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# Isotope geochemistry and paleobiology of the Devils Lake Basin, North Dakota

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**Isotope geochemistry and paleobiology of the Devils Lake Basin,  
North Dakota**

**Lent, Robert Mulvihill, Ph.D.**

**University of New Hampshire, 1992**

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ISOTOPE GEOCHEMISTRY AND PALEOBIOLOGY OF THE  
DEVILS LAKE BASIN, NORTH DAKOTA

BY  
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B.S. Radford University, 1982  
M.S. North Carolina State University, 1985

DISSERTATION

Submitted to the University of New Hampshire  
in Partial Fulfillment of  
the Requirements for the Degree of

Doctor of Philosophy  
in  
Earth Sciences/Geology

December, 1992

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Aug 21, 1990  
Date

## DEDICATION

To Pamela, Timothy, Patrick, Mom, Dad, Jim, Patricia, and Steve,  
without your love and support this would have never happened,

Thank You

## ACKNOWLEDGEMENTS

I would like to thank all of the members of the Earth Science Department, the Biogeochemical Research Group (RIP), the Glacial Research Group, and the Institute for the study of Earth, Oceans, and Space. Special thanks to Mark Hines, Frank Birch and Linda Hodley for their cooperation during the final months of this project, and to Paul Mayewski and Jack Dibb for the use of their laboratories.

I owe a large debt of gratitude to Berry Lyons and the rest of my dissertation committee---Mark Hines, Henri Gaudette, Ted Loder, and Bill Showers, each of whom shared freely their time, expertise, and friendship, Thank You. I will always be grateful to Berry who showed me that there was always more than one way to solve a problem, and more to data than just numbers. He provided me me friendship, and a unique perspective with which to look at the world---Cheers.

I would like to thank the people of the North Dakota District of the U.S. Geological Survey for their help, support, and friendship. In particular, I would like to thank Greg Wiche and Brad Sether for their help along the way.

I would also like to thank all of my friends and colleagues at the University of New Hampshire and beyond. Special thanks to Ted Sickley, Jeff Perkins, Tom Koch, and Steve Knollmeyer.

This research was supported by the U.S. Geological Survey Water Resources Research Program, and by grants from the University of New Hampshire and Sigma Xi.

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## ABSTRACT

# ISOTOPE GEOCHEMISTRY AND PALEOBIOLOGY OF THE DEVILS LAKE BASIN, NORTH DAKOTA

by

Robert M. Lent

University of New Hampshire, December, 1992

Devils Lake is located in one of the largest closed basins in the northern prairies. Water and sediment samples were collected to characterize present and past hydrologic and climatic conditions in the basin.

Precipitation in North Dakota exhibits a wide range of stable isotopic compositions. Precipitation samples clustered along two segments of the meteoric water line, illustrating the strong seasonal component of precipitation. Low deuterium excess in summer precipitation was indicative of higher relative humidity of the air masses originating over the Gulf of Mexico. High deuterium excess in winter precipitation is similar to the values found at Canadian stations located on the northern prairies, indicating that the origin of winter precipitation is Arctic air masses.

The isotopic composition of ground-water in the Spiritwood aquifer is lighter modern precipitation, indicating that the water was recharged

during colder, wetter periods. Surface water has experienced significant isotopic fractionation as a result of evaporation. Precipitation and runoff are not the only sources of recharge to Devils Lake. The intercept of the evaporation line for Devils Lake surface water and the precipitation, is more negative than precipitation and runoff.

Pore water in Devils Lake is enriched in major ions and nutrients. Two geochemical processes are primarily responsible for the large dissolved-solids and nutrient concentrations in the pore water: burial of saline sediments and pore water, and microbially-mediated sulfate reduction. Bottom sediment fluxes are the dominant source of major ions and nutrients to Devils Lake.

Based on, biogenic silica and the composition of organic matter (TOC, C:N,  $\delta^{13}\text{C}$ , and  $\delta^{15}\text{N}$ ) in sediment cores, the paleobiologic conditions of Devils Lake can be described. High lake level stands are characterized by; increased primary productivity, increased input of detrital organic matter, and nitrogen unlimiting conditions, and low lake level stands by; decreased primary productivity, decreased input of detrital organic matter, where algal matter dominates the sedimentary organic matter.

## CHAPTER I

### STABLE ISOTOPIC COMPOSITION OF PRECIPITATION IN NORTH DAKOTA

#### INTRODUCTION

Stable isotopic composition of natural waters are a valuable indicator of hydrologic processes in surface-water and ground-water systems (Mazor, 1991). For example, deuterium and O-18 concentrations are used to; identify the source of surface-water (Fritz, 1981; Himo and Hasebe, 1986; Kennedy and others, 1986), the timing and source of recharge to ground-water (Fritz and others, 1981; Gat, 1981; Frape and Fritz, 1982; Issar and others, 1994; Long and others, 1988; Banner and others, 1989), and provide information about subsequent physical and geochemical processes including evaporation, mixing, and movement of water (Gat, 1971; Fritz, 1981; Fritz and others, 1978). Stable isotope investigations also can be used to provide paleoclimate information concerning the climatic condition at the time precipitation occurred (Freidman 1953; Dincer and others, 1970; Freidman and Smith, 1970; Johnsen and others, 1972; Bath and others, 1979; Sonnetag and others, 1979; Fontes, 1981; Rozanski, 1985).

The reliable use of stable isotopic data in a particular hydrologic system depends on understanding regional and local variations in the stable isotopic composition of precipitation. In addition, identifying the

mean annual composition of precipitation is a critical component of many isotope-based hydrologic studies of surface-water systems which receive recharge through the entire year. In contrast, determination of seasonal variations in the isotopic composition of precipitation is critical to studies of ground-water systems that receive seasonal recharge. Historically, many stable isotope studies assumed that the isotopic composition of regional and local precipitation can be adequately described by the Global Meteoric Water Line defined by Craig (1961). Presumably, this assumption is made because of the expense and difficulty generating a meteoric water line specific to individual study areas. In particular, samples must be routinely collected for an extended period of time. However, a recent investigation using seven years of precipitation data from nine stations across Canada indicated that the assumption is not necessarily valid for continental stations in North America (Fritz and others, 1987).

The stable isotopic composition of precipitation can exhibit considerable spatial and temporal variability (Dansgaard, 1964; Erikson, 1983; Ingraham and Taylor, 1991; Jacob and Sanntag, 1991). The degree of depletion of the heavy isotopes, deuterium and O-18, is related to latitude, altitude, and the timing and intensity of the individual precipitation events (Siegenthaler, 1979; Yurtsever and Gat, 1981; Mazon, 1991). In general, there is a gradual decrease in  $\delta$ -D and  $\delta$  O-18 concentrations from lower to higher latitudes resulting from decreasing temperature ("latitude effect"). In addition, there is a general decrease in  $\delta$  D and  $\delta$  O-18 from coastal areas to inland areas ("continental effect"), and with increasing altitude ("altitude effect"). The  $\delta$ -D and  $\delta$  O-18 concentrations in precipitation exhibit seasonal and longer term

variations related to temperature ("temperature effect"). Based on the complexity of these different processes the amount of variability in the isotopic composition of precipitation is not surprising.

There are significant amounts of data describing the global variability in the stable isotopic composition of meteoric precipitation from sources including, the International Atomic Energy Agency (IAEA) network (Yurtsever and Gat, 1981), and the Atmospheric Environment Canada network (Fritz and other, 1987). The IAEA network, started in 1961, consists of 144 stations world-wide, 65 of which are still in operation. Two of the operating stations, Chicago, Illinois and Ottawa, Quebec are relatively close to North Dakota. The Atmospheric Environment Canada network consists of nine stations across Canada (Fritz and others, 1987). These stations were in operation between 1977 and 1982. The Atmospheric Environment Canada network included three stations relatively near North Dakota: Wynyard, Saskatchewan, Le Pas, Manitoba, and Gimli, Manitoba.

Little published data exist describing the stable isotopic composition of precipitation in North Dakota. As a result of the limited data, the meteoric water line in North Dakota is poorly defined, and little is known about the spatial and temporal variability in the isotopic composition of precipitation in the state. A limited number of stable isotopic measurements of precipitation in North Dakota are available (Hwang, 1982; Rehm and others, 1982; Patch and Knell, 1988; and Shaver, unpublished data). In addition to these data, precipitation samples were collected near Bismarck, North Dakota from April, 1990 to October, 1991. The purpose of this paper is to compile the existing published and unpublished data describing the stable isotopic composition of

precipitation in North Dakota, and to supplement the existing data with new data from the Bismarck, North Dakota site. The specific objectives of the research were to; (1) develop a general meteoric water line for North Dakota, (2) determine the seasonal and spatial variability of stable isotopic composition of precipitation in North Dakota, and (3) compare the results of this study with other existing data from the Canadian prairie provinces and extend the regional interpretation south to North Dakota.

### Climate of North Dakota

The seasonal variability of climatic conditions in the northern prairies have been described as part of a number of studies. Longley (1972) evaluated climatic conditions across the prairie provinces of Canada. Climatic variability in the Red River of the North Drainage was summarized by Blair (1989). Finally, Jensen (1972) summarized general temperature and precipitation patterns in North Dakota. The following discussion was taken from these studies.

North Dakota has a semi-arid continental climate characterized by long cold winters and short hot summers. Monthly normals of temperature and precipitation at two National Weather Service Stations near two of the sampling locations in this study, Bismarck, North Dakota and Oakes, North Dakota, are listed in Table 1.1. Generally, January is the coldest month (mean monthly temperature approximately  $-14.4^{\circ}\text{C}$ ) and July is the warmest month (mean monthly temperature approximately  $21.4^{\circ}\text{C}$ ). The five months from November through March have mean monthly temperatures below  $0^{\circ}\text{C}$ . The five warmest months, May through

September, have mean monthly temperatures greater than 12°C. The transitions from summer to winter and winter to summer are usually rapid. In general, the climate of North Dakota can be described by two seasons, simplifying isotopic interpretations.

Table 1.1. Monthly normals of temperature and precipitation for Bismarck, North Dakota and Oakes, North Dakota (1951-1980).

Bismarck						
	Jan	Feb	Mar	Apr	May	June
temperature (°C)	-14.0	-9.72	-3.33	5.55	12.7	17.9
precipitation (cm)	1.29	1.14	1.45	3.33	5.46	8.41
	Jul	Aug	Sep	Oct	Nov	Dec
temperature (°C)	21.3	20.3	14.1	7.83	-1.89	-9.22
precipitation (cm)	7.11	7.29	4.98	2.51	1.22	1.17
Oakes						
	Jan	Feb	Mar	Apr	May	June
temperature (°C)	-14.8	-10.9	-4.00	5.55	12.9	18.3
precipitation (cm)	1.52	1.57	2.36	5.66	6.81	8.97
	Jul	Aug	Sep	Oct	Nov	Dec
temperature (°C)	21.5	20.6	14.3	7.83	-1.89	-9.94
precipitation (cm)	6.02	6.22	4.93	2.84	1.75	1.47

The amount of precipitation in North Dakota is relatively small. Average annual precipitation ranges from approximately 36 cm in western North Dakota to approximately 50 cm in the eastern part of the state. Average annual precipitation in Bismarck, North Dakota is approximately 45 cm. The majority of precipitation in North Dakota occurs as large thunderstorms during summer months and as

infrequent snow events during the colder months. A large percentage of the total annual precipitation occurs during the warm months from May through September (approximately 74 % in Bismarck and 66 % in Oakes).

Precipitation in North Dakota is derived from three general sources, the Pacific Ocean, Arctic regions, and the Gulf of Mexico (Winters and others, 1984; Wiche and other, 1986). The Rocky Mountains to the west act as a barrier to the prevailing westerly flow of air across North America. Therefore, the temperature and moisture characteristics of air masses that originate over the Pacific Ocean are modified as the air rises over the Rocky Mountains. The cold, dry air masses that originate over Arctic regions, and the tropical air masses originating over the Gulf of Mexico often reach North Dakota with only minor modification (Winters and others, 1984; Wiche and other, 1986; Blair, 1989).

### Sampling Location

Precipitation samples for stable isotopic analysis were collected in a relatively open area approximately ten kilometers south of Bismarck, in south-central North Dakota, on the east bank of the Missouri River (Figure 1.1). The nearest meteorologic station to the sampling site is the National Weather Service Station which is located approximately four kilometers north of the sampling site.

A second data set comparable in size to the Bismarck data set was collected near Oakes, North Dakota (Figure 1.1) by the North Dakota State



Water Commission. Precipitation samples were collected at the Oakes Experimental Station from April, 1989 through April, 1990.

Precipitation data also is available near Falkirk, North Dakota (Rehm and others, 1982 and Hwang, 1982), which is located approximately 65 kilometers north of Bismarck, near the center of the state (Figure 1.1). Precipitation samples at Falkirk were collected sporadically from May, 1978 through March 1980. Three additional precipitation samples were collected near Harvey, North Dakota (Patch and Knell, 1988) and one snow sample was collected near Devils Lake, North Dakota.

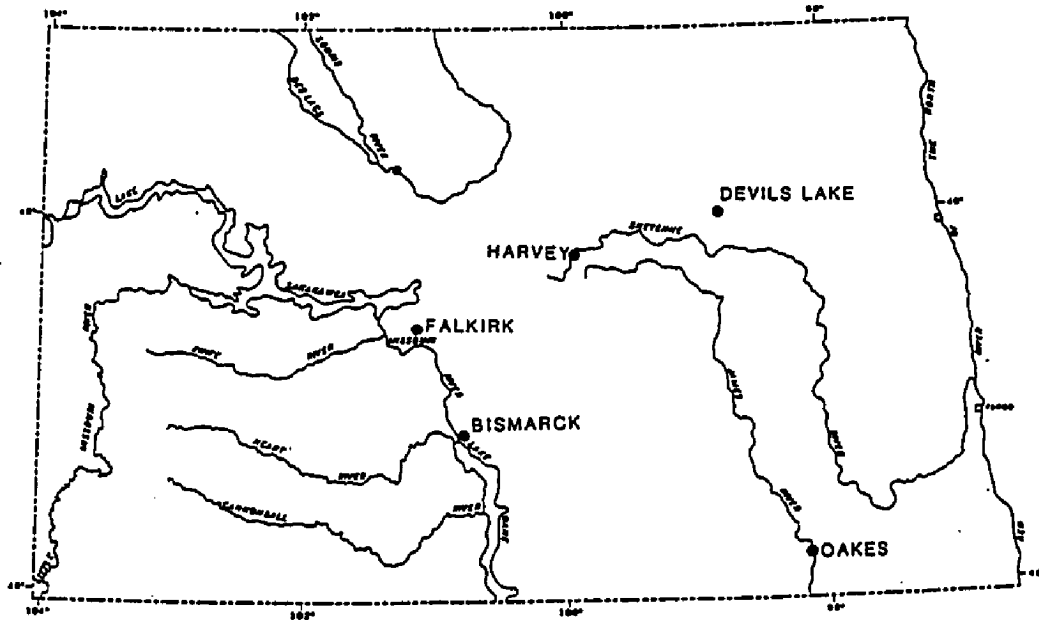


Figure 1.1. Location of precipitation sampling sites in North Dakota.

## METHODS

### Field Methods

Samples were collected using a 30 cm (29 cm interior diameter) "dish-shaped" Nalgene vessel. The vessel was set out in an open area after precipitation began, and was retrieved immediately after precipitation ended. The samples were decanted into 40 ml glass vials after preservation with HgCl. The samples were kept chilled at approximately 4°C until analyzed. Stable isotope analyses were performed at North Carolina State University. The analyses were performed less than four months after collection.

### Laboratory methods.

All samples were kept chilled until analysis. To measure  $\delta^{18}\text{O}$ , samples were equilibrated with isotopically constant purified tank  $\text{CO}_2$  according to a modified version of the method of Epstein and Mayeda (1953). During the equilibration phase, the sample bath was maintained at 50°C,  $\pm 0.1^\circ\text{C}$ , for at least 12 hours. The samples then were cryogenically purified through a double trap system. Isotopic analyses were performed with a Finnigan Mat 251 high sensitivity, moderate resolution mass spectrometer. Two internal standards, NCSU-SMOW

and IMSL-SMOW were processed along with the samples. Standard reproducibility was approximately  $\pm 0.1$  per mil.

Hydrogen gas for  $\delta$ -D analyses was extracted according to a modified version of the method of Coleman and others (1982). Approximately 60 mg of special zinc reagent F-20 (Indiana University Department of Chemistry) was weighed in a 9 mm glass breakseal, which was then pumped to ultimate vacuum on a water equilibration line. A 1  $\mu$ l aliquot of water was taken from the sample bottle using a capillary tube, which was immediately dropped into the 9 mm glass breakseal. The breakseals were immersed into liquid nitrogen for 15 minutes before pumping away nitrogen gas and sealing breakseals with a torch. Sample breakseals were placed in 500°C reaction oven for 30 minutes to allow reduction of the water by the zinc, and the resulting hydrogen gas was analyzed on the mass spectrometer. Two internal standards, V-SMOW (a distilled international standard water) and IMSL-SMOW (an internal marine standard water) were processed along with the samples. Standard reproducibility was approximately  $\pm 1$  per mil.

## RESULTS

The results of the stable isotopic analyses for the samples collected near Bismarck, along with existing stable isotopic data of the composition of precipitation in North Dakota are listed in Table 1.2. Statistical data, including maximum, minimum, and mean for the individual sampling locations in North Dakota are presented in Table 1.3. The isotopic composition of precipitation collected near Bismarck range from -18.8 to -0.096 ‰ for  $\delta$ O-18 and from -138 to -18 ‰ for  $\delta$ D during the sampling period April 1991 through August 1991. These data do not include any precipitation events from the colder months, September through March. Therefore, the Bismarck data can not, by themselves, be used to delineate yearly variations in the isotopic composition of precipitation in the state. The stable isotopic composition of precipitation near Oakes ranged from -25 to -3.5 ‰ for  $\delta$ O-18 and from -189 to -24.0 ‰ for  $\delta$ D during the sampling period April 1989 through April 1990. The stable isotopic composition of precipitation samples collected at Falkirk, Harvey, and Devils Lake all fall within similar ranges (Table 1.2).

Table 1.2. Stable isotopic composition of precipitation in North Dakota  
 (-- not available)

Location	Date	del O-18	del-D	deuterium excess
Bismarck				
	04/13/91	-8.72	-60.6	9.1
	05/03/91	-18.8	-138	12
	05/14/91	-0.096	-21.3	-20
	05/16/91	-6.35	-54.0	-3.2
	06/06/91	-3.15	-22.7	2.5
	06/14/91	-7.53	-57.9	2.3
	06/20/91	-8.09	-54.0	11
	06/24/91	-3.23	-20.8	5.0
	06/25/91	-2.87	-18.0	4.9
	06/28/91	-7.34	-64.3	-5.6
	06/30/91	-10.4	-88.1	-4.4
	07/11/91	-5.35	-35.9	6.9
	07/27/91	-4.87	-29.2	9.7
	07/27/91	-4.87	-29.3	9.7
	08/14/91	-4.64	-39.1	-2.0
	08/16/91	-10.6	-75.1	9.4
	08/19/91	-12.3	-90.0	8.4
	08/22/91	-9.61	-78.6	-1.7
Oakes				
	04/02/89	-10.2	-67	15
	04/25/89	-10.4	-73	10
	05/17/89	-6.1	-50	-1.2
	05/23/89	-6.2	-38	12
	06/11/89	-5.9	-43	4.2
	06/21/89	-6.3	-41	9.4
	07/11/89	-3.5	-24	4.0
	07/28/89	-6.4	-43	8.2
	08/19/89	-7.2	-45	13
	08/30/89	-8.1	-64	0.8
	09/20/89	-8.7	-61	8.6
	11/04/89	-21.5	-165	7.0
	11/22/89	-18.6	-130	19
	11/27/89	-21.7	-161	13
	01/17/90	-19.9	-149	10.2
	02/16/90	-25	-189	11
	03/14/90	-11.2	-70	20
	03/16/90	-21	-159	9.0
	04/16/90	-22.4	-177	2.2

Table 1.2 (continued). Stable isotopic composition of precipitation in North Dakota (-- not available)

Location	Date	del O-18	del-D	deuterium excess
Falkirk				
	04/21/78	-19.3	-148	7.1
	04/21/78	-18.6	-144	4.6
	05/25/78	-4.91	-16.6	23
	08/27/78	-4.49	-36.5	-0.58
	03/12/79	-26.2	-195	15
	03/12/79	-25.9	-206	1.4
	03/28/80	-21.4	-157	14
Harvey				
	--	-15.7	-116	9.6
	--	-10.2	-70	12
	--	-8.5	53	15
Devils Lake				
	--	-24.2	-175	19

Table 1.3. Yearly, summer, and winter means and ranges of isotopic composition of precipitation (-- not analyzed)

Location			mean	maximum	minimum
Total data	year	del O-18	-11.6	-0.10	-26.2
		del-D	-84.5	-15.2	-206
	summer	del O-18	-6.62	-0.10	-18.7
		del-D	-48.7	-15.2	-138
	winter	del O-18	-18.9	-8.72	-26.2
		del-D	-141	-61	-206
Bismarck	year	del O-18	-7.01	-0.10	-18.8
		del-D	-53.5	-15.2	-138
	summer	del O-18	-6.91	-0.10	-18.8
		del-D	-53.1	-15.2	-138
	winter	del O-18	--	--	--
		del-D	--	--	--
Oakes	year	del O-18	-12.6	-3.50	-25
		del-D	-92	-24	-189
	summer	del O-18	-6.49	-3.50	-8.7
		del-D	-45.4	-24	-64
	winter	del O-18	-18.2	-10.2	-25
		del-D	-134	-67	-189
Falkirk	year	del O-18	-17.3	-4.49	-26.2
		del-D	-129	-16.6	-206
	summer	del O-18	-4.70	-4.49	-4.91
		del-D	-26.5	-16.6	-36.5
	winter	del O-18	-22.3	-18.6	-26.2
		del-D	-170	-144	-206

The combined data were separated into summer months (May through September) and winter months (October through April) to determine seasonal variability in isotopic composition of precipitation in North Dakota. Winter and summer ranges of isotopic composition of precipitation were determined for Bismarck, Oakes, and Falkirk, North Dakota, based on the climate data in Table 1.1. Summer ranges were calculated using the data from May through September, the warmest and wettest months of the year. Winter ranges were calculated using the



data from remainder of the year. Precipitation samples collected during the summer months generally were less depleted in deuterium and O-18 in comparison to the remainder of the year (Table 1.3). One sample in March, three samples in April, and one May sample did not follow this simple pattern, emphasizing the variable nature of weather patterns in the northern plains during the spring months.

The data from all of the sampling locations were combined and the range and mean values of del-D and del O-18 for North Dakota were calculated (Table 1.3). The mean del O-18 concentration of the precipitation events sampled in North Dakota is -11.6 o/oo. The maximum del O-18 measured is -0.10 o/oo collected on May 14, 1991 near Bismarck. The minimum del O-18 measured is -26.2 o/oo collected on March 12, 1979 at Falkirk. The mean del-D concentration of precipitation events sampled in North Dakota is -84.5 o/oo. The maximum del-D measured is -15.2 o/oo collected on May 12, 1991 near Bismarck. The minimum del-D measured is -206 o/oo on March 12, 1979 at Falkirk. The mean del O-18 and del-D values of summer precipitation samples in the available data are -6.62 o/oo and -48.7 o/oo, respectively. The mean del O-18 and del-D values of the winter precipitation samples in the available data are -19.2 o/oo and -143 o/oo, respectively.

## DISCUSSION

Seasonal Variability in the Stable Isotopic Composition  
of Precipitation in North Dakota

Monthly precipitation in North Dakota exhibits strong seasonal variability (Table 1.1), and the isotopic composition of precipitation also exhibits seasonal variability (Table 1.3). There are isotope data for three or more precipitation events for seven months, March through August, and November. Maximums, minimums and means of  $\delta$  O-18 and  $\delta$ -D were calculated for these months (Table 1.4). Unfortunately, little data exist for the remaining months making detailed interpretation of seasonal variability in the isotopic composition of precipitation and the calculation of the weighted annual isotopic composition of precipitation difficult. However, these obstacles can be overcome using existing empirical relationships that relate the isotopic composition to climatic and geographic data. The seasonal relationship between mean monthly  $\delta$  O-18 composition of precipitation and mean monthly temperature is illustrated in Figure 1.2. A least-squares linear regression was calculated for the data as:

$$\delta \text{ O-18} = -17.1 + 0.55^{\circ}\text{C} \quad (1)$$

The correlation coefficient for equation 1 is 0.88. The large correlation coefficient indicates the strong relation of temperature to the isotopic composition of precipitation in North Dakota. The slope and intercept are similar to the slopes and intercepts calculated by Fritz and others (1987)

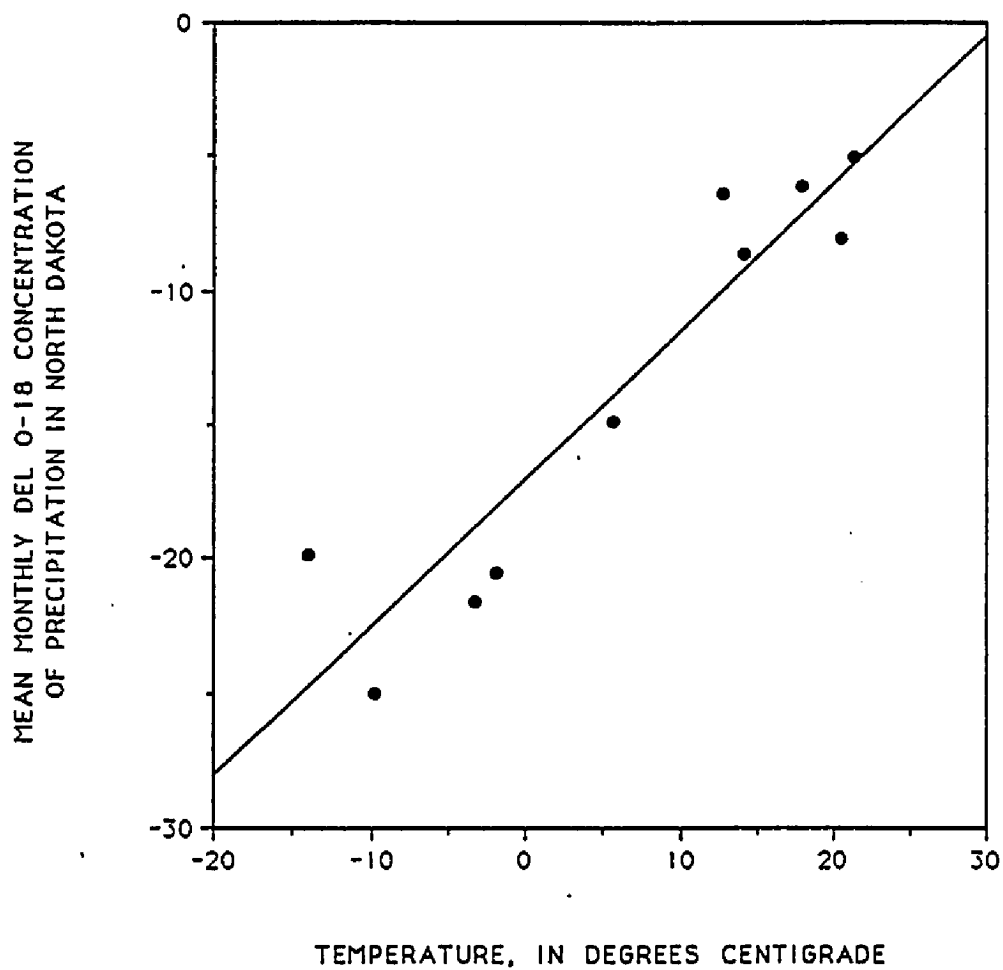


Figure 1.2. Variation in mean monthly del O-18 composition of precipitation with mean monthly air temperature.

for northern prairie stations in Saskatchewan and Manitoba. Fritz and others (1987) found that the relatively steep slope and negative intercept was characteristic of continental stations across Canada, in contrast to oceanic and eastern stations in Canada that are characterized by lower slopes (0.18 to 0.35) and less negative intercepts (-11.0 to -14.2).

Table 1.4. Mean monthly del O-18 and del-D composition of precipitation in North Dakota [-- not analyzed].

Month		mean	max	min	number
January	del O-18	-19.9	--	--	1
	del-D	-149	--	--	1
February	del O-18	-25	--	--	1
	del-D	-189	--	--	1
March	del O-18	-21.2	-11.2	-26.2	5
	del-D	-157	-70	-206	5
April	del O-18	-14.9	-8.71	-22.4	6
	del-D	-112	-60.6	-177	6
May	del O-18	-6.40	-0.01	-18.8	7
	del-D	-47.6	-15.2	-138	7
June	del O-18	-6.1	-2.9	-10.4	9
	del-D	-45.5	-18	-88.1	9
July	del O-18	-5.03	-3.5	-6.4	4
	del-D	-33	-24	-43	4
August	del O-18	-8.13	-4.49	-12.3	7
	del-D	-61.2	-36.5	-78.6	7
September	del O-18	-8.7	--	--	1
	del-D	-61	--	--	1
October	del O-18	--	--	--	--
	del-D	--	--	--	--
November	del O-18	-20.6	-18.6	-21.0	3
	del-D	-152	-130	-165	3
December	del O-18	--	--	--	--
	del-D	--	--	--	--

At any specific location, variations in temperature at the time of precipitation are the dominant influence on the isotopic composition of precipitation. Therefore, it is possible to estimate the isotopic composition of precipitation based on long-term climatic data used in conjunction

with geographic data. Yurtsever and Gat (1981) developed the following empirical equation that relates the isotopic composition of precipitation to temperature, precipitation, latitude, and altitude:

$$\delta \text{O-18} = -18.72 + (0.597)T - (0.0035P)(0.106L + (0.0012A)) \quad (2)$$

where: T=average monthly or yearly temperature (in °C)

P=average monthly or yearly precipitation (in mm)

L=latitude (in degrees)

A=altitude (in meters above sea level)

Mean monthly temperature and precipitation values for Bismarck and Oakes (from Table 1.1) were used to estimate theoretical mean monthly  $\delta \text{O-18}$  composition of precipitation using equation 2. The theoretical mean monthly  $\delta \text{O-18}$  values, along with the measured monthly mean  $\delta \text{O-18}$  composition of precipitation (from Table 1.4) are listed in Table 1.5. Theoretical mean monthly  $\delta \text{O-18}$  range from approximately -27 ‰ in January to -6.3 ‰ in July at Bismarck and Oakes. Measured monthly mean  $\delta \text{O-18}$  range from -25 ‰ in February to -5.03 ‰ in July. In most cases, the theoretical values agree reasonably well ( $\pm 2$  ‰) with the measured values. The notable exceptions are January and May, where the theoretical values are approximately 7 ‰ and 5 ‰ more negative than the measured values, and to a lesser degree June where the theoretical value is approximately 3 ‰ more negative than the measured value.

The theoretical mean monthly  $\delta \text{O-18}$  data in Table 1.5 can be used to calculate the mean annual  $\delta \text{O-18}$  composition of precipitation. Determining the mean annual isotopic composition of precipitation is critical to understanding the isotopic evolution of surface water and ground water. For example, in humid areas, where precipitation

exceeds evapotranspiration, the isotopic composition of recharge to ground water approximates the mean annual isotopic composition of precipitation (Gonfiantini and Gat, 1981). In contrast, in arid regions, where evapotranspiration is greater than precipitation, the isotopic composition of recharge can reflect seasonal isotopic composition of precipitation. For example, in the northern prairies of North America recharge to near surface aquifers appears to be dominated by winter and spring precipitation (Rehm and other, 1982; Hendry, 1988).

Table 1.5. Comparison of mean monthly  $\delta$  O-18 composition of precipitation in North Dakota and theoretical  $\delta$  O-18 composition of precipitation at Bismarck, North Dakota, and Oakes, North Dakota [-- not analyzed].

