**Date of Report: November 1, 2000**
**LCMR Work Program Final Report**

**Project Completion Date:** June 30, 2000

**LCMR Work Program 1997**

## I. PROJECT TITLE: Atmospheric and Nonpoint Pollution Trends in Minnesota Lakes

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**Total Biennial Project Budget:**

| | |
|---|---|
| **$ LCMR:** | $325,000 |
| **+ $ added from other funds** | $ 22,725 |
| **- $ Amount Spent:** | $347,725 |
| **= $ Balance:** | $0 |

**A. Legal Citation: ML 1997, Chap. 216, Sec. 15, Subd. 6(h)**
Atmospheric and Nonpoint Pollution Trends in Minnesota Lakes. $325,000.
**Appropriation Language:** This appropriation is from the trust fund to the pollution control agency to document geographic and historic trends in lake eutrophication and inputs of toxic metals and organic pollutants from land-use impacts and atmospheric sources. This appropriation is available until June 30, 2000, at which time the project must be completed and final products delivered, unless an earlier date is specified in the work program.

## II. PROJECT SUMMARY AND RESULTS:

This project documents geographic and historic trends in a) lake eutrophication and b) inputs of toxic metals and organic pollutants. Land-use impacts are separated from atmospheric sources in the 55-lake study of nonpoint pollution. This project leverages an investment that LCMR has already made in funding a $275,000 study to assess geographic and historic trends in mercury inputs to fifty lakes across Minnesota -- a project that involved collecting sediment cores from each lake, dating the last 150 years of sediment accumulation, and performing GIS analysis of the each lake's watershed for local land-use characteristics (five lakes were added in this study). The same sediment samples were used to assess the history of lake eutrophication and to quantify inputs of toxic chemicals in addition to mercury, including dioxins, furans, PCBs, chlorinated pesticides, and heavy metals.

This project addresses two major issues facing lake managers: (1) atmospheric inputs to lakes of metals (lead, cadmium, chromium, and others) and semivolatile organics (dioxins, PCBs, and other chlorinated hydrocarbons), and (2) eutrophication caused by soil erosion, urbanization, agricultural land-use practices, and atmospheric inputs of phosphorus and nitrogen. This monitoring and assessment project employs an elegant method to document environmental trends by using the location where the impact occurs (the lake) as the data archiving device. This approach is better (and less expensive) in many ways than trying to quantify inputs to lakes with automatic stream and precipitation monitoring devices on shore.

## III. PROGRESS SUMMARY:

This project has reached a successful conclusion. The additional data on modern lake chemistry has been successfully correlated with diatom taxonomy to reconstruct the history of total phosphorus and trophic change in Minnesota lakes. Heavy metals have been analyzed, and a procedure developed to separate the effect of soil erosion from atmospheric inputs. The analysis of semivolatile organics has been completed and interpreted.

## IV. OUTLINE OF PROJECT RESULTS:

**Result 1:** Characterize Modern Limnology
**Budget:** $44,800 Balance: $0
**Completion Date:** 6/98

All 55 lakes in the study were sampled during the spring during the course of the study. Lakes that have not been sampled extensively in the past for other reasons were also be sampled during the summer and fall of 1997 in order to accurately characterize trophic status. The trophic status is essential for the calibration of the trophic status model based on diatom analysis (below) and will be important for interpretation of landuse data and fish contamination patterns.

**Final Status:** A modern water-chemistry data set was compiled for the study lakes based on a minimum of two site visits between 1996 and 1998. Sampling was done between mid-May and early October. Additional water-chemistry data from 1993-1998 was available for 22 of the study lakes (MPCA, unpublished) and was incorporated into data set for the 55 study lakes.

**Result 2:** Coring, Metals Analysis, and Eutrophication Analysis
**Budget:** $146,250, increased to $174,850 with non-LCMR state funds. Balance: $0

**Completion Date:** 6/99
**Final Status:**.

*Diatom Reconstructions of Water Chemistry:* Relationships between water-chemistry variables and modern diatom assemblages were evaluated by using canonical correspondence analysis (CCA) in the program CANOCO (ter Braak, 1998). A total of 108 diatom taxa were used in these ordinations. Weighted averaging (WA) calibration with inverse deshrinking was used to develop transfer functions for reconstructing water-chemistry variables from fossil diatom assemblages in deeper core sections.

CCA results indicate that all 16 environmental variables collectively account for 42.7% of the variation in the diatom data. Based on forward selection a subset of six water-chemistry variables (Cl, ANC, color, TP, $SO_4$, pH, and $SiO_2$; in order of significance) explain independent variation in the diatom data and altogether account for 27.2% of the variation in the diatom data (64% of the variance explained by all 16 environmental variables). A CCA ordination shows that lakes cluster by ecoregion along the environmental gradients. Axis-1, which accounts for 32.8% of the explained variation is strongly aligned with Cl and TP, while Axis-2 accounts for an additional 19.6% of explained variation as is most strongly correlated with color, pH, and ANC. The first axis separates lakes in western and southern Minnesota from those in the northeastern part of the state, and represents underlying differences in bedrock geology (base-poor bedrock in NE Minnesota) as well as human impact. The more pristine lakes in the Northeast cluster toward the lower end of the TP and Cl gradients, opposite lakes in the southern part of the state, most of which are influenced by urban and agricultural land-use.

Reconstruction of water-chemistry variables from fossil diatom assemblages reveals marked changes in water quality for many of the study lakes between conditions existing prior to European settlement and those of today. These changes are clearly manifest in the metro and agricultural areas of southern and western Minnesota but are little evident in the northeastern part of the state where watersheds remain forested and largely undisturbed. Of the 20 metro-region lakes, 11 show increases in diatom-inferred TP between 1800 and today (six of which are statistically significant), eight are unchanged, and only one shows a decline. Half of the 15 lakes in agricultural areas of west-central and southern Minnesota show increases in TP from 1800 to present (three of which are statistically significant), three show modest declines and the others are unchanged. By contrast, the northeastern lakes show no systematic TP changes from 1800 to present; about half the lakes show modest declines in TP, while the others show modest increases or no change. It is also clear from the diatom reconstructions that TP levels in southern and western Minnesota, though currently enhanced by human impacts, have always been higher than those in the northeastern part of the state.

All of the metro-region lakes show increases in Cl concentrations from 1800 to present (ten of which are statistically significant), indicating the likely impacts of road-salt application and possibly leakage from septic systems in outlying areas. Ten of the 15 agricultural-region lakes show enhanced Cl levels over this same time period, again possibly owing to road salt, whereas all but two of the northeastern lakes show no change or decreasing Cl levels.

Many of the same lakes that show increases in diatom-inferred TP following European settlement also exhibit higher pH values today than they did in the early 1800s. pH increases are significant or nearly so in ten metro-region lakes and six agricultural region lakes. These pH increases probably reflect higher levels of algal productivity (caused by nutrient enrichment) which can raise pH by photosynthetic uptake of $CO_2$. There is no systematic direction to pH trends in the northeastern lakes, although three exhibit significant pH declines over the period of record. Because these pH declines predate 1970 (based on diatom analysis of core intervals from that period), and because ANC values in these lakes are not especially low, it is unlikely that the pH changes shown here are the result of acid rain.

The water-quality changes exhibited by many of the study lakes between 1800 and present almost certainly represent the cumulative impacts of land-used changes (agriculture and urbanization) that followed European settlement across much of the eastern US. Water quality conditions in Minnesota lakes were relatively stable prior to 1800 as shown by a comparison of diatom-inferred TP, Cl, and pH for 1750 and 1800. This fact coupled with results that show little water-quality change in most northeastern Minnesota lakes over the period of record provides a clear contrast to the pervasive and large-scale changes in water quality that have occurred throughout the rest of the state over the last century and a half.

These results along with associated water chemistry data have been compiled into a master's thesis by Joy Ramstack at Lehigh University, and two journal publications are currently in preparation from this research.

*Toxic Metals:* The compilation and preliminary synthesis of metal pollutants from four core intervals, representing approximate dates of 1997, 1970, 1800, and 1750, has been completed for all 55 study lakes. The interpretation of these results will be augmented by a two-year investigation of precipitation chemistry from four long-term NADP monitoring sites across Minnesota. Additional collection equipment suitable for clean trace-element sampling has been in place at these sites for one year and will continue in operation for a second year of collection. The samples are being analyzed for the same suite of heavy metals (plus P and N) that have been measured in the lake sediment cores. This additional work is supported by non-LCMR funding from the MPCA. Preliminary analysis of the core metals data indicates that lakes with substantial agricultural or urban land-cover have higher rates of metal accumulation that lakes with primarily forested watersheds. This additional metal loading is primarily derived from atmospheric deposition but is subsequently delivered to lakes attached to soil particles that are eroded from the watershed. Lakes in the metro region have received historically higher loadings of some metals (Pb, Cd, Zn) than lakes in outlying areas, although these anthropogenic inputs have declined in the last few decades (since 1970). Lead-isotopic analysis confirms the trends seen in total-Pb accumulation rates, with lower $Pb^{206}/Pb^{207}$ ratios in post-settlement sediments reflecting inputs of isotopically lighter lead from anthropogenic sources. Recent sediments from metro region lakes show a trend toward higher $Pb^{206}/Pb^{207}$ ratios since the 1970s, indicating a reduction of Pb pollution from combustion of leaded fuels.

