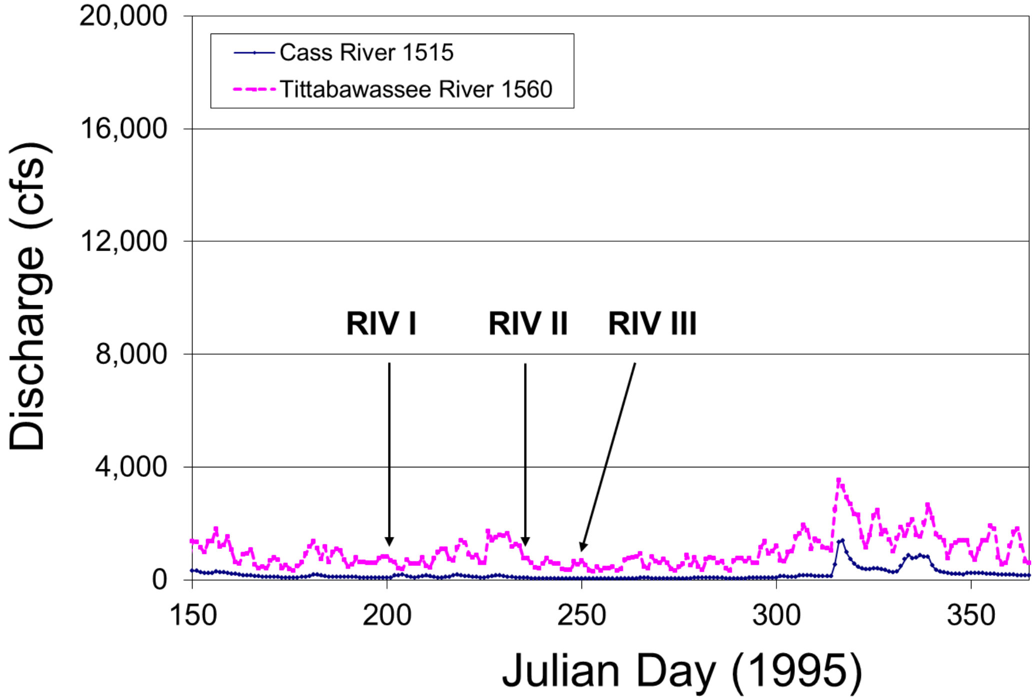


Figure 4.2: Stream hydrographs for the Rifle and Shiawassee Rivers



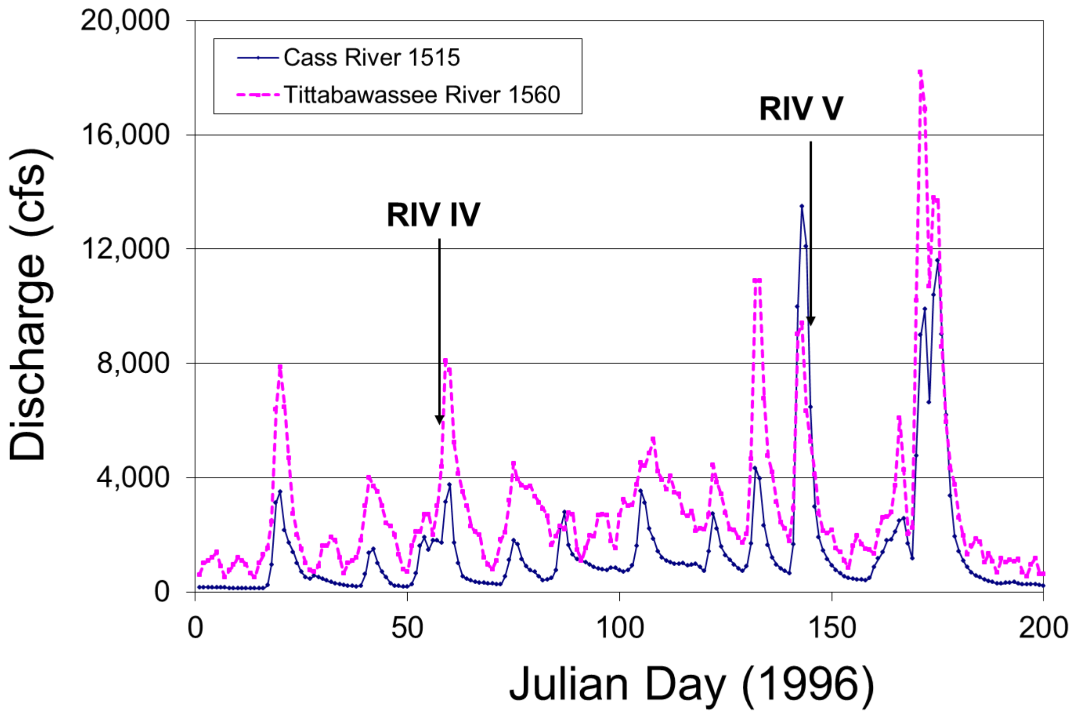


Figure 4.3: Stream hydrographs for the Cass and Tittabawassee Rivers

Watershed and Land Use Distribution

Land use and sampling points were related by GIS-based calculation of the up-gradient area contributing to a given sample location (Figure 4.4). The polygon layer created in these calculations was then intersected with land use data and proportions of each land-use type were exported to Excel for use in statistical analysis. Land use data were obtained from the 2001 IFMAP/GAP Lower Peninsula dataset (Michigan Department of Natural Resources, 2003) for each study catchment within the SBW. Land use was classified using the upper-most level Anderson classification and resulted in 7 land use types: (urban, agriculture, upland/openland, forest, water, wetland, and barren). Average land use in the study catchments closely reflected that of the total SBW. Land use/land cover in the SBW is agricultural (55%) followed by forested (26%) land use. Urban land use comprises only approximately 5% of the land use studied.

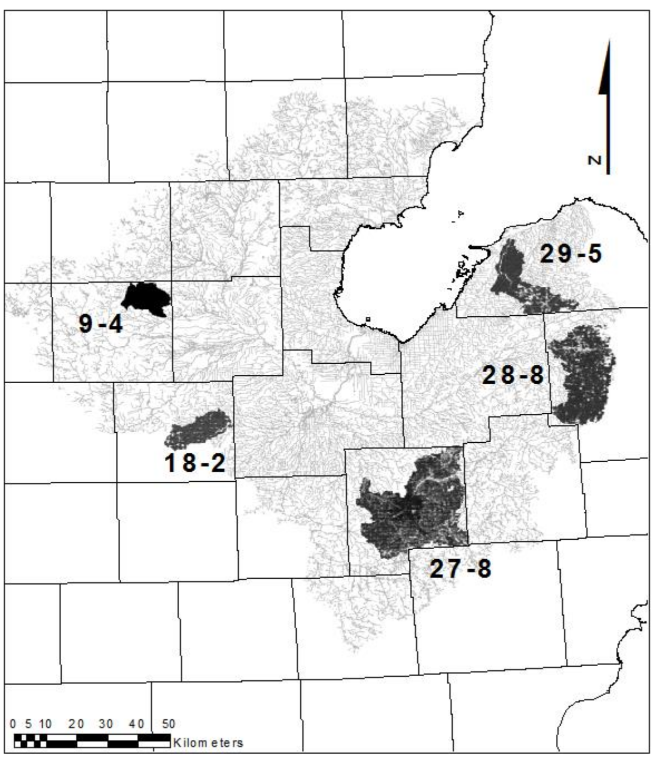


Figure 4.4: Example drainage area calculations for sample sites 9-4, 18-2, 27-8, 28-8, and 29-5.