Month		mean	Bismarck	Oakes
January	$\delta$ O-18	-19.9	-26.7	-27.2
February	$\delta$ O-18	-25	-24.1	-24.9
March	$\delta$ O-18	-21.2	-20.4	-20.9
April	$\delta$ O-18	-14.9	-15.4	-15.8
May	$\delta$ O-18	-6.40	-11.5	-11.6
June	$\delta$ O-18	-6.1	-8.89	-8.75
July	$\delta$ O-18	-5.03	-6.64	-6.33
August	$\delta$ O-18	-8.13	-7.20	-6.90
September	$\delta$ O-18	-8.7	-10.6	-10.4
October	$\delta$ O-18	--	-13.9	-13.9
November	$\delta$ O-18	-20.6	-19.5	-19.5
December	$\delta$ O-18	--	-23.8	-24.3

The theoretical yearly  $\delta$  O-18 compositions of precipitation near Bismarck and Oakes were calculated as weighted averages using measured monthly precipitation (Table 1.1), and theoretical monthly  $\delta$  O-18 compositions (Table 1.5). The theoretical yearly  $\delta$  O-18 compositions of precipitation near Bismarck is -11.4 o/oo. This value is similar to -11.6, the mean of the measured values of precipitation for

North Dakota (Table 1.3). The theoretical yearly  $\delta$  O-18 compositions of precipitation near Oakes is -12.3. While this value is more negative than both the measured value and the theoretical value for Bismarck, it is reasonable, based on the increased importance of winter precipitation to the yearly water budget in the eastern part of the state (Winters and others, 1984).

### Development of a North Dakota Meteoric Water Line

Stable isotope precipitation data commonly are plotted illustrating the variations in deuterium concentrations as a function of O-18 concentrations. Craig (1961) used this relationship to define the Global Meteoric Water Line as:

$$\delta\text{-D}=8 (\delta\text{ O-18})+10 \quad (3)$$

This equation was based on available data at the time. Yurtsever and Gat (1981) later refined the Global Meteoric Water Line:

$$\delta\text{-D}=8.17 (\delta\text{ O-18})+10.56 \quad (4)$$

Yurtsever and Gat (1981) also calculated the North American Meteoric Water Line as:

$$\delta\text{-D}=7.95 (\delta\text{ O-18})+6.03 \quad (5)$$

Fritz and others (1987) calculated the Canadian Meteoric Water Line as:

$$\delta\text{-D}=7.75 (\delta\text{ O-18})+9.83 \quad (6)$$

In general, the slopes of the various regional (or global) meteoric water lines are similar. The reason for the small differences in the slopes is that isotopic variations of global meteoric water are the result of atmospheric and oceanic conditions at the source of the water vapor, and

evaporative and isotopic equilibrium exchange reactions during transit and final condensation (Yurtsever and Gat, 1981; Welham, 1987). In particular, atmospheric water vapor maintains isotopic equilibrium, with respect to temperature, between water vapor and liquid water during condensation. The equilibrium occurs by isotopic exchange between water vapor and precipitation (Siegenthaler, 1979; Yurtsever and Gat, 1981; Welham, 1988). Dansgaard (1964) and Friedman and others (1964) modeled the variations in global isotopic composition of precipitation and showed that the slope of the Global Meteoric Water Line could be adequately explained as a Rayleigh distillation process, and that the slope of the line is primarily a function of near-surface air temperature. Yurtsever and Gat (1981) used a Rayleigh-batch separation model to include the relative amount and rate of water removal, thereby including rain-out history in the calculations (Welhem, 1988).

All the measured isotopic data from North Dakota are shown in Figure 1.3. A least-squares linear regression was calculated for the data as:

$$\delta\text{-D}=7.60 (\delta\text{ O-18})+2.59 \quad (7)$$

The correlation coefficient of the regression line is 0.98. The equation can be used as an estimate of the meteoric water line for North Dakota. The most striking feature of both lines is the fact that the data cluster along two distinct segments of the lines. The  $\delta\text{ O-18}$  compositions of these groups are between -26 and -18 ‰ and between -11 and 0 ‰ (Figure 1.3). The more negative data, with  $\delta\text{ O-18}$  concentrations between -26 and -18 ‰, are primarily the isotopic composition of winter precipitation. The more positive  $\delta\text{ O-18}$  concentrations between -11 and 0 ‰, are primarily the isotopic composition of summer precipitation.



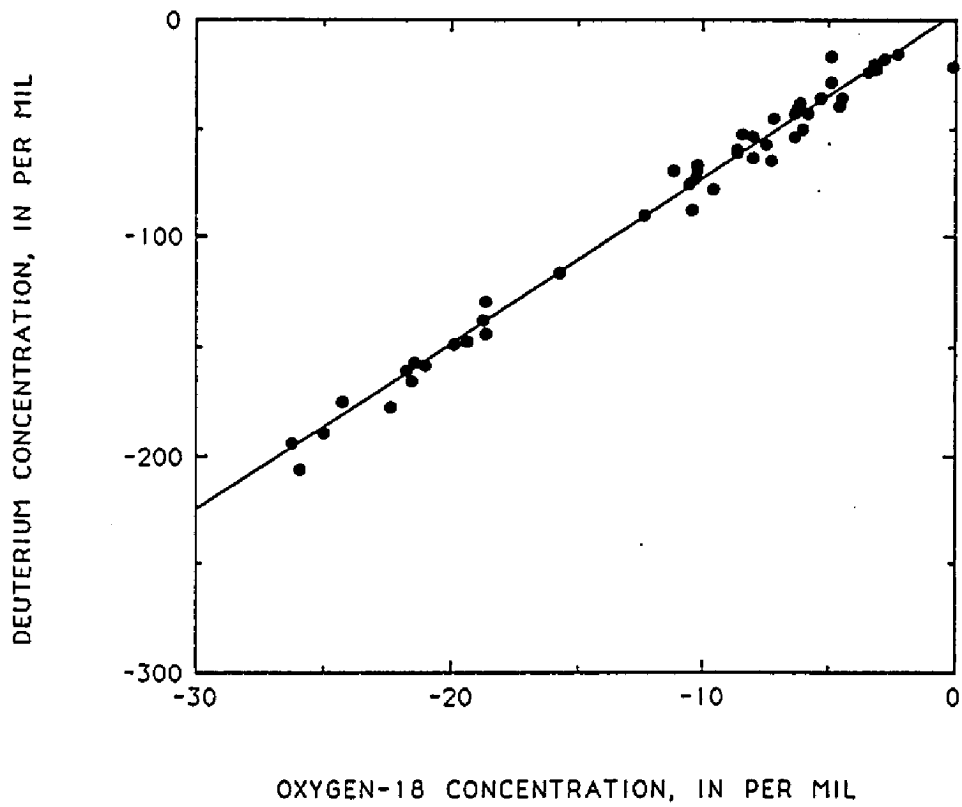


Figure 1.3. Variations in isotopic composition of individual precipitation events in North Dakota.

However, this may not be the best way to accurately determine the position of the line. This data set is biased by the larger number of samples from the summer months. Some of the bias can be removed using the mean monthly values for del O-18 and del-D. The mean monthly data are shown in Figure 1.4. A least-squares linear regression was calculated for the data as:

$$\text{del-D} = 7.51 (\text{del O-18}) + 1.79 \quad (8)$$

The correlation coefficient of the regression line is 0.997. While these considerations remove some the seasonal bias of the initial data, some bias still exists due to the lack of data for December, January, and February.

#### Seasonal variability in the North Dakota meteoric water line

The Canadian meteoric later line is actually a compilation of the individual meteoric water lines across Canada (Fritz and others, 1987). In addition, the individual meteoric water lines exhibited substantial seasonal variability. That is, there was a noticeable difference in the slope and intercepts of the individual meteoric water lines between winter and summer precipitation. The seasonal change in the meteoric water lines was most noticeable at the prairie stations in Saskatchewan and Manitoba.

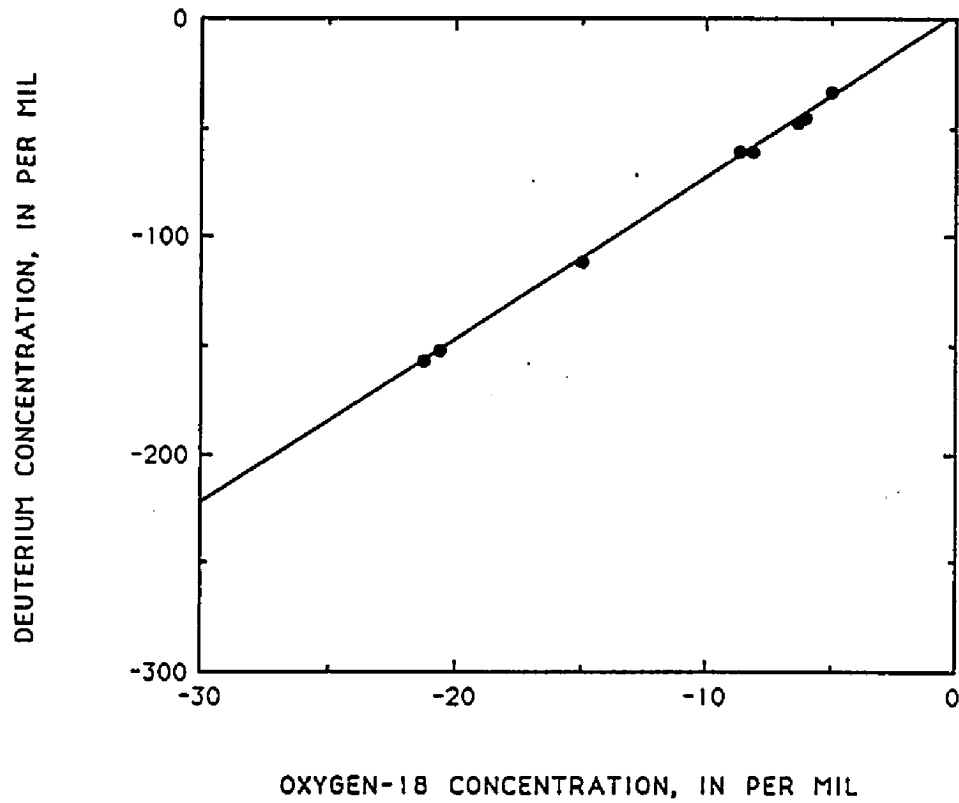


Figure 1.4. Variations in mean monthly isotopic composition of precipitation in North Dakota.

Yearly and seasonal (winter and summer) meteoric water lines for the individual sampling locations are tabulated in Table 1.6 and shown in figures 1.5-1.9. The meteoric water lines do not represent monthly averages, instead the lines were calculated using all available data due to the limited number of analyses. Winter was defined as October through April, while summer was defined as May through September. In some instances the yearly meteoric water lines are biased by uneven seasonal data. For example, the data from the Bismarck sampling location was collected almost entirely during the summer months. However, the total North Dakota data set, compiled from all the sampling locations in the state, is reasonably well distributed with respect to season. Therefore, the North Dakota meteoric water line based on Figure 4 is probably the most reasonable representation of the isotopic composition of precipitation in North Dakota.

The meteoric water line for North Dakota winter precipitation samples (Figure 1.10, Table 1.6) and the meteoric water line for North Dakota summer precipitation samples (Figure 1.11, Table 1.6) are noticeably different from the annual meteoric water line for North Dakota (Table 1.6). The meteoric water line for winter precipitation has a higher slope than the annual meteoric water line (8.12 compared to 7.60) and a much higher intercept (14.7 compared to 2.59). Individual winter meteoric water lines for winter precipitation, at Oakes and Falkirk, were calculated from the data. The Oakes meteoric water line for winter precipitation is similar to the North Dakota meteoric water line for winter precipitation. However, the Falkirk meteoric line for winter precipitation is almost identical to the meteoric water line for all precipitation sampled in North Dakota. The meteoric water line for

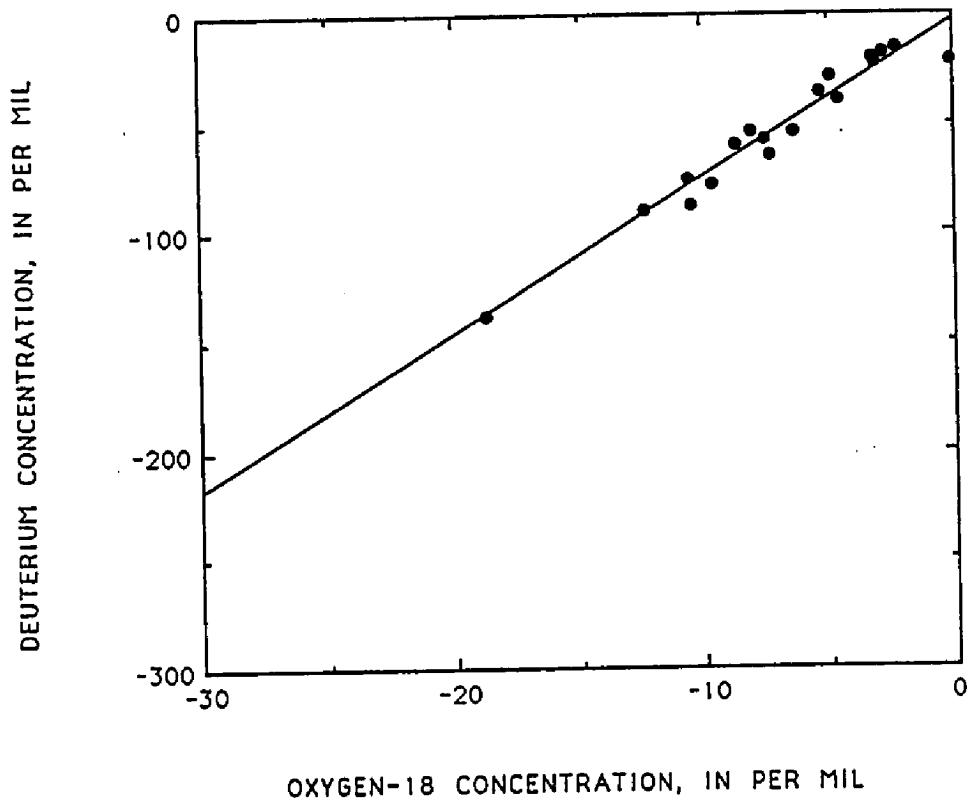


Figure 1.5. Variation in the isotopic composition of yearly precipitation events, Bismarck, North Dakota.

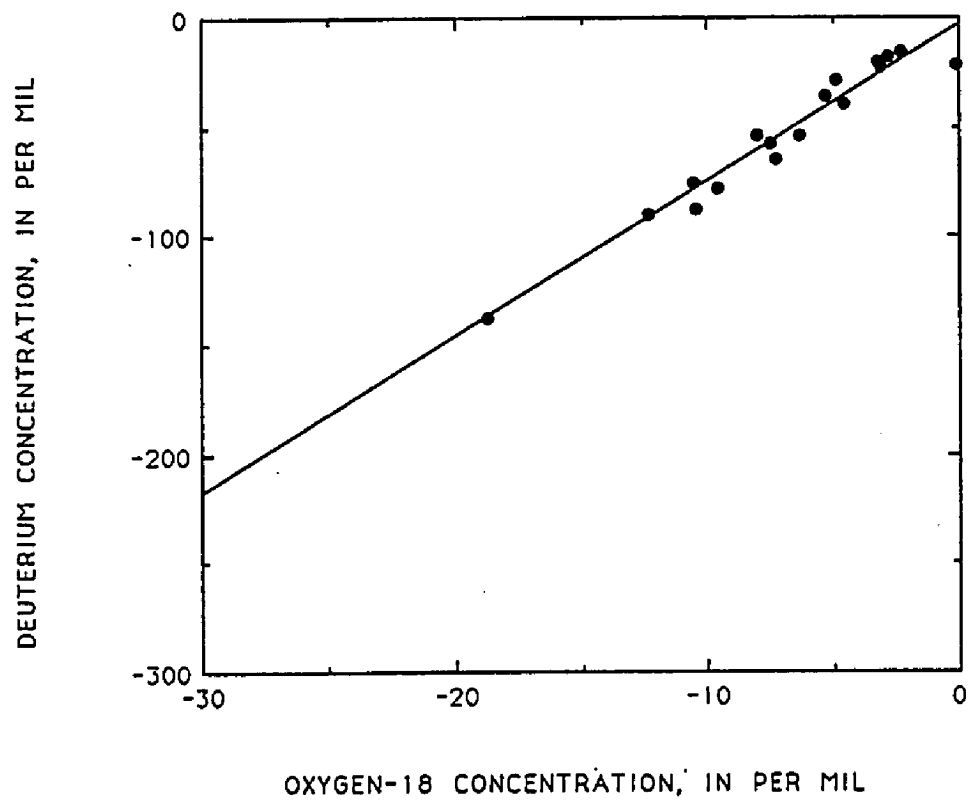


Figure 1.6. Variation in the isotopic composition of summer precipitation events, Bismarck, North Dakota.

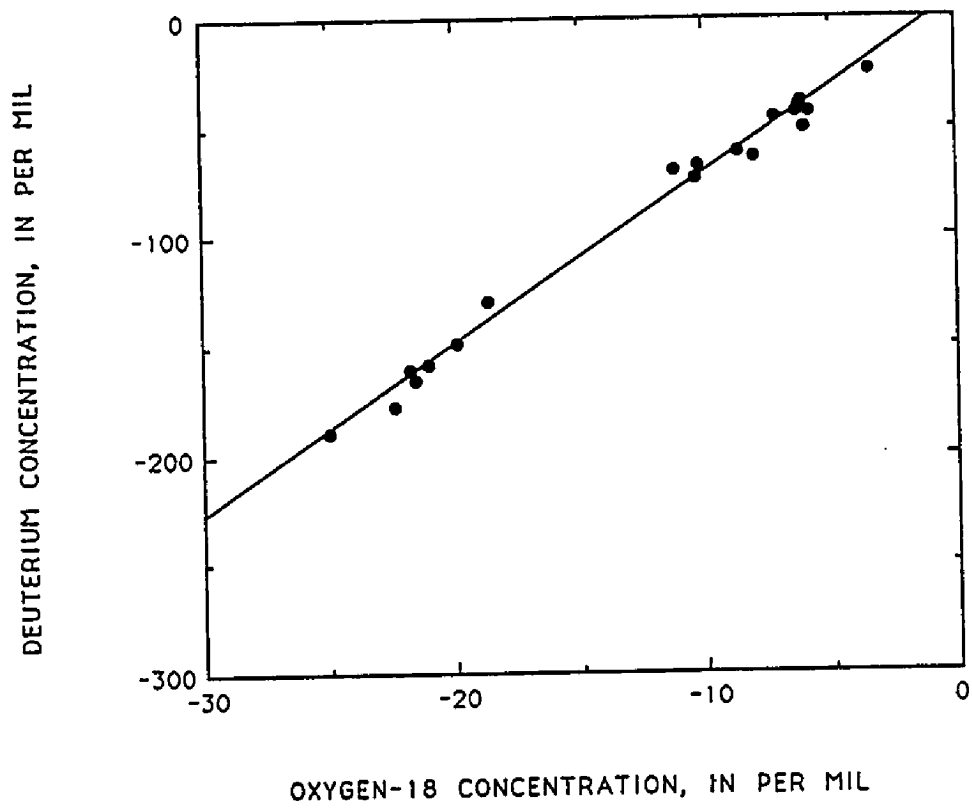


Figure 1.7. Variation in the isotopic composition of yearly precipitation events, Oakes, North Dakota.

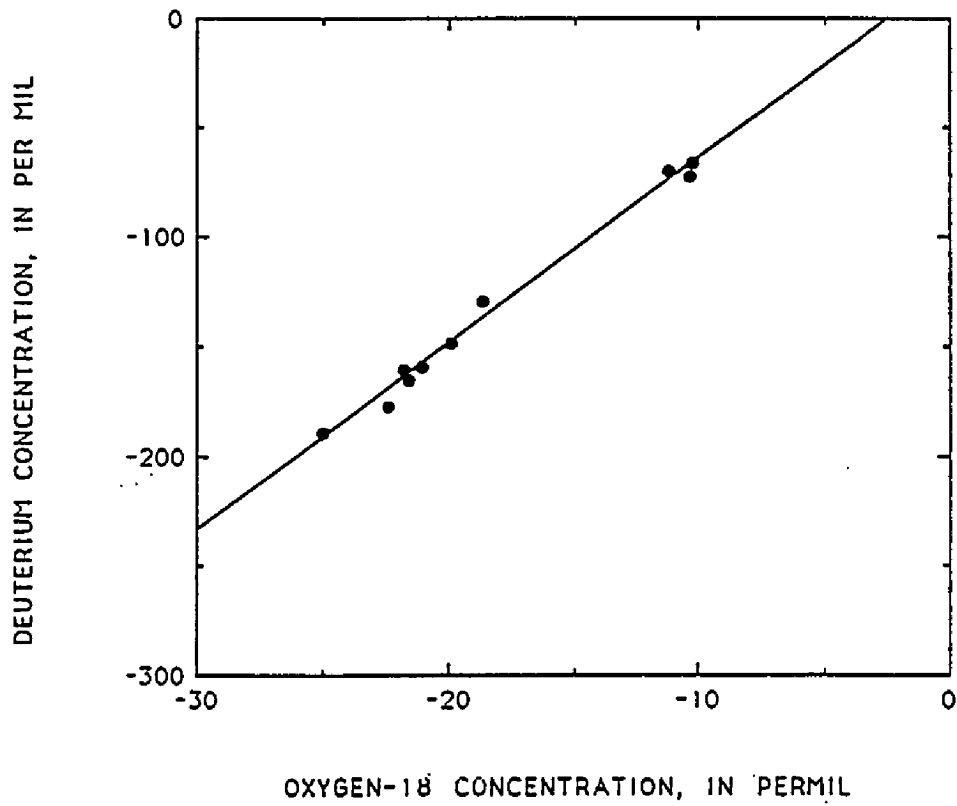


Figure 1.8. Variation in the isotopic composition of winter precipitation events, Oakes, North Dakota.



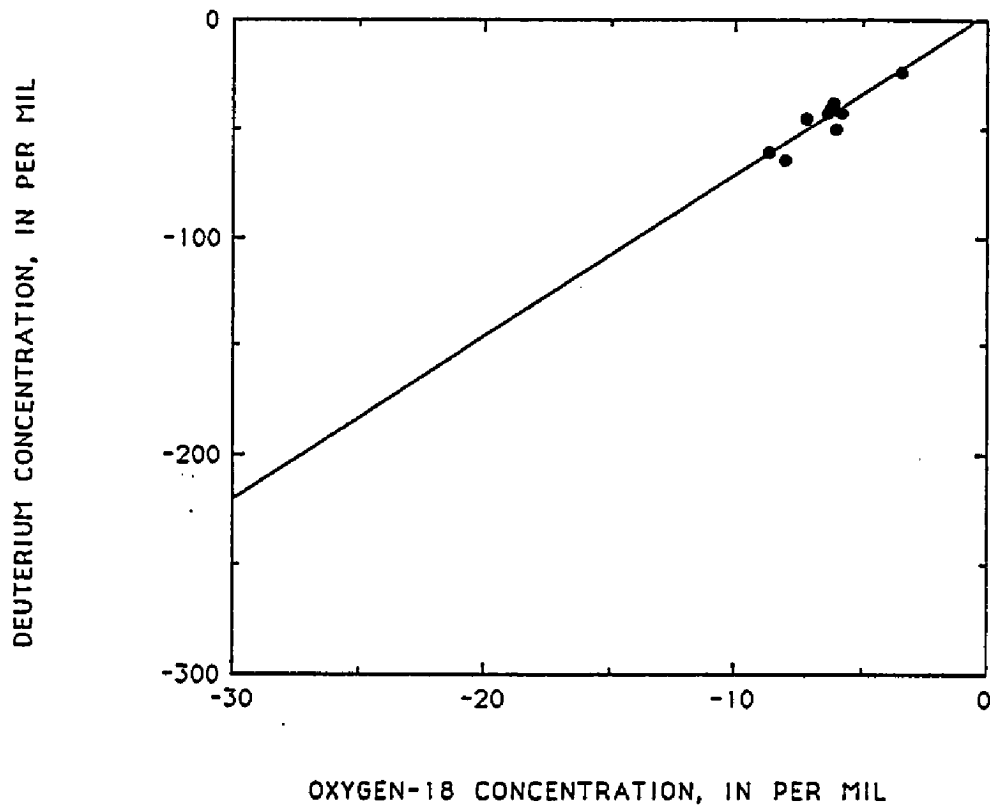


Figure 1.9. Variation in the isotopic composition of summer precipitation events, Oakes, North Dakota.

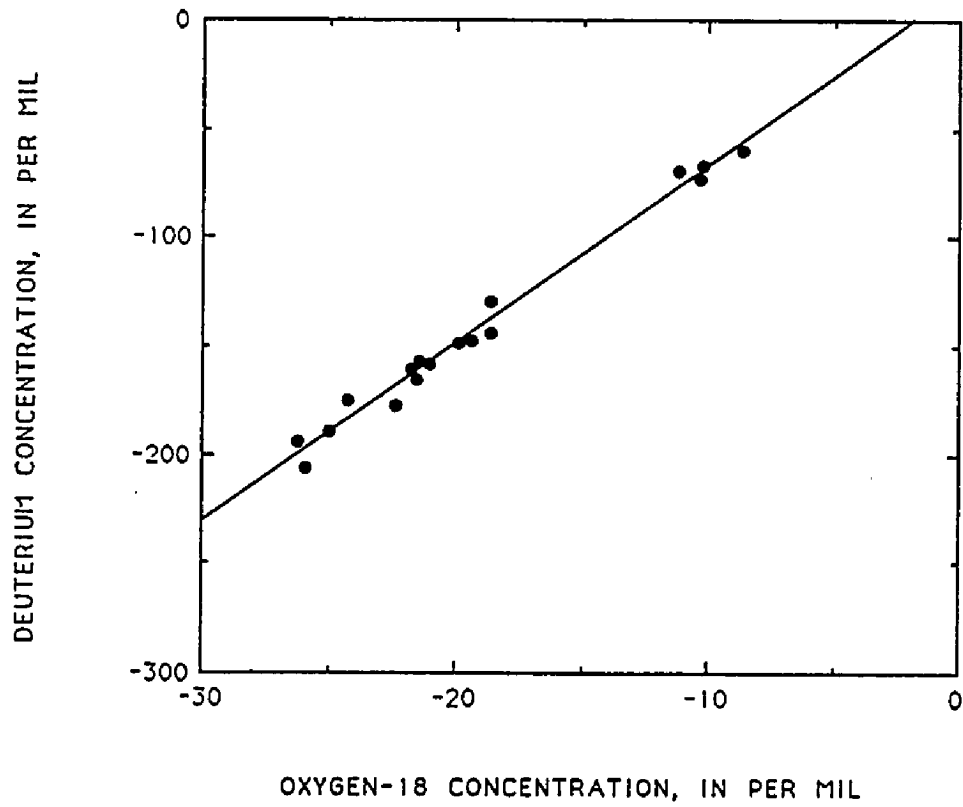


Figure 1.10. Variation in the isotopic composition of winter precipitation events in North Dakota.

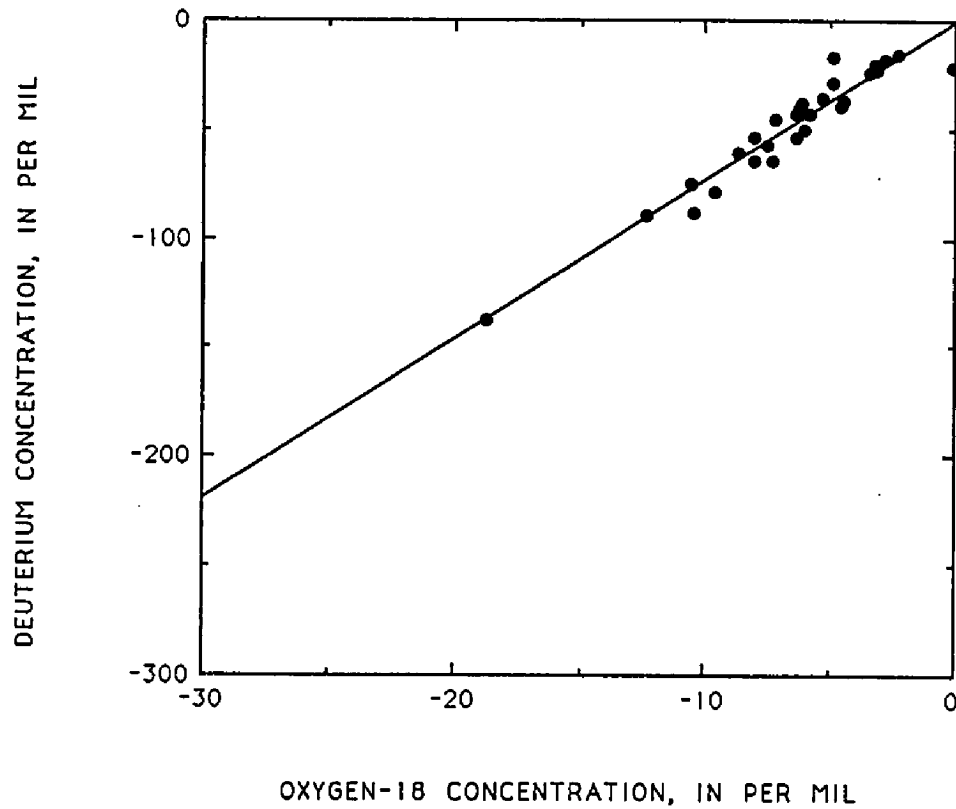


Figure 1.11. Variation in the isotopic composition of summer precipitation events in North Dakota.

summer precipitation has a lower slope than the meteoric water line for all precipitation (7.31 compared to 7.60) and a lower intercept (-0.35 compared to 2.59). Two individual meteoric water lines for summer precipitation, at Bismarck and Oakes, were calculated from the data. The meteoric water line for summer precipitation at Oakes is similar to the meteoric water line for summer precipitation in North Dakota. The meteoric water line for summer precipitation at Bismarck has a lower slope (7.15 versus 7.31) and a lower intercept (-3.34 versus -0.35).

Table 1.6. Calculated meteoric water lines for North Dakota and Canadian stations [-- not analyzed].

Location		Slope	Intercept	r <sup>2</sup>
North Dakota (Total data)	year	7.60	2.59	0.984
	summer	7.31	-0.35	0.925
	winter	8.20	14.71	0.987
Bismarck	year	7.15	-3.34	0.952
	summer	7.18	-3.44	0.954
	winter	--	--	--
Oakes	year	7.83	6.99	0.991
	summer	7.46	2.97	0.847
	winter	8.48	20.3	0.991
Wynyard (Saskatchewan)	year	7.63	0.07	0.985
	summer	7.61	-0.58	0.942
	winter	7.81	4.85	0.982
La Pas (Manitoba)	year	7.62	0.62	0.989
	summer	7.43	-3.04	0.940
	winter	8.04	11.2	-0.986
Gimli (Manitoba)	year	7.80	6.22	0.983
	summer	8.12	8.13	0.932
	winter	8.26	17.5	0.971
Atikokan (Ontario)	year	7.84	7.88	0.991
	summer	7.76	6.33	0.949
	winter	8.08	13.3	0.991

Not surprisingly, the meteoric water lines for the Canadian stations in the prairie provinces are remarkably similar to the North Dakota data. The slope and intercept of the meteoric water line for annual precipitation are similar to the three Canadian stations. The slope and intercept of the meteoric water line for summer precipitation in North Dakota are similar to the slope and intercept of the Wynyard, Saskatchewan meteoric water line for summer precipitation (Table 1.6). The slope and intercept of the winter meteoric water line for winter precipitation in North Dakota are similar to the slope and intercept of the Le Pas and Gimli, Manitoba meteoric water lines for winter precipitation (Table 1.6).