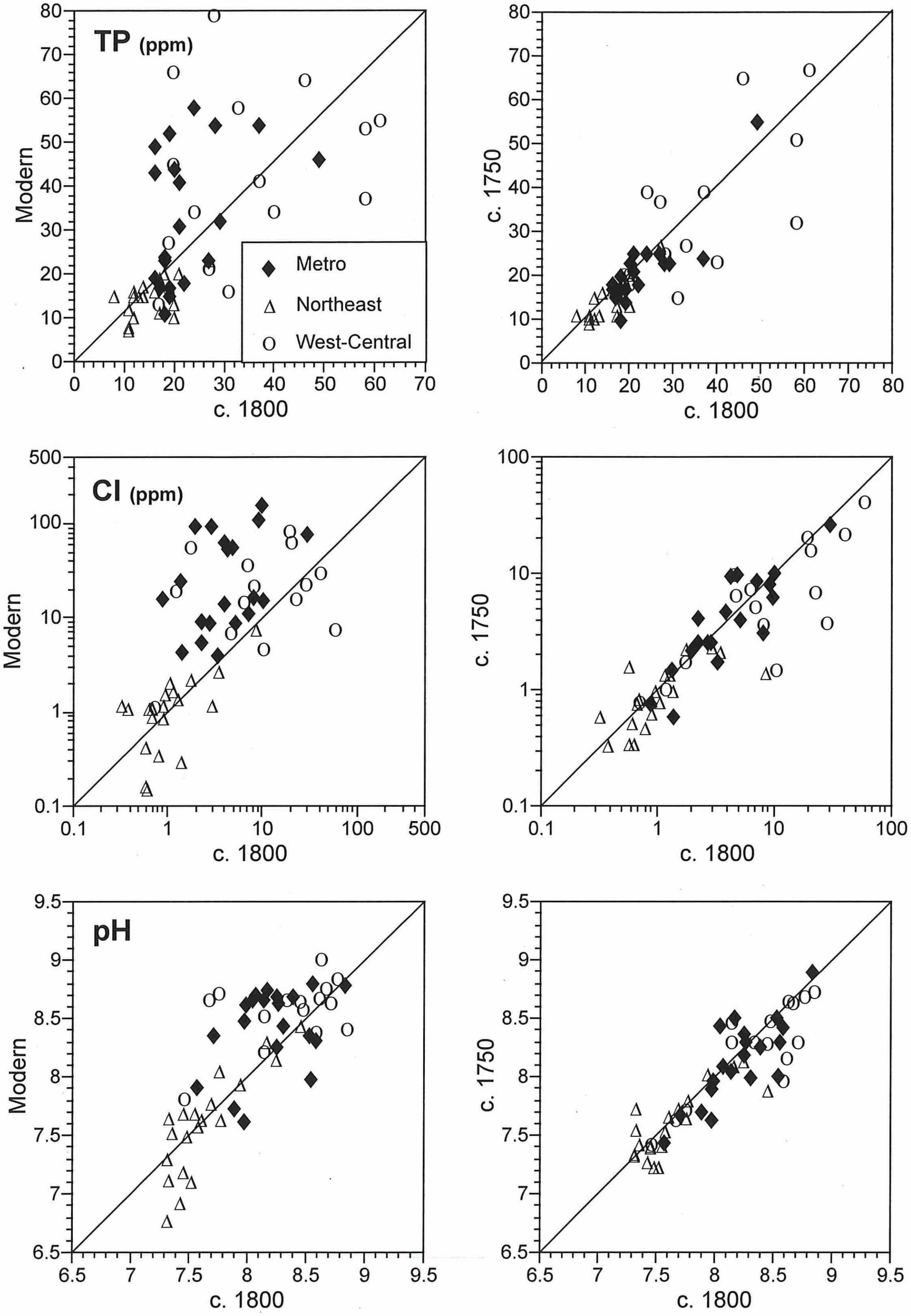


*Figure 1.* Diatom reconstructions of changes in water quality for 55 Minnesota lakes.

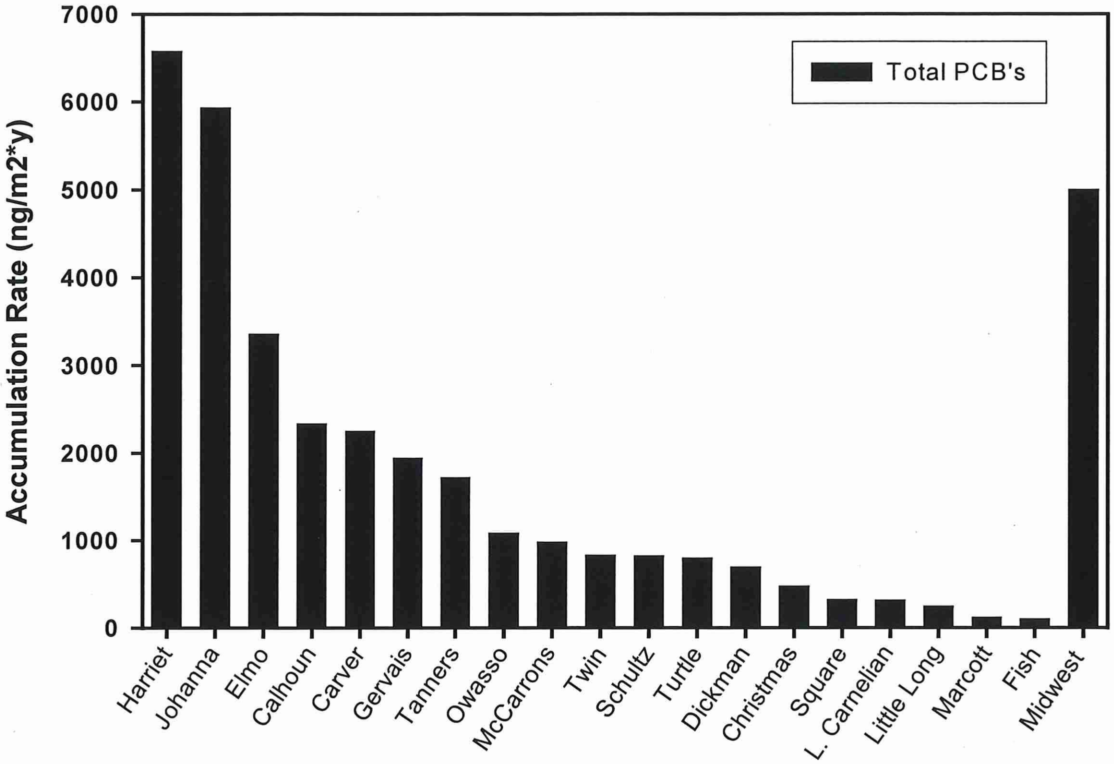
*Organic Contaminants:* The surface sediment samples from the 55 study lakes were delivered to Dr. Swackhamer's laboratory for analysis of chlorinated organics. These samples were collected at the same time that the lakes were cored, but were stored as wet sediment in glass jars so as preserve the more labile contaminants. In addition, three of the six study lakes from the North Shore subregion (Bear, Tettegouche, and Nipisiquit) were re-cored in September, 1999 to provide a complete profile of fresh sediment for detailed stratigraphic analysis of organic contaminants. These cores were collected from the same location as the original dated cores by re-location of coring sites with GPS instrumentation.

**Result 3:** Analyze and Interpret Organic Pollutants
**Budget:** $ 113,800 Balance: $0
**Completion Date:** 6/2000
**Final Status:**
We have completed the extraction and analysis of the 20 Metro lakes for PCBs, and the analysis of all 55 lakes for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), 4 technical chlordane compounds(cis- and trans-chlordane, cis- and trans-nonachlor), toxaphene, hexachlorocyclohexanes (including lindane), 6 compounds in the DDT family(o,p-DDT, p,p-DDT, o,p-DDE, p,p-DDE, o,p-DDD, p,p-DDD),and hexachlorobenzene. Sediments were exhaustively extracted with solvents, and analyzed by gas chromatographic mass spectrometry in negative ion mode except for PCBs which were analyzed by gas chromatography with electron capture detection. The results of these analyses indicate that, with few exceptions, the atmospheric deposition of these compounds has been very low, resulting in very low concentrations and accumulation rates around the state. The average value of accumulation of these compounds has been higher in the Metro region compared to the other regions of the state.

The products resulting from this study are the concentrations (ng chemical per dry weight of sediment) and accumulation rates (ng chemical per unit area per year) of PCBs, PCDD/Fs, and a suite of chlorinated pesticides in approximately 55 lakes in Minnesota. This allowed us to estimate the atmospheric deposition of these compounds to Minnesota lakes, to evaluate differences in the atmospheric deposition of these compounds near and far from sources, and to contrast urban vs. rural deposition. Not only are these data valuable to the state of Minnesota, but they have significance nationally and internationally. There are very few estimates of atmospheric deposition of these compounds, and none that evaluate the objectives stated above. We will present the individual results of each chemical class, and then summarize the results and address the study objectives at the end of the discussion.

PCBs. Polychlorinated biphenyls were used in a large variety of applications from 1929 until their ban in 1976 by the USEPA. Their most common use was as insulating fluids in capacitors and transformers, due to their stability when heated. They consist of a family of about 180 compounds (congeners) that have a similar biphenyl backbone with varying degrees of chlorination. These compounds are very resistant to abiotic or biological degradation, and thus have very long lifetimes in the environment. Like many of the compounds in this study, they also have physical-chemical properties that make them mobile in the environment. Thus they are found throughout the world due to long range atmospheric transport. They are lipophilic (fat-loving) and bioaccumulate in foodwebs with great efficiency. PCBs are one of many chemical families known as persistent, bioaccumulative compounds (PBTs in the US) or persistent organic compounds (POPs in Europe).

PCB concentrations ranged from 0.47 ng/g (Fish Lake) to 25.3 ng/g (Lake Harriet). The average concentration was 5.4 ± 5.8 ng/g. Their focus-corrected accumulations in the surface sediments (which serves as a surrogate of their atmospheric deposition rates) are shown in the figure below. The range in accumulations was 0.09 ug/m$^2$ yr (Fish) to 6.6 ug/m$^2$ yr (Harriet). The average accumulation was 1.6 ± 1.9 ug/m$^2$ yr. Lakes Harriet and Johanna had the highest concentrations and highest accumulation rates of all Metro lakes, and these accumulation rates are consistent with the background levels reported for other lakes in the upper Midwest. The accumulation rates for remote areas of the upper Midwest range from 1.3 ug/m$^2$ yr in Lake Superior (Jeremiason et al. 1994) to 1.9 ug/m$^2$ yr in pristine Wisconsin lakes (Swackhamer and Armstrong, 1986) to 5.6 ug/m$^2$ yr (Swackhamer et al., 1988). Thus, the accumulation rates throughout the Metro area are consistent with atmospheric deposition following long range transport. This indicates that the Twin Cities does not have significant points sources of PCBs from locations around the Metro region. This is in contrast to Chicago, which has significant localized sources of PCBs to the air currently (Holsen et al., 1991), probably a result of volatilization of PCBs from landfills where PCB-containing products were

