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J. M. Ramstack Lehigh University

Sherilyn C. Fritz University of Nebraska-Lincoln, sfritz2@unl.edu

D. R. Engstrom St. Croix Watershed Research Station, Science Museum of Minnesota, Marine on St. Croix MN, dre@smm.org

S. A. Heiskary Minnesota Pollution Control Agency, 520 Lafayette Road, St. Paul, MN

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# The application of a diatom-based transfer function to evaluate regional water-quality trends in Minnesota since 1970

J. M. Ramstack  $^{1,2,*}$ , S. C. Fritz<sup>3</sup>, D. R. Engstrom<sup>4</sup>, and S. A. Heiskary <sup>5</sup>

1 Department of Earth and Environmental Sciences, Lehigh University, Bethlehem PA-18015, USA

2 Current address: Department of Animal Ecology, Iowa State University, Ames IA 50011, USA

3 Department of Geosciences and School of Biological Sciences, University of Nebraska, Lincoln NE-68588 –0340, USA

4 St. Croix Watershed Research Station, Science Museum of Minnesota, Marine on St. Croix MN-55047, USA

5 Minnesota Pollution Control Agency, 520 Lafayette Road, St. Paul MN-55155, USA

\* Correspondence, email ramstack@iastate.edu

#### **Abstract**

Significant population growth over the last three decades, as well as efforts to improve surface-water quality mandated by the Clean Water Act, potentially have had opposing influences on aquatic ecosystems in the U.S. Because historical data on water-quality trends are limited over this time period, we developed a diatom-based transfer function to reconstruct chloride, color, acid neutralizing capacity (ANC), total phosphorus (TP), and pH in 55 Minnesota lakes. The lakes span three different ecoregions, as well as the Twin Cities metropolitan area, and differ in their history of settlement and land use, and in surficial geology, climate, and vegetation. Lakes in the Northern Lakes and Forest ecoregion are nearly pristine, whereas those in the other regions likely are strongly affected by urban or agricultural pollutants. Reconstructions of water-chemistry trends since 1970 suggest that recent human activities have had substantial impacts in both urban and rural areas. Chloride concentrations have increased in many Metro lakes, which may be due to road salts, and phosphorus levels have been steady or rising in agricultural regions. The majority of Metro lakes show some decline in TP, although many of the changes are not statistically significant based on our reconstruction techniques. There is no evidence that atmospheric deposition of sulfate or nitrate has caused acidification or changes in trophic state for remote lakes in the northeastern part of the state.

**Keywords:** acidification, diatoms, eutrophication, Minnesota lakes, phosphorus, transfer function

## **Introduction**

The period since 1970 has been one of dynamic change for water resources in North America. On one hand, intense human population growth has increased stress on aquatic systems, yet environmental laws have mandated cleaner surface waters. For example, the Federal Water Pollution Control Act of 1972 and the Clean Water Act Amendments of 1977 were aimed at improving surface-water quality (Fetter 1994).

Throughout the United States, a number of monitoring studies of individual or small clusters of lakes have been carried out during the last few decades

to assess changes in water quality (Edmondson and Lehman 1981; Jassby et al. 1995; Johengen et al. 1994). However, there are relatively few investigations that address large-scale regional trends in water quality over this time period, with the exception of studies of lake acidification (Kingston et al. 1990; Cumming et al. 1992; Hall and Smol 1996) and eutrophication in eastern North America (Dixit et al. 1999; Siver et al. 1999). Sparse data exist for agriculturally dominated landscapes in the North American mid-continent, with adjoining areas that experience the impacts of urbanization, mining and atmospheric pollution. Thus, it is currently not possible to evaluate regional patterns of water-quality change or to compare the extent of change attributable to differing human impacts and land-use histories.

We developed a diatom-based calibration data set (e.g., Charles and Smol (1994), Charles et al. (1994)) from 55 lakes in Minnesota (Figure 1) and use this data set to reconstruct historical trends in water chemistry over the last c. 30 years (Fritz et al. 1993; Reavie et al. 1995a; Reavie and Smol 2001) by comparing core sections equivalent to c. 1970 with modern conditions in each of the lakes. We chose this 30-year period to assess whether efforts to improve water quality over this time period have had a significant impact on the state's lake ecosystems. Nonpoint source pollution is a problem for Minnesota's aquatic ecosystems, as a result of agriculture, urban sprawl, lakeshore development, and deposition of atmospheric pollutants. The lakes that were used in this study range from nearly pristine sites in the northeastern part of the state to those strongly affected by urban and agricultural nutrient loading in the south. This range of lakes allows us to assess recent changes in water quality in a variety of ecosystems and to compare the extent of change attributable to different types of human impact. The limited historical data for this region can also be used to test the accuracy of our paleolimnological reconstructions.

#### *Study area*

The lakes in this study represent three of Minnesota's ecoregions: Northern Lakes and Forests, North Central Hardwood Forests, and Western Corn Belt Plains, as well as the Twin Cities (Minneapolis-St. Paul) metropolitan region (Table 1, Figure 1). These regions represent a gradient in vegetation, precipitation, geology, and land use from the northeast to the southwest portion of the state.

Fifty of the lakes in this study were selected for a previous study on mercury deposition across Minnesota (Engstrom et al. 1999). For this study, five additional lakes were added from agricultural regions in the southern portion of the state (those in the Corn Belt Plains ecoregion). The lakes were chosen in a non-random manner, but they are qualitatively representative of the larger population of lakes in each of the regions.