There are at least two plausible explanations for the seasonal differences in the meteoric water lines in the northern plains of North America. The decrease in slope of the meteoric water lines for summer precipitation may be due to local evaporative processes occurring during precipitation events (Fritz and others, 1987). Evaporation of falling rain drops could result in the enrichment of deuterium and O-18 in the residual liquid. This would result in a shift in isotopic composition to the right of the meteoric water line. If this process is restricted to summer precipitation, it would result in a lower slope and/or higher intercept of the meteoric water line (Fritz and others, 1987). The seasonal variations in meteoric water lines also may be the result of seasonal differences in climate patterns. The possibility is explored below.

Deuterium excess and the source of precipitation to North Dakota

The seasonal variations in climate patterns and the isotopic composition of precipitation can be evaluated by comparisons of the intercepts of seasonal meteoric water lines and calculation of the deuterium excess parameter. The deuterium excess parameter ( $d$ ) was originally defined by Dansgaard (1964) as:

$$d = \delta\text{-D} - 8 (\delta\text{-O}-18)$$

Deuterium excess (in ‰) describes the relationship between a single  $\delta\text{-O}-18$ - $\delta\text{-D}$  point to the Global meteoric water line. (Yurtsever and Gat, 1981). Deuterium excess is alternatively defined as the intercept of the local meteoric water line and the  $\delta\text{-D}$ -axis (Merlivat and Jouzel, 1979).

The deuterium excess present in an air mass primarily is a function of atmospheric and oceanic conditions present at the origin of the air mass (Merlivat and Coantic, 1975; Merlivat and Jouzel, 1979; Yurtsever and Gat, 1981; Fritz and others, 1987). Relative humidity of an air mass at its origin is the dominant factor in determining the deuterium excess of an air mass (Merlivat and Jouzel, 1979; Yurtsever and Gat, 1981; Fritz and others, 1987). Low relative humidity results in relatively high deuterium excess. A 10 % increase in relative humidity should result in a decrease of 6 ‰ in deuterium excess (Merlivat and Jouzel, 1979; Rozanski, 1985). Temperature, wind speed, and kinetic isotope effects also can exert minor influences on deuterium excess (Merlivat and Jouzel, 1979; Welham, 1987; Fritz and others, 1987). In addition, an inverse relation exists between deuterium excess and temperature during snow formation (Merlivat and Jouzel, 1979). Therefore, the intercept of a local meteoric water line with the  $\delta\text{-D}$ -axis,

and the deuterium excess of individual or grouped data can provide valuable insight into the source of moisture in air masses, and climatic conditions at their origin.

The precipitation samples in North Dakota exhibited a wide range of deuterium excess (Table 1.2). The mean deuterium excess in winter precipitation was 10.6 ‰. The mean deuterium excess of summer precipitation was 4.3 ‰. These values are similar to the deuterium excess values in the precipitation stations in Saskatchewan and Manitoba. However, a limited number of summer values in North Dakota were substantially lower than the values reported for Canada. Fritz and others (1987) proposed that the seasonal variations in deuterium excess indicated that summer precipitation was dominated by air masses originating over the Pacific Ocean, and winter precipitation was dominated by Arctic air masses. In addition, summer precipitation was modified further by evaporative processes due to semi-arid conditions in the northern prairies thus providing the wide range of deuterium excess values in summer precipitation.

The processes that are responsible for the isotopic character of precipitation in central Canada probably are similar in North Dakota. However one additional source of precipitation must be considered. As previously noted, precipitation in North Dakota is derived from three general sources, the Pacific Ocean, Arctic regions, and the Gulf of Mexico. During the summer, precipitation in North Dakota could be influenced by air masses originating over the Gulf of Mexico. Atmospheric conditions in the Gulf of Mexico are humid, therefore air masses originating in the region should be characterized by low deuterium excess. As previously noted, a number of the summer

precipitation samples collected in this study had negative deuterium excess values, one as low as -21 (Table 1.2). The negative deuterium excess values probably reflect the increased importance of precipitation derived from the Gulf of Mexico in North Dakota relative to Canada. In contrast to summer precipitation, the deuterium excess in winter precipitation was virtually identical the values reported by Fritz and others (1987) in Canada. This suggests that there is a similar source of winter precipitation to the northern prairies of North America.



## CONCLUSIONS

Precipitation in North Dakota exhibits a wide range of isotopic composition.  $\delta$  O-18 of precipitation in North Dakota ranged from -26.2 ‰ to -0.10 ‰, and  $\delta$ -D ranged from -206 ‰ to -15.2 ‰. In general, seasonal differences in the isotopic variability of precipitation were much greater than spatial differences within a season. Winter precipitation (October through April) was depleted in deuterium and O-18, relative to summer precipitation (May through September). A limited number of precipitation samples precluded detailed interpretation of the spatial variability in the isotopic composition of precipitation in North Dakota. However, the results do not preclude minor differences in the isotopic composition of precipitation across the state. Substantially more data are needed to evaluate if spatial variations exist, and if the variations are statistically significant.

A meteoric water line was estimated for yearly precipitation in North Dakota as:  $\delta$ -D=7.51 ( $\delta$  O-18)+1.79. This line was constructed using the mean monthly isotopic data for the entire State. The meteoric water line is similar to the regression for all the individual analyses. Individual precipitation samples clustered along two segments of the meteoric water line, illustrating the strong seasonal component of the yearly isotopic composition of precipitation in the state.

Seasonal variations in the isotopic composition of precipitation in North Dakota can be described using two separate meteoric water lines. One describing summer precipitation:  $\delta$ -D=7.31 ( $\delta$  O-18)-0.35, and one

describing winter precipitation:  $\delta\text{-D}=8.20 (\delta\text{-O-18})+14.7$ . The differences in slope and intercept between the summer and winter meteoric water lines are the result of local and regional meteoric processes. During the summer, local evaporation occurring while precipitation occurs may be responsible for moving individual samples to the right of the meteoric water line [(in  $(\delta\text{-O-18})$  versus  $(\delta\text{-D})$  space]. Evaporation would result in a decrease in slope and intercept.

The differences in slope and intercept between the summer and winter meteoric water lines are also the result of variations in climate patterns. The seasonal variations in isotopic composition in precipitation can be illustrated using the deuterium excess parameter. The mean deuterium excess in winter precipitation was 10.6, compared to 4.3 in summer precipitation. The shift toward lower deuterium excess values in summer is indicative of higher relative humidity at the origin of the air masses originating over the Gulf of Mexico. The high deuterium excess in winter precipitation is similar to the values found in precipitation further north at Canadian stations located on the northern prairies. The probable origin of the winter precipitation is Arctic air masses.

## CHAPTER II

### STABLE ISOTOPIC COMPOSITION OF SURFACE WATER AND GROUND WATER IN THE DEVILS LAKE CLOSED BASIN, NORTH DAKOTA

#### INTRODUCTION

Devils Lake, in northeastern North Dakota, is the terminal lake in a large closed-basin drainage system. The Devils Lake drainage basin is the largest closed basin in North Dakota, and one of the largest closed basins in the northern plains of North America. As with other closed basin-lakes, Devils Lake has experienced large fluctuations in lake level, water volume, and water quality (Jones, 1966; Mitten and others, 1968; Sando and Wiche, 1990, 1992). The water in Devils Lake is slightly saline to saline, and therefore is not suitable for drinking water supply or agricultural uses. However, Devils Lake supports an economically important recreational fishing industry critical to the vitality of the region. In addition to the unusual nature of the surface-water drainage, Devils Lake is located on top of the Spiritwood aquifer, the largest glacial aquifer in North Dakota. The Spiritwood aquifer is a large north-south trending buried-valley aquifer that extends from Canada to South Dakota, and is an important source of water in much of east-central North Dakota (Hutchinson and Klausning, 1980; Shaver, 1988; Kehew and Boettger, 1986; Ripley, 1988; Pusc, in review).

Since the mid 1980's Devils Lake has been the subject of intensive hydrologic and hydrogeochemical investigations designed to determine

water and chemical budgets of the lake (Wiche, 1986, 1991; Wiche and others, 1986; Sando and Wiche, 1990; Pusc, in review). While earlier work suggested that the lake is hydrologically separated from the regional ground water, more recent investigations, in particular the calculated water budgets for Devils Lake and the hydrologic study of the Spiritwood aquifer, indicate that the Spiritwood aquifer may be a significant contributor of water to the lake. However, due to the complexity of the hydrologic system in the Devils Lake area, there is uncertainty as to the amount of hydrologic interaction between the lake and the underlying glacial aquifer.

In an attempt to resolve some of the uncertainty in the hydrologic budget of Devils Lake, a stable isotopic investigation of surface water and ground water in the Devils Lake area was undertaken. The specific objectives of the study were to: (1) document the stable isotopic composition of surface water in the Devils Lake drainage basin, (2) document the stable isotopic composition of ground water in the Spiritwood aquifer and surficial aquifers associated with glacial tills in the vicinity of Devils Lake, (3) determine the variations in the stable isotopic composition of ground water along a flow path in the Spiritwood aquifer from a recharge zone to the lake, (4) determine the approximate timing of recharge (modern versus Pleistocene) to the Spiritwood aquifer by comparing the stable isotopic composition of water from the aquifer with stable isotopic measurements of precipitation in North Dakota, and (5) evaluate the potential for movement of water from the Spiritwood aquifer into Devils Lake.

### Local Geology

Devils Lake, West Stump Lake, and East Stump Lake are terminal lakes located near the southern edge of the Devils Lake drainage basin in northeastern North Dakota (Figure 2.1). The Devils Lake drainage is a large (approximately 10,000 square kilometer) closed basin located in the Red River of the North drainage basin. The Red River of the North drainage basin is located in the Central Lowland Province of the Interior Plains of North America (Winters and others, 1984). The Central Lowland Province in North Dakota is a glaciated area, covered by a combination of glacial till, lacustrine sediments, and glaciofluvial drift (Hobbs and Bluemle, 1987). The glacial sediments in North Dakota are Quaternary in age, and are collectively referred to as the Coleharbor Formation (Hobbs and Bluemle, 1987). The Holocene sediments in the Devils Lake area are referred to as the Oahe Formation. The maximum thickness of glacial material in the Devils Lake area is approximately 200 meters (Hobbs and Bluemle, 1987). The Cretaceous Pierre shale Formation underlies the glacial sediments in most of the Devils Lake area. In some areas of the Devils Lake drainage basin, where deep melt-water channels exist (such as the Spiritwood aquifer), shale of the Cretaceous Niobrara Formation underlies the glacial sediments (Hobbs and Bluemle, 1987).

The Spiritwood aquifer is a confined, buried channel system which extends roughly north-south through eastern North Dakota (NDSWC, 1986). The Spiritwood aquifer is believed to be a remnant of the north-flowing Cannonball River, which existed throughout the Quaternary

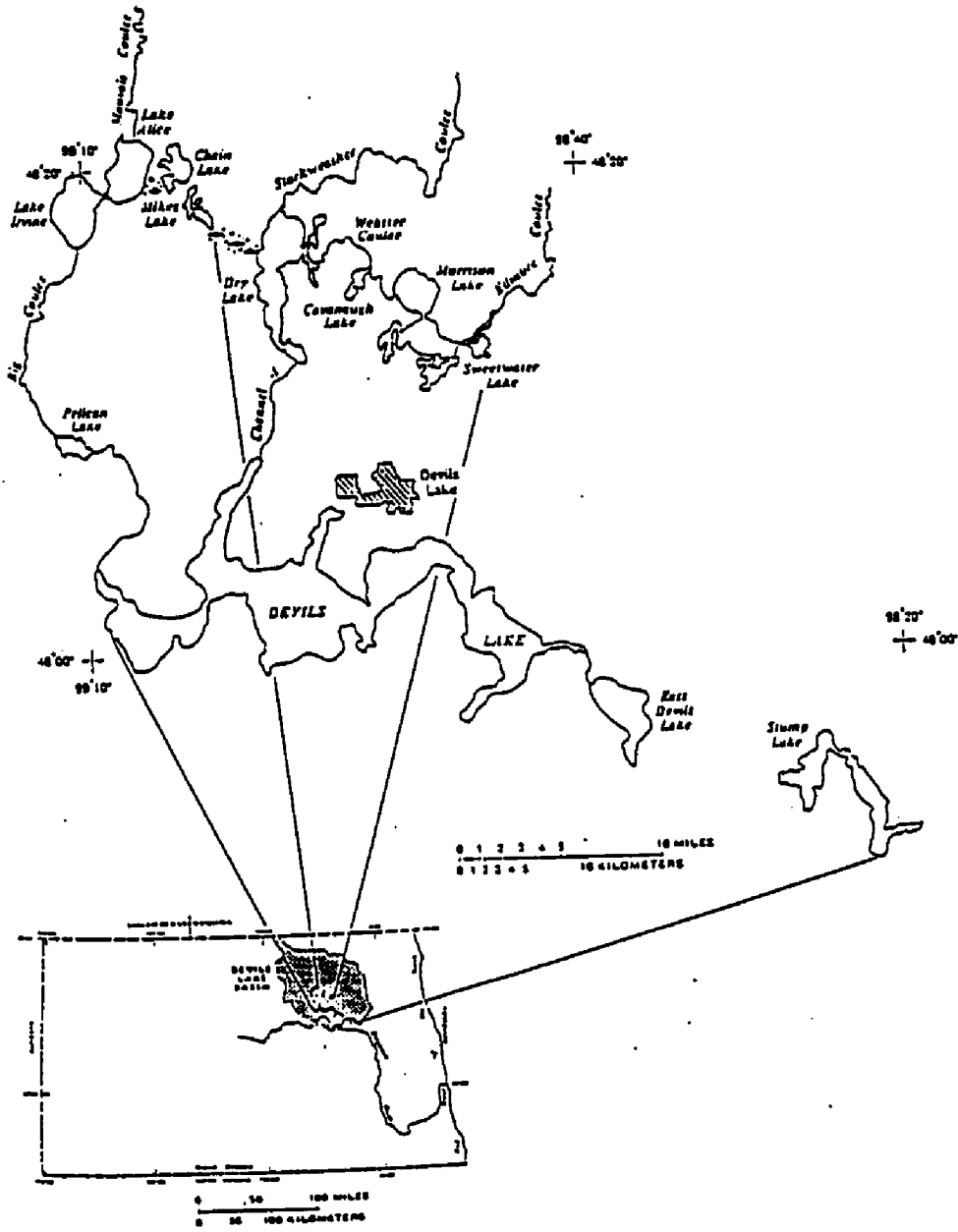


Figure 2.1. Map of North Dakota showing location of the Devils Lake drainage basin

(Hobbs and Bluemle, 1987). Multiple ice advances and retreats during the Pleistocene filled the Cannonball valley with a series of tills, glaciofluvial sediments and glaciolacustrine sediments (Carlson and Freers, 1975; Shaver, 1988; Hobbs and Bluemle, 1987). Scouring and thrusting action of glacial advances deepened the valley in the vicinity of Devils Lake, and built up the land immediately to the south of the lake. During periods when the Cannonball River's northward flow was blocked by ice, water was diverted to the southeast, forming a deep, narrow channel known as the Starkweather diversion trench, which enters the Spiritwood aquifer from the east, near East Devils Lake.

The Spiritwood aquifer is highly irregular in cross-section (Shaver, 1988; Hobbs and Bluemle, 1987). In the vicinity of Devils Lake the Spiritwood aquifer has an average thickness of approximately 27 meters, and a maximum thickness of nearly 100 meters. The width of the Spiritwood aquifer near Devils Lake ranges from five to fifteen kilometers (Hutchinson and Klausing, 1980).

The Spiritwood aquifer matrix material consists primarily of material of the Cando Formation, a series of sands and gravels sandwiched between clay-rich basal tills and the overlying glaciolacustrine sediments that form the confining layer of the system in the Devils Lake area (Hobbs and Bluemle, 1987). The Pierre Shale, a soft bentonitic material, provides the source of the shaley facies of the till in the local glacial material. As many as four separate ice advances have been identified in the area using the relative proportions of shaley material in the Cando Formation (Hobbs and Bluemle, 1987). As a result of these separate ice advances, the Spiritwood aquifer material has been

subjected to a great deal of reworking by glacial processes including shearing, thrusting, scouring, and fluvial action.

### Climate of North Dakota

The seasonal variability of climatic conditions in the northern prairies have been described as part of a number of studies. Longley (1972) evaluated climatic conditions across the prairie provinces of Canada. Climatic variability in the Red River of the North Drainage was summarized by Blair (1989). Jensen (1972) summarized general temperature and precipitation patterns in North Dakota. The following discussion was taken from these studies.

North Dakota has a semi-arid continental climate characterized by long cold winters and short hot summers. Generally, January is the coldest month (mean monthly temperature approximately  $-15^{\circ}\text{C}$ ) and July is the warmest month (mean monthly temperature approximately  $21^{\circ}\text{C}$ ). The five months from November through March have mean monthly temperatures below  $0^{\circ}\text{C}$ . The five warmest months, May through September, have mean monthly temperatures greater than  $12^{\circ}\text{C}$ . The transitions from summer to winter and winter to summer are usually rapid.

The amount of annual precipitation in North Dakota is relatively small. The average annual precipitation ranges from approximately 36 cm in western North Dakota to approximately 50 cm in the eastern part of the state. Average annual precipitation in the Devils Lake area is approximately 44 cm. The majority of precipitation occurs as large



thunderstorms during summer months and as infrequent snow events during the colder months. A large percentage (approximately 60 percent) of the total annual precipitation occurs during the warm months from May through September. Average annual evaporation in the Devils Lake area is approximately 86 cm (Winter and others, 1984). Potential evapotranspiration exceeds precipitation throughout most of the late spring, summer, and early fall.

### Hydrology of the Devils Lake Basin

Devils Lake is located in a closed drainage basin. Surface drainage in the Devils Lake basin is poorly defined (Wiche and others 1986). Approximately 87 percent of the basin is tributary to Devils Lake, and approximately 13 percent of the basin is tributary to Stump Lake (Wiche and others 1986). However, much of the northern portion of the basin is probably non-contributing to either Devils Lake or Stump Lake (Wiche, 1986). A number of semipermanent fresh-water lakes, collectively known as the Chain of Lakes, are located in the central region of the basin (Figure 2.1). The Chain of Lakes include, from west to east, Lake Irvine, Lake Alice, Chain Lake, Dry Lake, Morrison Lake, and Sweetwater Lake. During wet periods (high lake level) water moves from the northern portions of the basin into the Chain of Lakes by way of a series of intermittent streams known as coulees. Chain Lake, Lake Alice, and Lake Irving drain into the western end of Devils Lake through Big Coulee. Sweetwater Lake, Morrison Lake and Dry Lake drain into Sixmile Bay of Devils Lake through a man-made channel known as

Channel A. During dry periods the volume of water stored in these lakes decreases substantially.

Devils Lake is comprised of a series of basins. The basins are, from west to east, Minnewauken Flats (also known as West Bay), Main Bay, Mission Bay, East Bay, and East Devils Lake. Sixmile Bay and Creel Bay are small basins connected to Main Bay. During periods of high lake level, the basins are connected and the movement of water in the lake is generally to the east, resulting in a noticeable salinity gradient from west to east. In 1987 the dissolved solids concentrations in Devils Lake ranged from 2 grams per liter in Minnewauken Flats, to 10 grams per liter in East Devils Lake (Sando and Wiche, 1990, 1992). During dry periods, lake level drops, salinity increases, and the individual basins become isolated (Wiche and others, 1986).

Stump Lake is located to the east of Devils Lake. At water levels higher than 444 meters above sea level in Devils Lake, the Stump Lake basin becomes part of the Devils Lake Basin (Wiche, 1986). This has not occurred during European occupation of the area. In 1987 the dissolved solids concentrations in Stump Lake ranged from approximately 15 grams per liter in West Stump Lake, to approximately 75 grams per liter in East Stump Lake.

Detailed lake level measurements are available for Devils Lake dating back to 1901 (Figure 2.2). Prior to 1901, lake level measurements were made sporadically from 1867 (Wiche and others, 1986). The highest recorded lake level in Devils Lake, 438 meters above sea level, occurred in 1867. From 1867 to 1940, lake level steadily declined to a historic minimum of 427 meters above sea level. From 1940 to 1987 lake level generally rose, with one period of decline between 1956 and 1968. Lake

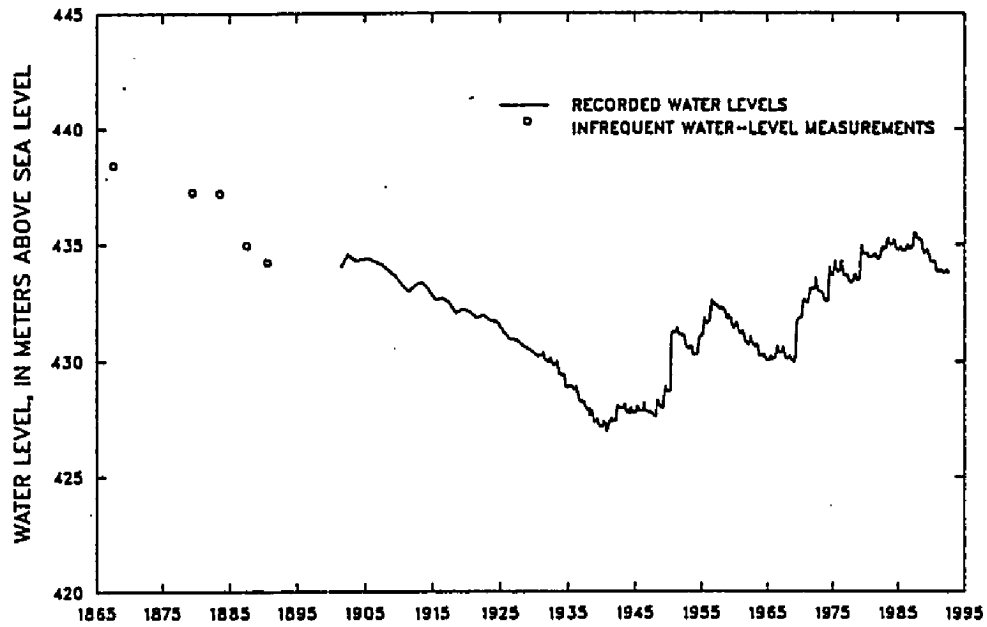


Figure 2.2. Historic water levels for Devils Lake, North Dakota, 1867-1991.

level in Devils Lake reached a recent maximum in 1987 of 435.5 meters above sea level, and has generally declined since 1987.

## METHODS

### Existing data compilation

From the early 1960's to the late 1980's, the North Dakota State Water Commission, the North Dakota Geological Survey, and the United States Geological Survey systematically evaluated the ground-water resources and geology of North Dakota. The results of these studies were published by the North Dakota State Water Commission as county reports. Well logs, water levels, and water quality data were taken from four of the North Dakota State Water Commission county reports which include data from five counties in the Devils Lake-Stump Lake area. The Ground-water Basic Data reports are for Benson County (Randich, 1971), Ramsey County (Hutchinson, 1977), Nelson County (Downey, 1971), and Eddy and Foster Counties (Trapp, 1966). Well logs, water levels, and water quality data from approximately 125 wells were used to construct the cross-sections, the piezometric surface map, and the chloride concentration map in this study.

### Field methods

Ground-water and surface-water samples were collected for stable isotopic analysis during three sampling periods. Ground-water and surface-water samples were collected in August, 1987, and September

1989. Surface-water samples also were collected during February 1988. During open water, surface-water samples were collected by wading out from shore as far as possible and collecting water in one liter polypropylene bottles. During the February sampling, surface water samples were collected through the ice near the center of each basin. The bottles were field rinsed at least three times prior to sampling. Water samples for stable isotopic analysis were sub-sampled from the one liter bottles in the field. Samples for stable isotopic analysis were decanted into 30 milliliter bottles. Care was taken to exclude any head-space during the transfer of water samples. The bottles were tightly capped and the caps were sealed with wax. These precautions were taken to minimize isotopic fractionation subsequent to sampling. Ground-water samples were collected from existing North Dakota State Water Commission and United States Geological Survey ground-water monitoring wells. Ground-water samples were collected using a 2.54 cm diameter PVC bailer. Sampling protocol for ground-water samples was similar to the protocol for surface-water samples.

#### Laboratory methods.

All samples were kept chilled until analysis. To measure  $\delta^{18}\text{O}$ , samples were equilibrated with isotopically constant purified tank  $\text{CO}_2$  according to a modified version of the method of Epstein and Mayeda (1953). During the equilibration phase, the sample bath was maintained at  $50^\circ\text{C}$ ,  $\pm 0.1^\circ\text{C}$ , for at least 12 hours. The samples then were cryogenically purified through a double trap system. Isotopic analyses

were performed with a Finnigan Mat 251 high sensitivity, moderate resolution mass spectrometer. Two internal standards, NCSU-SMOW and IMSL-SMOW were processed along with the samples. Standard reproducibility was approximately  $\pm 0.1$  per mil.

Hydrogen gas for  $\delta$ -D analyses was extracted according to a modified version of the method of Coleman and others (1982). Approximately 60 mg of special zinc reagent F-20 (Indiana University Department of Chemistry) was weighed in a 9 mm glass breakseal, which was then pumped to ultimate vacuum on a water equilibration line. A 1  $\mu$ l aliquot of water was taken from the sample bottle using a capillary tube, which was immediately dropped into the 9 mm glass breakseal. The breakseals were immersed into liquid nitrogen for 15 minutes before pumping away nitrogen gas and sealing breakseals with a torch. Sample breakseals were placed in 500°C reaction oven for 30 minutes to allow reduction of the water by the zinc, and the resulting hydrogen gas was analyzed on the mass spectrometer. Two internal standards, V-SMOW (a distilled international standard water) and IMSL-SMOW (an internal marine standard water) were processed along with the samples. Standard reproducibility was approximately  $\pm 1$  per mil.

## RESULTS AND DISCUSSION

### General Hydrology of the Spiritwood Aquifer

The well log data were plotted using the North Dakota state grid system (Figure 2.3). The upper boundary of the buried channels, including the Spiritwood aquifer, was operationally defined as 396 meter above mean sea-level. The approximate boundaries of present lake-shore boundaries were added for reference. A cross-section along the approximate axis of the buried channel (A-A', Figure 2.3) was generated to show the general stratigraphic relationships and geometry of the Spiritwood aquifer (Figure 2.4). The cross-section illustrates the irregular bedrock topography and the variable nature of the aquifer itself. Ground-water divides appear to correlate well with topographic highs, and the piezometric head data indicate that the regional flow is generally from the ground-water divides towards Devils Lake, suggesting that the lake is a discharge zone. The contention that Devils Lake is a discharge zone is supported by the presence of wells positioned as couplets suitable for use in calculating vertical gradients. These wells indicate discharge upward from the ground water near surface-water bodies, and downward to the ground-water aquifers further from the lakes. Recent data support this observation (Pusc, in review).



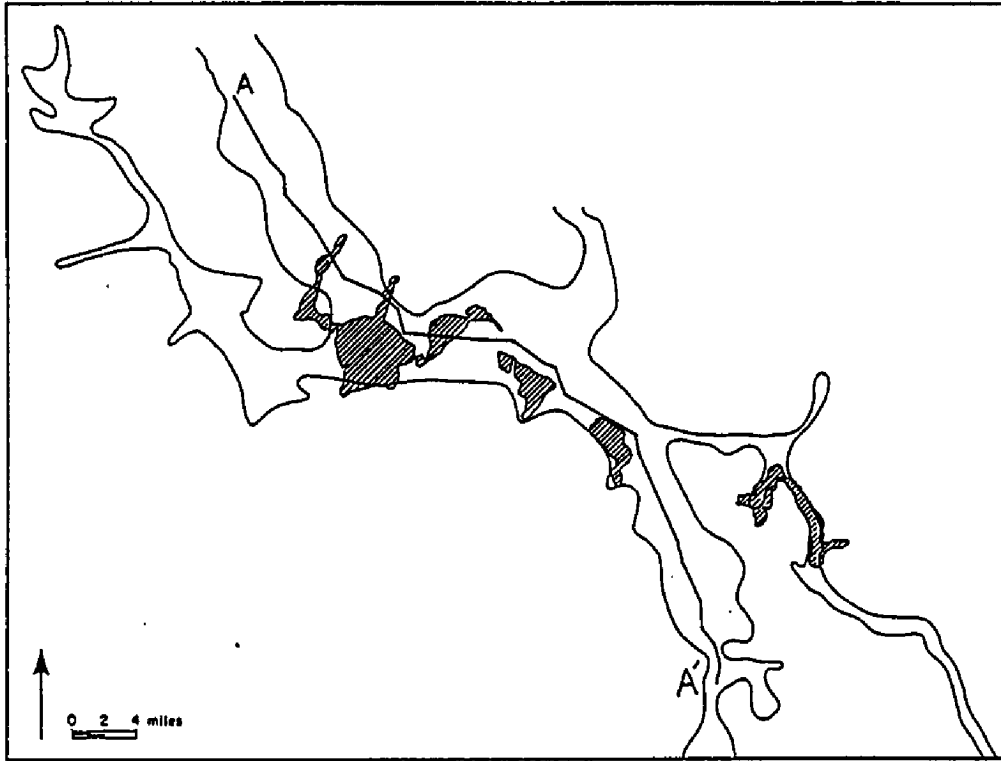


Figure 2.3. Location of the Spiritwood aquifer in the study area showing the position of cross section A-A'

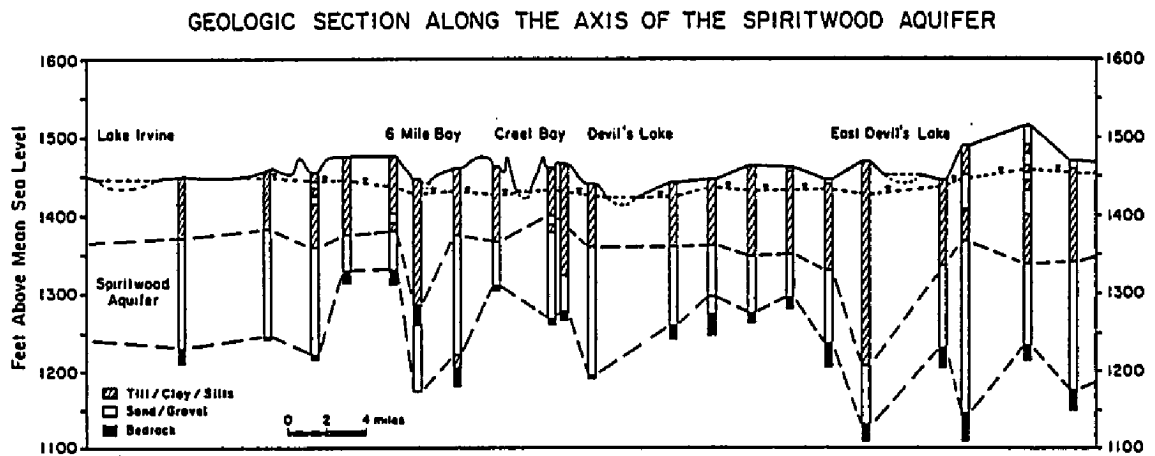


Figure 2.4. Geologic cross section along the approximate axis of the Spiritwood aquifer (A-A', Figure 3)

While the hydraulic gradient along cross-section A-A' is a reasonable representation of the regional ground-water flow in the vicinity of Devils Lake, a map of the piezometric surface shows that the flow fields are more complex (Figure 2.5). The generalized contours of the piezometric surface support the interpretation that local flow fields are superimposed on the regional flow in the Spiritwood Aquifer. Based on the geologic cross section and the piezometric surface map three ground-water divides have been identified (Figure 2.5). A more problematic ground-water flow divide appears to exist south-east of the junction of the Spiritwood and McVille aquifers and north of West Stump Lake. The uncertainty of this divide results from the subtlety of its expression and is compounded by the dynamics of historically fluctuating water levels.