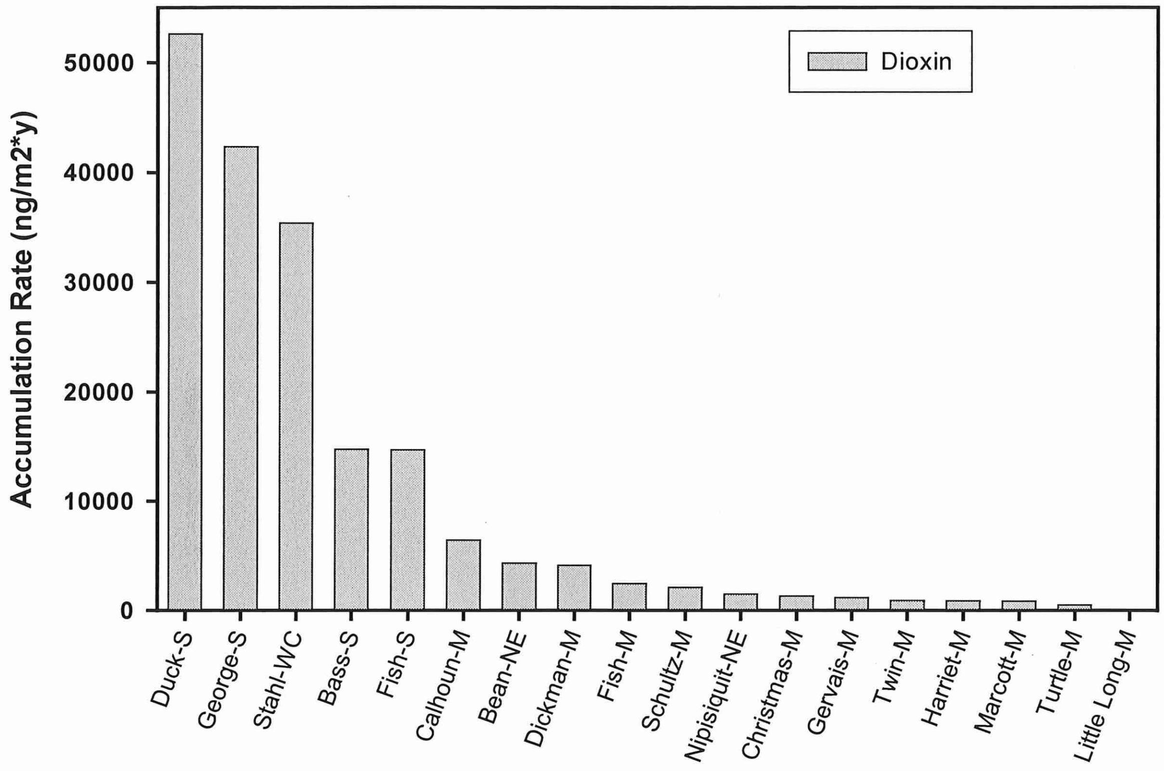


Total PCB Accumulation Rates
Metro Lakes
After Focus Factor Correction

deposited. Holsen et al. (1991) found deposition rates to Chicago that were up to a thousand times greater than those in non-urban areas in the upper Midwest.

PCDD/Fs. Polychlorinated dioxins and furans are somewhat unique pollutants, as they were never intentionally manufactured. They are incomplete combustion products in the incineration of waste, and can also be formed from bleaching of paper pulp using chlorine gas. They are byproducts in the manufacture of pentachlorophenol, in emissions from cement kilns, emissions from chloralkali plants, from sewage sludge, and were a contaminant in the manufacture of Agent Orange, the defoliant used in the Vietnam War. The dioxins and furans are both mixtures of many different congeners, and are also considered to be PBTs.

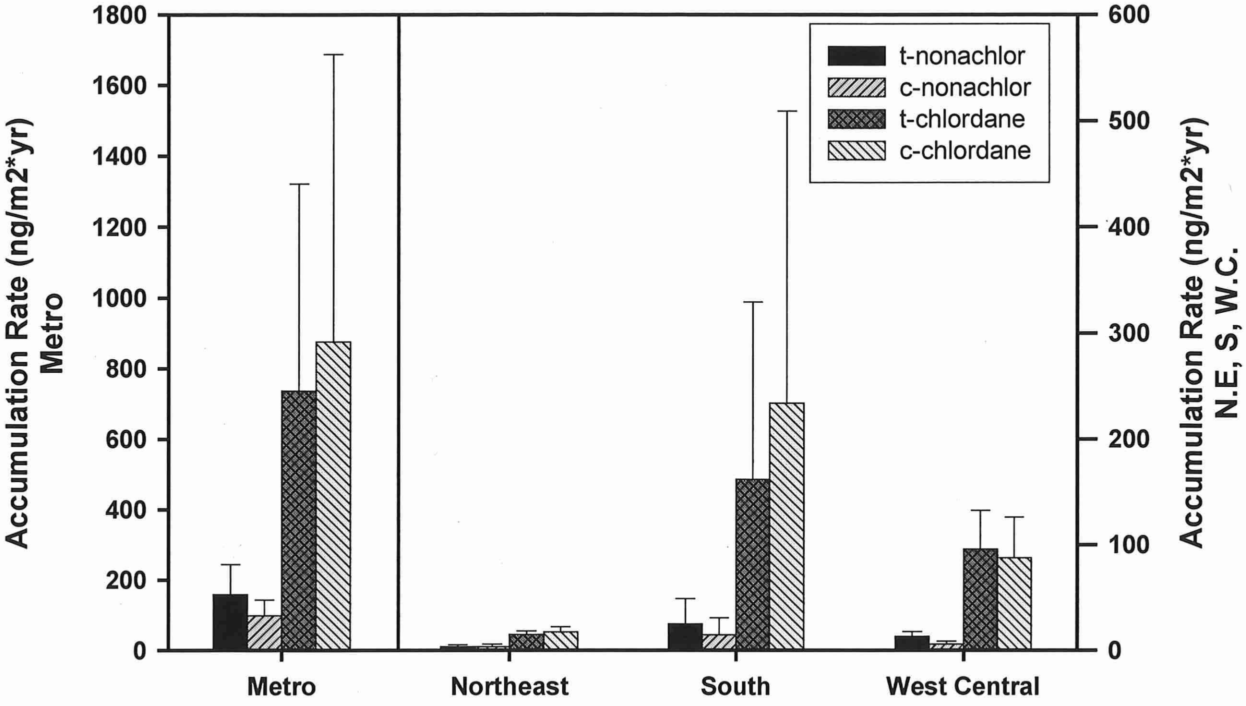
The concentrations of PCDDs and PCDFs ranged from non-detect (nd) – 65 ng/g and nd – 2.3 ng/g, respectively. The mean concentration was 18 ng/g PCDD and 0.41 ng/g PCDF for those lakes where the compounds were detected (about half of the lakes). The focus-corrected accumulation rates of PCDDs and PCDFs averaged 10 and 0.16 ug/m$^2$ yr in lakes where the compounds were detected. The PCDF accumulation rates are well within the Midwestern regional background, but the PCDD accumulations are considerably above the regional background of 0.05 – 0.4 ug/m$^2$ yr (Pearson et al., 1998). While the remote signature of PCDD/Fs usually has 5 –10 times more dioxin than furan, the enhanced dioxin signal in these sediments indicates that there may be a dioxin-enhanced source to the subregional atmosphere signal. The PCDDs were found in 11of 20 Metro lakes, and in 4 out of 5 of the southern region of the state. In fact, 4 out of 5 of the highest accumulation rates included the southern lakes.



**Dioxin Accumulation Rates**
**All Lakes Above LOD**
**After Focus Factor Correction**

<ins>Chlordanes.</ins> Technical chlordane is a mixture of 17 major chlorinated compounds. Four important components of this mixture were included in this study, and they are cis- and trans-chlordane and cis- and trans-nonachlor. Technical chlordane was produced in the US from 1948 until its ban in 1988 by the USEPA. Total US production was more than 10 million kg. It is used mostly on lawns and gardens, ornamental trees, and applied to foundations for termite control. It was also applied as a pesticide to protect corn and citrus crops. These compounds are also PBTs.

The concentrations of cis- and trans-chlordane averaged 1.2 and 1.1 ng/g, and the concentrations of cis- and trans-nonachlor averaged 0.15 and 0.23 ng/g. All compounds were detected in all lakes except for Beaver Lake. The accumulation rates averaged 0.35 and 0.30 ug/m$^2$ yr and 38 and 62 ng/m$^2$ yr for cis- and trans-chlordane and nonachlor, respectively. In general, the compounds co-varied with each other as would be expected since they all are components of the technical mixture. When compared across different geographical regions, the Metro region had significantly higher accumulations than all the other regions (see figure below). The southern lakes had the next highest accumulations followed by the west central region, with the northeast region having the lowest accumulations. Lake Harriet had the highest accumulations of all 4 compounds. The reasons for this may be due to residential lawn care applications in the Harriet watershed.



**Accumulation Rate of Contaminants**
**by Region**
**after Focus Factor Correction**

Toxaphene. Toxaphene is a broad spectrum pesticide that replaced DDT in the mid-1970s for control of cotton pests. This PBT was restricted in 1984 and banned in 1990. It was mostly used in the southern US, and accumulations in the upper midwest are mostly attributed to deposition following long range transport. "Hot spots" have been found in sediments from Canadian lakes that resulted from the use of toxaphene as a piscicide in the 1950s.

Our analyses found no detectable toxaphene in any of the lakes that were sampled. This is not surprising given the small amounts of sediments that were extracted. Our detection limit for toxaphene in these particular samples was approximately 10 ng/g, and background concentrations resulting from atmospheric deposition are 5-15 ng/g.

Lindane (γ-hexachlorocyclohexane). Lindane and its isomer α-HCH have been manufactured since 1949. It is used as an insecticide on fruit, vegetable, and forest crops (e.g. Christmas trees). It is still used as a treatment for head and body lice and scabies. It has not been manufactured in the US since 1977, but is still imported and formulated. Use is restricted to certified applicators in the US. It is still being produced in significant quantities globally, and is also a PBT. The HCHs were only found in five of the study lakes, with very low accumulations ranging from 0.1 to 4.2 ng/m$^2$ yr.

ΣDDT. The DDT family includes the o,p- and p,p- configurations of DDT, its aerobic degradation product DDE, and its anaerobic degradation product DDD. The degradation products are very persistent and have similar toxicities to the parent compound. All 6 of these compounds are considered to be PBTs. DDT was manufactured from 1948 to 1972 in the US when it was banned for all uses. It is a broad spectrum pesticide, and is also used for malaria-vector control (mosquitoes) in tropical regions of the globe. It is still used in developing countries, largely for the control of malaria-borne mosquitoes. Because of its public health significance, its global ban is highly controversial.