The Northern Lakes and Forests region is primarily forested, with only small tracts of land permanently cleared for agriculture and iron mining (Engstrom et al. 1999). There is little urban development, although the shores of some lakes are lined with resorts and cabins (Tester 1995). Lakes tend to be small and deep and are generally oligotrophic  $\langle 0.010 \text{ mg} \rangle$ L TP) to mesotrophic (0.010–0.030 mg/L TP) (Heiskary et al. 1987). Soils are very thin and overlie crystalline bedrock of the Canadian Shield. Many of these lakes have a very low-buffering capacity, making them potentially susceptible to acidification by acid rain (Kingston et al. 1990). Twenty of the study lakes are in this northern ecoregion (Table 1). Five of these lakes are clustered near the city of Grand Rapids, five are located within Voyageurs National Park, near the U.S./Canadian border, six are within the Lake Superior Highlands, within 5 km of the North Shore of Lake Superior, and the remaining four lakes are located within the Superior National forest.

The North Central Hardwood Forests region is characterized by a mosaic of land uses (Heiskary et al. 1987). The west-central portion is dominated by agricultural and forested use, while the eastern metropolitan area is dominated by urban, wetland, and forested areas (Engstrom et al. 1999). In recent decades, the proportion of land used for agriculture and urban development has increased. Currently the lakes in the North Central Hardwood Forests region range from oligotrophic to hypereutrophic (>0.100 mg/L TP) (Tables 1 and 2). Most lakes overlie calcareous glacial drift and consequently are high in alkalinity. Approximately 44% of the lakes in this ecoregion do not fully support swimable use because of eutrophication related impacts (Minnesota Pollution Control Agency 2000). Average annual evaporation exceeds precipitation in this region, so lake levels fluctuate seasonally and from year to year. Of the ten study lakes located in this region, half have large, agriculturally dominated watersheds and low water quality. The other half are not as heavily influenced by agriculture, have smaller watersheds, and higher water quality. All ten of the lakes are in rural areas, and all but two are at least partially ringed by summer cottages and year-round homes (Engstrom et al. 1999).

In the Western Corn Belt Plains ecoregion, agriculture is the primary land use, and more than 80% of the land has been under cultivation during the past few decades (Heiskary and Wilson 1989). The lakes in this region tend to be large and shallow and frequently receive runoff of sediment and nutrients from cultivated fields and animal feedlots. As a result of the combination of rich soils, shallow lake basins, and agricultural runoff, most lakes are classified as eutrophic (0.030–0.100 mg/L TP) or hypereutro-



**Figure 1.** Location of the fifty-five study lakes in Minnesota (key to lake numbers provided in Table 1), along with the ecoregions of Minnesota (modified from Tester (1995)).

phic (Tables 1 and 2). Five study lakes are located in this region, and all have watersheds dominated by agricultural lands, as is typical for the ecoregion (Engstrom et al. 1999). The five lakes, however, are slightly deeper (Table 1) than the norm for the region (Heiskary et al. 1987).

In the Minneapolis-St. Paul metropolitan area, al-

most all of the lakes are affected to some extent by urban runoff; many lakes receive direct, or indirect, input from storm sewers. Twenty of the study lakes are in this region, with roughly half in urban neighborhoods (within 10 km of the center of either Minneapolis or St. Paul). The other half are located in more rural landscapes.

**Table 1.** Location and size of each of the study lakes and their catchments (modified from Engstrom et al. (1999)). Metro = Twin Cities Metropolitan area, NL&F = Northern Lakes and Forests ecoregion {GR = Grand Rapids, NS = North Shore, SNF = Superior National Forest, and VNP = Voyageurs National Park}, HF = Hardwood Forests ecoregion {For = watershed is primarily forested, Ag = agriculturally dominated watershed}, and CBP = Corn Belt Plains ecoregion (refer to text for description of regions).