A generalized map of chloride concentrations in the Spiritwood aquifer was constructed to investigate the geochemical evolution of ground water in the aquifer (Figure 2.6). In general, the areal distribution of chloride concentrations in the Spiritwood aquifer is related to ground-water movement defined by the piezometric surface. The lowest chloride concentrations in the aquifer are located near the the inferred recharge zones, there are overall increases in chloride concentrations down gradient, with the highest chloride concentrations associated with the discharge zones near the lakes. This straightforward relationship of increasing chloride concentrations with distance away from the recharge zone suggests that chloride can be used to trace ground-water flow in the Spiritwood aquifer.

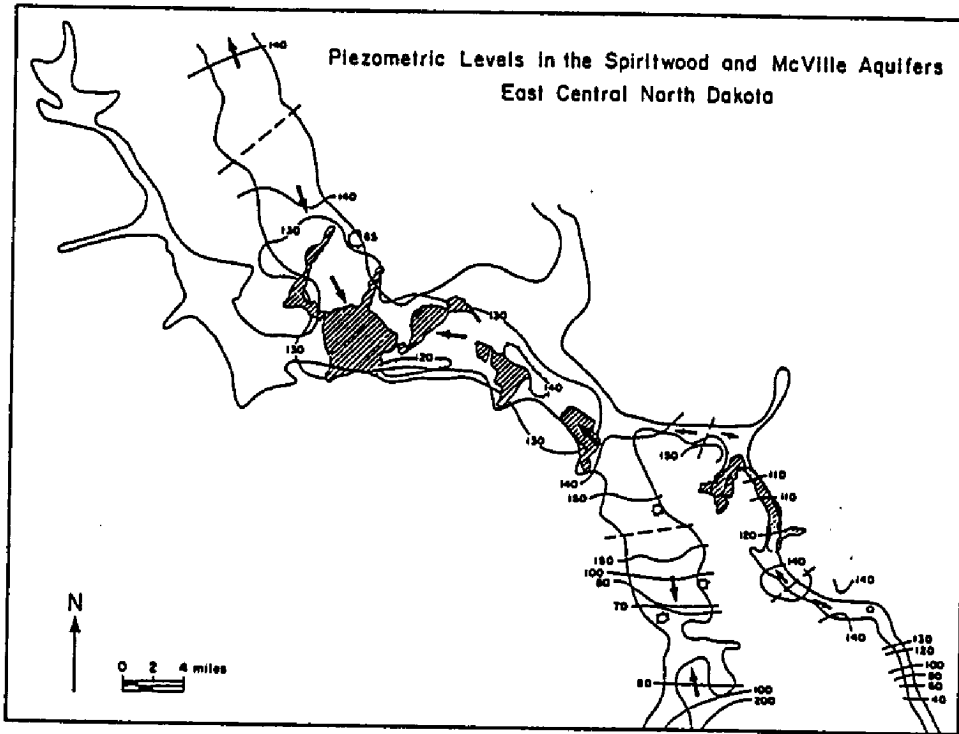


Figure 2.5. Approximate piezometric surface of the Spiritwood aquifer near Devils Lake

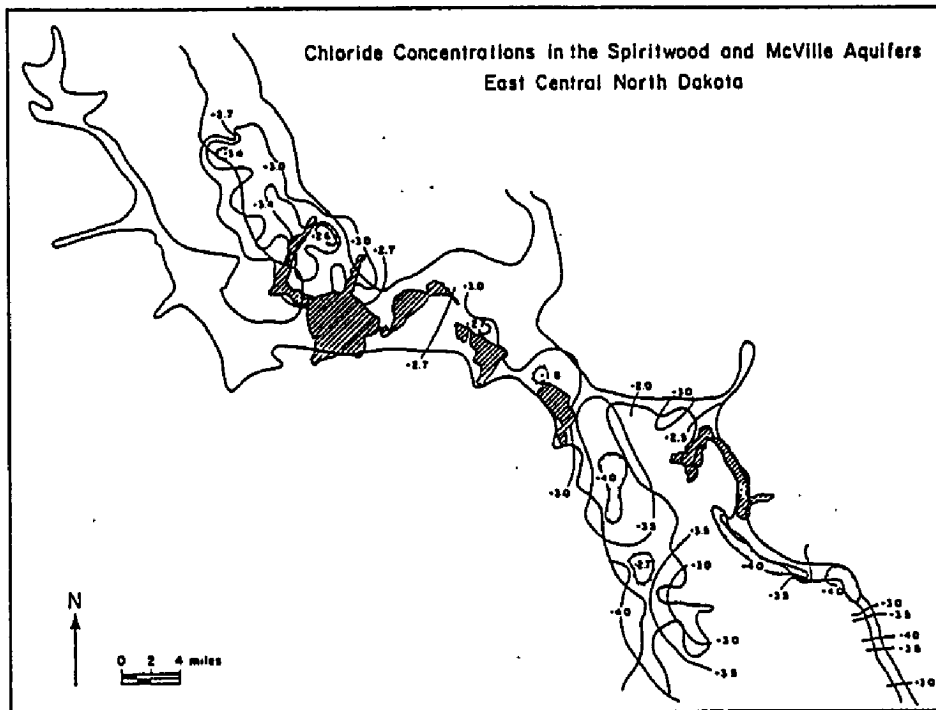


Figure 2.6. Approximate chloride distribution in the area near Devils Lake [concentrations in log (chloride molality)]

Together, the maps of the piezometric surface and chloride concentrations adequately define the ground-water system in the Spiritwood aquifer in the area around Devils Lake. The most important aspect of the ground-water system defined by the maps of the piezometric surface and chloride concentrations is the occurrence of ground-water divides north-east and south west of Devils Lake. Pusc (in review) found similar ground-water divides at approximately the same location. These ground-water divides apparently define the local ground-water system which separates the Spiritwood aquifer in the vicinity of Devils Lake, from portions of the aquifer to the north and south. The fact that these ground-water divides appear to be permanent (at least from the mid-1960's to the present) indicates that over the long term, the system is in dynamic equilibrium with recharge equal to discharge.

#### Stable Isotopic Composition of Precipitation in North Dakota

The stable isotopic composition of ground water can be a valuable indicator of the source of recharge to the aquifer (precipitation versus lake water) and the timing of recharge to the aquifer (modern versus Pleistocene, or seasonal precipitation versus annual precipitation) (Gat, 1971). The stable isotopic composition of surface water in lakes has been used to calculate water budgets for lakes, and to determine the contribution of lakes to local ground-water systems (Yurtsever and Gat, 1981; Krabbenhoft, 1992).

One of the most important, and often overlooked components of any stable isotope based hydrologic study, is a sound understanding of the

regional isotopic composition of precipitation (Mazor, 1991). Unfortunately, there is only a single measurement of the isotopic composition of precipitation in the Devils Lake area. One snow sample was collected in February, 1988 during this study. The isotopic composition of the snow event was -24.2 ‰ for  $\delta$ O-18 and -175 ‰ for  $\delta$ D. However, there are a number of hydrologic studies in other regions of North Dakota which included stable isotopic measurements of precipitation (Hwang, 1982; Rehm and other, 1982; Patch and Knell, 1988; Lent, chapter 1).

These data were compiled by Lent (chapter 1) and the following conclusions were reached. Precipitation in North Dakota exhibits a wide range of isotopic compositions. The  $\delta$ O-18 composition of precipitation sampled in North Dakota ranged from -26.2 ‰ to -0.10 ‰, and the  $\delta$ D composition ranged from -206 ‰ to -15.2 ‰. In general, the majority of the variations in the isotopic composition of precipitation were seasonal, as opposed to spatial. Therefore, the existing data is adequate to describe the isotopic composition of precipitation in the Devils Lake area. Winter precipitation (October through April) was depleted in the heavy stable isotopes relative to summer precipitation (May through September). Mean annual precipitation in North Dakota was estimated to have an  $\delta$ O-18 composition of approximately -12 ‰. Using the methods outlined in Lent (chapter 1), the theoretical  $\delta$ O-18 composition of precipitation in the Devils Lake area is approximately -13 ‰.

A meteoric water line was developed for North Dakota as :

$$\delta\text{-D} = 7.51 (\delta\text{O-18}) + 1.79$$

Individual precipitation samples clustered along two segments of the meteoric water line, illustrating the strong seasonal component to the

yearly isotopic composition of precipitation in the state. The isotopic composition of precipitation in North Dakota can be described best using two separate meteoric water line equations. One equation describing summer precipitation:

$$\delta\text{-D} = 7.31 (\delta\text{O-18}) - 0.35$$

and one equation describing winter precipitation:

$$\delta\text{-D} = 8.20 (\delta\text{O-18}) + 14.7$$

The differences in slope and intercept between the summer and winter meteoric water lines were attributed to a combination of local and region processes.

#### Stable Isotopic composition of ground water near Devils Lake

The results of the stable isotopic analyses of ground-water samples are presented in Tables 2.1 and 2.2. The stable isotopic composition of ground-water samples from the Spiritwood aquifer ranged from -15.5 o/oo to -7.74 o/oo for  $\delta\text{O-18}$ , and from -117 o/oo to -68.6 o/oo for  $\delta\text{-D}$  (Table 2.1). The stable isotopic composition of ground-water samples from tills in the Devils Lake area ranged from -16.2 o/oo to -11.5 o/oo for  $\delta\text{O-18}$ , and from -112 o/oo to 89.5 o/oo for  $\delta\text{-D}$ . (Table 2.2) In general, the samples from the Spiritwood aquifer fall along the meteoric water line for North Dakota, indicating that the water in the Spiritwood aquifer is meteoric water unaffected by evaporation. However, water from the Spiritwood aquifer appears to be depleted in deuterium and O-18 relative to mean annual precipitation. Generally, in ground-water systems where meteoric water is the principle source of recharge to an aquifer,



the isotopic composition of the ground water is similar to the isotopic composition of mean annual precipitation (Lloyd and Heathecote, 1985). This is particularly true in regions less arid than North Dakota where yearly precipitation exceeds yearly potential evapotranspiration (Gat, 1971; Mazor, 1991).

Table 2.1. Stable Isotopic Composition of Ground-Water Samples from the Spiritwood Aquifer

Sample	Well Name	del O-18	del-D
SA1	156-66-31DDD	-15.2	-115
SA2	115-66-09AAA	-15.3	-113
SA3	155-66-33CCC	-14.9	-108
SA4	154-65-17AAA	-13.1	-95.3
SA5	154-65-28DDD	-15.5	-116
SA6	154-66-23DDD	-15.5	-114
SA7	153-65-10BBB	-15.4	-117
SA8	153-65-11ADD	-15.5	-114
SA9	152-64-02CBC	-15.4	-114
SA10	152-62-33DDD	-7.7	-68.7

Table 2.2. Stable Isotopic Composition of Ground-Water Samples from Glacial Tillis near Devils Lake.

Sample	Well Name	del O-18	del-D
T1	154-65-28DDD	-13.6	-99.3
T2	153-65-12BCA	-16.2	-112
T3	153-64-07DCD	-12.2	-91.3
T4	153-064-35DCC	-13.7	-99.0
T5	153-64-36DCC	-11.5	-89.5

There are a number of possible explanations for the apparent depletions of deuterium and O-18 in the Spiritwood aquifer. The first

possibility is that recharge waters originated at a higher altitude where isotopic fractionation is more pronounced (Gat, 1981). While this is an appropriate explanation for the isotopic composition of some ground-water systems (for example ground water in central Missouri, Banner and others, 1989), it is not a reasonable explanation for the isotopic composition of ground water in the Spiritwood aquifer due to the north-south trend of the aquifer and the generally flat topography in the region. The second possibility is that the ground water originated in an area where the climate is significantly cooler (Mazor, 1991). Such regions do exist to the north in Canada. While the Spiritwood aquifer system does extend north into these regions, the possibility of uninterrupted flow for such distances seems unreasonable based on the local nature of ground-water flow in the Devils Lake area. In addition, travel times were estimated for these distances, based on the hydraulic characteristics of the Spiritwood aquifer in the Devils Lake area taken from county reports. The calculated travel times ranged from 40,000 to 50,000 years, apparently discounting this possibility.

Seasonal variations in the stable isotopic composition of precipitation and the ratio of the amount of precipitation to the amount of potential evapotranspiration also could explain the isotopically light ground water in the Spiritwood aquifer (Rehm and others, 1982). In North Dakota, the amount of precipitation exceeds the amount of potential evapotranspiration from late spring through early fall. Therefore, during the warmer months of the year, much of the precipitation that occurs probably does not recharge the aquifer. The isotopic composition of the Spiritwood aquifer is similar to the composition of a number of shallow, unconfined aquifers in North Dakota

(Rehm and others, 1982; Patch and Knell, 1988). Many of the shallow aquifers have detectable tritium activities indicating that modern recharge is occurring. Therefore, the isotopically light nature of the shallow aquifers could be due to recharge dominated by isotopically light winter precipitation and spring runoff. However, the confined nature of the Spiritwood aquifer, along with the thickness of the overlying tills seem to make this hypothesis unlikely.

A more likely explanation of the isotopically light nature of the Spiritwood aquifer is that the water in aquifer is paleo ground-water, recharged during colder climatic conditions (Gat, 1971). Potential sources of older, isotopically light water include Pleistocene meltwater generated during the last retreat of the Laurentide ice from the Devils Lake area approximately 13,000 years ago (Hobbs and Bluemle, 1987), or more recent periods of colder, wetter climate during the past few thousand years (Callender, 1968; Patch and Knell, 1988). Similar explanations have been used to interpret isotopically light ground water in numerous locations around the globe including; central Michigan (Long and others, 1988), Great Britain (Bath and others, 1978), and northern Sahara (Sonntag and others, 1978). While uninterrupted flow through the Spiritwood aquifer from Canada seems improbable, the recharge of the aquifer from either meltwater-derived surface water, or increased precipitation during colder, wetter periods appear to provide means for introducing isotopically light water into the aquifer.

The existence of large proglacial lakes is supported by the geological record (Hutchenson and Klausung, 1980). Geologic evidence also suggests that thrusting of sediments above the Spiritwood-forming Cando Formation was enhanced by hydraulic overpressures caused by

entrapment of existing formation water beneath a layer of permafrost (Hobbs and Bluemle, 1987). Therefore, the isotopically light water may have been introduced into the system prior to the final advance of the late Wisconsinian ice at approximately 10,000 to 13,000 years before present. The notion that the isotopically light water was the result of Holocene-age recharge during colder, wetter periods is supported by extensive sediment core data from Devils Lake (Callender, 1968; Fritz and others, 1991; Lent, chapter 4). These studies suggest that there were a number of colder, wetter periods during the past 6,000 years.

#### Spatial Variability in the Stable Isotopic Composition of Ground Water near Devils Lake

In general, there was little variability in the stable isotopic composition of ground-water samples from the Spiritwood aquifer near the ground-water divide located north of Devils Lake. The ground water closer to Devils Lake tended to be isotopically heavier, indicating that these samples may be from a different ground-water flow path, or represent mixing with an additional source of isotopically heavier water. The one exception to the isotopically light nature of ground water in the Spiritwood aquifer was the sample from southeast of East Devils Lake. The isotopic composition of this sample was substantially more positive (the  $\delta^{18}\text{O}$  of the sample was equal to  $-7.74$  ‰ and the  $\delta^2\text{H}$  of the sample was equal to  $-68.8$  ‰) than other samples from the Spiritwood aquifer, suggesting that the aquifer southeast of Devils Lake may have a different source of recharge. Unfortunately, only one well in this area

was sampled, therefore it is difficult to develop conclusive statements regarding the isotopic evolution of ground water southeast of the lake. In this area, portions of the Spiritwood aquifer are overlain by the Warwick aquifer, a shallow, unconfined glacial aquifer (Pusc, in review). The Warwick aquifer may provide recharge, with distinct isotopic composition, to the Spiritwood aquifer in this region of the study area. Based on the limited data it is unclear whether the variations in the isotopic composition of ground water from the Spiritwood aquifer is the result of variations in the timing of recharge, or mixing with isotopically heavier surface water from the lakes.

Five shallow ground-water samples were collected from well completed in shallow glacial tills to determine the isotopic composition of ground-water in tills near Devils Lake. The results of these analyses are presented in Table 2.1. In general, the ground-water samples from till were more positive (isotopically heavier) than ground-water samples from the Spiritwood aquifer. Four of the shallow ground-water samples plot to the right of the meteoric water line for North Dakota, indicating that the shallow ground water has experienced evaporation. In addition, the substantial differences between the isotopic composition of ground water from shallow tills and the ground water from the Spiritwood aquifer suggest that the Spiritwood aquifer is not recharged by shallow ground water near the lake. This supports the contention that Devils Lake is a discharge lake.

Stable Isotopic Composition of Surface Water  
in the Devils Lake Basin

Three categories of surface-water bodies were sampled for stable isotopic analysis during this study: fresh-water lakes including four lakes in the Chain of Lakes, and one pot hole; tributaries to Devils Lake including Channel A and Big Coulee; and saline lakes including Devils Lake, East Devils Lake, West Stump Lake, and East Stump Lake. The individual basins in Devils Lake also were sampled. The results of the stable isotopic analyses are presented in Table 2.3. In general, surface water in the basin became progressively enriched in the heavier isotopes with increasing salinity, suggesting that evaporation is an important process in the isotopic evolution of surface water in the basin. This is not surprising as a number of authors have shown that evaporitic concentration is an important process in the basin (Jones, 1966; Callender, 1968; Fritz and others, 1991; and Lent, chapters 3 and 4). There also were noticeable differences in the isotopic composition of the basins between the two consecutive fall period data sets.

The largest number of surface-water samples were collected during August, 1987. The data for the August 1987 samples are shown in Figure 2.7. The isotopically lightest samples in the basin were in the fresh water lakes north of Devils Lake. Four of these lakes were sampled in August, 1987; Dry Lake, Morrison Lake, Sweetwater Lake, and Lake Irvine (Figure 2.7). The isotopic composition of these lakes ranged from -9.62 to -7.64 ‰ for  $\delta^{18}O$  and from -74.6 to -58.5 ‰ for  $\delta^2H$ . Apparently, all of the lakes have experienced some evaporitic fractionation. Morrison Lake and Lake Irvine plot to the lower left of the diagram and near the

meteoric water line. Sweetwater Lake and Dry Lake plot further to the right and below the meteoric water line indicating a higher degree of fractionation. The two tributaries to Devils Lake also were measured in 1987 (Figure 2.7). Channel A, which drains Dry Lake, and Big Coulee, which drains Lake Irvine had similar isotopic compositions to the lakes they drain. Both Channel A and Big Coulee were isotopically lighter than Devils Lake.

Table 2.3. Stable Isotopic Composition of Surface Water in the Devils Lake Basin. {[the values are  $\delta$  O-18( $\delta$ -D)]; samples numbers refer to the locations on Figure 1}

Sample number	Location	August 1987	February 1988	September 1989
1	Minnewauken Flats	--	-7.71(-63.3)	--
2	Ziebach Pass	-5.96(-57.8)	-6.10(-61.4)	--
3	Sixmile Bay	--	--	-3.58(-41.3)
4	Creel Bay	--	--	-4.02(-43.3)
5	Main Bay	-5.86(-58.2)	-5.88(-58.6)	-3.69(-44.7)
6	Mission Bay	--	-6.15(-59.5)	--
7	East Bay (west)	-4.97(-53.0)	-6.14(-57.4)	-3.17(-43.9)
8	East Bay (east)	-4.97(-49.2)	-5.35(-51.2)	-3.08(-42.2)
9	East Devils Lake (west)	--	--	-2.73(-40.7)
10	East Devils Lake (east)	-5.27(-53.0)	-5.10(-55.3)	-4.02(-48.9)
11	West Stump Lake	--	-5.96(-43.8)	-3.09(-39.8)
12	East Stump Lake	-5.37(-54.0)	-6.69(-61.1)	-2.63(-41.7)
13	Dry Lake	-6.29(-60.3)	--	--
14	Morrison Lake	-9.62(-74.6)	--	--
15	Sweetwater Lake	-6.14(-58.5)	--	--
16	Lake Irvine	-7.64(-64.0)	--	--
17	Channel A	-6.22(-61.1)	--	-8.40(-81.7)
18	Big Coulee	-6.97(-54.7)	--	--
19	Black Swan	-5.82(-54.7)	--	--

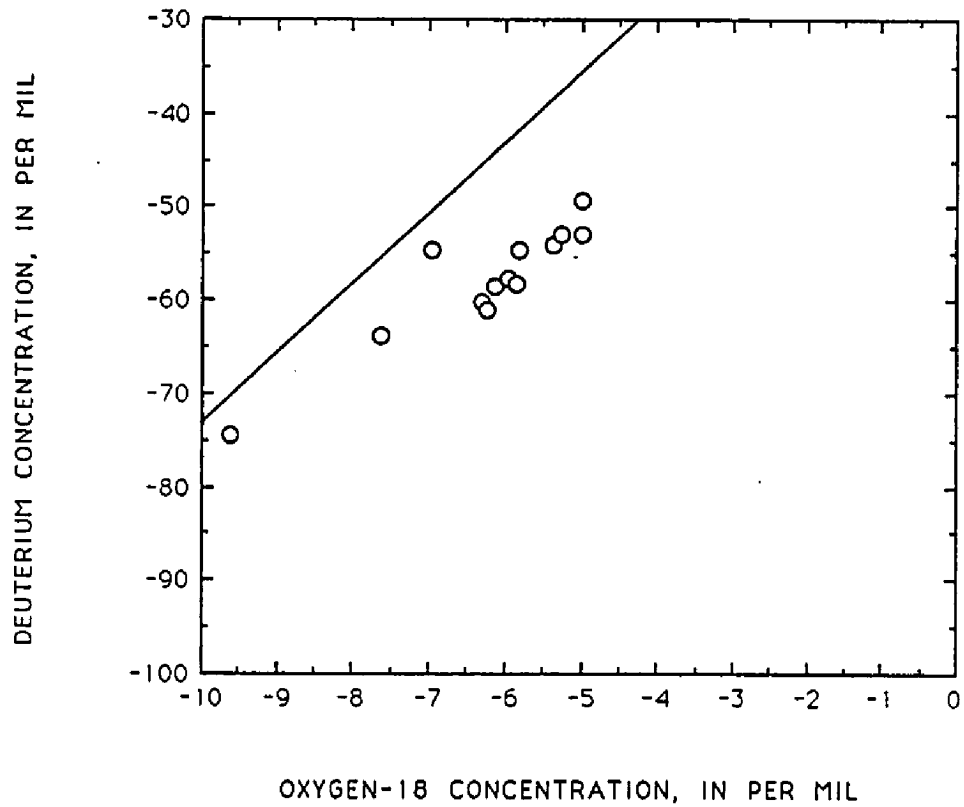


Figure 2.7. Isotopic composition of surface water samples from Devils Lake, August, 1987 (the solid line fits the meteoric water line for North Dakota).



The isotopic composition of surface water in Devils Lake became heavier from west to east (Table 2.3). This is consistent with increasing salinity and the general movement of water in the lake (Jones, 1966; Trapp, 1968 and Wiche, 1986, 1991). The isotopic composition of surface water in Main Bay and Ziebach Pass (located near the western end of Main Bay) were substantially lighter than water from East Bay. This trend toward heavier isotopic composition is attributed to evaporitic concentration as surface water moves through the lake.

In contrast, the isotopic compositions of surface water in East Devils Lake and Stump Lake were lighter than the water in East Bay, suggesting that surface water in East Devils Lake and Stump Lake had experienced less evaporation. This is inconsistent with the trend of increasing salinity from Devils Lake to East Devils Lake and Stump Lake. East Stump Lake is not connected by surface water flow to Devils Lake. These data support the contention that there is no hydrologic connection between Devils Lake and Stump Lake.

The fact that in 1987 surface water in East Devils Lake was isotopically lighter than the surface water in East Bay is somewhat disconcerting. In 1987, lake level was near the recent maximum, and East Devils Lake was separated from East Bay by a raised causeway with several culverts. Movement of surface water was generally unimpeded, and East Devils Lake was essentially an extension of Devils Lake. At the time the important sources of recharge to East Devils Lake appeared to be direct precipitation onto the lake surface, and surface water flow from Devils Lake. Therefore, the trend of heavier isotopic composition with increasing salinity from west to east in the basin would have been expected to continue. One plausible explanation for the relatively light

isotopic nature of East Devils Lake compared to East Bay is related to the fact that East Devils Lake is significantly deeper than East Bay (approximately 2-3 meters deeper). The amount of isotopic fractionation is related to the the volume of water evaporated relative to the amount of water remaining. As a result of the variations in water volume in the basins, similar amounts of evaporation from East Devils Lake and East Bay should not result in similar amounts of isotopic fraction.

The results of the isotopic analyses of the surface-water samples collected in February 1988 are shown in (Figure 2.8). In general the isotopic compositions of the surface-water bodies sampled are similar to the compositions measured in August, 1987. The similarities suggest that only limited isotopic fractionation occurred as a result of evaporative process during the time between sample periods. In fact, surface water at a few of the sample locations became isotopically lighter between the sample periods. This trend is particularly apparent in East Bay and East Stump Lake, and undoubtedly related to the removal of isotopically heavy water as ice during the winter. In concept, after ice melt in early spring, the isotopic composition of surface water should be near late autumn values. However, the additional isotopically light water added as winter precipitation should result in isotopically lighter surface water compositions throughout the basins.

The results of the isotopic analyses of the surface-water samples collected in September 1989 are shown in (Figure 2.9). The data plot further to the right and below the meteoric water line than the previous two data sets. The marked change in the stable isotopic character of surface water in the Devils Lake basin is the direct result of isotopic fractionation by evaporation. The climate in North Dakota during the

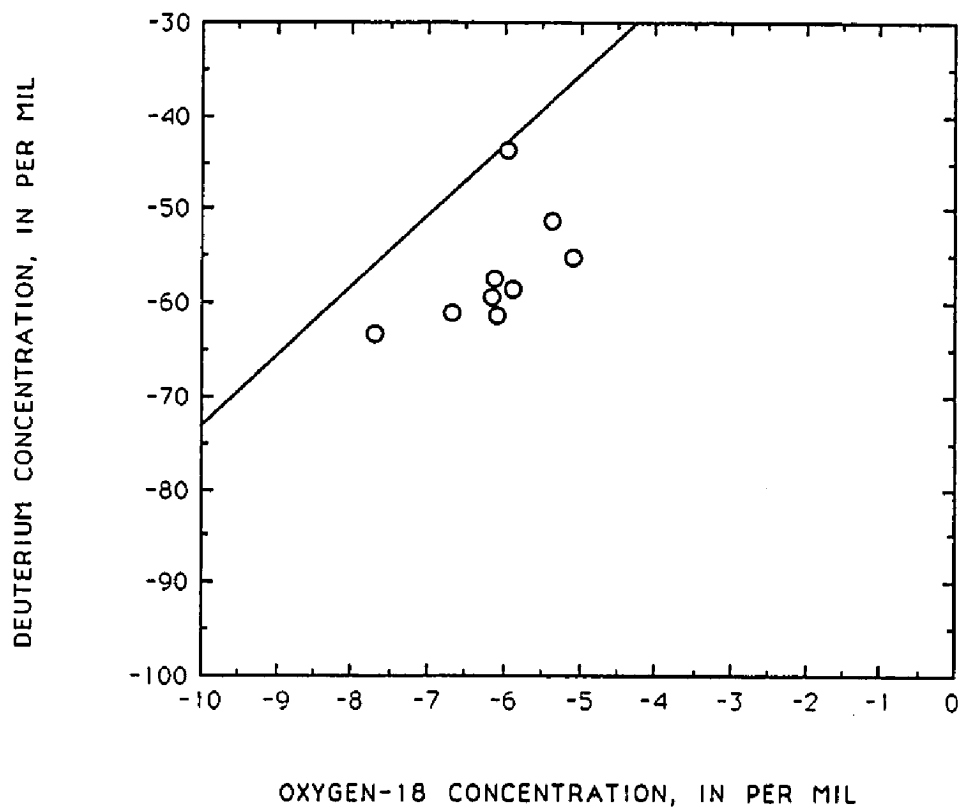


Figure 2.8. Isotopic composition of surface water samples from Devils Lake, February, 1988 (the solid line is the meteoric water line for North Dakota)

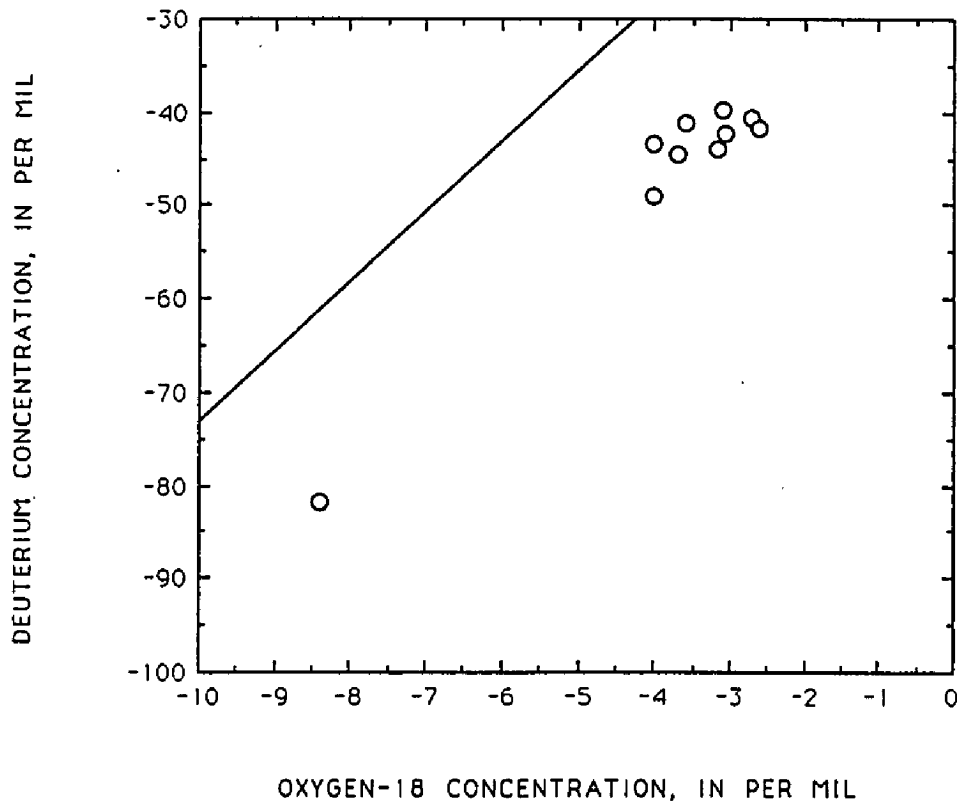


Figure 2.9. Isotopic composition of surface water samples from Devils Lake, September, 1989 (the solid line is the meteoric water line for North Dakota)

1980's generally was wetter than normal. the abundant precipitation resulted in extremely high lake levels throughout North Dakota (Wiche and others, 1986). As previously noted, lake level in Devils Lake reached a recent maximum in 1987. North Dakota experienced severe drought conditions in 1988, which resulted in a substantial loss of water in Devils Lake (approximately 0.4 meter decline in water level, Figure 2.2). The shift in the isotopic composition of surface water to less negative values in Devils Lake is a result of decreased water volume.

The effect of decreasing water volume in the basin on the isotopic composition of water in the lake is illustrated by comparing the isotopic composition of surface water between August, 1987, and September, 1989 (Figure 2.10). Four locations in Devils Lake and Stump Lake were sampled during both sample periods. These locations are; Main Bay, East Bay, East Devils Lake, and East Stump Lake. In each of the four basins the 1989 data plot further to the right and top of the diagram indicating enrichment of the heavier isotopes (Figure 2.10). The slopes of the lines defined by the four pair of data are less than the slope of the line defined by the meteoric water line for North Dakota (Lent, chapter 1). Yurtsever and Gat (1981) determined that the difference in slope between the meteoric water line and surface water in an evaporating basin primarily is the result of the relative humidity near the water surface.