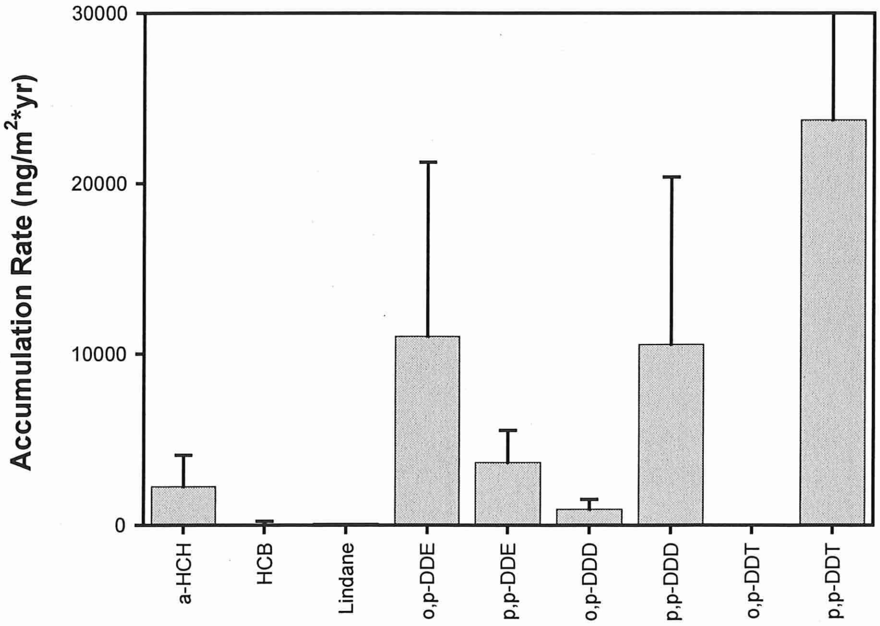
Only nine lakes were found to have detectable levels of any of the DDT compounds. Only 2 of the lakes had more than one DDT compound. These included Lake Harriet and Bass Lake. Of all of the DDT family of compounds, p,p-DDE or p,p-DDD usually is found most often and at the highest concentrations due to their greater resistance to degradation. However, this was only true in Harriet. The other detections were a smattering of different compounds, including those with o,p- configurations. All of them were very low concentrations. o,p-DDT was not detected in any lakeUnless DDT has been recently applied, it is usually in low concentrations in sediments relative to its degradation products. While generally the pattern observed in these lakes is typical of "aged" DDT, and at background levels, there are two lakes that only had detections of p,p-DDT (Square and Ninemile). This may indicate an isolated case of recent (last 10 years) application of old stocks of DDT in their watersheds.

Hexachlorobenzene. HCB is a manufactured chlorinated chemical and a waste product formed during the production of other chlorinated compounds. It was also used as a pesticide to protect grain seeds from fungus. HCB has been used in fireworks, ammunitions, and synthetic rubber. There have been no commercial uses of HCB in the US since 1986, but it is still being formed as a manufacturing by-product. HCB is considered a PBT.

Concentrations and accumulations of this compound were very low, and lakes with detectable HCB averaged 178 pg/g and 85 ng/m$^2$ yr. It was detected in 22 of the 55 lakes, and the highest accumulations were in Little Bass and Little Trout in the northeast region, and Macarrons and Turtle in the Metro region (200 – 650 ng/m$^2$ yr).

Overall, the atmospheric depositions of organic contaminants have been low in the state, and are representative of background conditions. The concentrations and accumulations of all compounds were log-normally distributed. The Metro area has higher accumulations of many of the compounds, but they are still low compared to other urban areas such as Chicago.

**AVERAGE FOCUS FACTOR CORRECTED ACCUMULATION RATES OF ORGANOCHLORINES**
**For All Lakes**
**(Excluding zeros)**



Error bars indicate standard deviation.

**Result 4:** Synthesis, Mapping, & Report Preparation
**Budget:** $ 20,150 Balance: $0
**Completion Date:** 6/2000

The synthesis of the above activities combined with data produced on the same lakes as part of an earlier LCMR-funded project (GIS, lead-210 dating, sediment accumulation rates) is a significant and essential effort. Maps of patterns in land use, non-point source watershed sources of pollutants, and atmospheric deposition of pollutants will be prepared and interpreted. Specific questions concerning the impact of nonpoint source pollution on Minnesota lakes will be answered, as outlined in "Dissemination," below.

**Final Status:**
Quantitative interpretation of the data is finished, and GIS-compatible databases are available. Papers for peer-reviewed publication are being prepared by the researchers.

## V. DISSEMINATION:

For each of the major nonpoint source issues (toxic organic compounds, heavy metals, and eutrophication), geographic and time trends will be displayed on maps, and the data will be available as a tool for environmental managers in the final report to the LCMR. For example, environmental scientists seeking to validate computer models of the effect of agriculture or urbanization on lakes may well use the data produced by this project. The results from individual lakes will be extrapolated to the regions in which they are located. Specific questions that will be answered include:

- Eutrophication:
  - How much shift has there been from natural benchmark conditions since settlement in the 1800s?
  - What nonpoint sources are responsible for eutrophication in the different regions of Minnesota?
  - Has atmospheric deposition of phosphorus and nitrate caused eutrophication of wilderness lakes?
- Heavy Metals:
  - How much metal loading is from the atmosphere versus soil erosion in different regions?
  - What was natural concentration of metals in different regions versus now?
  - Does urbanization funnel more metals to lakes?
- Toxic organic compounds:

Is atmospheric deposition constant across the state?
Does urbanization funnel more organics deposited from the atmosphere to lakes?
Does soil erosion increase loading of toxic organic compounds to lakes?

We also anticipate that this project will also address fundamental questions concerning the nature of nonpoint pollution, which will be disseminated to other scientists through scientific publications.

## VI. CONTEXT:

### A. Significance:

This project is a cost-effective way to quantify nonpoint source pollution and set benchmarks, especially when compared to the immense effort it takes to monitor inputs in real time, an effort that has been attempted for relatively few lakes. This effort is made even more cost-effective through its use of sediment-core samples collected and dated for an earlier project. The relative impacts of air pollution, soil erosion, and watershed development will be quantified for toxic organics, heavy metals, and nutrient enrichment. This method has been successfully used to address atmospheric mercury deposition, and we anticipate that the approach will be similarly productive with other nonpoint pollutants.

### B. Time:

An extra twelve months are requested for to complete this project because interpretation and integration of the different types of data (GIS, diatom, trace metal, toxic organics, erosion indicators, modern water samples) will consume considerable time after the time-consuming analysis of sediment stratigraphy from fifty-five lakes. The ending date will therefore be June 30, 2000.

**C. Budget Context:**

| | July 1995- June 1997 Prior expenditures on this project | July 1997- June 1999 Proposed expenditures on this project | July 1999- June 2001 Anticipated future expenditures on this project |
|---|---|---|---|
| 1. LCMR | $0 | $325,000 | $0 |
| 2. Other State | $10,000 | $15,000 | $0 |
| 3. Non State Cash | $10,000 | $0 | $0 |
| Total | $20,000 | $340,000 | $0 |

## VII. COOPERATION:

| Cooperator<br>(Project responsibility) | Salary Paid from LCMR funds<br>(% of total salary) | Affiliation | LCMR Project Funds | Additional Budget Items |
|---|---|---|---|---|
| Edward Swain[1]<br>(project management) | $12,000<br>(8%) | Air Quality Division, MPCA | $20,150 | Travel & supplies = $8,150 |
| Steven Heiskary[2]<br>(modern limnology) | $0<br>(0%) | Water Quality Division, MPCA | $44,800 | Unclassified staff = $11,200<br>Travel = $10,100<br>Water analyses = $23,500 |
| Deborah Swackhamer[3]<br>(organic pollutants) | $17,200<br>(8%) | Environmental and Occupational Health, University of Minnesota, Minneapolis | $113,800 | Technician, student = $67,640<br>Travel = $2,000<br>Analyses = $26,660<br>Publication costs = $300 |
| Daniel Engstrom[4]<br>(GIS, metals, diatoms) | $17,750<br>(12%) | St. Croix Watershed Research Station, Science Museum of Minnesota | $146,250 | Technician, students = $95,500<br>Travel = $3,500<br>Supplies = $6,500<br>Analyses = $23,000 |

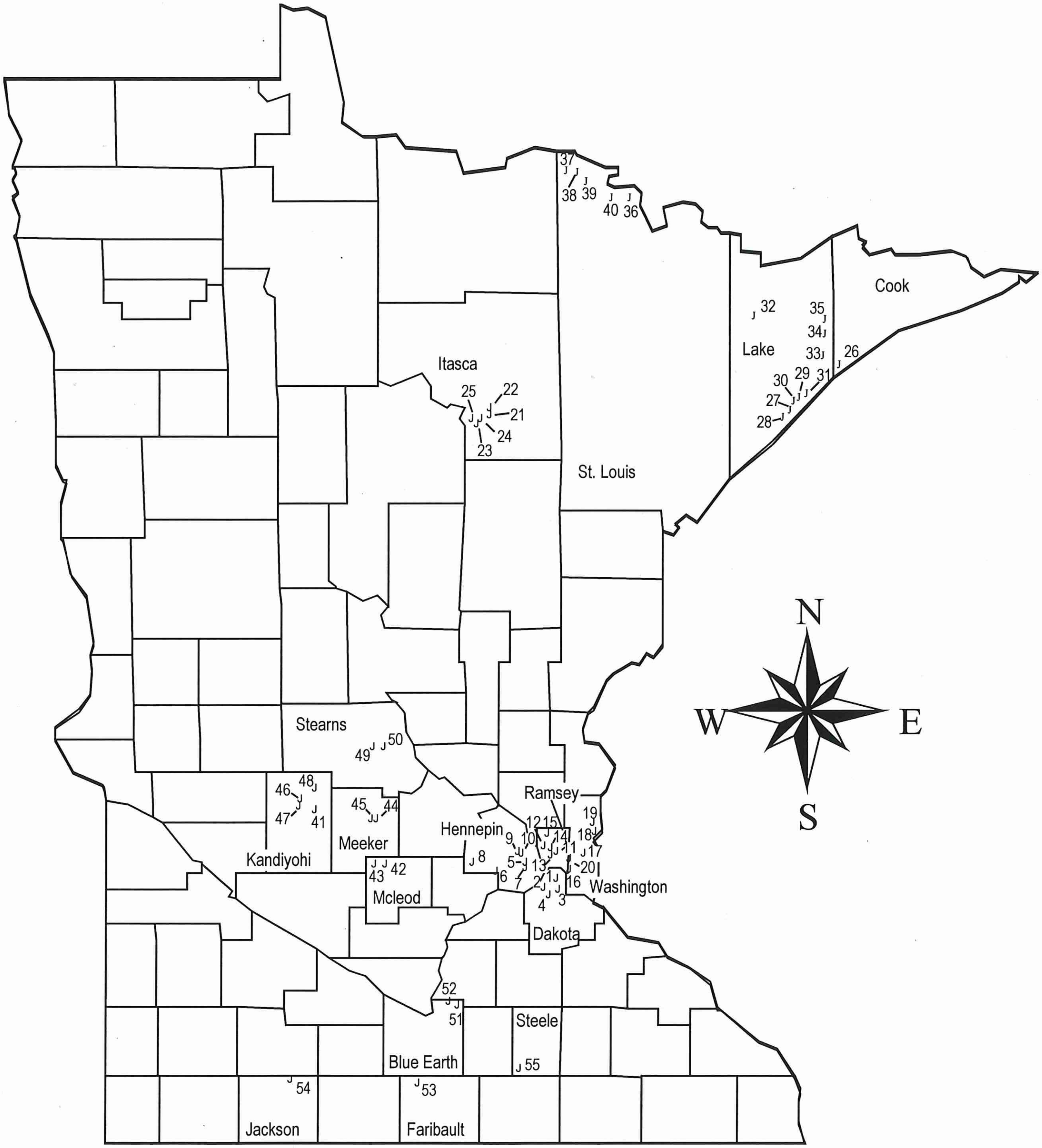
[1] Edward Swain is a classified employee at the MPCA. In this case, it is optimal to employ a classified employee and to displace part of his salary because it would be difficult to find an unclassified employee that can match Swain's qualifications: 1) Swain was manager of the LCMR project on which this one is based, and 2) he has technical expertise in each of the nonpoint pollutants being investigated, and is therefore an excellent choice for both project management and synthesis. The displaced salary will be used by the MPCA to partially fund an unclassified employee to investigate an air quality issue that Swain, with his training in paleoecology, might otherwise have time to pursue: global warming.