Map number	Ecoregion County		Lake	Latitude N	Longitude W area (ha)	Lake depth (m)	Max. catchment (ha)	Total catchment (ha)	Primary
1	Metro	Washington	Tanners	44° 57.00'	92° 58.88'	30.2	13.7	669	669
$\overline{2}$	Metro	Washington	Carver	44° 54.36'	92° 58.83'	19.6	11.0	864	864
3	Metro	Washington	Elmo	44° 59.37'	92° 52.96'	114.6	42.7	2076	569
$\overline{4}$	Metro	Washington	Square	$45^{\circ} 09.40'$	$92^{\circ}$ 48.26'	81.9	20.7	226	226
5	Metro	Washington	L. Carnelian	45° 07.07'	92° 47.79'	46.7	19.2	1854	162
6	Metro	Dakota	Dickman	44° 51.69'	93° 04.74'	9.1	2.4	57	57
$\tau$	Metro	Dakota	Fish	44° 49.35'	$93^{\circ} 10.03'$	12.5	10.1	1506	106
8	Metro	Dakota	Marcott	44° 48.95'	$93^{\circ} 04.02'$	7.5	10.1	251	56
9	Metro	Dakota	Schultz	44° 47.07'	$93^{\circ}$ 07.47'	5.3	4.9	69	18
10	Metro	Ramsey	Johanna	$45^{\circ}$ 02.43'	$93^{\circ} 09.93'$	86.4	12.5	1026	228
11	Metro	Ramsey	Turtle	45° 06.22'	93° 08.18'	133.3	8.8	180	180
12	Metro	Ramsey	Owasso	45° 02.28'	$93^{\circ}$ 07.45'	150.9	12.2	423	224
13	Metro	Ramsey	McCarrons	44° 59.85'	$93^{\circ} 06.67'$	30.1	17.4	412	43
14	Metro	Ramsey	Gervais	$45^{\circ}$ 01.05'	93° 04.30'	94.4	12.5	4028	243
15	Metro	Hennepin	Calhoun	$44^{\circ} 56.63'$	$93^{\circ} 18.79'$	168.5	27.4	2515	1236
16	Metro	Hennepin	Christmas	44° 53.85'	$93^{\circ} 32.47'$	105.7	26.5	189	189
17	Metro	Hennepin	Harriet	44° 55.15'	$93^{\circ} 18.58'$	138.6	25.0	387	387
18	Metro	Hennepin	Little Long	44° 56.88'	$93^{\circ}$ 42.47'	21.8	23.2	32	32
19	Metro	Hennepin	Sweeney	44° 59.44'	$93^{\circ} 20.48'$	28.3	7.6	1011	78
20	Metro	Hennepin	Twin	44° 59.52'	$93^{\circ} 20.17'$	8.7	17.1	33	33
$21\,$	NL&F	Itasca (GR)	Forsythe	47° 15.97'	$93^{\circ} 36.06'$	27.1	3.1	191	191
22	NL&F	Itasca (GR)	Snells	47° 14.46'	$93^{\circ} 40.16'$	35.8	15.2	288	288
23	NL&F	Itasca (GR)	Long	$47^{\circ}$ 13.63'	93° 39.39'	54.5	22.9	165	165
24	NL&F	Itasca (GR)	Loon	47° 13.95'	93° 38.42'	92.9	21.0	364	144
25	NL&F	Itasca (GR)	Little Bass	47° 17.05'	$93^{\circ} 36.09'$	64.5	18.9	540	540
26	NL&F	Cook (NS)	Dyers	47° 31.62'	$90^{\circ} 58.79'$	27.8	6.1	854	854
27	NL&F	Lake (NS)	Tettegouche	$47^{\circ} 20.66'$	$91^{\circ} 16.18'$	26.7	4.6	103	103
28	NL&F	Lake (NS)	Nipisiquit	47° 21.31'	$91^{\circ}$ 14.94'	23.7	5.5	298	60
29	NL&F	Lake (NS)	Wolf	$47^{\circ}$ 22.61'	$91^{\circ}$ 11.58'	13.1	7.3	68	68
30	NL&F	Lake (NS)	Bear	47° 17.05'	$91^{\circ} 20.62'$	18.3	8.8	60	60
31	NL&F	Lake (NS)	Bean	47° 18.51'	91° 18.02'	12.5	7.9	64	34
32	NL&F	Lake (SNF)	Ninemile	47° 34.55'	$91^{\circ}$ 04.88'	120.3	9.1	209	209
33	NL&F	Lake (SNF)	Wilson	47° 40.45'	$91^{\circ}$ 04.53'	257.1	14.9	719	719
34	NL&F	Lake (SNF)	Windy	$47^{\circ}$ 44.13'	91° 04.31'	184.6	11.9	1705	1464
35	NL&F	Lake (SNF)	August	47° 45.79'	$91^{\circ} 36.37'$	76.5	5.8	937	372
36	NL&F	St. Louis (VNP)	Shoepack	48° 29.82'	$92^{\circ} 53.27'$	155.4	7.3	1768	1635
37	NL&F	St. Louis (VNP)	Little Trout	48° 23.72'	$92^{\circ}31.63'$	107.6	29.0	140	140
38	NL&F	St. Louis (VNP)	Locator	48° 32.47'	93° 00.34'	54.1	15.9	1489	444
39	NL&F	St. Louis (VNP)	Loiten	$48^{\circ} 31.60'$	$92^{\circ} 55.61'$	39.0	14.9	242	242
40	NL&F	St. Louis (VNP)	Tooth	48° 23.88'	$92^{\circ} 38.59'$	23.6	13.1	151	151
41	HF	Stearns (For)	Kreighle	45° 34.72'	$94^{\circ} 28.69'$	41.0	17.1	88	88
42	HF	Stearns (For)	Sagatagan	45° 34.47'	94° 23.45'	88.7	14.3	252	252
43	HF	Kandyohi (For)	George	45° 14.55'	94° 59.06'	91.6	9.1	102	87
44	HF	Kandyohi (For)	Long	45° 19.87'	94° 51.13'	129.8	13.4	363	363
45	HF	Kandyohi (For)	Henderson	45° 13.82'	94° 59.56'	29.1	12.2	59	59
46	$\rm{HF}$	Kandyohi (Ag)	Diamond	$45^{\circ}$ 11.16'	94° 51.23'	644.8	8.2	3590	1850
47	HF	Mcleod(Ag)	Hook	44° 57.21'	94° 20.47'	133.1	5.5	620	399
48	HF	Mcleod(Ag)	Stahl	44° 57.18'	94° 25.24'	54.6	10.7	630	186
49	HF	Meeker (Ag)	Dunns	$45^{\circ} 09.50'$	94° 25.74'	63.0	6.1	1381	165
50	HF	Meeker (Ag)	Richardson	45° 09.57'	$94^{\circ} 26.40'$	48.3	14.3	1168	1168
51	CBP	Jackson	Fish	43° 50.82'	95° 02.67'	120.7	8.2	649	649
52	CBP	Faribault	<b>Bass</b>	43° 49.22'	94° 04.67'	75.7	6.1	136	136
53	${\rm CBP}$	<b>Blue Earth</b>	Duck	44° 13.07'	93° 48.89'	116.6	7.6	385	385
54	CBP	<b>Blue Earth</b>	George	44° 14.02'	93° 52.29'	36.2	8.5	54	54
55	CBP	Steele	Beaver	43° 53.52'	93° 20.90'	37.8	8.2	71	71