The fact that the data from the four different basins plot on lines with remarkably similar slopes supports the contention that temporal variations in the isotopic composition of surface water in the study basins are the result of climatic factors common to all the basins. The actual differences in the isotopic composition of surface water in the four basins

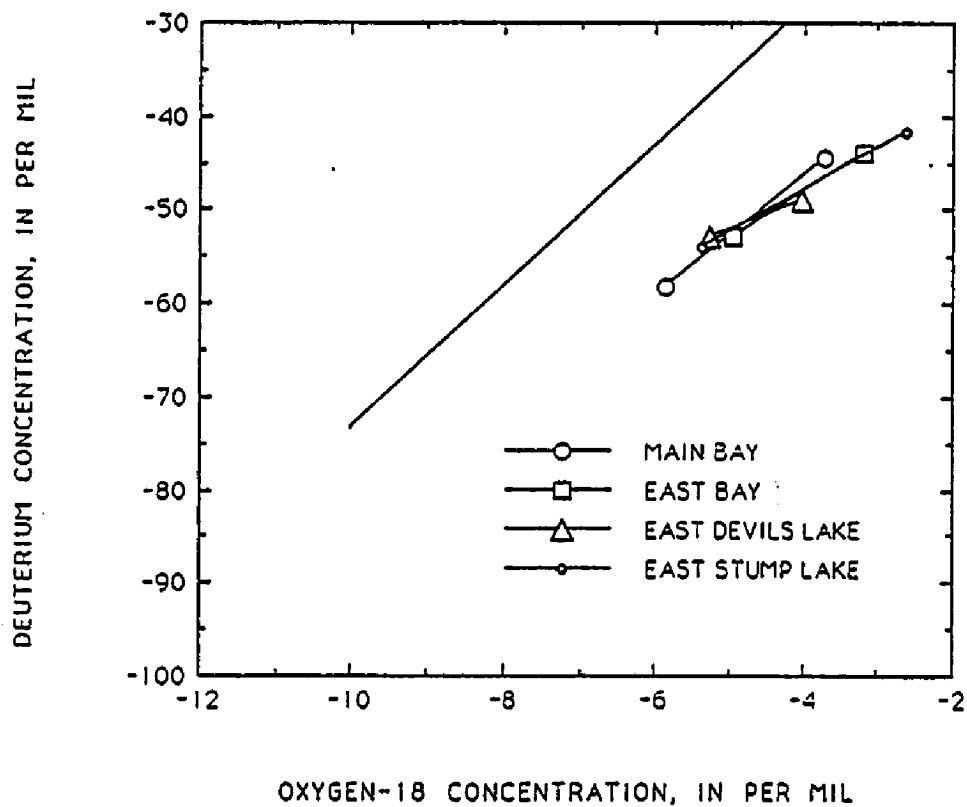


Figure 2.10. Variations in the stable isotopic composition of four surface-water stations in Devils Lake between August, 1987 and September, 1989. In all cases the values for the samples from 1989 plot towards the upper right corner. (the solid line is the meteoric water line for North Dakota)

(expressed as length of the lines in Figure 2.10) appears to be related to differences in the ratios of water volume to surface areas of the basins. The difference between the two years was greatest in East Stump Lake and smallest in East Devils Lake. East Stump Lake is generally shallow (water depths are less than two meters). In contrast, East Devils Lake is the deepest basin sampled. The fact that Main Bay also experienced significant variation may be related to the shallow nature of Minnewauken Flats.

#### Potential Sources of Recharge to Devils Lake

The relative importance of potential sources of recharge to a closed basin can be investigated through evaluation of the intersection of the line defined by the isotopic composition of surface water from the basin with the meteoric water line. By assuming that the lake is in isotopic equilibrium and that there is a single dominant source of recharge to the lake, the intersection of the two lines can be taken as the isotopic composition of lake water prior to evaporation (Mazor, 1991). The potential sources of recharge to Devils Lake are; ground water, surface runoff, and direct precipitation. Existing water budgets for Devils Lake indicate that the water budget is dominated by direct precipitation, even during high runoff periods (Wiche, oral communication).

Data from all the Devils Lake locations sampled were combined to provide additional information about sources of recharge to Devils Lake (Figure 2.11). these data include the samples from East Devils Lake. During the sampling period, water levels in the lakes were high enough

that Devils Lake and East Devils Lake were connected. The data fall on a line defined by the equation:

$$\delta\text{-D} = 5.72 (\delta\text{-O-18}) - 23.7$$

This line intersects the meteoric water line for North Dakota at  $\delta\text{-O-18}$  equal to -14.4. The range of compositions for the Spiritwood Aquifer (excluding the one sample south of East Devils Lake) and the value calculated for average annual precipitation also are shown on Figure 2.11.

If direct precipitation was the only source of recharge to Devils Lake, the intersection of the evaporation line for Devils Lake and the meteoric water line for North Dakota should be equal to the value of mean annual precipitation (direct precipitation onto the lake surface should not be effected by seasonal processes). The intersection of the two lines plots below (more negative) the value for annual precipitation, which indicates that direct precipitation may not be the only important source of recharge to Devils Lake. The only potential source of recharge to Devils Lake with an isotopic composition more negative than mean annual precipitation is the Spiritwood aquifer. During "wet" periods increased precipitation and runoff dominant recharge to Devils Lake. In contrast, during "dry" periods precipitation is less, and runoff is negligible. Therefore, during "dry" periods ground water may represent a significant contribution to the water budget of Devils Lake.

However, these conclusions are based on an extremely limited data set. Care must be taken to avoid over interpretation. More data is necessary to properly quantify ground-water contributions to Devils Lake. In particular, precipitation and surface water samples must be collected on a more regular basis to document the seasonal components of the



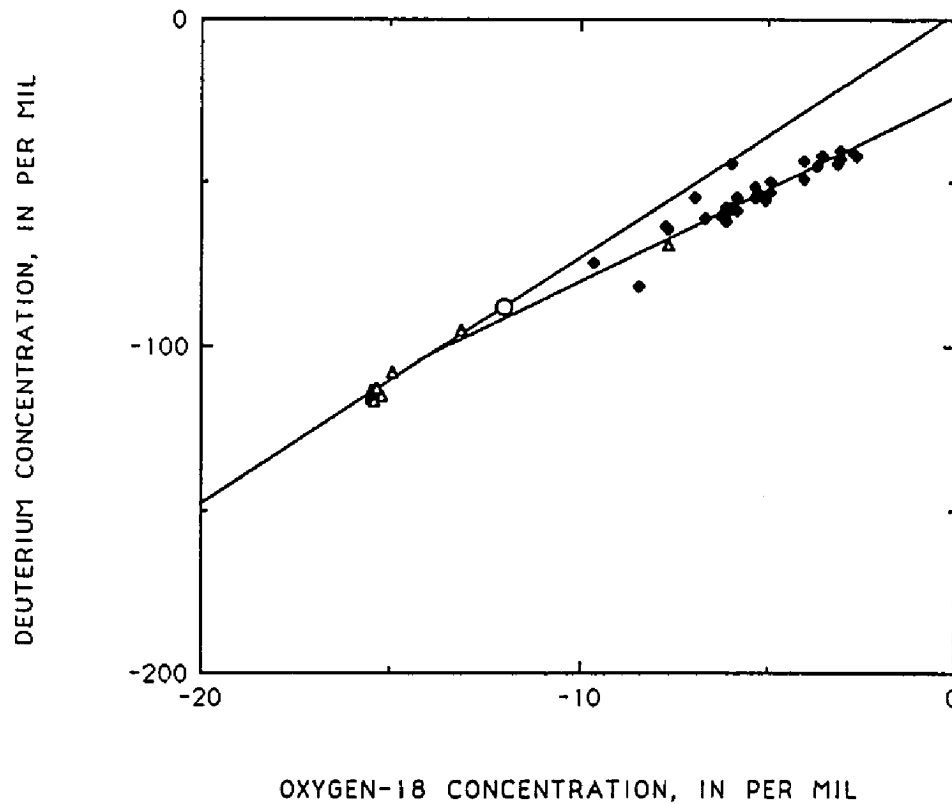


Figure 2.11. Comparisons between the stable isotopic composition of Devils Lake, the Spiritwood aquifer, and mean annual precipitation in North Dakota (the large open circle represent mean annual precipitation, open triangles are samples from the Spiritwood aquifer, and closed diamonds are surface-water samples).

isotopic budget. In addition, multiple samples from individual locations would allow the computation of separate evaporation lines for the different basins. Finally, an expanded data collection program would allow isotope mass-balance calculations which could be quantitatively compared to existing water budgets for the lake and ground water in the Devils Lake Basin.

## CONCLUSIONS

The Spiritwood aquifer is dominated by localized flow systems in the vicinity of Devils Lake. Ground-water divides, recharge zones and discharge zones can be identified by variations in chloride concentrations and existing ground-water head data. These data indicate that ground-water divides in the Spiritwood aquifer are located to the north and south of Devils Lake, effectively isolating the study area from regional ground-water flow. Generalized ground-water flow is from the ground-water divides to discharge zones associated with the lake. Chloride concentrations increase about two orders of magnitude along the described ground-water flow paths.

The isotopic composition of ground-water in the Spiritwood aquifer is lighter than present-day mean annual precipitation. The most likely explanation for the difference is that the water in the Spiritwood aquifer is old, recharged during colder, wetter periods. The timing of the recharge is difficult to ascertain without absolute age dating of the water. Possibilities include Pleistocene meltwater and more recent periods of colder wetter climate (6,000 to 500 years ago).

Surface water in the Devils Lake basin has experienced significant isotopic fractionation as a result of evaporation. The isotopic data for the Devils Lake basin plot along a single evaporation line suggesting a similar source of water to the different basins. However, the amount of evaporation (determined by the position on the evaporation line) is not consistent with dissolved solids data, indicating that the surface water basins are hydrologically separate.

Direct precipitation and surface-water runoff do not appear to be the only source of recharge to Devils Lake. The intercept of the evaporation line for Devils Lake surface water and the meteoric water line for North Dakota, is more negative (isotopically lighter) than either mean annual precipitation or measured surface water runoff. This suggests that there is an additional source of isotopically light water to Devils Lake. The only possible sources of isotopically light water appear to be either near surface ground water associated with glacial tills proximal to Devils Lake or ground water in the Spiritwood aquifer.

The ambiguity in the results of this study highlight the need for additional isotopic measurements in the Devils Lake basin. In particular, repeated measurements of surface water from selected basins need to be made to determine evaporation lines for specific basins. In addition, the isotopic composition of the Spiritwood aquifer south east of the lake should be determined.

## CHAPTER III

### PORE-WATER GEOCHEMISTRY AND SOLUTE FLUX FROM BOTTOM SEDIMENTS, DEVILS LAKE, NORTH DAKOTA

#### INTRODUCTION

Closed-basin lakes (lakes located in drainage basins that are not integrated with regional drainage systems) are located throughout the Great Plains of the western United States and Canada. These lakes often are brackish to saline and exhibit a wide variety of chemical concentrations. The hydrologic conditions (e.g., physical, chemical, and biological) in these closed-basin lakes can be strongly influenced by relatively small fluctuations in climatic conditions (Eugster and Hardie, 1978). The variations in hydrologic conditions caused by the fluctuations in climatic conditions are particularly evident with respect to lake level and salinity. Because of the variations in salinity, bottom sediments in closed-basin lakes are rarely in chemical equilibrium with the overlying lake water (Lerman and Jones, 1973; Barton and others, 1987).

In addition, many of the closed-basin lakes are eutrophic to hypereutrophic and, as a result, should have rapid rates of organic-matter production and decomposition (Armstrong and others, 1966; Dean and Gorham, 1976). The chemical disequilibrium between bottom sediments and the overlying lake water and the potential for significant

rates of microbially-mediated diagenetic reactions combine to make interactions between the bottom sediments and the overlying lake water important to the overall chemical budget of closed-basin lakes.

Although the chemical diagenesis of marine and freshwater sediments is well documented, little work has been done to characterize the diagenesis of lacustrine sediments from closed drainage basins. Even though models do exist to predict the chemical evolution of terrestrial waters (Eugster and Jones, 1979), these models usually are restricted to the evolution of surface water and neglect the influence of the underlying pore water. The chemical changes occurring in the pore water of saline-lake sediments can have a substantial impact on the chemical concentrations in the overlying lake water (Lerman and Jones, 1973).

Chemical mass-balance calculations are the predominant method used to characterize the chemical evolution of closed-basin lakes. Mass-balance calculations for saline lakes, such as Lake Chad (Eugster and Maglione, 1979), Lake Magadi (Jones and others, 1977), Lake Turkana (Yuretich and Cerling, 1983; Cerling, 1986), the Ethiopian rift valley lakes in Africa (Von Damm and Edmond, 1984), and Blue Lake in Australia (Ramamurthy and others, 1985) are similar to those used routinely for marine systems (Boyle and others, 1974). These calculations generally combine hydrologic water budgets with surface water and brine chemistries to describe the evolution of water as it undergoes evaporitic concentration.

Chemical budgets calculated for saline lakes often ignore the contributions of sediment pore water because of the lack of data. However, studies that include pore-water data have demonstrated the

large chemical flux possible from bottom sediments (Lerman and Jones, 1973; Barton and others, 1987). Chemical interaction between surficial bottom sediments and the overlying lake water is undoubtedly important throughout the history of saline lakes and may be extremely important during times of rapid lake-level fluctuations when the pore water and the overlying lake water would not be in chemical equilibrium (Lerman and Jones, 1973). For example, an increase in precipitation and no change in evaporation would result in a rapid rise in lake level and a decrease in salinity. This decrease in salinity would result in a larger salt content in the sediment pore water than in the overlying lake water and would result in a net flux of dissolved solids from the bottom sediments to the lake (Lerman and Jones, 1973).

The purpose of this investigation was to analyze the sediment pore water in Devils Lake, North Dakota, a brackish-water, closed-basin lake, to determine the diagenetic reactions occurring in the surficial bottom sediments (upper 30 centimeters) and to evaluate the impact of these reactions on the concentrations of chemical constituents in the overlying lake water.

### Study Area

The Devils Lake basin in northeastern North Dakota is a large [9,870 km<sup>2</sup> (square kilometers)] closed basin located in the drainage of the Red River of the North (Figure 3.1). About 8,600 km<sup>2</sup> (87 percent) of the total 9,870 km<sup>2</sup> is tributary to Devils Lake, and the remaining 1,270 km<sup>2</sup> (13 percent) is tributary to Stump Lake (Figure 3.1). The area around Devils

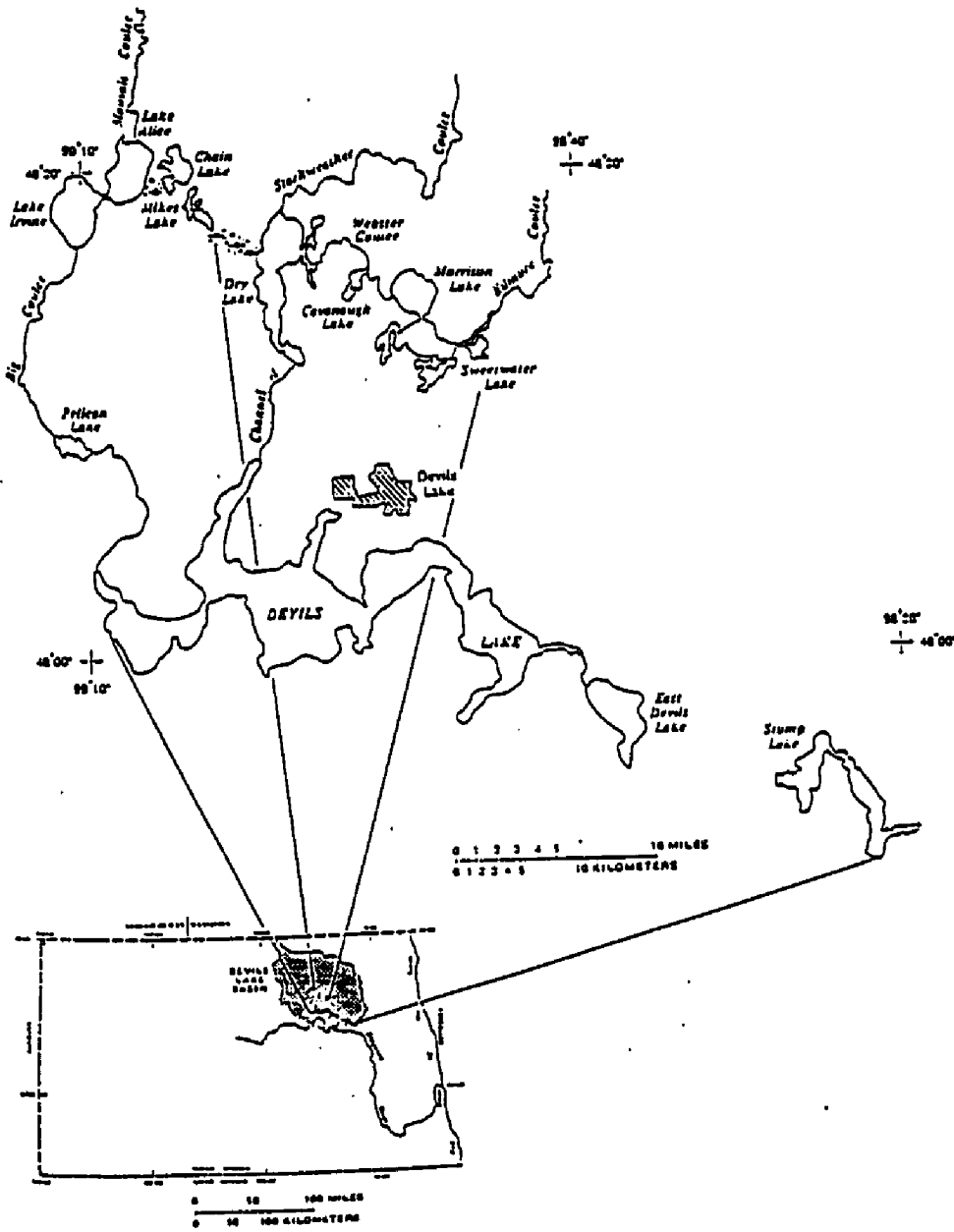


Figure 3.1. Location of Devils Lake, North Dakota.



Lake is blanketed by sediments of glacial origin, characterized by hummocky surfaces, shallow depressions, and poorly defined water divides (Callender, 1968; Hobbs and Bluemle, 1987). The till is comprised primarily of material from the Cretaceous Pierre Formation, a shale-rich formation underlying much of eastern North Dakota.

At water levels less than 434 m (meters) above sea level, Devils Lake is separated into a series of lakes. At water levels greater than 434 m above sea level, these lakes become interconnected, and Devils Lake is a single lake. Streamflow enters the west part of Devils Lake and moves toward the east, resulting in a salinity gradient that increases from west to east. Devils Lake is relatively shallow, and depths rarely exceed 10 m. Devils Lake is not integrated with regional drainage systems and, as with other closed-basin lakes, the volume of water and the water quality in Devils Lake is largely dependent upon local climatic conditions (Wiche, 1986, 1991; Wiche and others, 1986).

Historic records dating to 1867 show that the water level of Devils Lake has fluctuated by about 12 m (Figure 3.2). The water level generally declined from a historic maximum of 438.4 m above sea level in 1867 to 427.0 m above sea level in 1940. Since 1940, the water level has fluctuated considerably, reaching a maximum of 435.5 m above sea level in 1987 and then declining to 433.9 m above sea level by January 1991. The surface area of Devils Lake was about 363 km<sup>2</sup> in 1867, 26 km<sup>2</sup> in 1940, 233 km<sup>2</sup> in 1987, and 202 km<sup>2</sup> in 1990.

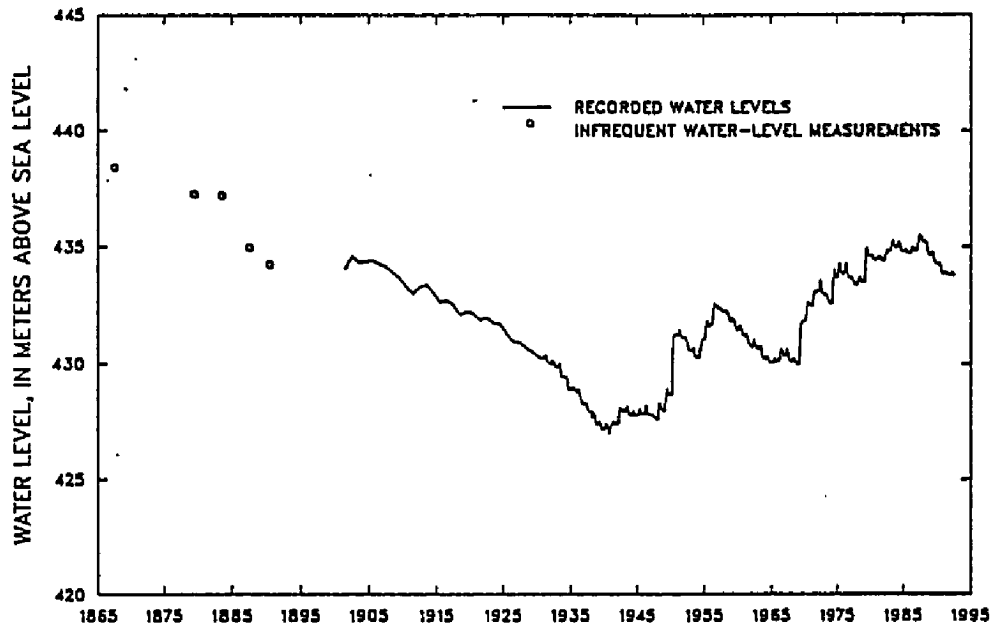


Figure 3.2. Historic waters for Devils Lake, 1867-1991.

## METHODS

### Sample Locations

In July 1986, four short cores (about 30 cm in length) were collected from the bottom sediments at the eastern end of Devils Lake (Figure 3.3). The locations where the sediment cores were collected were chosen so that the bottom sediments were sampled along the salinity gradient present in the overlying lake water. Core 1 was collected from the sediment underlying the relatively fresh water of Mission Bay at a water depth of about 6 m. Core 2 was collected from East Bay at a water depth of about 5 m, and core 3 was collected from East Bay at a water depth of about 5.5 m. Core 4 was collected from the sediment underlying the highest salinity water near the eastern end of Devils Lake at a water depth of about 4 m.

The sediment cores were collected from a small boat by using a hand-held sediment corer. The sediment corer was equipped with a 6-m metal extension and with 5-cm diameter core liners that were capped at both ends immediately after retrieval of the cores to minimize the effects of oxidation. Upon returning to shore, the sediment cores were extruded and divided into 3- to 5-cm sections. The pore water was extracted using nylon squeezers with Teflon parts and nitrogen gas (Lyons and others, 1988). About 3 to 7 ml (milliliters) of pore water was obtained from each section. The pore water was filtered before storage using 0.45- $\mu\text{m}$  (micrometer) membrane filters. Once filtered, the pore water was

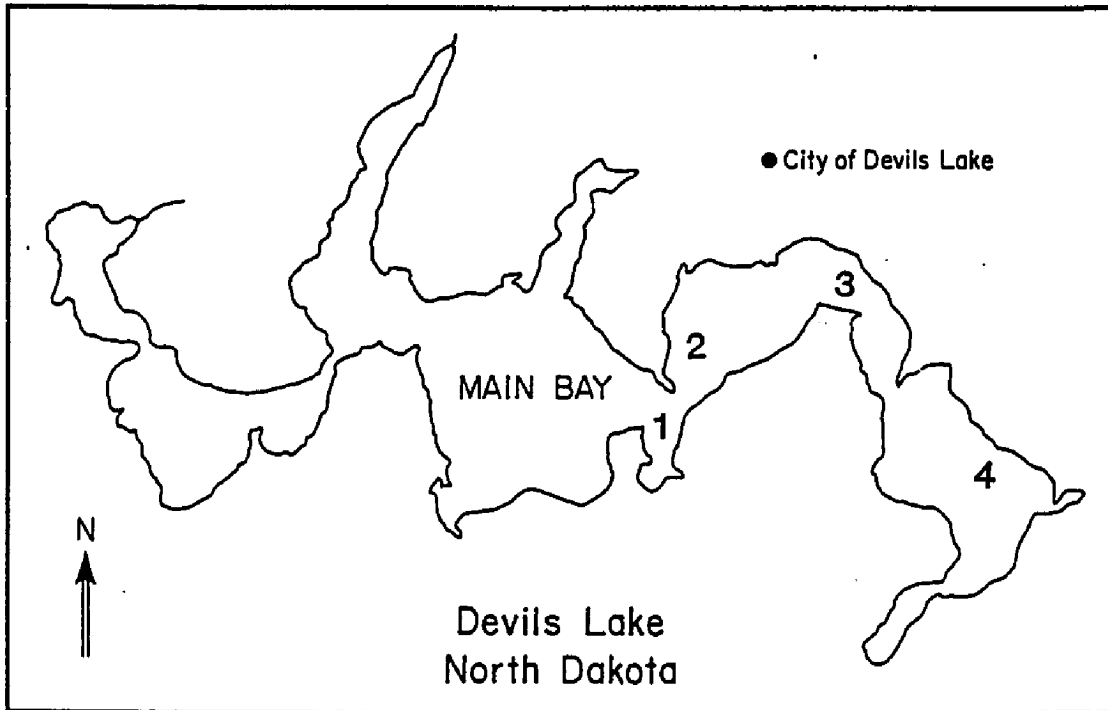


Figure 3.3. Location of sediment-cores sampling sites in Devils Lake, North Dakota. subdivided and stored in 30-ml polypropylene Nalgene bottles for later analysis.

All bottles were cleaned before use. Each bottle was rinsed with ultraclean water, filled with 10 percent solution of reagent-grade HCl (hydrochloric acid), and stored overnight. The bottles then were rinsed three times and filled with ultraclean water. The bottles remained filled until use.

### Chemical Analysis of Bottom-Sediment Samples

The rates of biogeochemical processes involving the degradation of organic material, such as  $\text{SO}_4^{2-}$  (sulfate) reduction, are affected by sedimentation rates (Berner, 1980). To determine sedimentation rates for the four sediment cores, 2- to 3-gm sediment samples were dried, powdered, and analyzed for Cs-137 (cesium-137) activity and excess Pb-210 (lead-210) activity. The Cs-137 and Pb-210 activities were measured for 8 to 24 hours using non-destructive gamma-counting spectrophotometry (Gasseler and others, 1976; Cutshall and others, 1983).

Sedimentation rates for the four cores were calculated on the basis of Cs-137 activity and excess Pb-210 activity. The presence of Cs-137 activity in sediments is the direct result of atmospheric testing of nuclear weapons occurring since the early 1950's. To determine the sedimentation rate from Cs-137 activity, the deepest sediment sample with measurable Cs-137 activity was identified. The midpoint of this sample then was assumed to correspond with an age of 34 years (1952). Atmospheric testing of warheads reached maximum in 1963, just before the ban on testing. Therefore, the midprofile maximum in Cs-137 activity

was assumed to correspond with an age of 23 years. The excess Pb-210 activity in the sediment was used to estimate the sedimentation rates by assuming a constant supply of Pb-210 and no sediment mixing (Jacobson and Engstrom, 1989).

In addition to the radiochemical analyses, the sediment samples were analyzed for environmentally-reactive trace-metal concentrations (Lyons and Fitzgerald, 1980). About 2-g sediment samples were weighed and then leached with 10 percent HNO<sub>3</sub> (nitric acid) at 25°C for 24 hours. Previous investigators (Carmody and others, 1973) have shown that HNO<sub>3</sub> leaching extracts as much as 80 to 85 percent of the total sedimentary metal in nearshore clastic sediments. This technique has been used successfully to estimate the trace-metal concentrations in estuarine sediments (Lyons and Fitzgerald, 1980) and carbonate-dominated sediments (Lyons and others, 1983). The leachates were filtered using glass-fiber filters and then analyzed by flame atomic absorption spectrophotometry for Cu (copper), Pb (lead), and Zn (zinc) concentrations. The leachates were analyzed colorimetrically for Fe (iron) using Ferrozine (Murray and Gill, 1978) and PO<sub>4</sub><sup>3-</sup> (phosphate) (Brey, 1973) concentrations after appropriate dilutions.

#### Chemical Analysis of Pore-Water Samples

Pore-water samples were analyzed for major ions, nutrients, and total Fe. Measurements of pH and titration alkalinity (HCO<sub>3</sub><sup>-</sup>) were made in the field immediately after the extraction of the pore water. Titration alkalinity concentrations in 5-mL samples were determined by titration

method using 0.197 N (normal) HCl. The acidified samples then were saved for subsequent chemical analyses including major cations Ca (calcium), Mg (magnesium), Na (sodium), and K (potassium)],  $\text{H}_4\text{SiO}_4$  (silicate),  $\text{NO}_2^-$  (nitrite),  $\text{NO}_3^-$  (nitrate),  $\text{NH}_4^+$  (ammonium),  $\text{PO}_4^{3-}$  (phosphate), and total Fe.

$\text{SO}_4^{2-}$  concentrations were determined gravimetrically after precipitation with BaCl (barium chloride). Cl (chloride) concentrations were determined on separate, nonacidified samples by ion chromatography. The small volume of pore water obtained from many of the samples limited the number of  $\text{SO}_4^{2-}$  and Cl analyses that could be performed.

Major-cation concentrations were determined by flame atomic absorption spectrophotometry after the addition of a Cs and La (lanthanum) matrix modifier.  $\text{H}_4\text{SiO}_4$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  concentrations were determined using colorimetric Auto Analysis techniques (Glibert and Loder, 1977).

Because of the length of storage time (about 12 weeks), DIN (dissolved inorganic nitrogen) was calculated as the sum of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ . This was done in case part of the  $\text{NH}_4^+$  present in the samples had oxidized. Total Fe was determined using ferrozine as described in Murray and Gill (1978).

The geochemical thermodynamic program WATEQ4F (Ball and Nordstrom, 1987) was used to calculate ion activities and mineral-saturation coefficients for the pore-water samples.

## RESULTS

### Sedimentation Rates

Cs-137 activity and excess Pb-210 activity data are presented in Table 3.1. Excess Pb-210 activity was detected in all four cores. In cores 1 to 3, the excess Pb-210 activity profiles exhibited near-surface maxima, indicating active sedimentation. Cs-137 activity was detected to a depth of 15 cm in core 1, a depth of 6 cm in core 2, and a depth of 3 cm in core 3. Cs-137 activity was not detected in core 4. Core 1 was the only core in which a midprofile Cs-137 activity maximum was detected (6 to 10 cm). Because of the lack of midcore Cs-137 activity maximums, sedimentation rates were calculated using the earliest (deepest) detected Cs-137 activity.

Sedimentation rates calculated on the basis of Cs-137 activity and excess Pb-210 activity are presented in Table 3.2. The sedimentation rates calculated using the two different radionuclide techniques are similar (Table 3.2). Core 1 has the largest sedimentation rate, and cores 2 and 3 have intermediate sedimentation rates. In core 4, there was no measurable Cs-137 activity, and, even though excess Pb-210 activity was detected, the activity was near background and did not vary significantly with depth, indicating that the sedimentation rate at this location is zero. Given the dynamic nature of the shallow water environments along with the relatively coarse sampling interval used in this study, these rates represent approximate sedimentation rates.