[2] Steven Heiskary will be able to spend 20 percent of his time on this project as part of his regular duties -- the $44,800 budgeted is for chemical analyses, traveling to the 55 lakes several times, and unclassified employees to help with sampling.

[3] Professor Swackhamer will oversee a graduate student and technician in the analysis and interpretation of organic pollutants.

[4] Dr. Engstrom is responsible for the collection and interpretation of GIS, trace metal, and diatom data. He will be coordinate the efforts of a full-time technician, plus a graduate student working on the analysis and interpretation of diatom microfossils.

**VIII. Location of Study Lakes:**



## IX. REPORTING REQUIREMENTS:

Periodic workprogram progress reports will be submitted not later than June 30 1998 and June 30 1999. A final workprogram report and associated products will be submitted by January 1, 2000, or by the completion date as set in the appropriation.

## X. RESEARCH PROJECTS:

A detailed description of work to be performed is attached.

# Detailed Description of Work to be Performed

## Atmospheric and Nonpoint Pollution Trends in Minnesota Lakes

### I. Abstract

This project documents geographic and historic trends in a) lake eutrophication and b) inputs of toxic metals and organic pollutants. Land-use impacts will be separated from atmospheric sources in the 55-lake study. This project leverages an investment that LCMR has already made in funding a $275,000 study to assess geographic and historic trends in mercury inputs to fifty lakes across Minnesota -- a project that involved collecting sediment cores from each lake, dating the last 150 years of sediment accumulation, and performing GIS analysis of the each lake's watershed for local land-use characteristics (five lakes will be added in this study). The same sediment samples will be used to assess the history of lake eutrophication and to quantify inputs of toxic chemicals in addition to mercury, including dioxins, furans, PCBs, chlorinated pesticides, and heavy metals such as lead, chromium, and cadmium.

The effects of nonpoint source pollution on lakes are notoriously difficult to assess, because (a) managers usually don't have pre-impact benchmarks against which to compare present-day lake conditions, and (b) monitoring inputs to lakes requires continuous sampling for several years to be meaningful. This project addresses two major issues facing lake managers: (1) it assesses atmospheric inputs to lakes of metals (lead, cadmium, chromium, and others) and semivolatile organics (dioxins, PCBs, and other chlorinated hydrocarbons), and (2) it quantifies eutrophication caused by soil erosion, urbanization, agricultural land-use practices, or atmospheric inputs of phosphorus and nitrogen. This monitoring and assessment project will employ an elegant method to document environmental trends by using the location where the impact occurs (the lake) as the data archiving device. This approach is better (and less expensive) in many ways than trying to quantify inputs to lakes with automatic stream and precipitation monitoring devices on shore. By using indicators of soil erosion (metals like aluminum or titanium), watershed inputs can be separated from air deposition of toxic metals. Eutrophication trends will be directly and unambiguously assessed by the use of bioindicators: diatom algae preserved in the sediments of each lake--the glass walls of diatoms, which make beautiful fossils, are powerful recorders of changing water quality. The diatom species that have dominated the last 3-5 years will be compared to the dominant species before agriculture and urban development changed the lake's watershed, and quantitative trends will be calculated using multivariate statistics on the bioindicator data.

Fifty-five Minnesota lakes distributed in geographic clusters will be analyzed for nonpoint source inputs: Twin Cities Metro (20 lakes); Agricultural region west of Metro (Kandiyohi, Meeker, Stearns counties, 10 lakes); Grand Rapids area (5 lakes); North Shore (5 lakes); Voyageurs National Park area (5 lakes); Northeastern Minnesota (5 lakes); Southern Minnesota (5 lakes).

### II. Background

Pollution from nonpoint sources is a major threat to aquatic ecosystems throughout Minnesota. Impacts range from nutrient enrichment and eutrophication to erosion and siltation and contamination from toxic metals and organic pollutants. While these impacts are expressed most strongly in urban and agricultural regions, aquatic habitats in more pristine areas also experience degradation from lake-shore home development and long-distance transport of atmospheric pollutants. The extent of these impacts for individual lakes -- or for a population of lakes in different regions of the State -- are poorly known, because (a) managers lack pre-impact benchmarks against which to compare present-day conditions, and (b) monitoring inputs to lakes requires continuous sampling over several years to be meaningful. This situation is not unique to Minnesota, and other states with abundant surface-water resources are equally ignorant of the degree of change that has occurred since time or European settlement. Synoptic surveys of present-day lake conditions in different ecoregions of the State (Heiskary & Wilson, 1990; Heiskary, 1996) provide a valuable baseline for assessing future impacts and are useful for assessing ecological "potential" within constraints imposed by prevailing land use. However, such surveys lack historic perspective and may give a misleading impression of background conditions for impacts that are extremely widespread.

Within the last decade, the paleolimnological analysis of lake-sediment cores has developed into an extremely powerful tool for assessing the magnitude and timing of impacts from nonpoint-source pollution (Charles *et al.*, 1994). During this period a variety of techniques have been refined to the point that quantitative assessment of eutrophication, erosion, and toxic pollution are now possible (e.g., Fritz *et al.*, 1993; Dearing, 1992; Swain *et al.*, 1992). Such methods have usually been applied at individual sites on an experimental basis to refine methodologies or to answer management problems unique to that lake. Few studies have utilized paleolimnological tools to survey historic changes in water quality for a large number of lakes -- the PIRLA study of lake acidification is a notable exception (Cumming *et al.*, 1992) -- largely because of the effort required for the analysis of a single sediment core.

The objective of this study is document through paleolimnological methods, geographic and historic trends in (a) lake eutrophication and (b) inputs of toxic metals and organic pollutants to a suite of 55 Minnesota lakes. This project leverages an investment that LCMR has already made in funding a study to assess historic trends in atmospheric mercury deposition across Minnesota. The LCMR mercury project, currently in progress, involves collecting sediment cores from each lake, dating the last 150 years of sediment accumulation, and performing GIS analysis of each lake's watershed for local land-use characteristics. Yet the same sediment samples can be used to assess historical changes in nutrient loading and to quantify inputs of toxic chemicals in addition to mercury, including dioxins, furans, PCBs, chlorinated pesticides, and heavy metals such as lead, chromium, and cadmium. By using indicators of soil erosion (elements like aluminum or titanium), watershed inputs can be separated from air deposition of toxic metals. Eutrophication trends will be directly and unambiguously assessed by the analysis of diatoms preserved in the sediments of each lake. The siliceous cell walls of diatoms are well preserved in the sediments of most lakes and are powerful recorders of changing water quality. The diatom species that have dominated the last 3-5 years will be compared to the dominant species before agriculture and urban development changed the lake's watershed, and quantitative trends will be calculated using multivariate statistics on the bioindicator data.

The persistence and continued inputs of chlorinated toxic chemicals into the atmosphere has led to air contamination and has resulted in a global reservoir of such chemicals (Swackhamer and Eisenreich, 1991). These chemicals include industrial chemicals such as polychlorinated biphenyls (PCBs); chlorinated pesticides such as DDT and chlordane; and combustion products such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F). These chemicals all share chlorine in their molecular makeup, and it is the chlorine that makes them toxic and also resistant to degradation or metabolism. These chemicals circulate in the environment to such an extent that they have been documented in air, water and biota in the Arctic and Antarctic.

These chemicals are removed from air by precipitation events (both rain and snow), by gravitational settling of particulates containing the chemicals, and by gas absorption to solid surfaces and water. Once in lakes (by direct deposition or by runoff to the lake) they sorb to particles and eventually settle to the sediments where they are sequestered, creating a history of the input of the chemical to the lake. In the sediments, they are quiescent and do not diffuse or move significantly in the sediment.

Isolated measurements of many of the chemicals in air have been made, but the long term trends of these chemicals over time are not documented. The air measurements that have been made have not addressed geographical variability. Because some of these chemicals have sources that correlate with human population and activity, the air concentrations and the deposition to surfaces will differ between areas in the state that are remote from human activity compared to the Twin Cities, for example. Also, different chemicals may be more elevated near specific activities. Thus we do not know the current accumulations of these chemicals, or the geographic differences in accumulation across the state.

A more direct measure of current exposure to these chemicals would be to monitor them at different sites around the state. However, to determine patterns or trends in the data would require the collection of samples at many sites and over long time periods. Because of the cost of the analyses for these compounds, such monitoring is prohibitively expensive. The use of lake sediments to tell us current accumulations and the history of accumulation in the past is both cost effective and provides more information than a monitoring program would.