	Ecoregion County	Lake	pH	ANC (ueq/l)	Color (PT-Co)	Cl (mg/l)	TP(mg/l)
Metro	Washington	Tanners	8.9	2370	26	99.0	0.056
Metro	Washington	Carver	8.7	2190	24	123.0	0.036
Metro	Washington	Elmo	8.5	2870	$\,$ $\,$	17.0	0.010
Metro	Washington	Square	8.7	2430	$\overline{4}$	5.6	0.012
Metro	Washington	L. Carnelian	8.8	2120	$\tau$	8.3	0.009
Metro	Dakota	Dickman	7.9	1480	13	58.0	0.105
Metro	Dakota	Fish	7.6	1613	19	101.0	0.079
Metro	Dakota	Marcott	7.8	2393	10	36.0	0.019
Metro	Dakota	Schultz	7.8	1690	18	32.0	0.026
Metro	Ramsey	Johanna	8.3	1620	17	119.0	0.036
Metro	Ramsey	Turtle	8.3	2320	$\,$ $\,$	22.0	0.027
Metro	Ramsey	Owasso	8.2	2030	15	81.0	0.040
Metro	Ramsey	<b>McCarrons</b>	8.6	1591	19	74.7	0.048
Metro	Ramsey	Gervais	8.3	2320	18	102.0	0.033
Metro	Hennepin	Calhoun	8.7	2150	9	117.0	0.028
Metro	Hennepin	Christmas	8.9	2620	$\boldsymbol{7}$	23.0	0.015
Metro	Hennepin	Harriet	8.9	2090	9	96.0	0.027
Metro	Hennepin	Little Long	8.8	1680	9	3.7	0.010
Metro	Hennepin	Sweeney	8.4	4200	18	183.0	0.046
Metro	Hennepin	Twin	8.6	2927	14	100.0	0.022
NL&F	Itasca $(GR)$	Forsythe	6.9	233	85	0.7	0.021
NL&F	Itasca (GR)	Snells	8.2	2507	18	6.3	0.024
NL&F	Itasca (GR)	Long	8.1	2294	10	2.1	0.013
NL&F	Itasca (GR)	Loon	8.6	2468	9	2.8	0.011
NL&F	Itasca (GR)	Little Bass	8.2	2421	17	1.8	0.013
NL&F	$Cook$ (NS)	Dyers	7.6	690	69	0.8	0.027
NL&F	Lake (NS)	Tettegouche	7.3	303	33	0.4	0.017
NL&F	Lake (NS)	Nipisiquit	7.4	486	23	0.3	0.016
NL&F	Lake (NS)	Wolf	7.8	610	18	1.9	0.014
NL&F	Lake (NS)	Bear	7.5	342	9	0.4	0.011
NL&F	Lake (NS)	Bean	7.6	526	8	0.3	0.017
NL&F	Lake (SNF)	Ninemile	7.4	356	17	$0.8\,$	0.017
NL&F	Lake (SNF)	Wilson	7.5	342	14	0.3	0.013
NL&F	Lake (SNF)	Windy	6.9	148	98	0.3	0.012
NL&F	Lake (SNF)	August	7.3	290	97	0.9	0.015
NL&F	St. Louis (VNP)	Shoepack	6.6	100	117	$0.2\,$	0.019
NL&F	St. Louis (VNP)	Little Trout	7.4	306	3	0.3	0.007
NL&F	St. Louis (VNP)	Locator	7.0	123	58	0.4	0.009
NL&F	St. Louis (VNP)	Loiten	7.1	150	29	0.3	0.008
NL&F	St. Louis (VNP)	Tooth	6.8	189	39	0.4	0.012
HF	Stearns (For)	Krighle	8.5	2008	$\mathfrak{Z}$	1.2	0.011
HF	Stearns (For)	Sagatagan	8.5	1741	$\overline{\mathcal{I}}$	3.7	0.027
HF	Kandyohi (For)	George	8.8	4548	5	28.4	0.015
HF	Kandyohi (For)	Long	8.5	3407	9	9.2	0.019
HF	Kandyohi (For)	Henderson	8.6	4176	$\boldsymbol{7}$	17.6	0.022
HF	Kandyohi (Ag)	Diamond	8.6	3365	16	16.1	0.080
$\rm{HF}$	Mcleod(Ag)	Hook	8.4	2952	15	25.3	0.068
HF	Meled (Ag)	Stahl	8.4	3107	20	11.6	0.046
$\rm{HF}$	Meeker $(Ag)$	Dunns	8.6	2232	15	17.5	0.139
HF	Meeker (Ag)	Richardson	8.3	2715	18	17.4	0.098
CBP	Jackson	Fish	8.8	3245	$\boldsymbol{9}$	20.2	0.038
CBP	Faribault	<b>Bass</b>	$9.0\,$	3338	$20\,$	15.0	0.081
<b>CBP</b>	<b>Blue Earth</b>	Duck	8.9	2892	12	16.3	0.065
CBP	<b>Blue Earth</b>	George	9.2	1982	$25\,$	11.2	0.130
CBP	Steele	Beaver	8.9	2501	$\boldsymbol{9}$	15.0	0.030

**Table 2.** Modern water-chemistry values for each of the reconstructed variables. Refer to Table 1 for explanation of region abbreviations.

## **Methods**

#### *Sediment cores and sample preparation*

Sediment cores were obtained with a piston corer from a deep flat region of each of the fifty-five study lakes. Cores from the original fifty lakes were obtained in 1995 and 1996. The additional five lakes added for this study were cored during 1997 and 1998. The cores were sectioned, freeze dried, and a chronology was established with  $210Pb$  dating, using the constant rate of supply model (Appleby and Oldfield 1978). Based on the 210Pb chronology and calculated sediment accumulation rates, samples were taken to represent equivalent time periods from the core top (ranging from the top 1 to 5 cm and representing 1–3 years of accumulation) and from the interval representing c. 1970 (see Engstrom et al. (1999) for detailed methods on core collection and 210Pb dating).