TABLE 3.1. Cs-137 activity and excess Pb-210 activity in bottom-sediment samples [NA, not analyzed]

Sediment core	Depth (centimeters)	Cs-137 activity (decays per minute per gram)	Excess Pb-210 activity (decays per minute per gram)
1	0-3	NA	NA
1	3-6	6.90	8.25
1	6-10	7.32	7.02
1	10-15	2.40	4.01
1	15-20	0	4.36
2	0-3	3.96	7.43
2	3-6	54	3.29
2	6-10	0	3.18
2	10-14	0	2.88
2	14-18	0	5.37
2	18-22	NA	NA
2	22-26	NA	NA
3	0-3	80	9.17
3	3-6	NA	NA
3	6-10	0	1.59
3	10-15	0	2.58
3	15-20	0	2.78
3	20-25	0	2.78
3	25-30	0	3.23
4	0-3	0	3.84
4	3-7	0	3.55
4	7-11	0	4.22
4	11-15	NA	NA
4	15-19	0	3.38
4	19-23	0	3.25

TABLE 3.2. Sedimentation rates for sediment cores 1 to 4 in Devils Lake, North Dakota

Sediment core	Cs-137 activity (centimeters per year)	Excess Pb-210 activity (centimeters per year)
1	0.44	0.3
2	0.18	0.12
3	0.18	0.11
4	0	0

### Bottom-Sediment Chemistry

Bottom-sediment chemistry data for sediment cores 1 to 4 are presented in Table 3.3. The Cu concentration varies from 5.0 to 16  $\mu\text{g/g}$  (micrograms per gram), the Fe concentration varies from 570 to 3,400  $\mu\text{g/g}$ , the Pb concentration varies from 0.42 to 16  $\mu\text{g/g}$ , and the Zn concentration varies from 9.8 to 40  $\mu\text{g/g}$ . The acid-leachable  $\text{PO}_4^{3-}$  concentration varies from 780 to 1,800  $\mu\text{g/g}$ . Generally, the concentrations of the various trace metals and  $\text{PO}_4^{3-}$  decrease from west (core 1) to east (core 4). In addition to the longitudinal variations between cores, the concentrations of trace metals and  $\text{PO}_4^{3-}$  generally are greatest in the near-surface samples and decrease with depth in all of the cores.

TABLE 3.3. Bottom-sediment chemistry data [cm, centimeters;  $\mu\text{g/g}$ , micrograms per gram]

Sediment core	Depth (cm)	Cu ( $\mu\text{g/g}$ )	Fe ( $\mu\text{g/g}$ )	Pb ( $\mu\text{g/g}$ )	Zn ( $\mu\text{g/g}$ )	$\text{PO}_4^{3-}$ ( $\mu\text{g/g}$ )
1	0-3	16	3,400	12	40	1,800
1	3-6	14	2,700	15	35	1,500
1	6-10	16	2,600	11	37	1,600
1	0-15	15	2,800	12	33	1,400
1	15-20	12	1,900	8.5	24	1,200
2	0-3	13	1,900	16	30	1,300
2	3-6	13	2,300	7.6	24	1,100
2	6-10	14	2,300	8.2	24	1,300
2	10-14	11	1,700	42	21	1,100
2	14-18	12	1,700	5.3	22	1,200
2	18-22	12	2,300	7.5	30	1,300
2	22-26	11	2,300	12	24	1,100
3	0-3	12	2,000	5.7	7	1,700
3	3-6	9.9	1,900	9.9	21	1,100
3	6-10	11	2,300	8.5	24	1,100
3	10-15	11	2,100	5.3	20	1,100
3	15-20	11	2,300	9.5	20	1,000
3	20-25	13	2,000	5.4	22	1,000
3	25-30	12	2,000	7.6	22	--
4	0-3	8.6	1,600	13	21	1,200
4	3-7	12	1,900	8.3	22	1,300
4	7-11	8.8	1,500	8.6	15	1,200
4	11-15	7.6	1,400	8.8	12	1,100
4	15-19	5.0	570	2.4	9.8	780
4	19-23	11	770	6.5	19	1,200

### Pore-Water Geochemistry

Pore-water geochemistry data are presented in Table 3.4. The pore-water samples can be characterized as a  $\text{Na-Mg-SO}_4^{2-}\text{-HCO}_3^-$  solutions. The pore water generally is alkaline, with pH values between 7.8 and 8.4. pH tends to increase with depth in all cores. Titration alkalinity increases with depth in cores 1 to 3 and remains relatively constant in

core 4. The concentrations of Ca, Mg, Na, K,  $\text{SO}_4^{2-}$ , and Cl in the pore-water samples are greater than the concentrations in the overlying lake water and generally increase with depth in sediment pore water, indicating that the bottom sediments may be a source of salts to the overlying lake water. A comparison of the pore-water samples taken from the top 3 cm of each core indicates that the concentrations of individual ions in the surficial pore waters tend to increase from west to east, consistent with the salinity gradient in the overlying lake water. However, the titration alkalinity concentration tends to decrease from west to east. There is little variation in the dissolved  $\text{H}_4\text{SiO}_4$  concentrations, which range from 0.72 to 1.54 mmol/L (millimols per liter).

DIN is calculated as the sum of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ . The nutrient concentrations are relatively low in all four cores, indicating slow rates of organic-matter decomposition. Core 2 has the largest concentrations of DIN [1,017 to 2,154  $\mu\text{mol/L}$  (micromols per liter)] and  $\text{PO}_4^{3-}$  (84.8 to 178.8  $\mu\text{mol/L}$ ). Core 3 has relatively small concentrations of DIN (534 to 1,263  $\mu\text{mol/L}$ ) and the smallest concentrations of  $\text{PO}_4^{3-}$  (4.6 to 26.1  $\mu\text{mol/L}$ ). Core 4 has the smallest concentrations of DIN (390 to 773  $\mu\text{mol/L}$ ) and relatively small concentrations of  $\text{PO}_4^{3-}$  (23.9 to 32.4  $\mu\text{mol/L}$ ). Core 1 has intermediate concentrations of DIN (629 to 1,331  $\mu\text{mol/L}$ ) and  $\text{PO}_4^{3-}$  (31 to 76.7  $\mu\text{mol/L}$ ). In cores 1 and 2, DIN and  $\text{PO}_4^{3-}$  increase with depth. In core 3, DIN and  $\text{PO}_4^{3-}$  decrease with depth. In core 4, located in the eastern end of the lake, DIN is extremely variable, and  $\text{PO}_4^{3-}$  is relatively constant.

TABLE 3.4. Pore-water geochemistry data [cm, centimeters; meq/L, milliequivalents per liter; mmol/L, millimols per liter;  $\mu\text{mol/L}$ , micromols per liter; DIN, dissolved inorganic nitrogen; --, not analyzed]

Sediment core	Depth (cm)	pH	HCO <sub>3</sub> <sup>-</sup> (meq/L)	Ca (mmol/L)	Mg (mmol/L)	Na (mmol/L)
1	0-3	8.2	14.4	3.07	5.19	52
1	3-6	8.2	16.5	3.32	5.77	64
1	6-10	8.1	18.7	3.23	6.01	60
1	10-15	8.4	21.4	2.86	7.67	74
1	15-20	8.3	23.6	2.98	11.3	97
2	0-3	8.0	19.3	2.71	5.58	64
2	3-6	8.1	20.3	2.95	6.28	85
2	6-10	8.2	22.7	4.25	9.29	92
2	10-14	8.1	28.9	4.22	9.52	105
2	14-18	8.4	30.9	4.52	11.6	103
2	18-22	8.4	31.8	4.83	12.3	105
2	22-26	8.4	33.1	5.21	13.0	112
3	0-3	7.8	14.5	3.92	5.95	54
3	3-6	8.0	16.3	3.73	5.88	52
3	6-10	8.2	15.3	4.32	8.48	76
3	10-15	8.1	19.7	6.80	13.7	108
3	15-20	8.3	18.8	9.78	20.1	138
3	20-25	8.1	20.6	13.2	29.4	155
3	25-30	8.2	22.5	13.3	29.2	173
4	0-3	7.9	12.5	8.07	8.93	75
4	3-7	8.0	12.7	12.7	11.2	86
4	7-11	8.2	12.7	14.0	14.5	103
4	11-15	8.1	10.1	14.0	15.2	109

TABLE 3.4. --Continued. Pore-water geochemistry data [cm, centimeters; meq/L, milliequivalents per liter; mmol/L, millimols per liter; umol/L, micromols per liter; DIN, dissolved inorganic nitrogen; --, not analyzed]

Sediment core	Depth (cm)	K (mmol/L)	SO <sub>4</sub> <sup>2-</sup> (mmol/L)	Cl (mmol/L)	H <sub>4</sub> SiO <sub>4</sub> (mmol/L)	Fe (umol/L)
1	0-3	3.98	24.1	2.23	0.72	3.04
1	3-6	5.06	19.9	10.7	1.25	5.34
1	6-10	5.10	25.8	4.57	1.14	8.38
1	10-15	5.99	26.4	3.10	0.76	3.33
1	15-20	7.68	44.2	5.16	1.07	5.89
2	0-3	5.27	17.6	3.24	0.99	1.61
2	3-6	5.61	22.0	3.67	1.02	1.99
2	6-10	7.48	27.6	--	1.11	1.06
2	10-14	7.31	35.3	--	1.12	1.40
2	14-18	7.80	38.4	14.1	1.33	--
2	18-22	7.87	46.1	7.05	1.24	0.84
2	22-26	8.28	56.3	6.04	1.30	1.67
3	0-3	4.35	22.5	--	0.91	0.30
3	3-6	4.53	23.5	--	0.98	--
3	6-10	6.00	34.2	6.18	1.28	0.41
3	10-15	8.24	52.1	--	1.15	6.64
3	15-20	9.96	75.1	--	1.52	19.5
3	20-25	10.7	95.0	--	1.54	33.3
3	25-30	11.4	108	8.01	1.34	32.4
4	0-3	5.74	35.5	4.57	0.96	0
4	3-7	6.39	47.5	3.10	1.18	0.47
4	7-11	7.36	51.5	5.02	1.30	0.79
4	11-15	7.73	66.6	8.83	1.22	0.95

TABLE 3.4. --Continued. Pore-water geochemistry data [cm, centimeters; meq/L, milliequivalents per liter; mmol/L, millimols per liter; umol/L, micromols per liter; DIN, dissolved inorganic nitrogen; --, not analyzed]

Sediment core	Depth (cm)	NO <sub>2</sub> <sup>-</sup>			
		NO <sub>3</sub> <sup>-</sup> (umol/L)	NH <sub>4</sub> <sup>+</sup> (umol/L)	DIN (umol/L)	PO <sub>4</sub> <sup>3-</sup> (umol/L)
1	0-3	168	461	629	31.0
1	3-6	336	655	991	42.9
1	6-10	172	627	779	41.8
1	10-15	227	810	1,040	69.3
1	15-20	222	1,110	1,330	76.7
2	0-3	231	786	1,020	88.6
2	3-6	310	830	1,140	84.8
2	6-10	349	1,070	1,420	103
2	10-14	240	944	1,180	99.8
2	14-18	337	1,340	1,680	176
2	18-22	285	1,390	1,680	178
2	22-26	275	1,880	2,150	179
3	0-3	185	1,080	1,260	26.1
3	3-6	305	252	557	20.9
3	6-10	248	286	534	24.9
3	10-15	261	231	492	13.7
3	15-20	195	472	667	8.6
3	20-25	417	578	995	4.6
3	25-30	264	664	928	5.8
4	0-3	178	212	390	32.4
4	3-7	462	311	773	30.2
4	7-11	172	231	403	32.2
4	11-15	182	364	546	23.9

## DISCUSSION OF PORE-WATER GEOCHEMISTRY

### Variations in Sedimentation Rates

Recently, a number of sedimentation-rate measurements have been made in Creel Bay and Main Bay of Devils Lake (Jacobson and Engstrom, 1989; Lent, chapter 4). Sedimentation rates calculated for the center of Creel Bay and Main Bay on the basis of excess Pb-210 activity were about 0.3 cm/yr (centimeters per year; Jacobson and Engstrom, 1989). On the basis of a discrepancy between the pollen stratigraphy and Pb-210 chronology, Jacobson and Engstrom (1989) suggested that the surficial bottom sediments in Main Bay may have undergone postdepositional redistribution or mixing. However, more recent calculations on the basis of Cs-137 activity and excess Pb-210 activity yielded a similar sedimentation rate of about 0.22 cm/yr (Lent, chapter 4).

The shallower bays sampled in this study appear to have greater variability in sedimentation rates than Creel Bay and Main Bay. The sedimentation rates in Creel Bay and Main Bay are between 0.22 and 0.3 cm/yr, and the sedimentation rates in the eastern part of Devils Lake are between 0 and 0.44 cm/yr (Table 3.2). In general, the sedimentation rates decrease from west to east. Two possible explanations for the variation between sedimentation rates in these different locations are: (1) A general decrease in sediment load from west to east as a result of increasing distance from the major tributaries to the lake; and (2) the physical reworking of bottom sediments (with the possible removal of



recent sediments) in the shallower eastern basins of the lake. Devils Lake has experienced extremely high water levels during the past 150 years (Wiche, 1986). As a result of large lake-level fluctuations, shallower regions of the lake should be more susceptible to sediment redistribution, wave-induced mixing, and nonsteady-state deposition. As acknowledged by Jacobson and Engstrom (1989), shallow depths, strong winds, and little shoreline protection combine to create an extremely high energy sedimentary environment in Devils Lake.

#### Chemical Concentrations in Devils Lake Bottom Sediments

The decrease in environmentally-reactive trace-metal concentrations from core 1 to core 4 undoubtedly is related to the increase in salinity from west to east and to the increase in distance from the major tributaries to Devils Lake. The principal sources of fresh water to Devils Lake are Big Coulee, located at the western end of Devils Lake, and channel A, a manmade inflow located at the northern end of Creel Bay (Figure 3.1). Although there are no published trace-metal data available for Devils Lake, it is likely that dissolved trace metals are introduced into the lake during spring runoff, when the volume of surface-water inflow is at a maximum and the salinity of surface-water inflow is at a minimum.

In addition to the general decrease in trace-metal concentrations along the surface-water flow path, the trace metals exhibit a general decrease with depth in the individual cores (Table 3.3). The lack of long-term data (i.e., trace-metal data from long cores representing more than

100 years of sedimentation) precludes a definitive interpretation concerning the input of trace metals to Devils Lake. However, the decrease in trace-metal concentrations with increasing depth may be the result of: (1) Increased anthropogenic activity in the drainage basin during the past 50 to 100 years; (2) variations in salinity of Devils Lake over time; or (3) postdepositional redistribution as a result of geochemical, physical, or biological processes.

Core 4 was collected from bottom sediments that were once subaerial exposed. A reddish oxidized layer occurs in this core at a depth of 20 cm. The oxidized layer differs in physical appearance from the other sediment samples and probably represents a "flooded" soil zone. In addition to the notable difference in physical appearance, core 4 has the smallest concentrations of sedimentary Cu and Fe as well as small concentrations of inorganic  $\text{PO}_4^{3-}$ . Unlike cores 1 to 3, core 4 has no inorganic  $\text{PO}_4^{3-}$  maximum in the top of the section (Table 3.3). The oxidized zone and the lack of an inorganic  $\text{PO}_4^{3-}$  maximum characterize an environment where little to no sediment deposition has occurred. The largest surficial concentrations of Cu, Fe, Zn, and inorganic  $\text{PO}_4^{3-}$  are in core 1, which has the largest sedimentation rate (Table 3.2) and is closest to the major tributaries.

#### Chemical Concentrations in Devils Lake Pore Water

A number of geochemical processes may be responsible for the chemical concentrations in sediment pore water. The primary geochemical process that is responsible for the chemical evolution of

surface water in closed-basin systems is evaporitic concentration (Eugster and Jones, 1979). As evaporation progresses, dissolved solids are concentrated in the fluid. Evaporitic concentration can result in the precipitation of various mineral phases which can be incorporated into bottom sediments (Eugster and Hardie, 1978). In brackish-water systems, such as Devils Lake (2 to 10 parts per thousand), mineral precipitation usually is restricted to the alkaline earth minerals [e.g.,  $\text{CaCO}_3$  (calcium carbonate)],  $\text{H}_4\text{SiO}_4$ , and possibly  $\text{SO}_4^{2-}$  minerals (Eugster and Hardie, 1978). In contrast, during periods of decreased salinity (higher lake levels), some of these authigenic minerals dissolve, resulting in the establishment of chemical gradients in the pore water and the subsequent diffusion of dissolved chemical constituents from bottom sediments to the lake. In addition to mineral precipitation and dissolution processes, the chemical concentrations in sediment pore water can be affected by a variety of chemical processes such as cation exchange, dissolution of inorganic biogenic material (such as opaline and carbonate tests and shells), and microbially-mediated decomposition of organic matter.

Comparisons of calculated mineral-saturation coefficients and measured ion activities can be used to evaluate the potential for the various mineral phases to precipitate (Drever, 1988). The mineral-saturation coefficient ( $Q$ ) is equal to the log of the ion-activity product (IAP) divided by the theoretical saturation product ( $K_{sp}$ ). When  $Q$ , for a specific mineral phase, is positive, the solution is considered to be supersaturated with respect to that mineral and precipitation is possible. When  $Q$  is negative, the solution is considered to be undersaturated with respect to the mineral and dissolution is possible.  $Q$  was calculated for

the pore-water samples using the chemical thermodynamic equilibrium program WATEQ4F (Ball and Nordstrom, 1987). The required input for WATEQ4F consists of complete chemical analyses including pH, temperature, titration alkalinity, major cations,  $\text{SO}_4^{2-}$ , and Cl. Q calculations were made for cores 1, 2, and 4. Calculations were not made for core 3 because of the small sample volume obtained. Results of the calculations for selected minerals are presented in Table 3.5.

TABLE 3.5. Mineral-saturation coefficients (Q) for selected minerals calculated for three cores in eastern Devils Lake (positive values indicate supersaturation, negative values indicate undersaturation)

core	Interval (cm)	Aragonite	Calcite	Gypsum	Amorphous silicate
1	0-3	1.00	1.15	-0.665	-0.066
1	3-6	0.974	1.12	-0.530	0.185
1	6-10	0.989	1.14	-0.575	0.140
1	10-15	1.25	1.40	-0.0627	-0.0040
1	15-20	1.10	1.25	-0.522	0.188
2	0-3	0.880	1.03	-0.677	0.079
2	3-6	0.948	1.10	-0.620	0.094
2	14-18	1.46	1.61	-0.362	0.213
2	18-22	1.47	1.62	-0.324	0.185
2	22-26	1.56	1.71	-0.322	0.202
4	0-3	0.925	1.07	-0.109	0.073
4	3-7	1.26	1.41	0.063	0.161
4	7-11	1.37	1.52	0.162	0.208
4	11-15	1.17	1.32	0.170	0.184

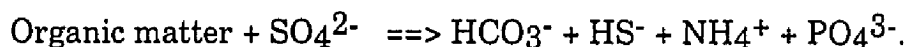
Cores 1 and 2 were collected in the least saline water. The pore water throughout these cores is supersaturated with respect to aragonite and calcite, indicating that  $\text{CaCO}_3$  may be precipitating. The possible removal of  $\text{CaCO}_3$  is consistent with the trend in chemical

concentrations in the overlying lake water where the ratio of  $\text{HCO}_3^-$  and Ca to Cl decreases with increasing Cl. The degree of saturation with respect to aragonite and calcite also increases with depth in the sediment cores (Table 3.5). The increase in the degree of saturation with depth is consistent with the increase in titration alkalinity, which probably is the result of microbial degradation of organic material. The pore water in cores 1 and 2 is undersaturated with respect to gypsum. In contrast, equilibria calculations indicate that the pore water in core 4 is slightly supersaturated with respect to gypsum. This suggests that even though gypsum is undersaturated in the surface water in the eastern end of Devils Lake, gypsum may be precipitating in the sediment in this area of the lake.

The distribution of  $\text{H}_4\text{SiO}_4$  in Devils Lake apparently is biologically controlled. The water column throughout Devils Lake is undersaturated with respect to  $\text{H}_4\text{SiO}_4$  (Sando, written commun., 1991) and the pore water is near saturation (Table 3.5). In addition, abundant diatom debris has been incorporated in the lake sediments (Stoermer and others, 1971; Fritz, 1990). Therefore, undersaturation of the water column with respect to  $\text{H}_4\text{SiO}_4$ , along with diatom debris in the bottom sediment, suggests that the removal of  $\text{H}_4\text{SiO}_4$  from surface water by biologic activity as amorphous  $\text{H}_4\text{SiO}_4$  is an important mechanism. In near-neutral lakes such as Devils Lake,  $\text{H}_4\text{SiO}_4$  is preserved in sediments (Eugster and Hardie, 1978). In Devils Lake, the increase in  $\text{H}_4\text{SiO}_4$  saturation between the lake water and the pore water suggests that  $\text{H}_4\text{SiO}_4$  is slowly dissolving in the sediment pore water and diffusing back into the overlying lake.

Microbial Processes in Devils Lake Bottom Sediments

The increase of nutrients with depth in the pore water extracted from cores 1 and 2 indicates that microbial decomposition of sedimentary organic matter is occurring in the bottom sediments at these locations. The sequence of decomposition reactions in sediments, with respect to depth, is well known (Berner, 1980). The occurrence, depth, and relative importance of the various biogeochemical zones are dependent on: (1) The amount and composition of organic matter buried; (2) the sedimentation rate; and (3) the availability of various electron acceptors (i.e., O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Fe<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup>, and CO<sub>2</sub>). Although both aerobic oxidation and denitrification probably occur in the bottom sediment, the large SO<sub>4</sub><sup>2-</sup> concentrations in the pore water suggest that a major biogeochemical pathway for organic decomposition may be SO<sub>4</sub><sup>2-</sup> reduction. SO<sub>4</sub><sup>2-</sup> reduction is a microbially-mediated reaction that involves the oxidation of organic matter to inorganic nutrients by the reduction of SO<sub>4</sub><sup>2-</sup> to S (sulfide). A generalized equation for SO<sub>4</sub><sup>2-</sup> reduction can be written as:



This equation describes the oxidation of organic matter by microbial SO<sub>4</sub><sup>2-</sup> reducers. In this reaction, organic matter is oxidized using SO<sub>4</sub><sup>2-</sup> as the terminal electron acceptor. Along with the transformation of SO<sub>4</sub><sup>2-</sup> to HS<sup>-</sup> is the production of HCO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3-</sup>. A decrease in SO<sub>4</sub><sup>2-</sup> concentration with depth was detected in only one pore-water profile (core 1). The increase in lake volume in Devils Lake along with the resulting decrease in dissolved solids in the water column have resulted in a relative enhancement of SO<sub>4</sub><sup>2-</sup> concentrations in the pore water. Therefore, the depletion of SO<sub>4</sub><sup>2-</sup> through microbial reduction

may be masked in the other cores. Even though all cores contain abundant Fe in the solid phase (Table 3.3), the largest dissolved Fe concentrations occur in the pore water of core 1. The large dissolved Fe concentrations and the decrease in dissolved  $\text{SO}_4^{2-}$  suggest that core 1 probably is the most reducing of the four cores. The dissolved Fe data from the other cores, with the exception of the 20- to 25-cm core section in core 3, are very low (less than  $2.0 \mu\text{mol/L}$ ) and probably reflect more oxidizing conditions in the bottom sediments at those locations.

When lake levels are high, the sediment pore water should have significantly greater concentrations of various chemical constituents than the overlying lake water. The difference between chemical concentrations in the water column and chemical concentrations in the sediment pore water is caused by the slow dissolution of saline sediments, at depth, deposited during periods of extremely low lake level. Thus, when lake levels are low, the difference in chemical concentrations in the water column and chemical concentrations in the pore water is much less. If the chemical constituents are biologically active, such as  $\text{SO}_4^{2-}$ , the difference between concentrations in the water column and concentrations in the pore water could be misinterpreted as a biological rather than a hydrologic (i.e., climatological) consequence. Therefore, it is uncertain whether the pore-water titration alkalinity and nutrient profiles from cores 1 and 2 are caused entirely by biogeochemical reactions such as organic-matter oxidation. However, because the pore water is supersaturated with respect to  $\text{CaCO}_3$  and there is no other logical explanation for the increases in DIN and  $\text{PO}_4^{3-}$ , it is assumed that the profiles are the result of organic-matter decomposition.

### Composition of Sedimentary Organic Matter in Devils Lake

Pore water TA:DIN:PO<sub>4</sub><sup>3-</sup> (titration alkalinity:dissolved inorganic nitrogen: phosphate) ratios have been used successfully to determine the C:N:PO<sub>4</sub><sup>3-</sup> (carbon:nitrogen:phosphate) ratio of organic matter undergoing decomposition in marine sediments (Sholkovitz, 1973; Martens and others, 1978) as well as in lake sediments (Gaillard and others, 1987). Core 1 is located in the part of Devils Lake where the largest sedimentation rate occurs (Table 3.2). At this location, an SO<sub>4</sub><sup>2-</sup> depletion of 4.2 mmol/L between the 0- to 3-cm and the 3- to 6-cm core section occurs. The increase in pore-water concentrations of titration alkalinity between these two sections was 2.10 meq/L, the increase in pore-water concentrations of DIN was 362 mmol/L, and the increase in pore-water concentrations of PO<sub>4</sub><sup>3-</sup> was 11.9 mmol/L. The C:N ratio was calculated as 5.8, and the N:PO<sub>4</sub><sup>3-</sup> ratio was calculated as 30.4. The C:N ratio is very similar to the ratio from Main Bay organic matter deposited during lake low stands (Lent, chapter 4). The N:PO<sub>4</sub><sup>3-</sup> ratio is similar to that in other temperate lakes dominated by burial of algal remains (Gaillard and others, 1987). In general, the input of organic matter to the sediments of Devils Lake is controlled by the lake level with an N-rich source such as algal material dominating during low stands and a more C-rich source, likely of terrestrial origin, dominating during high stands (Lent, chapter 4).

Using all of the pore-water data available from the four cores, the average C:N ratio is 20.7, and the average N:PO<sub>4</sub><sup>3-</sup> ratio is 28. The large C:N ratio implies that either the vast majority of organic matter undergoing decomposition is of terrestrial origin, the N has been



retained in the sediments, or there is another source of titration alkalinity. The dominant form of N in the pore water is  $\text{NH}_4^+$  which is readily adsorbed to particles (Berner, 1980). However, adsorption of  $\text{NH}_4^+$  does not explain the differences in the C:N ratios in Main Bay and the four cores from the eastern part of the lake. Another source of titration alkalinity can be discounted because pore water is supersaturated with respect to  $\text{CaCO}_3$ , and, if anything, some  $\text{CO}_3^{2-}$  has been removed from the pore water by authigenic mineral precipitation. The average C:N ratio of the four cores is about twice the C:N ratio of the Main Bay sediments and may suggest that more terrestrially-derived organic carbon is deposited in the shallower areas of Devils Lake than in the deeper, central parts of the lake. This terrestrial organic carbon may come from surface inflow or aeolian input.

## DISCUSSION OF SOLUTE FLUXES

Importance of Lake "Freshening" to Solute Concentrations

As previously stated, surficial bottom sediments are a critical component in the geochemical evolution of saline lake waters and in the salt budget of closed-basin lakes (Lerman and Jones, 1973; Cerling, 1986; Barton and others, 1987). The contributions of bottom sediments and pore water to a closed-basin lake would be particularly important as the lake level increased and diluted surface water came into contact with more concentrated pore water. For example, Lerman and Jones (1973) calculated that 45 percent of the dissolved solids in Lake Albet, Oregon, was contributed by sediment pore water diffusional flux over 25 years. By comparison, less than 1 percent of the total dissolved-solids flux into the lake over the same 25 years was attributed to external inflow. Lerman and Jones (1973) concluded that, during periods of high lake level, the diffusion of dissolved salts from the bottom sediment to the overlying lake water dominated the salt budget for the lake.

The diffusional flux of major ions,  $\text{H}_4\text{SiO}_4$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , and Fe was calculated using the technique outlined by Callender and Hammond (1982). Because of the lack of  $\text{SO}_4^{2-}$  and Cl measurements (in some cases) these constituents were excluded from the diffusion calculations. The diffusional flux ( $J_i$ ) of individual species can be calculated using the following equation:

$$J_i = f_0 D_{i, \text{sed}} dC_i/dx \quad (1)$$

where:

$J_i$  = the diffusional flux,

$f_0$  = the sediment porosity at the sediment surface,

$D_{i,osed}$  = the whole sediment diffusion coefficient, and

$dC_i/dx$  = the pore-water gradient.

Values for the pore-water gradients were calculated using linear regressions of the linear portions of the pore-water profiles. In most instances, the entire profile was used. However, in a few instances, the bottommost values were not used.  $D_{i0}$  then was calculated using the following equation by Callender and Hammond (1982):

$$D_i = D_{i0}/(f_0 F') \quad (2)$$

where:

$D_{i0}$  = the diffusional coefficient in water at infinite dilution (Li and Gregory, 1974), and

$F'$  = the modified formation factor of Krom and Berner (1980) corrected for viscosity and deviation from the Archie relation:

$$F' = 1.28/f_2 \quad (3)$$

where:

$f_2$  = the average sediment porosity.

The value 0.85 was used as an estimate of average porosity.  $D_{i0}$  values at 18 °C, with the exception of the  $D_{i0}$  value for  $H_4SiO_4$ , are from Li and Gregory (1974). The  $D_{i0}$  value at 25 °C for  $H_4SiO_4$  is from Lerman (1979). The diffusional fluxes calculated for the various chemical constituents are presented in Table 3.6. Results of the calculations are reported as  $mmol/m^2/d$  (millimols per square meter per day). Even though the diffusional-flux values must be taken as estimates because of the lack of

porosity and in-situ temperature measurements, the values represent a reasonable approximation. In general, cores 1 and 2 have similar fluxes. As previously stated, these cores were collected in areas of low salinity. The measured pore-water diffusional fluxes from these cores were dominated by Na. The Mg and K fluxes were similar in concentrations. Ca had the lowest flux rate of the major ions measured.

TABLE 3.6. Diffusional fluxes for selected chemical constituents [millimols per square meter per day].

	Core 1	Core 2	Core 3	Core 4	Creel Bay	Main Bay	(1968)
HCO <sub>3</sub> <sup>-</sup>	3.6	4.3	6.9	4.0	40	43	3.7
Ca	0.26	0.35	6.2	9.7	0.27	0.30	0.066
Mg	1.1	0.99	13	6.4	0.74	1.9	4.5
Na	61	11	120	56	4.4	16	--
K	1.7	1.0	11	5.6	0.56	1.2	--
SO <sub>4</sub> <sup>2-</sup>	--	--	--	--	-14.	7.9	16.
Cl	--	--	--	--	6.1	2.0	9.1
H <sub>4</sub> SiO <sub>4</sub>	16	0.072	0.46	0.82	0.62	0.73	--
NO <sub>2</sub> <sup>-</sup> +NO <sub>3</sub> <sup>-</sup>	-0.0019		0.0038	0.1145	-0.21	--	--
NH <sub>4</sub> <sup>+</sup>	0.30	0.36	0.74	0.30	4.5	9.0	--
PO <sub>4</sub> <sup>3-</sup>	0.010	0.017	-0.011	-0.012	0.52	0.15	--
Fe	2.1	0.0043	20	0.62	--	--	--
HS	--	--	--	--	7.0	2.4	--

The calculated diffusional fluxes for cores 3 and 4 are notably different (Table 3.6). The diffusional fluxes of Ca, Mg, and K in cores 3 and 4 generally are about 3 to 40 times greater than the fluxes in cores 1 and 2. The dramatic increase in flux rates between cores 1 and 2 and cores 3 and 4 is the result of the significantly larger ionic strength of the pore waters and the resulting large chemical gradient in the pore-water profiles in the eastern end of the lake. The differences between the calculated diffusional fluxes of Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> in cores 1 and 2 and cores

3 and 4 are not as great. The modest increase in the  $\text{HCO}_3^-$  diffusional flux suggests that the dissolution of  $\text{CO}_3^-$  minerals is not responsible, in itself, for the large increase in the Ca and Mg diffusional fluxes.