Fifty-five Minnesota lakes distributed in geographic clusters will be analyzed for nonpoint source inputs (Table 1): Twin Cites Metro (20 lakes); Agricultural regions west of the Metro area (Kandiyohi, Meeker, Stearns, and McLeod counties, 10 lakes); Grand Rapids area (5 lakes); North Shore (6 lakes); Voyageurs National Park area (5 lakes); Northeastern Minnesota (Lake and Cook counties, 4 lakes). These lakes, which represent three of Minnesota's seven ecoregions (North Central Hardwood Forest, Northern Lakes and Forest, and Northern Minnesota Wetlands), have already been selected and cores collected under the current LCMR mercury study. An additional set of five lakes will be chosen from the agricultural regions south of Mankato (Figure 1) to provide coverage for the Western Corn-Belt Plains ecoregion.

**Table 1. Proposed Study Lakes.** The focus, lake ID #, and lake name are noted. Five additional lakes and their watersheds will be chosen for study in the southern region of Watonwan - Blue Earth - Waseca - Martin - Faribault counties.

**Silver Bay/North Shore**
Lake and Cook Counties (6 Lakes)
38-0409 Bean
38-0405 Bear
16-0634 Dyers
38-0242 Johnson (Wolf)
38-0232 Nipisiquit
38-0231 Tettegouche

**International Falls/Voyageurs**
**(near Boise)**
St. Louis County (5 Lakes)
69-0682 Little Trout
69-0756 Tooth
69-0870 Shoepack
69-0872 Loiten
69-0936 Locator

**Cohasset/Grand Rapids**
**(near Clay Boswell)**
Itasca County (5 Lakes)
31-0560 Forsythe
31-0575 Little Bass
31-0570 Long
31-0571 Loon
31-0569 Snells

**South Central Minnesota**
**(low disturbance)**
Kandiyohi, Meeker, Stearns Counties (5 Lakes)
34-0142 George
34-0116 Henderson
34-0066 Long
73-0097 Kreighle
73-0092 Sagatagan

**South Central Minnesota**
**(agricultural)**
Meeker, Kandiyohi, McLeod Counties (5 Lakes)
47-0088 Richardson
47-0082 Dunns
34-0044 Diamond
43-0104 Stahls
43-0073 Hook

**NE Minnesota**
**(Control)**
Lake/Cook Counties (4 Lakes)
38-0691 August
39-0033 Ninemile
38-0047 Wilson
38-0068 Windy

**Twin Cities Metro**
**(Urban area)**
Dakota, Ramsey, Hennepin, Washington (20 Lakes)
19-0057 Fish
19-0046 Dickman
19-0042 Marcott(Ohman's)
19-0075 Schultz
19-0065 Holland
62-0007 Gervais
62-0054 McCarrons
62-0056 Owasso
62-0061 Turtle
62-0078 Johanna
27-0137 Christmas
27-0179-02 Little Long
27-0016 Harriet
27-0031 Calhoun
27-0035-01 Sweeney
27-0035-02 Twin
82-0014 Little Carnelian
82-0046 Square
82-0108 Elmo
82-0115 Tanners

**Figure 1. Study areas.** Shaded areas indicate counties in which lakes and their watersheds will be studied in this project to characterize nonpoint pollution. Five lakes and their watersheds will be chosen for study in the southern region of Watonwan - Blue Earth - Waseca - Martin - Faribault counties.

## III. Methods

### Site Selection and Mapping

Lakes were selected for investigation based on criteria established for the LCMR mercury study including proximity/distance from emission sources, degree of local watershed impact, present-day water quality (major-ion chemistry and trophic state), lake size, morphometry, and watershed area. Despite this prior selection, the array of study lakes is well suited to the investigation of other nonpoint source pollutants. In particular the lakes provide strong contrasts between highly impacted (urban, agricultural) and near-pristine (control) lakes with respect to both atmospheric emissions and nutrient runoff. Four of Minnesota's ecoregions are represented in this study by at least five lakes to provide a measure of variability within each region. Study lakes from agricultural and urban areas represent a broad range of trophic conditions, while lakes from more pristine areas of northern Minnesota are arrayed at varying distances from isolated emission sources (electrical utilities, pulp mills, and taconite processing plants). These northern lakes span a wide range in alkalinity and DOC. Most lakes occupy relatively small watersheds without major inflowing rivers and typically exceed 8 m in depth. The lakes were chosen in a non-random manner, so that results from this study cannot be applied in a statistical sense to the population of lakes as a whole.

Watershed characteristics are currently being mapped by GIS technology as part of the LCMR mercury study. The intent is to generate an ARC/INFO database with four thematic layers (base map, land cover, roads, and slope) for each of the 55 watersheds. Source data include 1991 NAPP color infrared stereo aerial photos, USGS 7.5' digital elevation maps, USGS Hydrological Investigation Atlas and Minnesota DOT roads data. The five sites to be added under this study will be analyzed in a similar manner.

Several issues will arise during the interpretation of the data collected in this project. For instance, how will we separate different types of nonpoint source pollution causing eutrophication if a watershed contains more than one type of nonpoint source pollution? Attribution of nonpoint sources as the source of contaminants and nutrients will only be made where GIS analysis indicates that one type of NPS clearly dominates a given lake. Contrasts of these systems that are dominated by one type of nonpoint source pollution will allow us to compare the delivery rates of different sources (e.g. agriculture, storm sewers, urban atmospheric deposition).

### Coring and Dating

A single sediment core spanning the last 200-300 years of lake history has been collected from the deeper region of each of the initial 50 lakes (five additional lakes in southern Minnesota will be cored for this project). The cores were collected during the open-water season by means of a piston corer fitted with a clear plastic core barrel and operated from the lake surface by rigid drive-rods. The sediments were extruded vertically from the top of the tube at 1-4 cm intervals and stored under refrigeration until subsampled for various analyses. At each coring site an additional sample of the uppermost 2-cm of sediment was collected with a Hongve drop-corer and stored in borosilicate jars for analysis of organic pollutants. Sediment's are currently being dated by $^{210}$Pb methods to determine age and sediment accumulation rates for the past 150-200 years. Lead-210 is measured by $^{210}$Po distillation and alpha spectroscopy (Eakins & Morrison, 1978), and dates are calculated by the constant rate of supply (c.r.s.) model (Appleby & Oldfield, 1983). Sediment cores from the five new sites will be collected and dated in a similar manner, analyzing a minimum of 60 samples for lead 210 activity over the five new cores.

Where appropriate, secondary dating markers will be used to verify lead-210 dating of cores. Charcoal and pollen are not always appropriate for a given site, and rarely supply definitive confirmation of dating. Lead 210 will thus be relied on for dating unless a) the areal inventory of lead 210 does not match that of nearby sites, b) the lead 210 curve indicates disturbance in the watershed that could affect dating, or c) if obvious change in the qualitative nature of the sediment (color, loss-on-ignition, etc.) does not match the known date of settlement. If local vegetational change or fire history indicates a reliable unique marker, we will make use of such markers in any cases where the lead-210 dating requires verification.

## Water Quality Monitoring

All lakes in the study will be sampled during the spring during the course of the study. A subset of the lakes that have not been sampled extensively in the past for other reasons will also be sampled during the summer and fall of 1997 in order to accurately characterize trophic status. The trophic status is essential for the calibration of the trophic status model based on diatom analysis (below) and will be important for interpretation of landuse data and fish contamination patterns. This subset will be determined after a review of existing data for each lake. The spring collections will provide at a consistent temporal sample for each lake for statistical purposes.

Samples will be collected near the point of maximum depth. Lake surface samples will be collected with an integrated sampler, which is a PVC tube 6.6 feet (2 meters) in length with an inside diameter of 1.24 inches (3.2 centimeters). Near-bottom samples for total phosphorus will be collected with a two-liter PVC Kemmerer. Dissolved oxygen and temperature profiles will be taken at one meter intervals on each sample date with a meter. Transparency will be measured by a Secchi disk.

Sampling procedures will be employed as described in the MPCA Quality Control Manual. Laboratory analyses will be performed by the laboratory of the Minnesota Department of Health (MDH) using U.S. Environmental Protection Agency (EPA)-approved methods. Pertinent information from the Minnesota Department of Health Chemical Laboratory Handbook (1995) is summarized below. Samples will be analyzed for total phosphorus (TP), total Kjeldahl nitrogen, nitrite+nitrate-N, color, dissolved organic carbon, solids, pH, alkalinity, turbidity, conductivity (field), chloride, chlorophyll-a, and phaeophytin (Table 2). Chlorophyll-a samples will be field filtered and frozen. Dissolved organic carbon (DOC) samples will be field filtered through a 0.45 micron filter. DOC samples will then be stored in 250 mL plastic bottles and acidified. Information on bottles, holding times, and other information may be found in MDH (1995).

All water quality data will be stored in STORET, the EPA's national water quality data bank. STORET parameter numbers are noted in Table 2. This will provide the opportunity to make comparisons with previously collected MPCA and Citizen Lake-Monitoring Program (CLMP) data for these lakes and allow the investigators to characterize inter-annual variability in some of the water quality variables used in this study. Data will be summarized using the statistical analysis software - SAS and made available to other investigators in a spreadsheet format.

## Quality Assurance for Water Samples

Two of the most important parameters in this study are total phosphorus and chlorophyll-a. Duplicate samples analyzed at MDH for total phosphorus in 1994 revealed a mean difference of 7 µg/L and a percent difference of 16 percent. For chlorophyll a duplicate samples, the mean difference was 1.36 µg/L and the percent difference was ten percent Recent (1996) MDH analysis of spiked TP samples found good spike recovery (Table 3):

**Table 2. Water Quality Parameters, MDH Lab #, STORET Code, and MDH Report Levels**

| Parameter | MDH # | STORET # | Report Levels |
|---|---|---|---|
| Total P | 59 | 665 | 0.01 mg/L |
| Total P, low level | 58 | 665 | 0.002 mg/L |
| Total Kjeldahl N | 68 | 625 | 0.1 mg/L |
| Nitrite+Nitrate - N | 69 | 630 | 0.05 mg/L |
| Chlorophyll-a | 450 | 32211 | |
| Phaeophytin | 451 | 32218 | |
| Total Suspended Solids | 3 | 530 | 1 mg/L |
| Suspended Volatile Solids | 4 | 535 | 1 mg/L |
| Color | 12 | 80 | 5 Pt-Co |
| Alkalinity | 22 | 410 | 10 mg/L |
| Dissolved Organic Carbon | 99 | | 1 mg/L |
| Chloride | 23 | 940 | 1 mg/L |
| Turbidity | 11 | 76 | 0.2 NTU |

**Table 2. Spike recovery for Total Phosphorus as the Minnesota Department of Health laboratory.**

| Spike | April Spike Recovery | June Spike Recovery |
|---|---|---|
| 10 µg/L* | 16 µg/L | <10 µg/L |
| 25 µg/L | 25 µg/L | 26 µg/L |
| 50 µg/L | -- | 50 µg/L |
| 100 µg/L | 99 µg/L | -- |
| 204 µg/L | -- | 204 µg/L |
| 400 µg/L | 411 µg/L | -- |

* MDH was not requested to run low-level analysis in either case

Low level analysis for TP and alkalinity will be used when concentrations are anticipated to be near the detection limit for the conventional technique, µg/L.