Statistical Procedures

Interpretations of factors in the context of biogeochemical sources and processes can be difficult (Drever, 1997). Varimax rotation was used as this solution simplifies the interpretation of the factors allowing variables to identify with a single factor. A loading close to +/- 1 indicates strong correlation between a variable and a factor, while loadings close to 0 indicate weak correlation (Davis, 1986; Evans et al., 1996). Variables that exhibit a rotated loading greater than 0.5 was considered moderately loaded on a factor, while variables greater than 0.75 were considered strongly loaded on a factor. In this research, factor analysis for each sample event individually and for all sample events together was performed using SYSTAT software (Wilkinson, 2008). A chemical fingerprint (chemical grouping) was sought for each land use type using this methodology.

Examination of the literature has shown there to be a large number of multivariate statistical methods applied to environmental data (Howell, 2007; Skrbic and Durisic-Mladenovic, 2007; Onuska and Davies, 1991). It is suggested that use ranked data is useful for describing compositional data (such as those data used here) as it avoids many problems associated with the analysis and interpretation of raw compositional data (Howell, 2007). Rank order has the greatest influence on the correlation matrix upon which factors are based (Gorsuch, 1974) and as factor analysis should be most sensitive to rank order, all factor analysis reported in this paper were reported on ranked data.

Results

Temporal Chemical Variability

The RIV-I sample event was only tested for bromide, chloride, and sodium. The remaining sample events were subject to an expanded suite of analytes to include major cations. The summary statistics for all sample events is presented as Tables 2. It appears from the data that elevated dissolved concentrations were not confined to either low or high flow regimes, rather, RIV-I (high flow) and RIV-I (low flow) showed average dissolved concentrations of many of the chemicals studied in excess of the other sample events. This is true for bromide, chloride, sodium, magnesium, and SiO_2 but not for potassium (RIV-I and RIV-IV had highest average). This variability was not expected as all high flow events were expected to have the lowest concentrations due to dilution by meteoric water. Concentrations of several dissolved ions, including chloride, potassium, and sodium, varied within each sample event by an order of magnitude or more between the minimum and maximum levels. Calcium was not as temporally variable possibly related to the dissolution of carbonate minerals from widespread glacial deposits present across the portion of Michigan occupied by the SBW (Phillips, 1988; Long et al., 1988). Geochemical modeling provided by Kolak (2000) found that RIV-III samples throughout the SBW were at equilibrium or supersaturated (SI >0) with respect to calcite, supporting this interpretation. In addition to the glacial geology of the SBW, agricultural applications (e.g. field liming) may also have a significant influence on the prevalence of Ca^{2+} in the measured samples given the prevalence of agricultural land use in the SBW (see Table 1).

Table 4.2. Basic statistics organized by sample event.

	RIV-I Sampling (Summer Low Flow)					RIV-II Sampling (Summer High Flow)				
Variable	**No. of Samples**	**Min.**	**Mean**	**Max**	**CV**	**No. of Samples**	**Min.**	**Mean**	**Max**	**CV**
Cl^-	50	1.80	44.41	156.00	0.80	64	1.90	55.31	689.00	1.62
Br^-	50	0.11	0.44	2.75	0.99	64	0.13	0.58	7.36	1.89
Na^+	49	0.50	18.90	94.64	1.04	64	0.80	19.00	118.00	0.87
Ca^{2+}						64	22.80	79.31	125.00	0.30
Mg^{2+}						64	7.00	26.63	40.40	0.29
K^+						64	0.90	4.56	16.40	0.58
SiO_2						55	0.10	3.33	8.10	0.46
Temp										
pH										
Alkalinity										

	RIV-III Sampling (Summer Low Flow)					RIV-IV Sampling (Winter High Flow)				
Variable	**No. of Samples**	**Min.**	**Mean**	**Max**	**CV**	**No. of Samples**	**Min.**	**Mean**	**Max**	**CV**
Cl-	68	4.80	78.51	800.00	1.49	72	4.70	30.82	164.00	0.89
Br-	68	0.10	0.72	9.65	1.86	72	0.11	0.35	1.35	0.65
Na+	68	3.30	31.41	204.00	1.20	72	0.50	12.10	95.50	1.28
Ca2+	68	41.50	88.65	169.00	0.28	72	0.40	46.40	135.00	0.46
Mg2+	68	8.50	30.48	52.00	0.31	72	4.00	15.08	38.40	0.47
K+	68	0.70	4.57	13.40	0.63	72	1.10	6.50	35.20	0.72
SiO2	68	0.30	3.23	18.60	0.79	71	1.10	2.60	5.98	0.44
Temp	59	8.14	18.63	25.90	0.16					
pH	14	7.35	7.90	8.14	0.03					
Alkalinity	14	231.00	291.08	412.00	0.17					

	RIV-V Sampling (Spring High Flow)				
Variable	**No. of Samples**	**Min.**	**Mean**	**Max**	**CV**
Cl-	63	1.70	37.48	255.00	0.88
Br-	63	0.06	0.37	4.73	1.56
Na+	63	0.20	13.40	80.50	0.98
Ca2+	63	22.00	79.92	135.00	0.28
Mg2+	63	6.00	22.21	35.00	0.27
K+	63	0.30	3.48	8.80	0.43
SiO2	63	0.64	2.84	4.36	0.27
Temp					
pH					
Alkalinity					

Factor Analysis of Individual Sample Events

Factor analysis results for individual sampling events are shown Table 3a through Table 3e. The seasonal and hydrologic characteristics of the five analyses are not identical although some similarities can be observed amongst them. Two sample events were conducted during summer low flow (RIV-I and RIV-II) to observe the chemical characteristics of the surface water body during the maximum contribution of groundwater (baseflow). The km^2 variable is included to ascertain whether watershed size would correlate to contribution of dissolved solids. Chloride/bromide and chloride/sodium concentration ratios (Cl:Br, Cl:Na, respectively) were included as a means of attributing salt concentrations to source. These were calculated as ratios of the concentrations determined by the analytical results of the respective ions. Waters affected by halite dissolution tend to have an elevated Cl:Br ratio, often exceeding 3,000 (Wilson and Long, 1985). Waters influenced by a brine source, such as those in the Michigan basin, have a Cl:Br ratio of 400 to 600 (Wahrer et al., 1996; and Meissner et al., 1996).

The RIV-I data set was limited in analytical scope and the only elemental correlation made was between chloride, bromide, and sodium, which were all positively loaded together. These analytes do not exhibit a strong statistical correlation with any particular land use indicating they are potentially 'disconnected' from land use during summer baseflow hydrologic regimes. However, Cl/Br concentration ratios behave differently and exhibited factor loading by itself in this data set.

The RIV-II data set was collected during the recession limb of a summer high flow event for most of the rivers included in this study. However, the hydrologic response to the precipitation event driving the summer high flow in these rivers was not uniform across the entire SBW. For example, the Cass River (Figure 25; Kolak, 2000) illustrates an instance of a minimal hydrographic response to the precipitation event. Given the large spatial area incorporated in this project, this is an important consideration as differential precipitation and snow melt has the potential to disrupt consistent biogeochemical associations between river chemistry and land use.