The calculated diffusional fluxes of the nutrients ( $\text{NO}_2^- + \text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$ ) appear to be low in all cases. The fluxes are low, in part, because the majority of the organic matter buried at these locations is derived from terrestrial sources. This organic matter has, in general, lower C:N and C: $\text{PO}_4^{3-}$  ratios than algal remains and is more recalcitrant in nature.

#### Comparison of Calculated Flux Rates to Existing Flux Rates

In addition to the sampling conducted in this study, pore-water samples have been collected in Devils Lake on two other occasions. Callender (1968) collected a single core from the center of Main Bay during the summer of 1966. This core was sampled on about 10-cm intervals and analyzed for Ca, Mg,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$  and Cl. Callender's data were used to calculate diffusional-flux rates for the five constituents. An average porosity of 0.85 and a constant temperature of 18°C were used in the calculations. The diffusional fluxes calculated are presented in Table 3.6. The calculated Mg and titration alkalinity flux rates are remarkably similar to rates calculated in this study. However, the rate calculated for Ca is about 4 to 150 times less than the rate calculated in this study. This difference may be due to differences in the  $\text{HCO}_3^-$ :Ca ratio between the 1960's and the 1980's, or may represent misleading results due to coarse sampling interval used in 1966.

Creel Bay and Main Bay were sampled during the summer of 1990 (Komor, 1992a,b). The diffusional-flux rates presented in table VI for Creel Bay and Main Bay were calculated using data from Komor (1992b). We used a measured average porosity of 0.90 and a measured temperature of 12 °C to calculate the diffusional-flux rates. The cation (Ca, Mg, Na+, and K) flux rates are similar to the calculated flux rates in cores 1 and 2, reflecting the similar chemical concentrations in the overlying lake water in these areas.

As previously stated, the magnitude of the calculated diffusional-flux rates of major cations increases from core 1 to core 4. The calculated diffusional-flux rates for Creel Bay and Main Bay are consistent with this observation. In addition, the increases in diffusional-flux rate from west to east in Devils Lake are greater than the increases in cation concentration in the overlying lake water (Sando, written commun., 1991). This suggests that the variations in the bottom-sediment contributions may be partly responsible for the salinity gradient in the overlying lake water. This is in sharp contrast to previous interpretations that suggest that the salinity gradient from west to east in Devils Lake is caused by evaporitic concentration alone.

However, the  $\text{HCO}_3^-$  and nutrient flux rates are notably different. The  $\text{HCO}_3^-$  flux rate was about 5 to 12 times greater in Main Bay during the 1990 study than in this study. In addition,  $\text{NH}_4^+$  flux rates were about 5 to 15 times greater in Main Bay during the 1990 study, and  $\text{PO}_4^{3-}$  flux rates were more than 100 times greater. The differences between  $\text{HCO}_3^-$  and nutrient flux rates for cores 1 and 2 from this study and  $\text{HCO}_3^-$  and nutrient flux rates for the core from Main Bay in 1990 are related to biogeochemical reactions occurring in the sediment.  $\text{SO}_4^{2-}$

reduction could account for the notable differences in the pore water chemical concentrations in the cores from this study and the cores from Creel Bay and Main Bay. Komor (1992b) suggested that, based upon the pore-water profiles of  $\text{SO}_4^{2-}$  and other nutrients in Creel Bay and Main Bay,  $\text{SO}_4^{2-}$  reduction was a dominant process in Devils Lake sediments during the summer of 1990. This conclusion is in contrast with the earlier observation that  $\text{SO}_4^{2-}$  reduction was not a dominant process in at least three of the four cores from the eastern part of Devils Lake. Therefore, in areas where  $\text{SO}_4^{2-}$  reduction is an important process (Creel Bay and Main Bay), titration alkalinity and nutrient fluxes are large and  $\text{SO}_4^{2-}$  fluxes are negative. In contrast, in areas where  $\text{SO}_4^{2-}$  reduction is not important (cores 3 and 4), titration alkalinity and nutrient fluxes are much smaller and  $\text{SO}_4^{2-}$  fluxes are positive.

#### Controls on Sulfate Reduction in Devils Lake Bottom Sediments

The implication that the occurrence of microbial  $\text{SO}_4^{2-}$  reduction is responsible for the differences in chemical concentrations in cores from this study and in chemical concentrations in cores from earlier studies of Creel Bay and Main Bay suggests that  $\text{SO}_4^{2-}$  reduction occurs only in specific areas of Devils Lake or is intermittent with respect to time. There are at least three explanations for the occurrence of sulfate reduction: variations in the quality (labile versus refractory) of sedimentary organic matter; variations in the sedimentation rate; and variations in the water column stability.

The occurrence or absence of  $\text{SO}_4^{2-}$  reduction in the bottom sediments of Devils Lake may be related to the quality of sedimentary organic matter and the rate of sediment deposition. More abundant lake-produced organic matter, which has a lower C:N ratio relative to the C:N ratio of detrital organic matter, would result in a larger rate of organic-matter decomposition. The larger rate of microbial activity would quickly deplete the dissolved  $\text{O}_2$  and  $\text{NO}_3^-$  in the pore water and result in a change to anaerobic conditions that are favorable for  $\text{SO}_4^{2-}$  reduction. The sedimentary organic matter in Main Bay definitely is more labile than the sedimentary organic matter in the eastern part of Devils Lake. As previously stated, the C:N ratio of organic matter from Main Bay is about 8.5, indicating that the organic matter is derived from aquatic, lake-produced, organic matter. In contrast, the C:N ratio of organic matter from cores 1 to 4 averages 21, indicating that the organic matter is derived from detrital, terrestrial organic matter.

Variations in sedimentation rates also appear to influence the occurrence of  $\text{SO}_4^{2-}$  reduction in Devils Lake. Although the quality of organic matter in cores 1 to 4 is similar, pore-water data indicate that  $\text{SO}_4^{2-}$  reduction is occurring in core 1 but not in cores 2 to 4. The occurrence of  $\text{SO}_4^{2-}$  reduction in core 1 probably is related to the larger sedimentation rate measured in core 1. If all other environmental conditions are similar, increased sedimentation rates can trigger  $\text{SO}_4^{2-}$  reduction in sediments by rapidly moving organic matter out of oxidizing conditions into reducing conditions favorable for  $\text{SO}_4^{2-}$  reduction (Berner, 1980). Therefore, the occurrence of  $\text{SO}_4^{2-}$  reduction in Devils Lake bottom sediments, along with the increased flux of titration alkalinity and nutrients from bottom sediments to the lake, appears to be the result of



both the quality of sedimentary organic matter and sedimentation rates. The occurrence of water-column stratification could intensify  $\text{SO}_4^{2-}$  reduction.

Komor (1992b) suggested that temporary stratification of the overlying lake water, along with depletion of dissolved  $\text{O}_2$  in the bottom water, is responsible for reducing conditions in the surficial bottom sediment. This explanation suggests that  $\text{SO}_4^{2-}$  reduction is an ephemeral process in Devils Lake and is related to the stability in the overlying lake water. Detailed water-column information has been available for Devils Lake since 1986 (Sether and Wiche, 1989). During periods of relatively low wind velocity, Devils Lake can stabilize for short periods of time (Wiche, written commun., 1991). When the lake stabilizes,  $\text{O}_2$  may become depleted in deeper lake water. Dissolved oxygen depletion in the overlying water leads to a depletion of electron acceptors near the sediment/water interface. Therefore, the organic matter transformations (such as sulfate reduction) may be occurring in the water column. Thus, the physical character of the overlying lake water (e.g., the degree of water-column stability) may have a major influence on the magnitude of the bottom sediment diffusional-flux rates for certain chemical constituents.

### Chemical Mass-Balance Calculations for Devils Lake

Chemical mass balances can be calculated for closed-basin lakes by combining hydrologic data with water-chemistry data (Lerman and Jones, 1973; Yuretich and Cerling, 1983; Barton and others, 1987). The mass balances then can be used to evaluate the relative importance of the various sources and sinks to a system and to determine residence times for chemical species. Chemical mass balances for two ions (Ca and Na) in Devils Lake were calculated for the year 1986 by combining measured pore-water flux data, available surface-water concentrations, and information about the hydrologic balance (Wiche, 1986). The mass-balance calculations were restricted to Ca and Na because of the uncertainties associated with the nutrients and biologically active constituents (such as bicarbonate and sulfate).

To calculate the mass balances for Ca and Na, Devils Lake was assumed to be in steady state. This approach was chosen because of the lack of chemical data for the beginning and the ending of the study period. This lack of data also precluded more dynamic calculations, which included changes in the storage of salt in the lake. The general hydrology and water budget of the lake for 1986 is well constrained (Wiche, 1986, 1991). During 1986, Devils Lake rose about 20 cm. Chemical data for the surface runoff and for the lake itself were taken from the 1983-85 study. The average chemical concentrations in the samples from Main Bay were used to compute the average chemical concentrations in the entire lake. This simplification is reasonable because Main Bay is the largest basin in the lake and is located near the center of the salinity gradient. The annual runoff during 1986 for all of

Devils Lake was used in conjunction with the average chemical concentrations in the 1985 spring runoff in Mauvais Coulee to estimate the surface-runoff component of the chemical mass balances. The chemical concentrations in the spring runoff were used because of the intermittent nature of the streams during the remainder of the year. During the summer, streamflow into Devils Lake decreases rapidly, and dissolved solids increase because evaporation exceeds precipitation and inflow. During the summer, streamflow is often zero. Estimates of the yearly precipitation are taken from two NOAA meteorologic stations located on the James River and the Red River near Devils Lake. The hydrologic and meteorologic data used in the mass-balance calculations are presented in Table 3.7.

TABLE 3.7. Hydrologic and meteorologic data used to calculate chemical mass balances for Devils Lake, North Dakota (the values are representative of conditions present in 1986)

Parameter	Value
Surface area	$2.15 \times 10^2 \text{ m}^2$
Precipitation	0.585 m
Inflow	$4.25 \times 10^7 \text{ m}^3/\text{yr}$
Capacity	$9.25 \times 10^8 \text{ m}^3/\text{yr}$

The assumption was made that there were three possible sources of dissolved solids to Devils Lake: (1) Precipitation onto the lake surface, (2) streamflow into the lake, and (3) diffusion into the water column from bottom sediments (Table 3.8). Once dissolved solids enter the lake, they accumulate as dissolved solids in the lake water, are removed to the lake

sediment as precipitated minerals, or occur as dissolved solids in pore water.

The total volume of Ca and Na used in the mass-balance calculations is dominated by diffusion from the bottom sediments (Table 3.8). The relative importance of the pore-water contributions to the overall input of dissolved solids varies from about 68 percent for Ca to about 93 percent for Na. Streamflow contributes the remainder of the dissolved solids to the lake. These data suggest that even though pore-water contributions are the largest source of salts to Devils Lake, streamflow contributions also must be accounted for in chemical studies in brackish lakes. This is in contrast to Lake Albet, where streamflow contributions are insignificant compared to the calculated pore-water contributions (Lerman and Jones, 1973). Together, these studies suggest that the relative importance of pore-water contributions to the total dissolved-solids budget may be related to salinity and the disequilibrium that exists between the salinity of the sediment pore water and the overlying lake water.

TABLE 3.8. Amount of Ca and Na in Devils Lake and calculated fluxes of Ca and Na for precipitation, streamflow, and sediment pore water, Devils Lake, North Dakota (moles per year)

Ion	Devils Lake	Direct precipitation	Streamflow	Sediment pore water
Ca	$1.52 \times 10^9$	$1.56 \times 10^6$	$7.45 \times 10^7$	$1.6 \times 10^8$
Na	$1.99 \times 10^{10}$	$6.48 \times 10^5$	$2.65 \times 10^8$	$2.4 \times 10^9$

The residence times of Ca and Na were calculated as the total mass of the ion in the lake divided by the input of the ion for the entire year (Table 3.9). The calculations were made with and without pore-water contributions. Together, the two sets of calculations demonstrate the importance of the sediment pore water to the response time of the basin. Without the pore-water data, the residence time would be greatly overestimated. The pore-water profiles were collected near the lake-level maximum when the disequilibrium between the chemical concentrations in the sediment pore water and in the overlying lake water should be the most pronounced. This should have resulted in the maximum flux rate between the pore water and the overlying lake water. In addition, 1986 was a high water year, and there were significant quantities of tributary and precipitation inflow to Devils Lake. Since 1987, the Devils Lake drainage basin has experienced severe drought conditions. During this period, pore-water contributions should be even more dominant in the chemical budget of the lake.

TABLE 3.9. Calculated residence times with and without pore-water contributions

Ion	Residence time without pore-water contributions (years)	Residence time with pore-water contributions (years)	Percent pore water of total flux
Ca	20	6.2	67.8
Na	75	7.5	93.4

### Source of Dissolved Solids in Devils Lake Pore Water

Even though pore-water contributions dominant the chemical budget of Devils Lake, the source of dissolved solids in the pore water is still largely unknown. The lack of detailed temporal and spatial data, along with the lack of deeper cores, precludes any absolute determinations of the source. However, general observations derived from available data indicate there are two principal sources of dissolved solids to the pore water of Devils Lake. The dominant source of major ions (with the exception of titration alkalinity and to a lesser degree  $\text{SO}_4^{2-}$ ) in the pore water appears to be related to high salinity sediments that were deposited during periods of low lake level and high salinity. Callender (1968) measured dissolved  $\text{SO}_4^{2-}$  and Cl in pore water to a depth of 6 m in Main Bay. A horizon of high salinity pore water was detected at a depth of 30 cm. Lent (chapter 4) measured sediment conductivity to a depth of 85 cm in Main Bay. A horizon of high salinity pore water was detected at a depth of 64 cm. These near-surface high-salinity layers are probable sources of dissolved solids in the pore water.

The dominant source of nutrients and biologically-active ions such as titration alkalinity appears to be the remineralization of organic matter. The magnitudes of the microbially-mediated fluxes are related to the redox condition in the sediment as well as to the amount and type of organic matter that is buried. The magnitudes of these fluxes are significantly greater under reducing conditions (i.e., during  $\text{SO}_4^{2-}$  reduction). In addition, the change in redox condition may influence the fluxes of a wide variety of trace constituents associated with organic matter and iron oxyhydroxides. The exact hydrologic conditions

responsible for  $\text{SO}_4^{2-}$  reduction are still unclear, but high. nutrient-rich runoff along with calm conditions probably promote increased  $\text{SO}_4^{2-}$  reduction in the bottom sediments. During these times, nutrients may be regenerated more rapidly than during low lake-level stands when wind mixing limits the reintroduction of nutrients as a result of  $\text{SO}_4^{2-}$  reduction.

## CONCLUSIONS

Sediment pore water in Devils Lake is enriched in major ions and nutrients relative to the overlying lake water.

Two geochemical processes are primarily responsible for the large dissolved-solids concentrations in the pore water in Devils Lake: (1) Burial of saline sediments and pore water with subsequent upward diffusion, and (2) microbially-mediated decomposition of organic matter.

The principal source of major ions (excluding titration alkalinity) appears to be high salinity sediments located in the upper 1 meter of bottom sediment. Little information exists concerning the variability in composition of pore water and bottom sediments at depth in Devils Lake. Mineral-dissolution processes in Devils Lake bottom sediments probably are restricted to carbonate and sulfate minerals.

Microbial decomposition of sedimentary organic matter is the principal source of titration alkalinity and nutrients to pore water in Devils Lake. The concentration of nutrients and the rates of nutrient regeneration in bottom sediments are highly variable. The sediments in the eastern part of Devils Lake have relatively small nutrient concentrations and nutrient diffusional-flux rates. In contrast, the bottom sediments in Main Bay have significantly larger nutrient concentrations and nutrient diffusional-flux rates. The larger nutrient concentrations and the larger nutrient diffusional-flux rates in Main Bay are the result of more labile sedimentary organic matter and the occurrence of sulfate reduction.



The absolute concentrations of major ions in bottom sediment pore water increases from west to east. In addition, the calculated diffusive fluxes increase from west to east. These trends suggest that the observed concentration gradient in the lake are not the result of just evaporitic concentration as water moves through the system.

Bottom sediment diffusional fluxes are the dominant source of major ions and nutrients to Devils Lake. Calculated bottom-sediment diffusive fluxes of calcium and sodium are substantially greater than calculated fluxes for either direct precipitation or surface runoff. Estimated residence times based on the calculated flux rates indicate that any attempt to "improve" water quality in Devils Lake by importing fresh water will not result in significant decreases in nutrient or major ion concentrations in the lake.

## CHAPTER IV

### HIGH PRECISION PALEOCLIMATIC AND PALEOBIOLOGIC RECORDS FROM SEDIMENTS OF DEVILS LAKE, NORTH DAKOTA

#### INTRODUCTION

Lacustrine sediments provide a medium in which temporal variations in climatic conditions can be discerned. For example, lake-sediment cores have been used to document the acceleration of geochemical cycles due to anthropogenic activities. Geochemical stratigraphies derived from sediment core data have allowed the historic interpretation of such activities as eutrophication, deforestation, fossil fuel burning, and watershed acidification. More recently, with worldwide interest in global change, lake sediments have been used to develop historic records of climatic variability (for example, Spencer, and others, 1984; Krishnamurthy and others, 1986; Leonard, 1986; Fort and others, 1989; Benson and others, 1990; Meyers, 1990).

The northern Great Plains region of North America is an extremely important agricultural area vital to both the United States and Canada. The climate of the region is characterized by long cold winters and short hot summers and minimal precipitation (in the Devils Lake area approximately 44 centimeters per year). Agricultural activity in the northern Great Plains is dependent on shallow glacial aquifers and lakes

which apparently respond rapidly to climatic fluctuations (Wiche, 1986, 1991; Wiche and others, 1986). An understanding of the variations in climate and the effect of these variations on water resources is imperative to the development of agricultural and recreational activities in the region.

Recently, significant efforts have been made to relate predicted global climatic changes to water resource management (Solomon and others, 1987; El-Ashry and Gibbons, 1988; Revelle and Waggoner, 1989). All of the major general circulation models that have been developed predict that a doubling of atmospheric greenhouse gases would result in an increase in mid-continent summer dryness with a possible substantial decrease in soil moisture (Gleick, 1989). In addition to the increase in summer dryness, the general circulation models predict a decrease in winter precipitation. Because the majority of recharge to shallow glacial aquifers in the Great Plains is during the winter and early spring, the predicted decrease in winter precipitation has potentially grave consequences for agricultural activity in the region. Specifically, a shift in the regional patterns of agriculture and increased irrigation usage are potential consequences the predicted climate change (Adams and others, 1990). Revelle and Waggoner (1989), using a scenario of 2°C temperature increase and a 10% reduction of precipitation, predict an 18% deficiency in water needs for the Missouri River water region (e.g., the northern Great Plains). If these predictions are at all reasonable, water quantity, as well as water quality, will be greatly affected in the Great Plains with a decrease in available water as well as an increase in salinity.

Numerous closed-basin lakes are located throughout the Great Plains of North America (Dean, 1981; Gorham and others, 1983; Last and Schweyen, 1983; Swanson and others, 1988; LaBaugh and others, 1987; Last, 1990). Small changes in the balance between inflow and evaporation in these closed-basins can result in large changes in both lake level and salinity (Wiche, 1991; Wiche and others, 1986). Large variations in environmental conditions can, in turn, result in rapid changes in lake biota as well as the composition of sediment deposited on the lake bottom. Long-term (>100 years) records of lake level and water chemistry are only available for a few of these closed basin lake systems, including the Great Salt Lake in the western United States and Devils Lake in North Dakota. Visual comparisons of water-level records for the Great Salt Lake and Devils Lake illustrate the remarkable similarity during the past 100 years (Figure 4.1). The similarity in lake level history in two geographically separated closed-basin lakes suggest that the two lakes are responding to large-scale climatic fluctuations, and not just local variability (Wiche and others, 1986).

Previous studies in closed-basin systems have demonstrated relationships between temperature, salinity, and lake-level to geologic criteria preserved within sediments. Therefore, sediment cores from saline lakes may prove to be important paleoclimatic recorders. Interpretive data from sediment cores can be used to extend climatic histories beyond existing historical records, resulting in an increased understanding of climatic change within a basin. By combining a number of paleoclimatic histories from adjacent basins regional trends in climate can be discerned (Eugster and Hardie, 1978). Because of the 'climatic fragility' of the Great Plains, paleoclimatic studies can provide

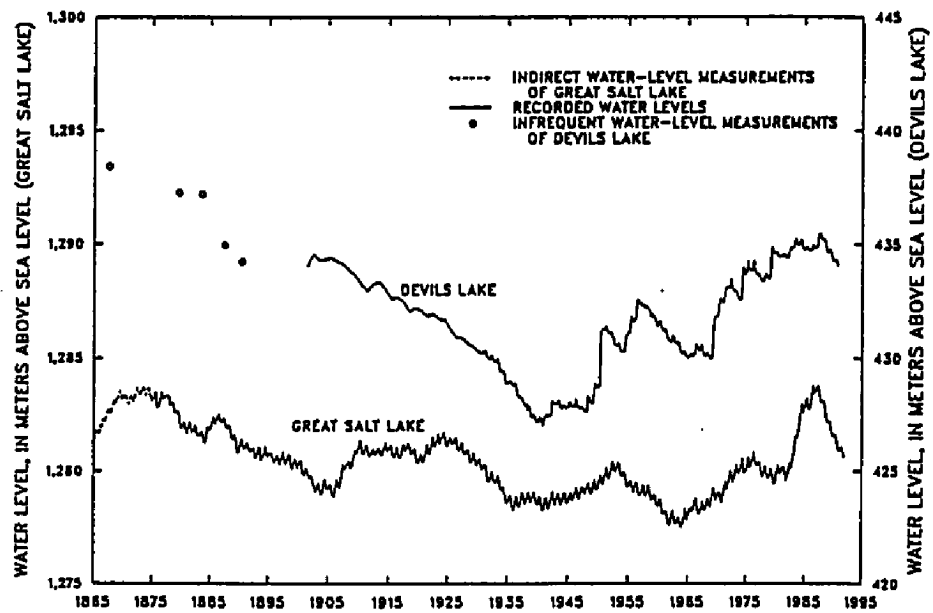


Figure 4.1. Historic water levels for Devils Lake, North Dakota (1867-1991) and the Great Salt Lake, Nevada ((1865-1991) (Figure adapted from Wiche, 1986)]

useful information about climatic variation and assist in the management of this important agricultural region. The objective of this research was the development of high resolution paleoclimatic information based upon geologic and biogeochemical sediment data to establish a climatic history for the Devils Lake, North Dakota region. A short sediment core (approximately 84 cm) representing approximately 500 years was collected from the main basin in Devils Lake. The core was analyzed for Cs-137 and excess Pb-210 activity, sediment conductivity, biogenic silica content, total organic carbon content, carbon:nitrogen ratio of the total organic fraction, and isotopic ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) composition of the total organic fraction.

### Great Plains Holocene Climate

Histories of Holocene climatic change have been developed in a number of lakes in the Great Plains of North America. The lakes studied include; Devils Lake, North Dakota (Callender, 1968; Engstrom, 1988; Jacobson and Engstrom, 1989; Fritz, 1990; Fritz and others, 1991), Lake Wabamun, Alberta (Hickman and others, 1984), and Waldsea Lake, Saskatchewan (Last and Scheweyen, 1985). Similar work has been undertaken elsewhere in North America in Lake Mendota, Wisconsin (Winkler and others, 1986), and Walker Lake, Nevada (Meyers, 1990). In general, prior to 6,500 years before present (y.b.p.), regional climate was warmer and drier than present climate. A broad period of cooler and wetter climate occurred between 6,500 and approximately 2,500 y.b.p. A brief warm period occurred approximately 2,500 y.b.p. This warm

episode was followed by a period of oscillating lake levels and a gradual shift toward cooler wetter climate. Approximately 2,000 y.b.p. there was a brief warming event followed by another period of oscillating climate. However, little detailed information is available for the past 1,000 years. Many lakes throughout the northern Great Plains experienced drying and desiccation between approximately 4,000 and 8,000 y.p.b (Aronow, 1957; Last and Slezak, 1986).

Previous paleoclimatic studies using lacustrine sediments were based on a variety of geologic, geochemical, and biologic criteria (Callender, 1968; Bartlein and others, 1984; Dean and others, 1984; Fritz and others, 1991; Last and Slezak, 1986; Last and Schweyen, 1983). Variations in grain size, bulk sediment composition and mineralogy of the authigenic components have been utilized as indicators of lake level and salinity. Paleoclimatic reconstructions based upon biologic criteria in saline lake sediments are usually restricted to pollen data (Jacobson and Engstrom, 1989), diatom assemblage data (Stoermer and others, 1971; Forester and others, 1987; Fritz, 1990; Fritz and others, 1991), ostracod data (Forester, 1983; Forester and others, 1987), and identifiable organic material such as tree detritus (Aronow, 1957; Callender, 1968). While these studies have provided valuable climatic information, their usefulness is often limited by a lack of resolution and/or non-unique interpretations. Although samples taken at intervals of 10's and 100's of years result in important climatic information, this work, in part, was to assess if smaller time horizons could be sampled, analyzed, interpreted, and then applied to determine more detailed paleohydrologic histories.

### Study Area

The Devils Lake drainage basin, located in northeastern North Dakota, is a large internally drained basin located within the Red River of the North drainage (Figure 4.2). The northern section of the Devils Lake drainage basin is comprised of interconnected fresh water lakes and other poorly defined surficial drainage. The area around Devils Lake is blanketed by sediments of glacial origin, comprised of material from the Cretaceous Pierre Shale and Pleistocene lacustrine sediments (Hobbs and Bluemle, 1987). Surficial features can be characterized by hummocky topography with shallow depressions and poorly defined water divides (Wiche, 1986; Hobbs and Bluemle, 1987).

Devils Lake is comprised of a series of lake basins (Figure 2). During periods of high water (e.g. the present) these basins are interconnected and the movement of water within the lake is generally to the east, resulting in a noticeable salinity gradient increasing from west to east. In 1987 the salinity of Devils Lake varied from approximately 2 parts per thousand (ppt) in West Bay to 10 ppt in East Devils Lake. During drier periods, the individual basins become isolated, and the lakes are significantly smaller and more saline (Wiche, 1986). The Stump Lake drainage basin is located to the east of Devils Lake. At water levels greater than 444 meters above sea level (m.s.l.) it becomes part of the Devils Lake basin. In 1987 the salinity of Stump Lake varied from approximately 75 ppt in West Stump Lake to 150 ppt in East Stump Lake.



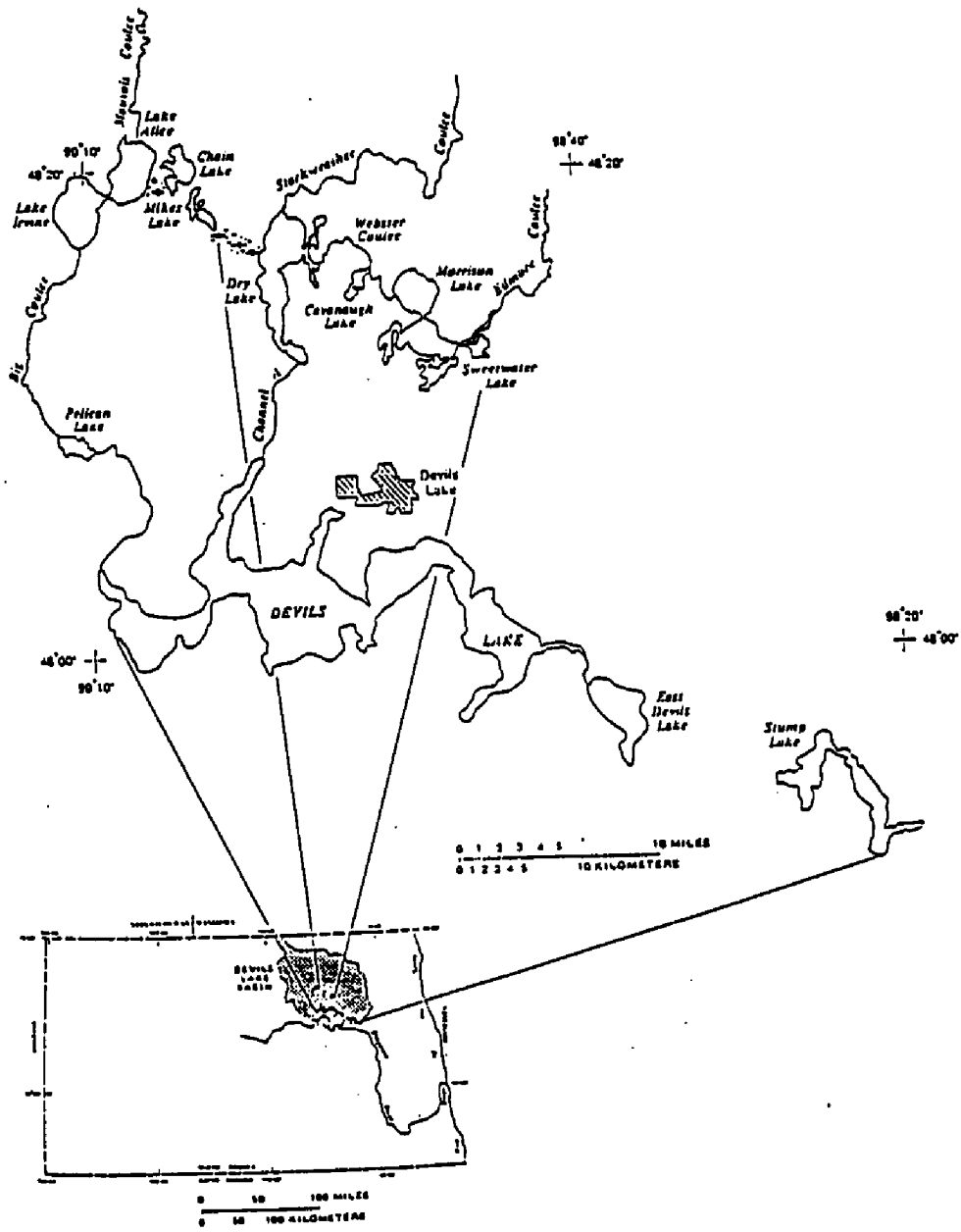


Figure 4.2. Location of Devils Lake, North Dakota.

Detailed lake level measurements are available for Devils Lake dating back to 1901 (Figure 4.1). Prior to 1901, lake level and salinity were recorded sporadically since 1867 (Wiche, 1986). The highest recorded lake level, 438 m.s.l., occurred in 1867. From 1867 to 1940 lake level steadily declined to a minimum of 427 m.s.l. Since that time, lake level has generally risen, with one period of decline from 1956 to 1968. Devils Lake water level reached a recent maximum of 435.5 m.s.l. in 1987. (Wiche, 1991).

## METHODS

### Field methods

A short (84 cm) sediment core was collected near the center of Main Bay in Devils Lake (water depth approximately 10 m) during the summer of 1987 (Figure 4.2). The coring operation was performed from a small boat using a ~12 m section of 5 cm diameter PVC tubing. After collection, the core was capped and transported back to the University of New Hampshire.

### Laboratory methods

The sediment core was extruded, and sectioned into 1 cm horizons, and allowed to air dry. After drying, the sediment samples were disaggregated using a mortar and pestle and stored in capped vials. Estimates of sedimentation rate were obtained by measurements of the activity of Cs-137 and excess Pb-210. The sediment was carefully weighed and the activity of Cs-137 and excess Pb-210 in the sediment was determined using non-destructive gamma spectrophotometry. In addition, two samples from the core (33-36 cm and 80-84 cm) were analyzed for C-14 activity to obtain an estimate of the long-term sedimentation rate.

Measurements of sediment conductivity, biogenic silica, and total organic carbon (TOC), of the sediment were made to identify changes in bulk sediment chemistry. Downcore variations in sediment conductivity were estimated by leaching a small sediment sample (approximately 100 mg) with 50 ml of MilliQ® water. Specific conductivity of the leachate was measured after 30 minutes using a standard conductivity meter.