A 10% hydrochloric acid solution was used to dissolve carbonates in the samples, and hydrogen peroxide was used to oxidize organic matter. After the chemical treatments, samples were rinsed and stored in distilled water. The diatom suspensions were settled onto coverslips, and the coverslips were affixed to slides with Naphrax®. At least 400 diatom valves were counted along transects in the modern samples. In the c. 1970 core sections, 300 valves were counted, except when the concentration of diatoms was extremely low. In these cases, 10 transects were counted. Due to poor diatom preservation, reconstructions for Marcott Lake (Dakota County) and Sagatagan Lake (Stearns County) were based on 145 and 80 diatom valves, respectively. Diatoms were identified to species following primarily (Krammer and Lange-Bertalot 1986 to 1991; Patrick and Reimer 1966).

#### *Water*-*chemistry analysis*

A modern water-chemistry data set was compiled for the study lakes by the Minnesota Pollution Control Agency (Table 2). Lakes were sampled a minimum of two times between 1996 and 1998. Sampling was done between mid-May and early October (the vast majority of samples were collected between June and September, the few samples taken in May were collected well after spring turnover). In addition, a limited set of water-chemistry data from 1993–1998 is available for 22 of the lakes (Minnesota Pollution Control Agency, unpublished data), and some of these values are incorporated here.

Epilimnetic water samples were collected just below the lake surface in 10L plastic cubitainers, placed on ice, and analyzed within one to four days of collection. Conductivity (temperature corrected), pH (closed head-space), and true color (Pt-Co units) (Standard Methods 2120B; American Public Health Association, American Water Works Association, and Water Environment Federation (1995)) were measured in the lab. Acid neutralizing capacity (alkalinity) was determined by fixed end-point titration, dissolved organic carbon (DOC) was measured with a carbon analyzer (UV-persulfate digestion), and chlorophyll *a* was measured with a spectrophotometer (EPA method 446.0). Major ions were measured on filtered (0.45m) subsamples by ion chromatography (Cl and  $SO_4$ ) and flame AA (K, Mg, Ca, Na). Total phosphorus (TP), total nitrogen (TN), and  $SiO<sub>2</sub>$ were determined by colorimetric methods (EPA parameter number 365.2) using either an autoanalyzer or spectrophotometer (American Public Health Association, American Water Works Association, and Water Environment Federation 1995).

Limited historical water-quality data exist for thirteen of the study lakes (eleven lakes in the Metro region, one in the Hardwood Forest, and one in the Corn Belt Plains). This data set consists of a compilation of TP, chlorophyll *a*, and Secchi depth measurements made over the past few decades (Heiskary, unpublished data summarized from STORET). These data are used for comparison with our core reconstructions.

## *Statistical analysis*

Modern diatom species assemblages were compared to the following water-chemistry variables: pH, acid neutralizing capacity (ANC), conductivity, K, Mg, Ca, Na, Cl,  $SO_4$ ,  $SiO_2$ , Secchi depth, color, dissolved organic carbon (DOC), total phosphorus (TP), total nitrogen (TN), and chlorophyll *a*. Some variables had a non-normal, skewed distribution (Na, Cl,  $SO_4$ ,  $SiO<sub>2</sub>$ , color, TP, TN, and chlorophyll *a*) and were log transformed to achieve a normal distribution prior to any further statistical analyses.

Relationships between water-chemistry variables and diatom assemblages were evaluated using canonical correspondence analysis (CCA) in the program CANOCO (ter Braak 1987). Taxa that occurred in at least two of the modern samples and had a maximum abundance greater than or equal to 1% of the diatom sum were included. In addition, three species

that had only one occurrence, but that represented more than 5% of that lake's total diatom assemblage were added. A total of 108 diatom taxa were used in these ordinations. Species with rare occurrences were downweighted (rare was defined as a species with <20% abundance of the most common species). Because some of the environmental variables are highly correlated, forward selection was used to select a subset of variables that best explained statistically the variation in the species data ( $p < 0.05$ ). For this subset of variables, a series of constrained CCAs were conducted to test the significance of each variable on the first axis, using Monte Carlo permutation tests with 199 permutations. In addition, partial CCAs were conducted for all pairs of variables. Weighted averaging (WA) calibration with inverse deshrinking was used to develop a transfer function that was applied to the 1970 core section.

The strength of the transfer function is reported in terms of the squared correlation  $(r^2)$  and the root mean square error (RMSE). Because the same data are used cipitation to generate the model and test it, the RMSE usually underestimates the RMSE of prediction (RMSEP), and the validation step of jackknifing was used. precipitation. Jackknifing reruns the model multiple times, each time leaving one sample out of the model and reconstructing that lake's chemistry. This approach gives a more realistic error for reconstructions (Fritz et al. 1999). Outliers were detected by examining plots of residuals and were removed before performing the reconstructions. The WA calibration and reconstructions were performed using the program CALIBRATE (Juggins and ter Braak 1999).

### **Results**

## *Calibration data set*

Canonical correspondence analysis (CCA) indicates that the 16 environmental variables collectively account for 42.7% of the variation in the diatom data. Forward selection indicates that Cl, ANC, color, TP,  $SO<sub>4</sub>$ , pH, and  $SiO<sub>2</sub>$  (in order of the amount of variation explained) explain independent variation in the diatom data and together account for 27.2% of the variation in the diatom data (64% of the variance explained by all environmental variables). In the constrained CCAs, all variables (Cl, pH, ANC, TP, and color) had a statistically significant ( $p < 0.005$ ) influence on diatom distribution. The ordination indicates that Cl was the strongest explanatory variable (explains 8.5% of the variation in the species data), followed by pH (7.6%), ANC (6.9%), TP (6.5%), and color (4.5%). In the partial CCA analyses, the ratios of the first to the second eigenvalues were large for all pairs of variables, and Monte Carlo permutation indicated significance ( $p \leq 0.01$ ), except for ANC with pH as a co-variable, which was only marginally significant ( $p = 0.065$ ).