Despite this, agricultural land use showed positive correlation with the Cl:Br ratio, as well as calcium and magnesium. These chemical loadings may reflect agricultural control via landscape manipulation (e.g., tilling) and flushing from the larger hydrologic event, possibly including the influence of fertilizer application as well. As magnesium is often considered a proxy for erosion or landscape denudation (Long et al., 2010, Tipper et al., 2008), this can be interpreted as the season exhibiting elevated erosion rates from this land use type. The reason for a positive correlation between agricultural land use and Cl:Br ratio is unclear as much of the relic road salt applied during the previous colder months is expected to have been flushed from the system. Septic effluent inputs from these rural localities offer a possible explanation as city sewer systems commonly associated with the more population-dense urban environments. Sodium concentrations measured during RIV-I showed the weakest correlation to Br and Cl, suggesting the possible influence of other significant sources such as natural erosional sources or, more likely, the lack of correlation is the result of differences in environmental behaviors (e.g. Na adsorptive tendencies versus chloride conservative tendencies).

The RIV-III data set, like RIV-I, was also collected during a summer low flow period, but with an expanded suite of analytes (Table 2). Here agricultural land use is moderately correlated to calcium and magnesium, and strongly with potassium and alkalinity. Cl, Br and Na again correlated strongly with one another under a separate factor. Cl:Br ratios were moderately well correlated with both agriculture and urban land use types. The statistical disconnect between the ratios of these elements from their given concentrations is difficult to explain as one would expect a correlation between the two. Interestingly, the ratios appear to be driven by agricultural land use, suggesting a common source amongst these sample location even if the concentrations are variable.

Finally, this sampling event had a statistical correlation between watershed size and dissolved SiO_2. This result seems logical as the larger size of a catchment area would tend to have deeper groundwater flow paths, enabling more mineral dissolution to occur than areas of low groundwater retention. This same factor was also negatively correlated to pH which also seems plausible as the smaller the catchment size, the less opportunity for waters in that catchment to interact with the terrain carbonates that can raise pH.

The RIV-IV sampling was performed during a winter high flow event in the SBW. Here results show a negative correlation between agriculture and SiO_2. The implications of the negative correlation here is unclear. The factor analysis exhibits strong loadings of urban in relation to Cl, Br, and Na suggesting application of road salt as a deicer during the winter months to play a dominant role in the quantities of salts in surface water bodies during this time of year. Calcium and Mg correlated well together under Factor III with SiO_2 factoring moderately. However, these analytes did not correlate strongly to any particular land use type. This means a common source for the cations and SiO_2 but, whatever the source, is not restricted to a single land use. Finally, %wetlands and %water show moderate control over the Cl:Br ratios. This suggests the possibility of groundwater-surface water interaction playing a role in the presence of the two elements, likely bromide, as the Cl:Br ratio is much lower in area brines (400 to 600) than in the significantly more pure halite used as a road deicer (1,200 to 10,000) (Kolak et al., 1999).

Factor loading for RIV-V (spring high flow) exhibited moderately strong correlation between agricultural land use and Ca, Mg, and K. This result was expected initially for all sampling events but only observed in loadings greater than 0.5 in RIV-III (summer low flow) and RIV-V. Since the RIV-III sampling event was conducted in early September and RIV-V was conducted in late May, these sampling events may have followed particular agricultural field activities (fertilizer distribution, planting, harvesting, etc.) possibly contributing to soil disturbance and run off from agricultural fields. The RIV-V data set also exhibited the typical factor connection between Na, Br, and Cl. The elemental salt components were expected to factor strongly with an urban environment as this landscape continues to hydraulically rid itself of the road deicers built up during the winter. However, it appears the smaller hydrologic peaks in the watersheds in the time period of RIV-IV and later, in the month of March (refer to Figures 2 and 3), removed road deicers enough that it did not agree as strongly with an urban environment. There was a moderate correlation between Cl:Br ratios and %urban, suggesting some influence of this landscape type over the presence of these ions in the watershed, but it is not clear if this signature is sourced from relic road salt or other sources such as landfill and septic effluent.

Table 4.2a: Factors for the RIV-I data collected 10-11 July 1995. Numbers in bold indicate strong loading on a factor (loading > 0.75). Only loadings >0.5 or <-0.5 are shown.

RIV-I Sampling (Summer Low)

	FACTORS					
VARIABLE	**I**	**II**	**III**	**IV**	**V**	**VI**
Urban			**0.769**			
Agriculture	**-0.922**					
Upland Openland	**0.915**					
Forest	**0.908**					
Water						
Wetland						**-0.925**
Barren					**0.931**	
Total Km2			**0.900**			
Cl		**0.911**				
Br		**0.929**				
Na		**0.933**				
Cl:Br				**0.958**		

Table 4.2b: Factors for the RIV-II data collected 20-21 July 1995. Numbers in bold indicate strong loading on a factor (loading > 0.75). Only loadings >0.5 are shown.

RIV-II Sampling (Summer High Flow)

	FACTORS					
VARIABLE	**I**	**II**	**III**	**IV**	**V**	**VI**
Urban			**0.875**			
Agriculture				0.703		
Upland Openland		0.684				
Forest			**-0.750**			
Water		**0.773**				
Wetland			-0.714			
Barren		**0.933**				
Total Km2					**0.936**	
Cl	**0.946**					
Br	**0.962**					
Na	0.683					
Cl:Br				0.723		
Ca				0.653		
Mg				0.729		
K	0.638					
SiO2						**0.775**

Table 4.2c: Factors for the RIV-III data collected 1-5 September 1995. Numbers in bold indicate strong loading on a factor (loading > 0.75). Only loadings >0.5 are shown.

RIV-III Sampling (Summer Low Flow)

	FACTORS					
VARIABLE	**I**	**II**	**III**	**IV**	**V**	**VI**
Urban					**0.943**	
Agriculture	**0.939**					
Upland Openland	**-0.850**					
Forest	**-0.920**					
Water			**-0.806**			
Wetland						0.694
Barren						**-0.809**
Total Km^2				**-0.890**		
Cl		**-0.953**				
Br		**-0.960**				
Na		**-0.890**				
Cl:Br	0.537				0.577	
Ca	0.710					
Mg	0.688					
K	**0.786**					
SiO_2				**-0.869**		
T (°C)			**-0.792**			
pH			-0.555	0.583		
Alk (HCO_3-)	**0.780**					

Table 4.2d: Factors for the RIV-IV data collected 21-25 February 1995. Numbers in bold indicate strong loading on a factor (loading > 0.75). Only loadings >0.5 are shown.

RIV-IV Sampling (Winter High Flow)

	FACTORS					
VARIABLE	**I**	**II**	**III**	**IV**	**V**	**VI**
Urban		**0.853**				
Agriculture	**-0.943**					
Upland Openland	**0.911**					
Forest	**0.951**					
Water						-0.625
Wetland	0.575					-0.566
Barren				**0.943**		
Total Km^2					**0.983**	
Cl		**0.978**				
Br		**0.923**				
Na		**0.958**				
Cl:Br		0.539				0.671
Ca			**0.926**			
Mg			**0.882**			
K						
SiO_2	0.548		0.577			

Table 4.2e: Factors for the RIV-V data collected 23-25 May 1995. Numbers in bold indicate strong loading on a factor (loading > 0.75). Only loadings >0.5 are shown.