## Diatoms and Eutrophication

In the last few decades diatom analysis has become an increasingly important technique for evaluation of the extent of limnological change through time (Dixit et al., 1992). Diatom analysis has been used to document the impact of land-use change, such as forest clearance, agriculture, sewage inputs, or urban development (Bradbury, 1975; Brugam, 1978; Engstrom et al., 1985; Fritz, 1989; Smol, 1981; Stoermer et al., 1985), of atmospheric pollution from fossil-fuel burning (Battarbee & Charles, 1987; Charles et al., 1989), as well as of natural perturbations resulting from forest disturbance or vegetation change (Boucherle et al., 1986; Whitehead et al., 1989) or climate fluctuations (Bradbury, 1991; Fritz et al., 1991) on aquatic ecosystems. Diatoms have short generation times and colonize rapidly. Thus they respond virtually without lags to changes in the aquatic environment and for this reason are probably unparalleled as indicators of limnological change.

Originally diatom-based reconstructions of limnological conditions through time were qualitative in nature, but within the last few years multivariate statistical techniques that relate diatom distributions in surface-sediment samples to measured environmental gradients have provided a tool for the quantitative reconstruction of changes in lakewater acidity (Birks et al., 1990; Cumming et al., 1992; Stevenson et al., 1989), trophic state (Anderson et al., 1993; Fritz et al., 1993; Hall & Smol, 1992; Whitmore, 1989), and salinity (Fritz, 1990; Fritz et al., 1991), as well as a means of validating process-oriented models (Sullivan et al., 1991). The most widely used technique for quantifying the relationship between diatoms and environmental variables is canonical correspondence analysis (CCA) (ter Braak, 1986), an ordination method that allows one to identify the environmental variables that are strongly correlated with diatom distribution. The optima and tolerance of individual diatom species with respect to a given environmental parameter, such as trophic state, can be calculated with weighted averaging regression (ter

Braak & VanDam, 1989), an extension of CCA, and these data can then be used to derive a transfer function to reconstruct the environmental variable from diatom assemblages in cores (Birks et al., 1990).

### *A. Calculation of a Transfer Function for Quantitative Reconstruction of Limnological Conditions from Diatom Assemblages:*

Diatoms will be analyzed in the surficial sediment of each lake to characterize the modern community, and ordination of the diatom data and associated limnological data from the same suite of lakes will be used to quantify the relationship between diatom distributions and measured environmental variables, particularly those related to trophic state (nutrient concentrations and Secchi depth). We will use canonical correspondence analysis (ter Braak, 1986; ter Braak, 1987) to identify the major environmental gradients correlated with diatom distributions, as well as major groupings of lakes within the regional data set. The data set will be enlarged and made statistically more robust with forty lakes from a previous study in Michigan and from additional lakes studied for other reasons in Minnesota. Forward selection and Monte Carlo permutation tests will be carried out to test which environmental variables account for a statistically significant amount of variance in the diatom data (ter Braak, 1990). Trophic variables, including TP, TN, chlorophyll a, and Secchi depth, will be tested to determine whether they account for statistically significant variation in the diatom data, and a calibration equation will be derived with weighted-averaging regression (ter Braak & VanDam, 1989) for the most significant trophic variables. Published equations for TP reconstruction in various regions have root mean square errors of 0.15-4.0 µg g-1 (Anderson et al., 1993; Fritz et al., 1993; Hall & Smol, 1992). Although trophic state has been identified as the most important limnological variable of interest, reconstructions can be carried out easily for other parameters of regional significance, dependent on the nature of regional environmental settings and stresses.

### *B. Reconstruction of Pre-settlement Conditions and Evaluation of the Extent of Limnological Change:*

The extent to which lakes have been perturbed relative to their pre-disturbance state will be assessed by comparing the modern (approximately 1991-1996) diatom assemblage of each lake with assemblages at depth in the sediment core, from intervals prior to regional disturbance. Ideally one would analyze multiple sediment intervals from each lake and reconstruct a complete limnological history. However, the time required for paleolimnological analyses is considerable, and reasonable time and financial constraints permit analysis of only one or two lakes within each region at this level of detail. An alternate approach is to analyze just a few core levels from each lake and to compare of the top of each core with one or two pre-disturbance levels. This approach, which is commonly referred to as the core-top/ core-bottom technique, has been used to determine broad regional patterns of lake acidification in the eastern United States (Cumming et al., 1992; Dixit et al., 1992; Dixit & Smol, 1995), and forms the basis of the paleolimnological portion of the USEPA EMAP Surface Waters Program for monitoring ecological trends (Dixit & Smol, 1994).

In this study four stratigraphic samples will be analyzed from each core, one representing the last 5 years (1991-1996), one approximately 20 years prior to coring, and two samples from sediments representing pre-settlement times. This sampling strategy is intended to assess 1) the trajectory of change over the past two decades, 2) the magnitude of trophic change from preindustrial to modern times, and 3) the two pre-settlement samples will provide a measurement of the variation possible in diatom assemblages due to natural variation in the environment alone. An additional 40 samples will be analyzed for diatoms to provide a more detailed time-trend of trophic change in lakes that are identified, in consultation with the project manager, as particularly suitable for more analysis. The transfer function(s) will be applied to diatom data from pre-settlement horizons of each core to reconstruct trophic state in each lake prior to regional landscape disturbance. An assessment of the magnitude and direction of trophic or limnological change since pre-settlement times and two decades ago can be determined by comparing for each lake the reconstructed conditions with modern. Error estimates for reconstructed values can be generated based on the root-mean square error of the prediction or with bootstrapping techniques (Birks et al., 1990) and used to determine if modern conditions are significantly different from those in the past. These data can be summarized to describe and characterize the condition of regional populations at the time of settlement and to determine the proportion of regional lakes that have changed significantly in trophic state or some other variable.

One can also derive from ordination data an index of the magnitude and direction of change within the diatom community of each lake by measuring the distance in multivariate space between the pre-settlement and modern sample. This number is a measure of the amount change in the diatom assemblage through time. These calculations allow one to compare the magnitude of biological change between lakes and between regions, regardless of the nature or cause of the perturbation. This approach has been widely used to determine rates of change in plant communities (Jacobson et al., 1987) and has been applied recently to stratigraphic diatom data (Battarbee et al., 1988) to estimate the magnitude, direction and rate of limnological/biological change.

## Toxic Metals

Numerous studies have shown lake sediments to be excellent archives for historic changes in the industrial discharge of potentially toxic metals such as Hg, Zn, Pb, Cu, Ni, Cd and Co (Rippey et al., 1982; Norton et al., 1990; Engstrom et al., 1994). Most heavy metals have short residence times in the water column and are quantitatively retained in the sediments, making stratigraphic interpretations relatively straight-forward (but see (Carignan & Tessier, 1985; White et al., 1989). Sediment records have provided compelling evidence for the role of atmospheric deposition in contaminating aquatic environments far removed from direct (point-source) industrial influence (Evans, 1986; Rada et al., 1989). These studies have been used to document the history of emissions, the effect of abatement, and the geochemical cycling of trace-metals in the aquatic environment (Carignan & Nriagu, 1985; Renberg, 1986; Johnson, 1987).

Sediments will be analyzed for a suite of metals, bulk density, and elements derived from erosion of watershed soils. These data in combination with results from $^{210}$Pb dating will be used to reconstruct time-trends in metal inputs from atmospheric deposition and watershed erosion. Freeze-dried subsamples will be digested in 0.5 M HCl following oxidation of organic matter with hydrogen peroxide (Engstrom and Wright, 1984), and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for cadmium, lead, chromium, zinc, copper, and nickel. Four stratigraphic samples will be analyzed from each core, one representing the last 5 years (1991-1996), one approximately 20 years prior to coring, and two samples from sediments representing pre-settlement times. This sampling strategy is intended to assess 1) the trajectory of change over the past two decades, 2) the magnitude of change in pollutant inputs from preindustrial to modern times, and 3) the two pre-settlement samples will provide an measurement of the variation possible due to natural variation alone. An additional 60 samples will be analyzed for metals to provide a more detailed time-trend of metal pollution in lakes that are identified, in consultation with the project manager, as particularly suitable for more analysis. Geochemical analysis of the same sediment intervals for elements associated with the erosion of mineral soils (sodium, potassium, titanium, aluminum) are currently under way as part the LCMR mercury study. Bulk density, organic matter, and carbonate content of all sediment intervals will also be available from the mercury study.

A practical approach for estimating atmospheric deposition from a single core is to normalize contaminant accumulation by the 210Pb accumulation rate in the core to correct for different degrees of sediment focusing within and among lakes (e.g., Wong et al. 1995). Focusing is the preferential transport and deposition of fine-grained sediments into deeper parts of a lake basin. In this method, core-specific contaminant accumulation is divided by a focusing factor (F), where

$$F = 210\text{Pb accumulation (core)}/210\text{Pb deposition (atmospheric)}.$$

This correction assumes that both the specific contaminant and 210Pb are associated with fine-grained particulates and are focused to the same degree within the lake basin.

Trends in metal concentrations and accumulation will be compared among lakes within each of the study regions to determine if sites near emission sources are more highly impacted by atmospheric metal deposition than those more distant. Lakes will be stratified according to watershed impacts and erosion rates to determine whether urbanization, agriculture, and other land-use changes increase metal inputs from watershed soils.