In the CCA biplot (Figure 2), lakes cluster by ecoregion along the environmental gradients. Axis 1 accounts for 32.8% of the explained variation in the diatom data, while axis 2 accounts for an additional 19.6% of the explained variation. The first axis represents the maximum variation in the data set and is most closely correlated with log Cl and log TP; log Cl accounts for more of the variation in the species data than does log TP (represented in Figure 2 by the longer vector). The Cl gradient represents a gradient of ionic concentration from lakes in base-poor areas in the northeastern part of the state, which receive precipitation well in excess of evaporation, to lakes in western portions of the state with more easily weathered soils and where evaporation equals or exceeds precipitation. The lakes in the more pristine Northern Lakes and Forests region cluster toward the lower end of the TP and Cl gradients compared to the other three regions. Lakes also array themselves along the second axis, which is correlated most strongly with color, pH and ANC. The majority of lakes in the Northern Lakes and Forests region plot low along the pH/ANC gradient.

Table 3 summarizes the performance of the transfer function. The results indicate a high correlation between the observed and estimated values for all seven environmental variables. The RMSE values are higher for ANC, because this is the only variable that is not presented on a log-based scale.

#### *Modern diatom assemblages*

In the Northern Lakes and Forest ecoregion, modern samples from the North Shore (Table 1) are dominated by *Fragilaria construens* var. *venter* (Ehrenberg) Grunow and *Aulacoseira ambigua* (Grunow) Simonsen. Both of these species are common in oligotrophic to mesotrophic waters (Reavie et al. 1995b; Reavie and Smol 2001), although Brugam (1979) has argued that, in Minnesota, *Aulacoseira ambigua* is unrelated to trophic state. Lakes within Voyageurs National Park are dominated by *Asterionella formosa* Hassall, *Cy-*



*Figure* 2. Canonical Correspondence Analysis of the fifty-five study lakes with forward selection of environmental variables. Lakes are coded by ecoregion.

*clotella stelligera* Cleve and Grunow, and *Tabellaria flocculosa* (Roth) Kützing, which generally have mesotrophic TP optima (Hall and Smol 1992; Reavie et al. 1995a). The four lakes within the Superior National Forest are dominated by a combination of species found in both the North Shore and Voyageurs National Park areas. *Fragilaria crotonensis* Kitton is one of the dominant species in four of the five lakes clustered near the city of Grand Rapids and is not a dominant part of any of the other lakes in the Northern Lakes and Forests region. This diatom is often associated with nutrient enrichment in lakes of low to moderate alkalinity (Bradbury 1975; Brugam 1979).

In the Metro region of Minneapolis-St. Paul, many the of the modern samples are dominated by small *Stephanodiscus* species, which are known to have high phosphorus requirements (Bradbury 1975; Bennion et al. 1996). Bradbury (1975) found increases in four *Stephanodiscus* species in a sediment core from a lake in northeastern Minnesota, coincident with increased inputs of domestic and municipal wastes. Eleven of the Metro lakes are in urban areas within 10 km of the center of Minneapolis or St. Paul; *Stephanodiscus parvus* Stoermer and Håkansson makes up at least 30% of the count in six of these lakes. The remaining nine lakes in the Metro region are in more rural or suburban landscapes, and only two of these have *Stephanodiscus parvus* as 30% or more of the assemblage. The majority of lakes in the rural part of this region are dominated by *Asterionella formosa, Frag-*

**Table 3.** Results of the Weighted Averaging (WA) Regression. The strength of the transfer function is reported in terms of the squared correlation  $(r^2)$ , the root mean square error (RMSE; observed -inferred), and the jackknifing root mean square error (RMSE of prediction).

Environmental variable	$r^2$	Root mean square error (apparent)	Root mean square error of prediction
log Cl	0.77	0.43	0.55
ANC	0.79	476	597
log Color	0.68	0.20	0.28
log TP	0.68	0.19	0.25
log SO <sub>4</sub>	0.65	0.29	0.37
pH	0.80	0.28	0.35
log SiO <sub>2</sub>	0.69	0.28	0.42

*ilaria crotonensis,* and *Cyclotella bodanica* var. *lemanica* (O. Miiller) Bachmann, which are common in mesotrophic systems (Reavie et al. 1995).

In the Corn Belt Plains ecoregion, samples are dominated by *Aulacoseira ambigua* and small *Stephanodiscus* species, which have moderate to high phosphorus requirements (Hall and Smol 1992; Reavie et al. 1995a). One of the five lakes in this region has a high percentage of *Fragilaria crotonen- sis.* 

The agricultural lakes in the Hardwood Forests region (Table 1) show a similar species composition to those in the Corn Belt Plains, with *Aulacoseira* species and small *Stephanodiscus* species dominating the modern assemblage in these lakes. The lakes of this region that are in smaller, less agricultural water- sheds tend to be dominated by *Fragilaria crotonensis,* and only two of these five lakes have high percentages of *Stephanodiscus minutulus* (Kiitzing) Cleve and Moller.