RIV-V Sampling (Spring High Flow)

	FACTORS					
VARIABLE	**I**	**II**	**III**	**IV**	**V**	**VI**
Urban			0.506			
Agriculture	**0.935**					
Upland Openland	**-0.888**					
Forest	**-0.882**					
Water				0.594		
Wetland	-0.543		-0.582			
Barren				**0.902**		
Total Km2					**0.979**	
Cl		**0.954**				
Br		**0.911**				
Na		**0.949**				
Cl:Br			**0.850**			
Ca	**0.797**					
Mg	0.745					
K	0.606					
SiO_2						**0.944**

Factor Analysis of Combined Data Sets

Combining datasets from all five sampling events is included to investigate the statistical loadings amongst the variables across an entire year. Though this would likely obscure seasonal-dependent observations, more persistent influences have the potential to be revealed. Factors for rank-ordered data from the combined sampling events are shown in Table 6. RIV-II included the additional analytes temperature, pH, and alkalinity. Samples collected for RIV-I were analyzed for an abbreviated suite of constituents: Cl, Na, and Br. The combination of data sets resulted in a total of 317 individual samples. Proportions of agricultural land use, along with alkalinity, exhibited strong loadings on Factor I; K was moderately loaded on this factor. Factor I can possibly be explained by increased dissolution of soil minerals as a result of soil cultivation. This process could increase concentrations dissolved calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and potassium feldspar (KAl_2SiO_8). Because of this, it was questioned by Ca or Mg was not strongly loaded as well on Factor I. More likely, K correlations with agricultural land use are the result of application of potassium-containing fertilizers. This explanation agrees with Panno's findings (Panno et al., 2006) where a mass balance calculation was performed showing consistencies between KCl application and water chemistries analyzed from tile drains of croplands.

Ca and Mg were shown to be loaded strongly on Factor VI which also has the agricultural land use type loaded at 0.425, a little below the threshold of its reported value in the tables of 0.5. All other land use types were reported as a weaker negative value (closer to 0 than -0.5) on Factor VI. Other researchers have noted similar loadings of alkalinity, Ca, and Mg together under a given factor and interpreted the results as mineral weathering (Fitzpatrick et al., 2007; Wayland et al., 2003; Puckett and Bricker, 1992; Schott and Van der Wal, 1992).

Factor II had strong loadings of Na, Cl, and Br together. As suggested previously, sources of these ions could include road deicers, landfill leachate, septic effluent, and possibly even subsurface brine interaction with surface water. A closer examination of potential source of these ions is included in the next section. Factor III showed %water on the landscape to be loaded with temperature and pH while inversely loaded with SiO_2. Dissolved SiO_2 and pH are more difficult to explain. One possible explanation is that groundwater in the region is more basic has a higher pH due to mineral-water interactions (e.g. calcite dissolution) that have the potential to raise pH. Surface water has the potential to have a lower pH due to CO2 dissolution in the surface water and the precipitation. Factor IV shows urban land use correlating to the Cl:Br ratio. However, Cl, Br, and Na are all loaded together on a different factor (II) suggesting a disconnection between urban land use and Na.

The individual analyses show that Ca, Mg generally seem to load on same factor with agriculture (aside from winter high flow which can possibly be explained by frozen ground and strength of urban signature. However, in the combined analysis of all data sets, Ca and Mg are disconnected from agriculture. It is not clear if this disconnection is real or an artifact of the strength of urban influence. If this is the case, the combined analysis may signify that the combined analysis works to obscure interpretations of results.

Table 4.3: Factors for data from all sampling events combined. Numbers in bold indicate strong loading on a factor (loading > 0.75). Only loadings >0.5 are shown.

RIV-I – RIV-V: Combined Data

VARIABLE	I	II	III	IV	V	VI	VII
Urban				0.920			
Agriculture	0.765						
Upland Openland	-0.720						
Forest	-0.760						
Water			0.577				
Wetland							-0.852
Barren					-0.887		
Cl		0.971					
Br		0.980					
Na		0.898					
Cl:Br				0.533		0.579	
Ca						0.889	
Mg						0.860	
K	0.699						
SiO_2			-0.795				
T (°C)			0.570		0.593		
pH			0.874				
Alk (HCO3-)	0.927						

Sodium, Bromide, and Chloride Sources in the SBW

Results from the statistical analyses performed indicate that Na, Br, and Cl were significantly correlated to one another within each season the samples were collected. It has been shown by others that ground and surface water contamination by road deicers is localized to these waterbodies near roadways and the extent of the salt contamination is directly proportional to the mass of salts applied (Foos, 2003). Given the chemically conservative nature of Cl and Br, the anions have the potential to provide excellent fingerprints of urban land use (Smart et al., 2001). However, these ions do not appear to have a strong relationship with any given land use with the noted exception of urban during RIV-IV. This begs the question, what is the source of these ions in the SBW?

If the source of these ions were simply attributed to road deicer application, Br would likely not have been as strongly loaded with Na and Cl (Panno, 2006). Likewise, if wastewater were a strong influence on these ions, a significant quantity of samples should plot above the halite line as septic systems and animal waste are typically enriched in Na relative to Cl (Vengosh and Keren, 1996). However, it has been observed in studies of deicing salts (Shanley, 1994; Driscoll et al., 1991) and waste water (Vengosh and Keren, 1996) that the ratio of Na to Cl is reduced due to uptake of Na via cation exchange whereas Cl is relatively conservative. Thus, the molar ratio of Na:Cl in halite is initially 1:1 and should decrease due to cation exchange as the dissolved salt moves through the subsurface. The data show a generally reduced presence of Na relative to Cl (Figure 4.5) and, while the samples collected from the SBW plot are scattered, they appear to plot primarily along the brine ratio of 0.61 to 1. Given that this study encompassed both small and large catchment areas above a given sample location (Smallest = 2.64 km^2, Largest = 912.46 km^2), exchange alone probably did not account for the nearly exclusive loss of Na relative to Cl. Rather, it is possible that a localized influence of groundwater from the glaciofluvial aquifer with enriched salinity from subsurface brines played a role in dissolved salts present.

Also supporting the argument of cation exchange as the likely large loss of Na ions from the surface water is in the trend lines plotted for each of the sampling events. These plots are shown to overlay the halite and brine ratio lines in Figure 5. One would expect cation exchange to provide the largest loss of Na during summer low flows when the potential mineral-water interaction is at its peak. Conversely, cation exchange should be the least during winter high flow events due to the increased amount of surface runoff. The latter is shown to be true with the winter high flow (RIV IV) to overall exhibit the closest values of Na and Cl to that of halite.

However, the former argument is not supported by the data with a summer high flow (RIV II) showing the most suppression of Na versus Cl. It's possible that brine influenced areas of the glacialfluvial aquifer are providing sufficient salts to confound the chemical results, raising the Na concentrations relative to the Cl in the summer low flows (RIV I and RIV III). The RIV II trend line is shown to plot much lower (largest loss of Na or gain of Cl) than the other event trends possibly the result of maximized cation exchange in shallow subsurface hydrologic flow and interactions with active landscape biota, while the contribution of salinized deeper aquifer waters are diluted.