Analytical results from sediment dating and metal analyses will be used to calculate metal accumulation rates for each core for modern and preindustrial times. The change in metal accumulation between these two periods will provide a relative measure of the increase in metal inputs to the lakes. Historic changes in atmospheric loading will also be inferred from concentration ratios normalized to a conservative tracer of soil erosion (e.g., aluminum):

$$E.F. = \frac{Me_m / Al_m}{Me_p / Al_p}$$

where $Me_m$ and $Al_m$ are modern (1986-1996) metal and Al concentrations and $Me_p$ and $Al_p$ are their preindustrial concentrations. These calculations correct for changes in metal inputs from soil erosion by assuming that metal:aluminum ratios in soils are constant over time for a given lake. Accumulation ratios and enrichment ratios are independent of individual lake characteristics (size, chemistry, morphometry, etc.) that otherwise affect the absolute flux of metals to the core-site and can be compared among lakes to assess spatial trends in atmospheric deposition.

## Organic Pollutants

All sediment samples underwent Soxhlet extraction for 24 hours with DCM following several cycles of methanol rinse. Approximately 5-7 g wet sediment was mixed with anhydrous sodium sulfate prior to extraction. Surrogate compounds (PCB congeners #14, 65, and 166, $^{13}$Cl-PCDD/Fs, $^{13}$Cl-lindane, $^{13}$Cl-HCB, $^{13}$Cl-DDE, and $^{13}$Cl-chlordane) were added at the beginning of the extraction to monitor the efficiency of the extraction process. The methane fraction was batch extracted with hexane to reduce water content, and the solvent fractions were combined and solvent exchanged to hexane.

The extract was reduced in volume to approximately 10 mL. Extracts were then cleaned by liquid-solid chromatography. The extract was passed over a column containing anhydrous sodium sulfate (1 g) over 1% deactivated alumina (7 g) over anhydrous sodium sulfate (1 g) over 0% deactivated silica gel (5 g) over anhydrous sodium sulfate (1 g). The alumina was activated at 450 °C for a minimum of 4 hr. and deactivated with organic-free water (w/w); the silica gel was activated at 350 °C for a minimum of 4 hr.; the sodium sulfate was cleaned by ashing at 450 °C for a minimum of 4 hrs. The column was eluted with 85 mL hexane followed by 95 mL of 40% DCM-in-hexane. The first fraction contained PCBs and several non-polar chlorinated compounds; the second fraction contain edpolar organochlorine compounds, PCDD/Fs, and toxaphene. Fractions are reduced in volume to approximately 1 mL and solvent exchanged to hexane. Extracts has elemental sulfur removed by passing them over a micro-column containing activated granulated copper and eluted with hexane. Extracts were stored in the freezer until analysis. Just prior to instrumental analysis, extracts were reduced to approximately 300 μL by gentle nitrogen stream and internal standards were added (PCB #204). All data were reported corrected for surrogate recovery.

The extracts were first analyzed for PCBs. PCBs were quantified by individual congener using the method of Mullin (1985) and Swackhamer (1988). Analysis was accomplished using a Hewlett Packard gas chromatograph equipped with an $^{63}$Ni electron capture detector (ECD) and a 60 m x 25 mm, 0.25 μm film thickness high resolution glass capillary column (DB-5) with $H^2$ carrier gas. The individual congener data were processed by the Millenium (Millipore-Waters) data system. Total PCBs and homolog distributions are reported as the sum of the individual congeners. All data were transferred electronically to spreadsheet and database software for further reduction and processing. All data are reported corrected to surrogate standard recovery. All of these methods have been approved in Quality Assurance Project Plans by the U.S. EPA, and have been used successfully by this laboratory for many years (e.g. Pearson et al., 1996).

The first and second fractions of each extract (see above) were then recombined and analyzed for the compounds shown in Table 3. The secompounds were analyzed by gas chromatographic mass spectrometry in electron capture negative ionization mode (Hewlett Packard 5988A) using the quantification method described in Swackhamer et al. (1987) with a few improvements regarding interference corrections. The ionization gas was methane, with the source operated at 100 °C and approximately 0.9 torr pressure. A 60 m x 0.25 mm MS-5, 0.25 um film thickness columnwas used with helium carrier gas. Selected ions weremonitored to maximize sensitivity and selectivity.

Table 3. Compounds analyzed by gas chromatographic mass spectrometry.

| | |
|---|---|
| o,p-DDT | PCDD/Fs |
| o,p-DDE | cis-chlordane |
| o,p-DDD | trans-chlordane |
| p,p-DDT | cis-nonachlor |
| p,p-DDE | trans-nonachlor |
| p,p-DDD | hexachlorobenzene (HCB) |
| α-HCH | toxaphene |
| γ-HCH (lindane) | hexachlorobenzene |

In this study each of the 55 lakes was characterized by the analysis (for the compounds in Table 3) of one modern sample from the top two centimeters of sedimentPCB analyses were performed on modern samples from the twenty lakes in the metropolitan area and compared to the PCB accumulation rates in other pristine areas in the upper Midwest. .

*Quality Assurance for Organic Analyses:* Duplicate analyses were done for all compounds of interest on sediments from Lakes Harriet, Square, Bass, and Stahl.. The precision of these analyses was acceptable given the extremely low levels of contaminants that were being measured.

Surrogate standards were added at the beginning of the sediment extractions to monitor for losses incurred during the procedures. Recoveries of $^{13}$Cl-lindane, $^{13}$Cl-DDE, and some of the $^{13}$Cl-PCDD/Fs were below detection (we had to guess at what the expected ambient concentrations were) and could not be calculated. We used the $^{13}$Cl-chlordane recoveries for toxaphene and all chlordane compounds, and $^{13}$Cl-HCB recoveries for the HCH and DDT compounds as well as for HCB. The average surrogate recoveries were within the acceptable limits for such analyses.

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## IV. Results and Products

### General Results

For each of the major nonpoint source issues (toxic organic compounds, heavy metals, and eutrophication), geographic and time trends will be displayed on maps, and the data will be available as a tool for environmental managers. For example, environmental scientists seeking to validate computer models of the effect of agriculture or urbanization on lakes may use the results of this project. The results from individual lakes will be extrapolated to the regions in which they are located.

Specific questions that will be answered include:

- Eutrophication:
  - How much shift has there been from natural benchmark conditions since settlement in the 1800s?
  - What nonpoint sources are responsible for eutrophication in the different regions of Minnesota?
  - Has atmospheric deposition of phosphorus and nitrate caused eutrophication of wilderness lakes?
- Heavy Metals:
  - How much metal loading is from the atmosphere versus soil erosion in different regions?
  - What was natural concentration of metals in different regions versus now?
  - Does urbanization funnel more metals to lakes?
- Toxic organic compounds:
  - Is atmospheric deposition constant across the state?
  - Does urbanization funnel more organics deposited from the atmosphere to lakes?
  - Does soil erosion increase loading of toxic organic compounds to lakes?

### Specific Products

This project will also address fundamental questions concerning the nature of nonpoint pollution, which will be disseminated to other scientists through scientific publications.

*Diatoms and Eutrophication:*

The extent to which lakes have been perturbed relative to their pre-disturbance state will be assessed by comparing the modern diatom assemblage of each lake with assemblages at depth in the sediment core, from intervals prior to regional disturbance. The transfer function(s) will be applied to diatom data from pre-settlement horizons of each core to reconstruct trophic state in each lake prior to regional landscape disturbance. An assessment of the magnitude and direction of trophic or limnological change since pre-settlement times can be determined by comparing for each lake the reconstructed conditions with modern. Error estimates for reconstructed values can be generated based on the root-mean square error of the prediction or with bootstrapping techniques (Birks et al., 1990) and used to determine if modern conditions are significantly different from those in the past. These data will be summarized to describe and characterize the condition of regional populations at the time of settlement and to determine the proportion of regional lakes that have changed significantly in trophic state or some other variable.

We will also derive from ordination data an index of the magnitude and direction of change within the diatom community of each lake by measuring the distance in multivariate space between the pre-settlement and modern sample. This number is a measure of the amount change in the diatom assemblage through time. These calculations allow one to compare the magnitude of biological change between lakes and between regions, regardless of the nature or cause of the perturbation.

*Toxic Metals:*

We will reconstruct time-trends in metal inputs from atmospheric deposition and watershed erosion. Trends in metal concentrations and accumulation will be compared among lakes within each of the study regions to determine if sites near emission sources are more highly impacted by atmospheric metal deposition than those more distant. Lakes will be stratified according to watershed impacts and erosion rates to determine whether urbanization, agriculture, and other land-use changes increase metal inputs from watershed soils.

Analytical results from sediment dating and metal analyses will be used to calculate metal accumulation rates for each core for modern and preindustrial times. The change in metal accumulation between these two periods will provide a relative measure of the increase in metal inputs to the lakes. Historic changes in atmospheric loading will also be inferred from concentration ratios normalized to a conservative tracer of soil erosion (e.g., aluminum):

$$\text{E.F.} = \frac{Me_m / Al_m}{Me_p / Al_p}$$

where $Me_m$ and $Al_m$ are modern (1986-1996) metal and Al concentrations and $Me_p$ and $Al_p$ are their preindustrial concentrations.

*Organic Pollutants:*

The products that will result from this study will be the concentrations (ng chemical per dry weight of sediment) and accumulation rates (ng chemical per unit area per year) of PCBs, PCDD/Fs, and selected chlorinated pesticides in approximately 50 lakes in Minnesota, and in vertical cores from three selected lakes. This will allow us to evaluate differences in the atmospheric deposition of these compounds near and far from sources, and to contrast urban vs. rural deposition. Not only will these data be valuable to the state of Minnesota, but they will have significance nationally and internationally. There are very few estimates of atmospheric deposition of these compounds, and none that evaluate the objectives stated above.

## VI. Budget

## VII. Principal Investigators and Cooperators.

| Cooperator | Affiliation |
|---|---|
| Edward Swain<br>(project manager, synthesis) | Air Quality Division,<br>MPCA |
| Steven Heiskary<br>(modern limnology) | Water Quality Division,<br>MPCA |
| Deborah Swackhamer<br>(organic pollutants) | Environmental and Occupational Health,<br>University of Minnesota, Minneapolis |
| Sherilyn Fritz<br>(diatoms, eutrophication) | Department of Earth & Environmental Sciences,<br>Lehigh University, Bethlehem, Pennsylvania |
| Daniel Engstrom<br>(GIS, metals, synthesis) | St. Croix Watershed Research Station,<br>Science Museum of Minnesota, Marine on St. Croix, MN |

A resume for each of the cooperators is attached.