#### *Fossil diatom assemblages*

In the Northern Lakes and Forests ecoregion, sites do not show major changes in species assemblages in the 1970 samples compared with the modern samples, although two of the lakes in the North Shore region show an increase in *Cyclotella pseudostelligera* Hus-tedt. Otherwise, there are no apparent changes in species assemblages in any of the other lakes of this ecoregion.

Shifts in species assemblages from 1970 to modern times are evident in the Metro region. For example, *Stephanodiscus pawus* or *S. minutulus* occur as at least 10% of the species count in 10 of the modern samples, as compared with 14 of the 1970 samples. Three of the lakes closest to the urban core show decreases in these small *Stephanodiscus* species over the past few decades. In the more rural areas of the Metro region, *Stephanodiscus* species declined as a significant part of the diatom flora in two lakes but increased in one other lake from 1970 to the present.

Within the Corn Belt Plains ecoregion, the lakes are dominated by *Aulacoseira* species and small *Stephanodiscus* species in both the modern and 1970 samples. However, the small *Stephanodiscus* species are more prevalent in modern samples, whereas *Aulacoseira ambigua* and *Aulacoseira granulata* (Ehrenberg) Simonsen decrease in abundance.

Few significant changes occur within the Hardwood Forests ecoregion. However, in the less agricultural sites, *Fragilaria crotonensis* is more prevalent in the modern samples compared with the 1970 samples.

#### *Water-chemistry reconstructions*

Water-chemistry reconstructions are expressed as the change from 1970 to the present (Figure 3). Reconstructions were performed for five water-chemistry variables that are most interesting limnologically, and potentially impacted by cultural influences (Cl, ANC, color, TP, and pH). Even though pH and ANC are often highly correlated in aquatic systems, we chose to include ANC because the constrained ordination suggested it exhibited some independent influence as an explanatory variable (see Section 3 on Calibration Data Set). Although the statistical analyses indicate that the influence of TP is weaker than Cl, pH, or ANC, we reconstruct this variable because its influence is statistically significant and clearly it is of strong interest to those concerned with water quality trends.

With the exception of ANC, the water chemistry reconstructions are based on log-transformed data. Thus, the changes are shown as log minus log values, which is an expression of the ratio of change. Because the errors are also log-based (with the exception of ANC), significance is likewise expressed in terms of the ratio of change. We also back-transformed the variables that were originally log-transformed (Cl, color, and TP) to look at the magnitude of change (Figure 4). In Figure 4, the lakes that are starred as showing significant change over time are simply those that showed significance on the log scale.

Most of the changes in Cl have occurred in the Metro region. When we look at the magnitude of change (Figure 4), it is obvious that there has been little change in Cl in the other three ecoregions.

Twelve of the lakes show statistically significant changes in ANC over the past few decades, and slightly more than half of them also show a change in lake pH. However, there are no clear regional trends in these variables.

Most of the lakes do not show statistically significant changes in color over this time period, and there do not appear to be clear regional trends in this environmental variable (Figure 3). Most of the lakes in the Northern Lakes and Forests region show a decrease in color; however, this is not statistically significant.

Some regional trends do occur in TP. Only six of the study lakes have shown statistically significant change in log TP over the past few decades (Fig-









ure 3). However, when we look at the magnitude of change in this variable (Figure 4), it is evident that little change has occurred in the Northern Lakes and Forests region; the majority of change has taken place in the other three ecoregions.

## *Comparisons with historical data*

Historical data from Wilson Lake, in Lake County (in the Northern Lakes and Forests region), exist from a water-chemistry survey from 1968 (Bright 1968). Although TP was not measured, Secchi depth measurements for Wilson Lake in 1966 and 1967 are 4.4 m and 3.1 m, respectively; the modern Secchi depth value for Wilson Lake is 4.0 m. Secchi depth and TP are commonly inversely correlated, as a lake increases in trophic status (TP), water transparency (Secchi depth) often decreases (Wetzel 1983). When compared with Bright's results, our modern Secchi depth value suggests that this lake's trophic status has not changed significantly over the last three decades; this is reflected in our TP reconstruction which shows that TP has not changed significantly since 1970. Species assemblages in this study and Bright's are consistent in that *Aulacoseira ambigua*  was the dominant diatom in both Bright's sample and our 1970 core section. Wilson Lake was also intensively studied in the early 1980's by the Minnesota Pollution Control Agency as part of an acid rain program. Based on eleven measurements from 1981– 1984, TP averaged 0.01 9 mg/l, and ranged between 0.011 and 0.030 mg/L (Minnesota Pollution Control Agency, unpublished data). Our modern TP measurement for Wilson lake is 0.013 mg/l. This is again consistent with the results of our reconstructions, which suggest that the trophic status of Wilson Lake has not changed significantly over the past few decades.

Historical data on TP exist for eleven lakes in the Metro region, as well as for one lake in the Hardwood Forest ecoregion and one lake in the Corn Belt Plains (Heiskary, unpublished data summary, drawn from STORET). For the Metro region, our data show that three lakes recorded a significant change in TP (Figure 3,4). Lake Elmo, which had a significant decrease in TP according to our data, showed a decrease in measured TP since 1951, although the change was only marginally significant  $(p = 0.079)$ . Only two lakes in the historical dataset show significant changes in TP, both Lake Calhoun (Hennepin County) and Lake Owasso (Ramsey County) had a significant decrease in measured TP since 1971. From 1971–1972, TP concentrations in Lake Calhoun averaged 0.059 mg/l; in contrast, from 1991–1995, TP averaged 0.032 mg/L (Minnesota Pollution Control Agency, unpublished data summary, drawn from STORET). The TP concentration in Lake Owasso averaged 0.083 mg/l during a period from 1971 to 1981 (based on 31 observations). In contrast, during a period from 1990–1995, TP averaged 0.049 mg/ l (based on 38 observations) (Minnesota Pollution Control Agency, unpublished data summary, drawn from STORET). Based on our reconstructions, both of these lakes show declines in TP that were not statistically significant.