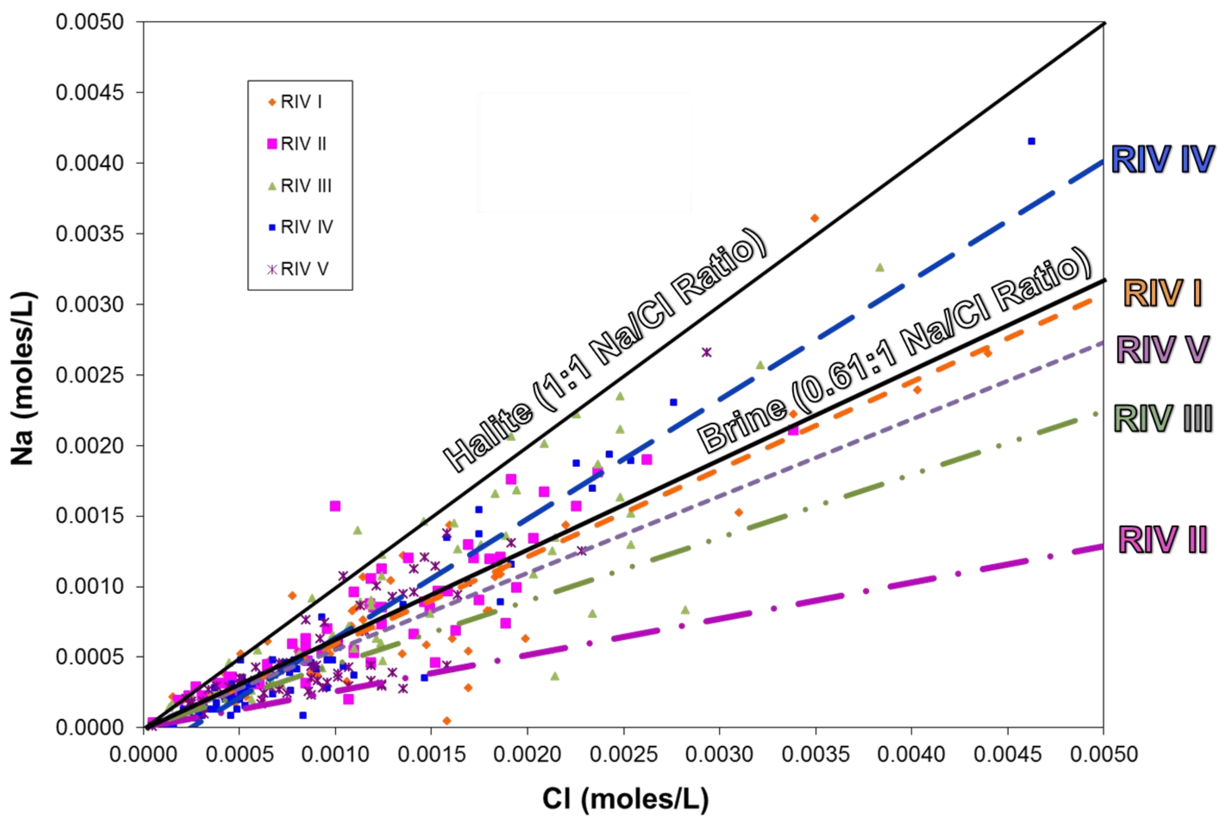


Figure 4.5: Ratio of Na+ to Cl- (moles/L) in all samples collected in the SBW. Simple halite dissolution would show a 1:1 molar ratio. The brine ratio is represented by 0.61 to 1 which is typical of Michigan Basin brines (Wilson, 1989).

Another technique used to reconstruct history or provenance of water systems is in the examination of Cl:Br ratios. Cl and Br behave conservatively in both ground and surface water and ratios of these two elements typically remain unaltered until a water of a dissimilar ratio is mixed into the system (Davis et al., 1998). Thus, most small catchment basins and shallow ground water tables reflect the Cl and Br concentrations of regional precipitation. In these cases, Cl:Br ratios are usually between 80 and 160. Oil field waters typically have ratios between 200 and 400; sewage: 300 to 600; waters directly affected by halite dissolution: 1,000 to 10,000 (Davis et al., 1998). Cl:Br ratios versus Cl concentrations of all samples collected from the SBW are shown as Figure 6. Lines indicate approximate regions where groups of samples have a tendency to plot as depicted by Panno et al. (2006). The vast majority of the samples collected plot in the 'landfill leachate' range of the figure. Given that urban land use of the watershed studied amounted to merely 5% and the land use majority being agricultural and forested (55% and 26%, respectively), it seems unlikely that landfill leachate could provide the Cl:Br chemistry necessary for such ubiquitous results of the surface water samples collected. The Cl:Br ratios would likely present a chemistry representative of a mix of sources. However, the tendency of the Na/Cl ratio to plot along the brine signal (Figure 4.5) gives indication that a process is present diminishing the Na concentrations or enriching the Cl concentration. With this in mind, it seems more likely that this signal is representative of a mixture of halite inputs along with other sources/processes (e.g. cation exchange) on a basin-wide scale. These processes of enrichment of Cl or loss of Na have suppressed the Na:Cl ratios and manipulated the Cl:Br ratios to provide surface water chemistry that may be interpreted as influenced by basin brines via ground water-surface water interactions. However, the Na:Cl ratios of the independent sample events show the event with ratio closest to halite dissolution (Na:Cl ratio = 1.0) occurred during the RIV-I sampling (Summer Low Flow I). The Na:Cl ratio mean for RIV-I was the highest at 0.63 and the Na:Cl ratio for RIV-IV (Winter High Flow) was the lowest at 0.33. While RIV-I averaged to have higher concentrations of both Na and Cl, concentrations of Na were elevated with respect to Cl for this event. This result was not anticipated because it would seem that road deicers in the winter and cation exchange during periods of low flow (larger contributions of baseflow) would provide the opposite mean ratios. The results give some indication that the elevated levels of Cl relative to Na observed during the high-flow events are related to surface runoff and shallow groundwater; not from interaction with basin brines.

Independent observations of the Cl:Br ratios from each sampling event also show the highest flow events showed the lowest Cl:Br ratios. RIV-III (the second Summer Low Flow) resulted in the highest mean Cl:Br ratio of approximately 119.02 (dimensionless) while the RIV-IV (Winter High Flow) resulted in the lowest mean Cl:Br ratio of 81.73. The remaining sample events followed a similar pattern (RIV-I = 108.77, RIV-II = 102.34, RIV-V = 109.40). This finding is counterintuitive as waters influenced by halite dissolution generally have a Cl:Br ratio in excess of 3,000 (Wilson and Long, 1985). If halite road deicers alone dictated the ratio of Cl:Br in the winter high flow observations, mean Cl:Br ratios during this sampling event should exceed samples collected during other periods. Given the agricultural land use majority, the potential exists for the legacy contributions of methyl bromide (a soil fumigant) to complicate Br chemistries (methyl bromide was phased out by the EPA in 2005 [EPA, 2014]). However, application of this compound would be used during the crop growing season exclusively, promoting Br release to the environment during this period or briefly afterward. Ratios of Cl:Br measured in river samples should be the most reduced then during the spring or summer months, but again, the opposite is observed here. More likely, additions of KCl used primarily for making liquid starter fertilizers in agricultural areas serve as the confounding source for Cl:Br ratio observations.

It appears that simple assignment of Na-Cl-Br provenance in the SBW is confounded by many factors. Others have proved successful in delineating similar solute sources in watersheds (Herczeg et al., 1993), but, complications arise in the SBW given the variation of land uses, seasonal change in fertilizer and road deicer application. These, along with the potential presence of basin brine interaction with the surface water, prevent an easy definition to linking a specific Na-Cl-Br chemistry with a particular land use. Supplementing the already extensive data set with other geochemical analyses may be necessary to provide a definitive source of these specific solutes. Panno suggested more distinctive separations of sodium and chloride sources to be possible with analysis of boron (B) and iodine (I) as the septic effluent and effluent-affected ground water samples plot near the origin, whereas animal waste is enriched in B and I_2 (Panno et al. 2005). Reviewing the data as a whole, there are several potential geochemical mixing pathways. However, if based on spatial analysis of land use and amount of agricultural land use in SBW, perhaps agricultural drainage seems most plausible, but more data are needed to support this statement.

Despite this, synoptic sampling events in the SBW did document seasonal trends in dissolved solids amongst the expanded sets of analytes. The factor analysis shows many of the expanded set of water chemistry analytes to be directly attributed to land use but only on a seasonal basis. Land-use analysis of the data primarily associates the strongest biogeochemical fingerprint with urban centers and agricultural land use. The lowest concentrations of solutes were observed in association with a high proportion of forested land use within a catchment.

Overall, the hypothesis was proven true and the relative strength of a biogeochemical fingerprint for a particular land use type to be dependent upon season. Agricultural land use exhibited its most significant fingerprint during a summer low-flow event and a spring high-flow event, both of which possibly coincided with agricultural practices involving disturbance of the soils during this time. This implies that the recent disturbances of the soil by agricultural activity allows for manifestation of a discernable biogeochemical fingerprint in water bodies local to these activities. The agricultural fingerprint included calcium, magnesium and potassium for several synoptic events during of the study, as well as, alkalinity in the RIV-III analysis. The RIV-IV analysis (winter high flow) was the only other high flow measurement that did not correlate agricultural land use to any dissolved solids (negatively correlated to silica), however the surface landscape at this latitude is typically frozen during much of the winter months possibly preventing significant erosion from this land use.

Urban land use was well correlated to Cl, Br, Na, and Cl:Br ratio in the winter sample event (RIV-IV) only. As this suite of chemicals is strongly associated with urban land use only during winter months it can be interpreted as likely sourced from road deicer application. Urban land use type was not factored to water chemistry at any other period with the noted exceptions of a more moderate correlation to Cl:Br ratios during one summer low flow (RIV-III) and the spring high flow (RIV-V). Several studies have shown that anthropogenically sourced Na and Cl in groundwater and surface water bodies is often attributed to urban land use (Panno et al., 2006; Mason et al., 1999; Buttle and Labadia, 1999). Our observations allow for a similar conclusion in this study but the degree to which urban environments influence dissolved Na and Cl levels appears to be heavily dependent on the season of which the sample is collected. It is unclear why Br is linked to %urban as halite distributed as a road deicer would have little Br included in it. Organic matter decomposition could contribute some Br to the surface water confounding results, but it is difficult to conclude this as a reasonable source during the winter months. The inclusion of Br with the suite of cations is possibly an indication of the influence of regional baseflow chemistry (which, in turn, may be influenced by subsurface brines) on the surface waters. This interference may be the reason %urban land use does not correlate well with Na and Cl except winter months harboring discreet events (e.g. road deicing) producing a strong, localized signal overprinting that of the background signal. It is also interesting to note that %urban land use did not correlate with Na, Cl, and Br during the spring high flow but did correlate to the Cl:Br ratio, indicating that the watersheds seem to rid themselves of the largest quantities of salt deicers applied during the winter months, yet retain some control over the salt concentrations into the spring.

Figure 4.6 shows the plotting ranges of different Cl and Br source (from Panno, et al., 2006). Cl:Br ratio is plotted on the y-axis and Cl concentration along the x-axis. The data collected from this study is plotted over the source divisions showing that many of the of the data gathered plot in the range of landfill leachate boundary with brines and animal waste. This figure alone would indicate that urban and agricultural centers to dominate the Cl Br chemistries of the SBW surface water. However, it is clear that this conclusion is true only seasonally.

Figure 4.7 shows the triplot of the glaciofluvial aquifer studied by Wahrer et al., 1996. As TDS increases (up to >1,000 mg/L), water chemistry shifts from mostly Ca-dominant, to no dominant, to mostly Na+K dominant facies. Overplotting Wahrers data is samples collected from four of the five RIV events. RIV I was not included as it was simply Na, Br, and Cl data. In SBW, most samples (even those with TDS approaching 1,000 mg/L) plot in Ca-dominant to no-dominant facies (especially at higher TDS). This may indicate a disconnect between SBW and the Glaciofluvial aquifer in which case surficial inputs (landscape, surface runoff, interflow, etc.) are a more important influence on hydrochemical facies

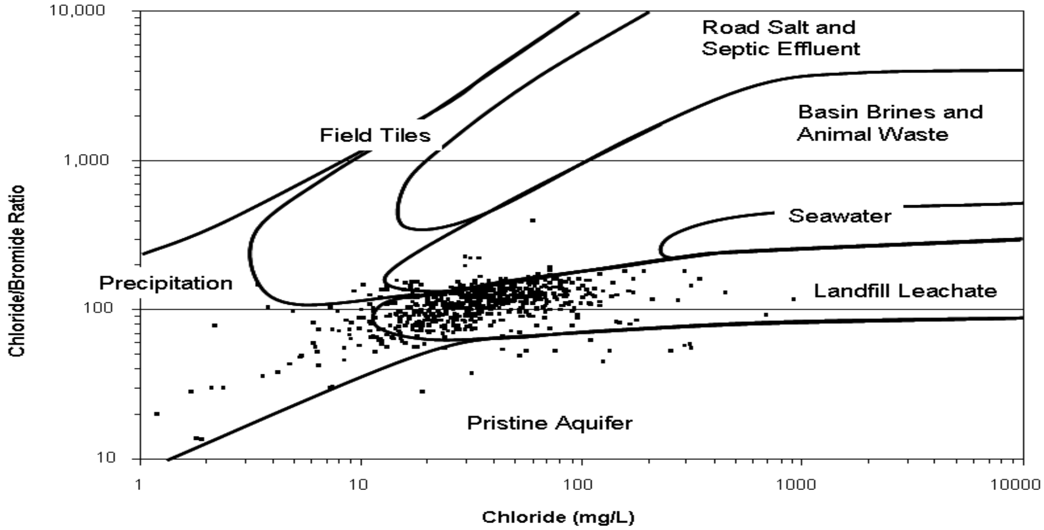


Figure 4.6: Cl:Br ratios vs Cl- concentrations of all samples collected from the SBW. Lines indicate potential sources based on Panno et al., 2006.