George Lake (Kandyohi County), in the Hardwood Forest ecoregion shows a decline in TP, which is statistically insignificant in both our and Heiskary's results (historical data for this lake go back to 1979). Fish Lake, in the Corn Belt Pains, records a statistically insignificant post-1985 decrease in TP in historical data and a statistically insignificant post-1970 increase in ours.

#### **Discussion**

Our diatom-based reconstructions suggest that a number of lakes in the metropolitan area of Minneapolis-St. Paul and in the agriculturally dominated Corn Belt Plains have changed significantly since 1970, whereas limnological change in the Northern Lakes and Forests and Hardwood Forests areas has been limited.

The greatest changes in Cl occur in the Metro region (Figure 4). Cl is a conservative ion, and changes in concentration can result from evaporative concentration or dilution driven by climate or from seepage of road salts into the lake basins. It seems more likely in this case that the change has been due to the seepage of road salts, because the changes in Cl are confined to the Metro region (Figure 4).

Only a few lakes show significant shifts in color, in terms of the ratio of change. However, many lakes in the Northern Lakes and Forests region show a substantial shift in color, in terms of magnitude of change in Pt-Co units (Figure 4). The lakes that show changes greater than  $+/-$  10 Pt-Co units all have high modern color values (greater than 17 Pt-Co units). Declines in color may result from vegetation change (Pienitz et al. 1999) (which is unlikely in this region), or from changes in climate such as drought (Schindler et al. 1996) that may affect color via a variety of processes, such as increased water residence time or altered catchment inputs of dissolved organic matter.

Although a few lakes in each ecoregion show a shift in ANC, only five of the study lakes record a change in pH (Figure 3). None of the lakes in the Northern Lakes and Forests region show a significant change in pH, and only about half of the lakes show any decrease at all. The naturally low buffering capacity of these northeastern lakes makes them potentially susceptible to acidification by acid rain. However, these results suggest that there has been no significant acidification in this region in the past few decades. These results are consistent with the findings of the PIRLA project (Paleoecological Investigation of Recent Lake Acidification; Kingston et al. (1990)), which included three lakes from the Northern Lakes and Forests region (in St. Louis and Lake counties) and found no significant change in 20thcentury diatom-inferred pH.

Only one lake in the Northern Lakes and Forests region showed a significant change in TP (Figure 3), and, in terms of the magnitude of change (Figure 4), little change in TP is evident in the Northern Lakes and Forests region. This is a relatively pristine region, with very little agriculture or urban development, and hence land-use disturbances are minimal. A decrease in TP was expected in the Metro region (Figure 4) because of considerable efforts to reduce non-point source nutrient inputs, but most reconstructed changes were not statistically significant. Because many of these lakes are now eutrophic, the magnitude of decrease in TP is not large relative to the range of lakes surveyed, and the reconstructed change is not sufficient to shift these lakes into the mesotrophic category. Although only two lakes in this region showed a statistically significant decrease in TP in terms of a ratio of change, 14 out of 20 of these lakes did show some decrease in this variable. For example, seven of the Metro lakes record a decline in TP of at least 0.007 mg/l P (Figure 4), but these changes were not significant, because the ratio of change was not greater than the error of the reconstruction. Although not statistically significant, the decline in TP may be real and likely reflects successful reduction of nonpoint phosphorus inputs. The species data support the notion that subtle changes in TP have occurred in these Metro lakes over the past few decades. Small *Stephanodiscus* species, which are associated with high TP levels, dominated a larger percentage of lakes in the 1970s than in the modern core sections.

Historic TP trends in Metro lakes (Heiskary, unpublished data) and our reconstructed values generally show similar trends, but are not always the

same. The differences may occur because the historical dataset includes years with limited limnological sampling. A few spot measurements may not represent an accurate average of lake conditions for that year. Thus, diatom-based reconstructions may be more reliable, because the species assemblage in a core section integrates a longer period of time than a single sampling date.

In the Corn Belt Plains ecoregion, as well as in agricultural lakes from the Hardwood Forest region, a few of the lakes do show decreases in TP; however there are some lakes that show substantial increases in TP (Figure 4). Since 1970, small *Stephanodiscus*  species have become more prevalent, which suggests intensified agricultural influences in some of these systems. Although pesticides can have significant influences on diatom community structure in agricultural landscapes, we did not have data available to evaluate these impacts (Spawn et al. 1997).

This regional approach has allowed us to compare water-chemistry changes among regions with differences in land use. Results indicate that modern landuse practices are having substantial impacts on Minnesota lakes. In urban areas, road salts, and increases in impervious surfaces, have likely increased Cl levels, which are not substantially increasing in other regions. TP levels are declining in many urban lakes, suggesting that efforts to reduce non-point nutrient inputs (as well as reduction in development activity in some areas) may be having a noticeable effect. However, in the agricultural areas, TP levels are rising in some of the lakes, suggesting that landuse practices in these regions need to be evaluated. No significant acidification in the Northern Lakes and Forests region is evident in recent times nor are changes in trophic state. Thus, lakes in this region have not been significantly influenced by atmospheric deposition of strong acids, and the impact of other land-use changes have been minimal.

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## **Appendix 1**

The 108 diatom taxa that were used in the CCA ordination, the water-chemistry optima within the fifty-five Minnesota lakes, as determined by weighted averaging (see text), and the number of lakes in which each taxon occurred. Optima are not given for groups not resolvable to species level (ex. *Stephanodiscus* spp.).







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