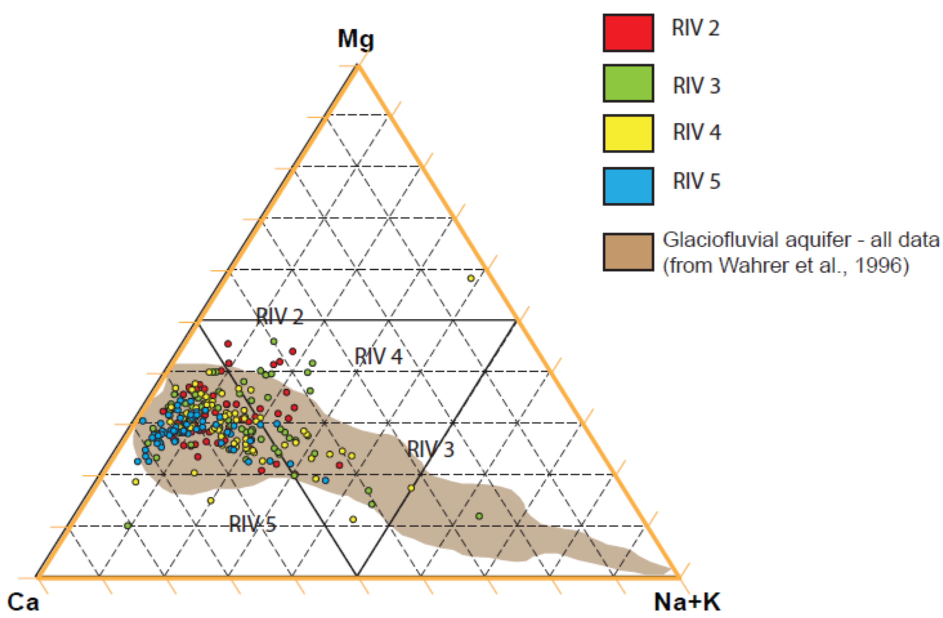


Figure 4.7: Triplot showing Glaciofluvial aquifer data collected by Wahrer et al., 2006 in the SBW overprinted with RIV II, RIV III, RIV IV, and RIV V samples. RIV I was not included as the analytes tested during this event did not include Ca, Mg, Na or K.

A combination of all available data into a statistical model provides an normalization for seasonal variation in activities associated with a given land use average set of correlations. These calculations were performed for the observation of any persistent (e.g. multiple seasons or the full year) biogeochemical signatures. The combined data set shows agriculture to be correlated most often with K and alkalinity. Again, this correlation is interpreted as the result of landscape disturbance and fertilizer distribution. Urban land use is closely correlated to the Cl:Br ratio showing that urban environments elicit some control over this ratio. However, observations made amongst the individual sample events show the correlation between %urban and the Cl:Br ratio to exist only the winter and spring high flows.

Changes in the biogeochemical fingerprint associated with land use throughout the year could also be the result of significant changes in the amount of surface water chemistry interaction with the environment. As discussed, there has been documented evidence of ion exchange due to interaction of a dissolved solid with its environment. Thus reduction in the Na:Cl ratios have been shown to decrease with increasing surface water residence time and distance traveled as groundwater (Vengosh and Keren, 1996; Shanley, 1994; Driscoll et al., 1991). This suggests the variability of Na, Cl, and Br preventing a statistical assignment to any particular land use is driven by regional baseflow and, aside from road salting, there is not a significant regional land use signal competing with the baseflow chemistry. This is shown by the strong statistical correlation of %urban to Na, Cl, and Br only during the winter high flow.

Conclusion

Overall, we conclude that studies attempting to link chemical concentrations to a particular land use should give consideration to coordinating surface water analytes to the hydrologic regime and time of year the sample collection is to be undertaken. The seasonal changes in surface water chemistry are clearly modified by anthropogenic activities, particularly during high flow regimes, when baseflow chemistry is overwhelmed with land use signals. This study provides further evidence that surface water studies quality must give careful consideration to both spatial and temporal factors before field activities are executed.

Continued research in this vane is needed as modeling scenarios in similar watersheds in Michigan have shown deicing practices to have a more widespread effect on watershed chemistry than anticipated and there could be a time lag on the order of decades or more before the water chemistry impacts of past chemical distributions are realized (Boutt et al., 2001). This study also documents several samples exceeding chloride concentrations of 250 mg/L, illustrating the need to better understand Cl sources as the potential for adverse effects on aquatic ecosystems exists

Table 4.4: Sample ID, location, and land use distribution for sampling of Saginaw Basin Watershed, MI, USA. Values in bold indicate highest land use percentage. Dominant land use is defined as land use percentage >50%. Those sample IDs without a land use >50% are defined as 'mixed'.

Sample ID	Latitude	Longitude	% Urban	% Agriculture	% Upland	% Forest	% Water	% Wetland	% Barren	Dominant Land Use
DTL	43.6753	-84.7081	5.4	**86.2**	2.6	3.8	0.1	1.8	0.1	Agriculture
1-1	44.3721	-84.1061	2.7	25.6	10.0	**60.7**	0.0	1.0	0.1	Forest
1-1a	44.3775	-84.1056	1.4	11.6	11.1	**71.2**	0.9	3.7	0.0	Forest
1-5	44.3342	-84.0636	2.5	7.1	17.3	**63.0**	2.1	8.0	0.1	Forest
1-5a	44.3675	-84.0517	2.6	6.6	17.9	**63.4**	1.9	7.5	0.1	Forest
2-1	44.0331	-84.0678	3.3	8.7	16.0	**49.0**	0.0	23.0	0.0	Mixed
2-4	43.9450	-84.0210	2.4	**41.5**	20.5	32.8	0.0	2.5	0.2	Mixed
3-1	43.8844	-84.0256	4.5	24.0	20.9	**41.6**	0.1	8.8	0.1	Mixed
3-1a	43.9050	-84.0210	3.1	**55.9**	7.3	31.3	0.0	1.6	0.8	Agriculture
3-2	43.8944	-83.9379	6.6	**57.9**	9.0	22.3	0.2	3.7	0.2	Agriculture
4-1	43.8069	-84.0864	3.8	23.2	13.8	**57.1**	0.0	1.9	0.1	Forest
4-2	43.7969	-84.0461	3.6	33.9	16.5	**44.0**	0.0	1.8	0.1	Mixed
4-2a	43.8010	-83.9640	4.9	**56.6**	9.4	26.7	0.2	2.0	0.2	Agriculture
4-3	43.8442	-84.0264	3.2	**53.6**	10.9	30.6	0.0	1.4	0.3	Agriculture
5-1	43.8925	-84.1856	2.0	2.5	23.6	**64.1**	0.0	7.8	0.0	Forest
5-1a	43.8636	-84.1864	2.1	7.6	19.5	**65.0**	0.0	5.7	0.0	Forest
5-2	43.7925	-84.2272	0.3	0.7	9.6	**67.2**	5.9	16.3	0.0	Forest
5-3	43.7544	-84.1447	1.8	8.9	13.8	**67.4**	1.0	7.0	0.1	Forest
5-4	43.6674	-84.1670	4.0	34.0	15.8	**43.3**	2.5	0.3	0.0	Mixed
5-6	43.6675	-83.9701	3.7	31.0	13.9	**46.3**	0.5	4.4	0.3	Mixed
5-7	43.6386	-83.9778	7.2	**65.6**	7.0	17.5	0.2	2.2	0.2	Agriculture
5-8	43.6299	-84.0503	6.9	**58.9**	9.0	22.3	0.3	2.3	0.2	Agriculture
8-2	43.7408	-85.1450	2.5	**39.4**	32.9	23.4	0.0	1.8	0.0	Mixed
8-2b	43.7619	-85.1478	1.8	20.2	16.6	**45.1**	8.6	7.6	0.0	Mixed
8-4	43.6458	-84.9775	3.6	**86.5**	3.9	5.1	0.0	0.8	0.1	Agriculture
9-1	43.6647	-84.7878	5.1	**74.6**	3.6	10.7	0.1	5.8	0.1	Agriculture
9-1b	43.6690	-84.6910	5.8	**78.9**	4.9	7.4	0.1	2.6	0.2	Agriculture
9-2	43.7569	-84.7064	5.9	**79.2**	4.0	6.7	0.1	4.0	0.1	Agriculture
9-2a	43.7570	-84.6690	5.8	**67.0**	10.4	11.9	0.7	4.0	0.2	Agriculture
9-3	43.6783	-84.6875	5.9	**81.9**	3.3	5.5	0.1	3.1	0.2	Agriculture
9-3b	43.6700	-84.6828	5.8	**78.5**	5.1	7.7	0.1	2.6	0.2	Agriculture
9-4	43.6922	-84.6275	4.9	**71.7**	6.1	13.1	0.2	3.9	0.1	Agriculture
9-7	43.6983	-84.7550	6.2	**79.7**	3.0	6.6	0.2	4.0	0.3	Agriculture
12-1	43.5533	-85.1055	2.8	**39.3**	19.9	34.4	0.6	3.0	0.0	Mixed
17-1	43.3429	-84.5080	5.0	**85.9**	1.9	5.6	0.0	1.6	0.0	Agriculture
17-2	43.3722	-84.4301	4.3	**89.7**	1.2	3.6	0.0	1.0	0.0	Agriculture
18-1	43.2430	-84.5829	3.6	**81.6**	2.6	9.7	0.0	2.5	0.0	Agriculture
18-2	43.3072	-84.3694	5.5	**86.3**	1.5	4.7	0.2	1.6	0.1	Agriculture
20-1	42.8760	-83.8673	4.5	**70.7**	3.5	17.5	0.2	3.5	0.1	Agriculture
20-7	43.0864	-84.1397	3.8	**77.4**	2.2	14.7	0.0	1.8	0.1	Agriculture
21-1	42.8950	-83.6578	4.1	**48.8**	11.7	29.3	0.0	6.0	0.1	Mixed
21-2	42.8855	-83.7542	8.9	**47.6**	10.4	24.6	0.4	7.6	0.4	Mixed
21-3	42.9425	-83.8580	12.1	**51.0**	9.5	22.1	1.5	3.8	0.0	Agriculture
22-1	43.0242	-83.9100	9.9	**71.6**	4.9	12.3	0.0	1.0	0.3	Agriculture
22-1b	43.0082	-83.9303	11.1	**68.9**	5.1	13.0	0.0	1.7	0.1	Agriculture
22-2	42.9783	-83.9878	2.7	**93.4**	1.0	2.6	0.1	0.1	0.1	Agriculture
22-4	43.0931	-84.0267	3.2	**88.5**	0.6	6.3	0.0	1.3	0.0	Agriculture
22-4a	43.0619	-84.0897	3.2	**92.1**	0.5	3.5	0.0	0.8	0.0	Agriculture
23-1	42.8302	-83.5615	6.1	15.3	13.0	**49.3**	2.9	7.1	6.2	Mixed
23-2	42.8625	-83.5152	3.8	17.7	11.0	**56.4**	2.4	8.6	0.0	Forest
26-2	42.9325	-83.4206	1.3	22.8	10.2	**52.0**	0.3	13.2	0.0	Forest
26-2a	42.9353	-83.3797	4.5	**40.9**	11.7	37.2	0.5	5.2	0.0	Mixed
26-3	42.9340	-83.3315	3.6	**49.2**	8.9	30.8	0.3	7.1	0.0	Mixed
27-1	43.1442	-83.1722	1.3	**43.9**	9.3	37.5	0.0	7.9	0.1	Mixed
27-1a	43.1872	-83.1350	2.5	**53.3**	7.7	28.3	0.5	7.7	0.0	Agriculture
27-2	43.1482	-83.2333	1.4	15.5	8.2	**58.3**	1.7	14.9	0.0	Forest
27-8	43.1158	-83.8598	21.4	**33.5**	14.0	25.2	1.0	4.5	0.4	Mixed

Table 4.4 (cont'd):

Sample ID	Latitude	Longitude	% Urban	% Agriculture	% Upland	% Forest	% Water	% Wetland	% Barren	Dominant Land Use
27-8a	43.1333	-83.7522	**46.2**	14.6	12.1	24.4	0.5	2.1	0.1	Mixed
27-8b	43.1172	-83.8356	19.3	**31.1**	16.6	29.5	0.4	2.9	0.1	Mixed
27-9	43.2062	-83.7987	19.5	**34.0**	15.3	28.2	0.4	2.4	0.2	Mixed
28-1	43.2708	-83.0238	2.9	**80.0**	4.5	9.9	0.0	2.6	0.1	Agriculture
28-2	43.4300	-83.0665	3.1	**87.6**	1.7	5.4	0.0	2.2	0.0	Agriculture
28-3	43.5445	-82.9757	2.2	**68.9**	5.2	17.6	0.0	6.1	0.1	Agriculture
28-4	43.5323	-83.0442	3.1	**84.5**	3.1	6.6	0.0	2.5	0.1	Agriculture
28-5	43.7237	-82.9330	2.5	**77.6**	3.6	10.8	0.1	5.4	0.1	Agriculture
28-6	43.6643	-82.9997	3.1	**66.8**	5.8	16.7	0.1	7.5	0.1	Agriculture
28-7	43.6428	-82.9997	2.0	**54.4**	6.1	23.7	0.0	13.8	0.0	Agriculture
28-8	43.5675	-83.1128	2.7	**75.7**	4.4	13.1	0.0	4.1	0.1	Agriculture
29-lake	43.9704	-83.2149	0.7	0.5	2.5	**82.9**	0.0	13.4	0.0	Forest
29-1	43.7022	-83.1000	2.9	**79.8**	2.8	10.2	0.0	4.2	0.0	Agriculture
29-2	43.7022	-83.1740	3.2	**84.3**	3.6	6.5	0.0	2.4	0.0	Agriculture
29-3	43.5997	-83.3612	3.1	**86.8**	2.0	6.6	1.5	0.0	0.0	Agriculture
29-3a	43.6564	-83.3056	3.3	**78.9**	3.9	11.3	0.0	2.6	0.0	Agriculture
29-3b	43.6564	-83.3389	3.2	**88.1**	2.0	5.1	0.0	1.5	0.0	Agriculture
29-4	43.7008	-83.3946	4.0	**93.7**	0.3	1.3	0.0	0.4	0.3	Agriculture
29-4a	43.8019	-83.2889	3.7	**95.8**	0.1	0.1	0.0	0.1	0.2	Agriculture
29-4b	43.7680	-83.3690	4.4	**91.4**	1.1	2.3	0.0	0.6	0.1	Agriculture
29-5	43.9380	-83.2427	3.9	**81.8**	2.7	8.6	0.0	2.9	0.1	Agriculture
29-6	43.8283	-83.1000	7.9	**67.3**	5.2	13.4	0.2	5.8	0.2	Agriculture
31-5b	43.5360	-83.7113	6.3	**90.1**	0.9	1.9	0.1	0.6	0.0	Agriculture
32-6	43.4083	-83.6486	6.2	**86.3**	2.1	4.7	0.0	0.5	0.1	Agriculture

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