Biogenic silica content was measured using the technique outlined by DeMaster (1981). Approximately 20 mg sediment samples were leached in 1% Na<sub>2</sub>CO<sub>3</sub> over time. Aliquots were taken at 2, 3 and 5 hours. The aliquots were then analyzed for their silica content using the reduced molybdsilicate acid spectrophotometric method (Strickland and Parsons, 1968) as discussed by DeMaster (1981). Weight percent silica was plotted versus time and the extrapolated intercept (at time equal to zero) was taken as the amorphous silica content of the sediment.

TOC measurements were made on approximately 0.1 milligram sediment samples using the chemical combustion technique as described by Gaudette and others (1974).

Separate sediment samples were leached for approximately 24 hours with 10% reagent grade HCL for subsequent organic carbon to organic nitrogen ratios (C:N) and  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  isotopic analyses of the total organic matter. The C:N (w/w) ratios were determined with a Carlo Erba 1108 CHN analyzer at the University of North Carolina in Chapel Hill, North Carolina.

Carbon and nitrogen isotopic analyses were performed using the method described by Showers and Angles (1986) and Showers and others (1990).

## RESULTS

The results for Devils Lake sediments are presented in Table 4.1. Replicate analyses were performed on biogenic silica, C:N ratio, del C-13, and del N-15 measurements to establish estimates of precision. Estimates of precision were calculated by using the standard deviation of the replicates divided by the mean of the replicates. This value was then converted to a percent. A single estimate of precision was then calculated for each analysis (i.e., soluble salt, biogenic silica, C:N, del C-13, and del N-15) by taking the mean of the individual estimates of precision.

TABLE 4.1. Means, ranges, and precisions of geochemical analyses of sediments from Devils Lake sediment core

	Soluble Salt ( $\mu$ MHOs/gm)	Biogenic Silica (% dry wt.)	Total Organic Carbon (% dry wt.)
Mean	1020	3.26	3.4
Range	378 to -1750	0.77 to -7.51	1.87 to -5.12
Precision	$\pm 3.5\%$	$\pm 7.1\%$	$\pm 4.4\%$
	Carbon to Nitrogen	del C-13 (per mil)	del N-15 (per mil)
Mean	8.38	-25.2	4.6
Range	6.26 to -9.95	-27.5 to -23.9	8.50 to -28.0
Precision	$\pm 7.9\%$	$\pm 0.93\%$	$\pm 5.8\%$

### Sedimentation Rate Measurements

Variations in the downcore activity of Cs-137 and Excess Pb-210 were measured to determine the long-term sedimentation rate in Main Bay, Devils Lake. Based upon these measurements, a sedimentation rate of 0.22-0.25 cm/yr was calculated for the Main Bay core. The calculated sedimentation rate is in reasonable agreement with other sedimentation rate measurements from Devils Lake. Pb-210 sedimentation rates from the center of Main Bay and Creel Bay were determined by Jacobson and Engstrom (1989) to be approximately 0.3 cm/yr. Jacobson and Engstrom (1989) also calculated sedimentation rates for Main Bay and Creel Bay on the basis of pollen data. The pollen data was in good agreement with the Creel Bay core, but the pollen derived sedimentation rate for Main bay suggested a much higher sedimentation rate. Additional Cs-137 and excess Pb-210 for other sediment cores measurements are available for the eastern end of Devils Lake (Lent, chapter 3). These data indicate that in three locations the sedimentation rate is higher and that in another location there has been no net sediment accumulation over the past ~40 years.

Results of the C-14 analyses indicate that the sediment at 33-36 cm has an age of  $225 \pm 50$  years, and that the sediment at 80-84 cm has an age of  $1185 \pm 210$  years. Calculated long-term sedimentation rate based on these samples is approximately 0.05 cm/yr, substantially lower than the short-term sedimentation rates derived earlier using Pb-210 and Cs-137. Additional long term sedimentation rates based upon C-14 are available for Main Bay and Creel Bay (Callender, 1968, Fritz and others, 1991). The uppermost samples dated by Callender (1968) were the intervals 66-86 cm

and 175-208 cm. Based upon C-14 analyses these samples were  $1120 \pm 60$  years and  $1940 \pm 125$  years old respectively. Based on these data the sedimentation rate for the top 1-2 m of the cores was between 0.06 and 0.10 cm/yr, suggesting that the bottom of the core in this study may be significantly older than the approximately 400 years calculated using the Pb-210 and Cs-137 information. In addition, Fritz and others (1991) measured C-14 to a depth of 28 meters in Devils Lake. Based on these data, sedimentation rates in Devils Lake decreased from approximately 0.30 cm/yr for the top 300 cm of the core, to approximately 0.23 cm/yr for the interval between 300 and 1000 cm. The sedimentation rate continued to decrease with depth to approximately 0.16 cm/yr between 1500 and 2100 cm.

#### Sediment Conductivity Measurements

Results of the sediment conductivity analyses are presented as a time series in Figure 4.3. There is a general increase in sediment conductivity with depth, with a maximum at 63 cm, presumably reflecting the period of maximum salinity. By extrapolating the Pb-210 derived sedimentation rate of 0.20 cm/yr (accurate only for the top 20 cm of the core) an approximate age of 315 years can be calculated for the 63 cm high salt event. This calculated age is in reasonable agreement with the 500 year old drying event in Devils Lake suggested by Callender (1968) and similar events in other lakes in the area (Aronow, 1955). The apparent discrepancy in age between the the postulated 500 year drying event and the high salt layer at 63 cm may be explained by the

SOLUBLE SALT, IN  
MICRO MHOS PER  
MILLIGRAM

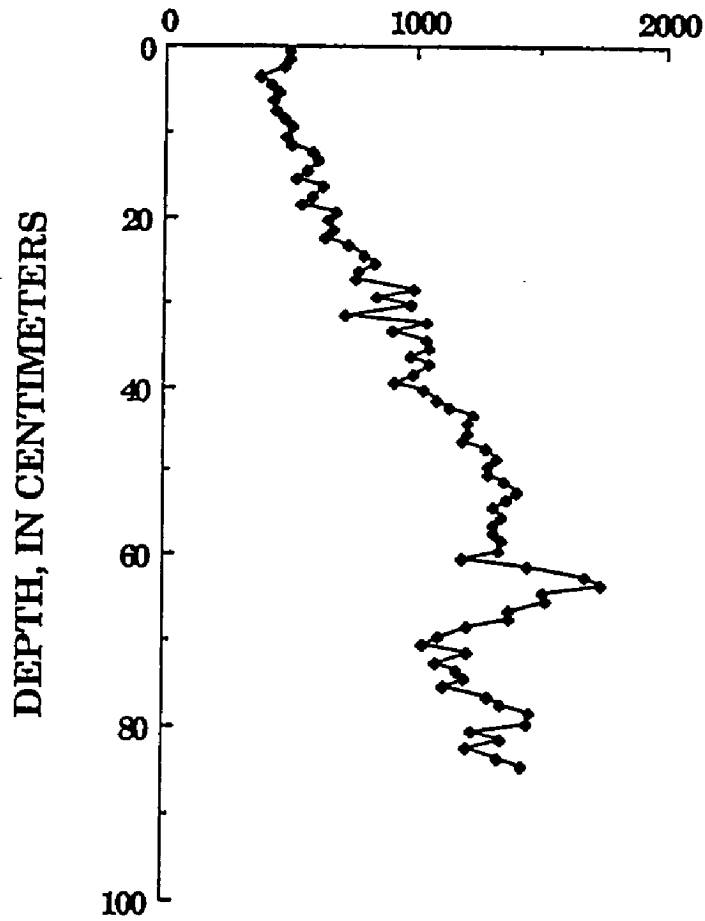


Figure 4.3. Down-core variations in sediment conductivity in Main Bay.



extrapolation of Pb-210 sedimentation rate calculations to depth. For comparison, the C-14 based sedimentation rate calculations result in an age of approximately 800 years for the 63-64 cm interval.

The sediment conductivity data appear to adequately identify episodes of high salt deposition. Not only is there the extremely prominent event at 63-64 cm, but additional high salt events may occur at 79-80 cm, 84-85 cm and possibly 52-53 cm (Figure 4.3). Low salt events are more difficult to identify because of the diffusion of salt from areas of high salt content to areas of lower salt content. However, the data does suggest the occurrence of low salt episodes at 3-4 cm, 31-32 cm, 39-40 cm, 60-61 cm, 70-71 cm and 82-83 cm.

#### Biogenic Silica Measurements

The amorphous silica content of lake sediments is primarily biogenic silica produced by diatom activity (Conley, 1988). Therefore, measurements of the amorphous silica content of lacustrine sediments can provide direct estimates of the biogenic silica content and an indirect estimate of paleo-diatom abundances (Conley, 1988). In previous studies, composition of diatom assemblages in lake sediment cores have been used as a paleolimnologic tool to identify major fluctuations in climate (Hecky and Kilham, 1973), variations in pH of the lake (Elnor and Ray, 1987), and changes in lake productivity due to anthropogenic influences (Schelske and others, 1983). In the Laurentide lakes, an increase in the silica content near the top of sediment cores is related increased nutrient content due to agricultural activity (Schelske and others, 1983). Recent

studies have documented identifiable variations in the composition of diatom assemblages with changes in salinity in Devils Lake (Stoermer and others, 1972; Fritz, 1990; Fritz and others, 1991). While these studies demonstrate that diatom assemblages respond rapidly to changes in lake level and salinity they do not evaluate variations in primary productivity with changing salinity. DeMaster and others (1983) showed that an increase in the total biogenic silica content of marine sediments was observed in upwelling areas with increased surface primary productivity. Based upon these observations it seems reasonable that variations in the total biogenic silica content in the Main Bay core are related to variations in climatic or lake conditions.

The results of the biogenic silica analyses are presented in Figure 4.4. The plot of the biogenic silica content does not appear to reflect the influence of increased agricultural activity in the Devils Lake area during the last 100 years. Instead, minima in the biogenic silica profile seem to correlate with maxima in the sediment conductivity profile. In particular, the two periods of the most pronounced increased sediment conductivity (63-64 cm and 79-80 cm) have the lowest observed amorphous silica content (less than 1 %). In contrast, the core section with decreased salt content between 69 and 76 cm contains extremely high amorphous silica content (almost 8 %). These observations suggest an inverse relationship between amorphous silica and sediment conductivity. This inverse relationship implies a positive relationship between amorphous silica and lake level. In addition, there is good agreement between biogenic silica profile (Figure 4.4) and lake level (Figure 4.1). The two periods of low biogenic silica at approximately 3-5 cm and

**BIOGENIC SILICA, IN  
WEIGHT PERCENT**

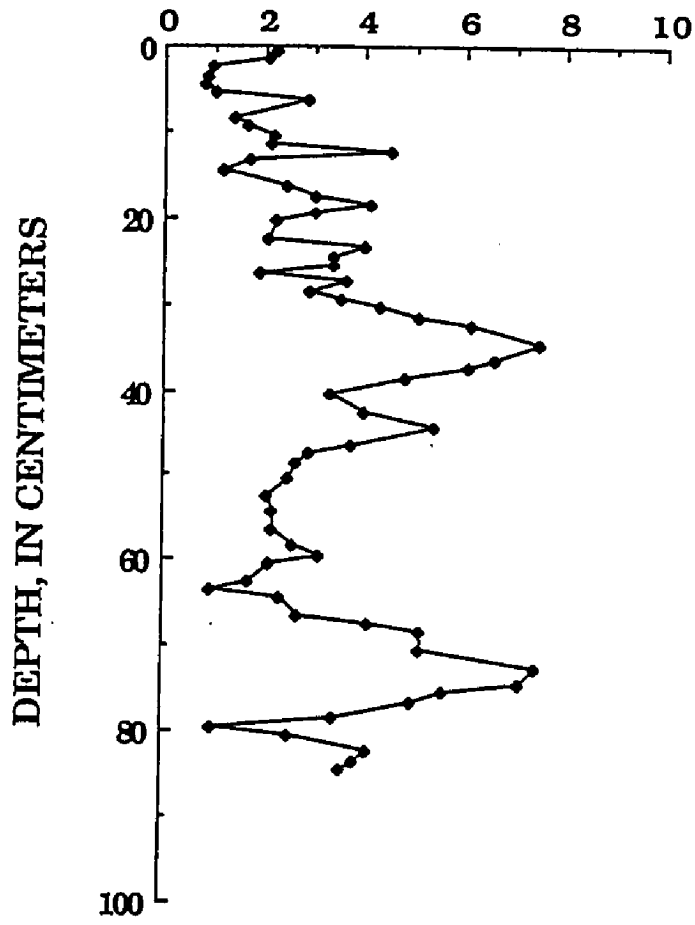


Figure 4.4. Down-core variations in biogenic silica concentrations in Main Bay.

8-10 cm depths correspond well with the two most recent periods of low lake level that occurred in 1960's and early 1940's respectively.

Variations in the biogenic silica content may be the result of various geologic and/or biogeochemical processes. Silica dissolution does not appear to be an important contributing factor to variations in biogenic silica concentrations. Most importantly, biogenic silica concentrations do not appear to decrease with depth. In addition, previous studies have identified well-preserved diatom frustules to a depth of 28 meters (Fritz and others, 1991). The variations in the biogenic silica content also may be the result of sediment dilution due to fluctuations in the sedimentation rate. Detailed Pb-210 sedimentation rate data available for Main Bay (Jacobson and Engstrom, 1989) seem to discount this as the only cause of silica variability. While Jacobson and Engstrom did identify fluctuations in average sediment accumulation between 50 and 150 mg/ cm<sup>2</sup> /yr over a ~180 year period, these fluctuations were much more gradual and of lower magnitude than the rapid fluctuations in biogenic silica. The biogenic silica profile could also be the result of changes in primary productivity as evidenced in marine environments (DeMaster, 1981). If this were the case the amount of organic carbon present in the sediment should also reflect similar variations with depth.

#### Organic Matter Geochemical Measurements

There are maxima in the profile of the total organic carbon (TOC) concentrations at the surface, 6.5, 16.5, 32.5, and 70.5 cm and minima at 4.5, 20.5, 52.5, and 80.5 cm. The ratio of biogenic (Figure 4.5) silica to

**TOTAL ORGANIC CARBON  
IN, WEIGHT PERCENT**

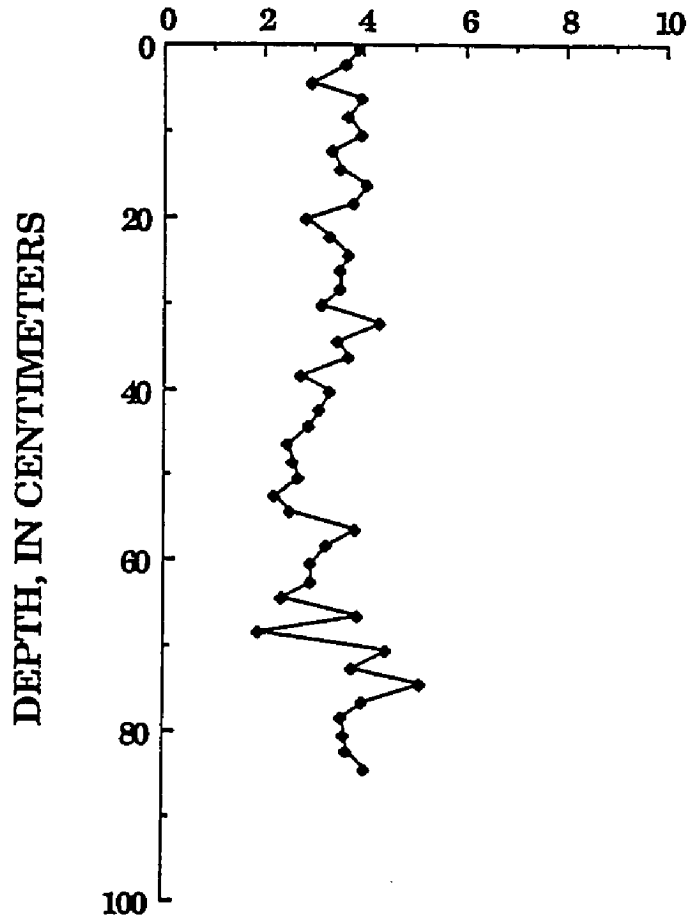


Figure 5. Down-core variations in total organic carbon concentrations in Main Bay.

total organic carbon (TOC) does not remain constant with depth in the Main Bay core. Instead, the ratio of biogenic silica to TOC is similar to the plot of biogenic silica versus depth, suggesting that variations in the ratio may also be related to change in lake salinity. Variations in the biogenic silica to TOC content of diatoms have been documented in marine and freshwater diatoms (Conley and others, 1989). While Conley and others could not positively identify the cause of this variability they suggested three possibilities: (1) differences in sinking strategy of the diatoms (2) the adaptation of marine diatoms to low dissolved silica environments; and (3) deviations in the salinity of the water. Variations in the biogenic silica to TOC ratio in Devils Lake sediments also may be the result of variations in diatom assemblages or variation in the source of organic matter to the lake.

Variations in the C:N content of sedimentary organic matter can be used in conjunction with  $\delta^{13}\text{C}$  to identify the source of the organic matter. Organic matter derived from aquatic organisms generally have lower C:N ratios, reflecting the relatively large amount of nitrogen-rich compounds such as proteins. Terrestrial plant material usually has a much higher C:N ratio due to the abundance of N-poor compounds associated with their structural parts. The C:N ratios from the Main Bay core and other organic material associated with Devils Lake are presented in Table II.

The C:N ratios of the organic matter in the Main Bay core vary from approximately 6.2 to 10 with a mean of 8.4 (Figure 6). Callender (1968) found similar values in long cores from Main Bay and Creel Bay. While the C:N ratios of organic matter in Main Bay sediments are similar to the

### CARBON TO NITROGEN COMPOSITION OF ORGANIC MATTER

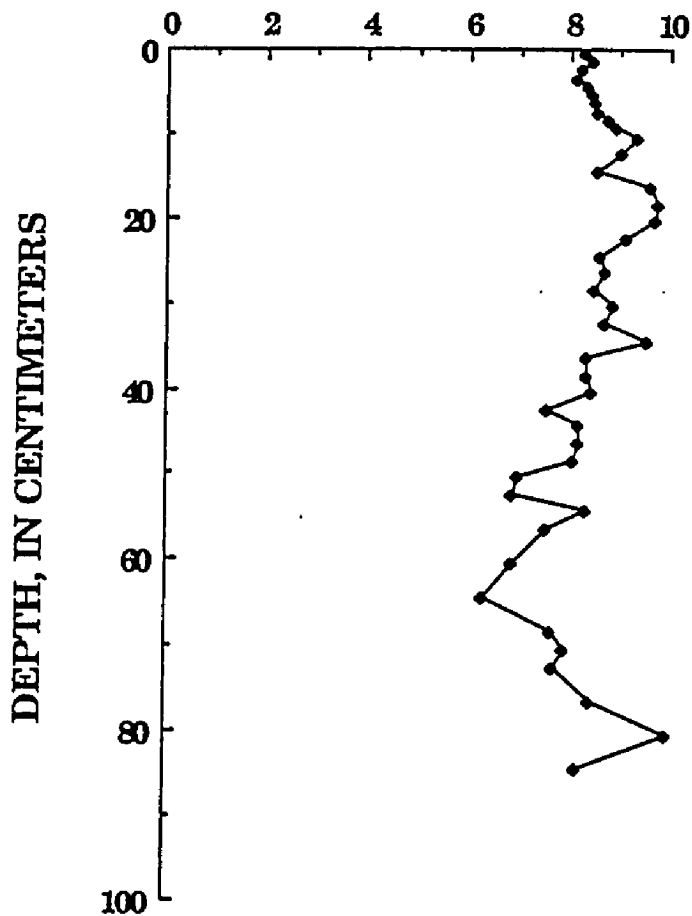


Figure 6. Down-core variations in the ratio of organic carbon to organic nitrogen in Main Bay.

composition of diatoms (Meyers, 1990) and marine organic matter (Jasper and Gagosian, 1980), they are in contrast to sedimentary organic matter from shallow water in Devils Lake (Lent, chapter 3), littoral vegetation (Meyers, 1990) and temperate soil organic matter (Post and others, 1985) that have higher ratios. These data suggest that the organic matter in the Main Bay core is derived primarily from aquatic productivity and that the variability in composition may be due in part to minor contributions by terrestrial organic matter. Degradation of organic matter by bacterial action cannot, by itself, account for the variations in TOC or C:N ratio. If bacterial oxidation of organic matter was the primary cause of variations in TOC and the C:N ratio, TOC should generally decrease with depth, and the C:N ratio should increase with depth as a result of the removal of labile, high nitrogen concentration organic matter.

#### Organic Matter Isotopic Measurements

The  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  composition of sedimentary organic matter were measured to determine variations in the source of the organic material in the sediment with changing climatic conditions. Variations in the  $\delta^{13}\text{C}$  composition of lacustrine organic matter are the result of changes in the source of the organic matter (detrital versus aquatic) and the total alkalinity of the lake (Stuiver, 1975; Krishnamurthy and others, 1982; Meyers and Benson 1988; Meyers, 1990). In general, there are two sources of organic material to lake sediments, detrital organic matter which includes terrestrial plant material and soil



organics, and aquatic organic matter that has been produced in-situ (primarily plankton and plant material).

The initial  $\delta$  C-13 composition of terrestrial plant material is the result of the pathway by which the plant photosynthetically fixes CO<sub>2</sub> from the atmosphere. There are three primary pathways for the fixing of CO<sub>2</sub> by terrestrial plants, the C-3, C-4 and CAM pathways (Deines, 1980; DiNero, 1983). Each pathway has a characteristic  $\delta$  C-13 composition due to varying amounts of fractionation during photosynthesis. The  $\delta$  C-13 composition of organic matter derived from the C-3 (Hatch-Slack) pathway, the most common pathway for CO<sub>2</sub> fixation by terrestrial plants, is typically -24 to -37 per mil, with a mean of -27 per mil. Plants using the C-4 (Calvin-Benson) pathway, primarily tropical grasses and salt marsh plants, have  $\delta$  C-13 compositions between -9 and -16 per mil, with a mean of -12 per mil. CAM pathway plants, primarily succulents, typically have  $\delta$  C-13 compositions between -9 to -19 per mil with a mean of -17 per mil (Deines, 1980; Hoefs, 1980; Deniro, 1983; Anderson and Arthur, 1983). Floating aquatic plants that fix atmospheric CO<sub>2</sub> have  $\delta$  C-13 compositions similar to terrestrial plants (Stuiver, 1975). However, the  $\delta$  C-13 composition of submerged aquatic plants and plankton may be related to the alkalinity of the lake. In lakes with high alkalinity, submerged plants and plankton tend to use bicarbonate instead of dissolved CO<sub>2</sub> resulting in up to a 10 per mil increase in the  $\delta$  C-13 composition of the organic matter (Stuiver, 1975).

Therefore, the two sources of organic matter, detrital and aquatic, can have variable  $\delta$  C-13 composition which can make the interpretation of stable isotopic information more difficult. Stuiver (1975) found that  $\delta$  C-13 composition of sedimentary organic matter in lakes

was more negative during colder climatic episodes. In addition, variation in climate can result in a switch from the Calvin-Benson photosynthetic pathway to the Slack-Hatch pathway with a concurrent shift in  $\delta^{13}\text{C}$  to more positive values (Meyers and Benson, 1988). Climatic change can also result in a change in the  $\delta^{13}\text{C}$  composition of aquatic plants (Stuiver, 1975). The C:N composition of sedimentary organic matter can be used along with the  $\delta^{13}\text{C}$  composition to identify the source.

The carbon isotopic ( $\delta^{13}\text{C}$ ) composition of sedimentary organic matter has been used in other lakes to identify climatic variations (Stuiver, 1975; Krishnamurthy and others, 1986; Meyers, 1990). The downcore  $\delta^{13}\text{C}$  composition of organic matter in Devils Lake shows considerable variation (Figure 4.7). In general, the organic matter is isotopically lighter (-26 to -27‰) near the top of the core, and becomes isotopically heavier (-24 to -25‰) with increasing depth. This overall increase in  $\delta^{13}\text{C}$  may be reflecting long-term climatic change. In addition to the gradual shift in  $\delta^{13}\text{C}$  with depth, there are a number of short duration positive episodes (5-7 cm, 12-14 cm, 24-26 cm, and 42-44 cm) and negative episodes (near-surface, 8-10 cm, 12-24 cm, 36-38 cm, and 62-64 cm).

While the variations in  $\delta^{13}\text{C}$  are visually similar to the variations in the other measured variables, there are no direct statistical correlations between  $\delta^{13}\text{C}$  and either biogenic silica, TOC or C:N. The lack of correlation between  $\delta^{13}\text{C}$  and the other biogenic indicators is not surprising. As previously stated, the isotopic composition of lacustrine organic matter can be effected by variations in: the source of organic matter (detrital vs aquatic); the isotopic composition of aquatic

**C-13 COMPOSITION OF  
ORGANIC MATTER  
PER MIL**

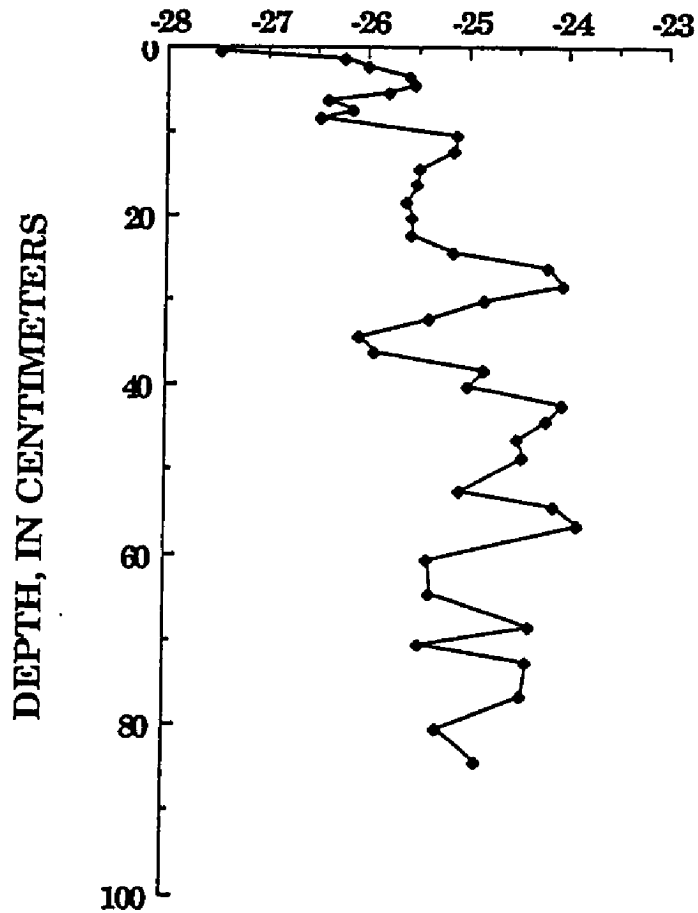


Figure 4.7. Down-core variations in the  $\delta^{13}\text{C}$  composition of sedimentary organic matter in Main Bay.

organics due to changes in temperature and alkalinity; variations the relative importance of plankton species (in particular, C3 vs C4 species); and geochemical processes including bacterial decomposition.

The carbon isotopic data does not, in itself, identify a definitive source of the organic material in the sediment core. Unfortunately, there are no available measurements of the  $\delta^{13}\text{C}$  compositions of biologic material in the Devils Lake drainage basin. However, these measurements were made in Walker Lake, Nevada (Meyers, 1990). The average  $\delta^{13}\text{C}$  composition of sedimentary organic matter from Devils Lake (-24 to -27 ‰) is similar to both deciduous trees common in the Devils Lake area, and mixed (C3) plankton (Table 4.2). The sedimentary organic matter in Devils Lake is distinctly different from blue-green algae (C4) from Walker Lake. These observations indicate that the variation in the  $\delta^{13}\text{C}$  composition of sedimentary organic matter is the result of either variations in the composition of C3 plankton, or variations in the relative importance of detrital and aquatic organic matter. The data seems to exclude the possibility of periods of increased blue-green algae production as a cause of the variations in the  $\delta^{13}\text{C}$  signal.

The  $\delta^{13}\text{C}$  composition along with the C:N data can be used to identify the source of organic matter at different lake levels. During periods of high lake level (identified by high biogenic silica) the C:N ratio is generally large, and the  $\delta^{13}\text{C}$  composition is more negative. Combined, these trends indicate a larger detrital component to the total sedimentary organic matter input to Devils Lake during periods of high lake level. In contrast, during periods of low lake level (identified by low biogenic silica) the  $\delta^{13}\text{C}$  composition, and the C:N ratios are more characteristic of aquatic organic matter.

Table 4.2. Composition of organic matter from Devils Lake, North Dakota, and Walker Lake, Nevada. (Data for Walker Lake taken from Meyers 1990).

Material	C:N	del C-13
<u>Devils Lake, North Dakota</u>		
Shallow sediments	18 to 23	-27.5 to -23.9
<u>Walker Lake, Nevada</u>		
Deciduous Trees		
willows	38	-26.7
cottonwoods	22	-25.0
poplar	62	-27.9
Shurbs (C3)	30 to 57	-23.1 to -26.4
Shurbs (C4)	68 to 160	-12.5 to -14.1
Blue-green Algae (C4)	13	-18.6
Mixed Plankton (C3)	8	-22.8

The del N-15 composition of organic matter can also be used as an indicator of source for the organic matter in marine environments (Peters and others, 1978; Altabet and Deuser, 1985; Rau, and others, 1987), in estuaries (Mariotti and others, 1984), and in lake sediments (Pang and Nriagu, 1976, 1977; Collister and Hayes, 1989). The del N-15 composition in plant material varies with the isotopic composition of the inorganic nitrogen utilized and the amount of fractionation that occurred during uptake and assimilation (DeNiro, 1983). Terrestrial plants utilize atmospheric nitrogen, soil ammonium and soil nitrate. In most instances the residual organic matter of vascular plants have del N-15 compositions near 0 per mil (Kaplan, 1983). Table 4.3 presents the del N-15 composition of organic matter from a variety of environments. As a result of active nitrogen recycling, soil nitrogen can exhibit a wide range of isotopic values (Sweeney and others, 1978). The del N-15 composition of soil organic material from a variety of locations throughout Saskatchewan averaged 9.4 per mil. Pang and Nriagu (1977) determined

the average  $\delta$  N-15 compositions for the major nitrogen pools in Lake Superior. They reported mean  $\delta$  N-15 compositions of surface water (+0.6 per mil), phytoplankton (+1.6 per mil), zooplankton (+5.7 per mil) and sedimentary organic matter (+5.0 per mil). The stepwise increase in the  $\delta$  N-15 composition of organic matter is seen in other food chains (Mingawa and Wada, 1984) and in marine environments (Peters and others, 1978).

Table 4.3.  $\delta$  N-15 composition of various organic matter

Sample	$\delta$ N-15	Source
Soils, United States	+9.2	Shearer et al., 1978
Soils, Saskatchewan	+9.4	Karamanos et al., 1981
Sediment, Lake Michigan	+5.5	Pang and Nriagu, 1977
Sediment, Scheldt Estuary	+8.0	Mariotti et al., 1984
Suspended sediment Sargasso Sea	+2.0	Altabet and Deuser, 1985
Nearshore Sediments	+3.2 to 9.9	Peters et al., 1978
Green River Formation	+10.8 to 20.7	Collister and Hayes, 1989
Lake Hoare, Antarctica	-2.1	Wharton, unpublished
Devils Lake,	+10.7	This study
East Stump Lake	+6.3	This study
West Stump Lake	+7.4	This study

The organic matter from Devils Lake exhibits unusually high  $\delta$  N-15 compositions (Figure 4.8). The extremely positive  $\delta$  N-15 values are similar to values of organic matter from the Green River Formation (Collister and Hayes, 1989). Collister and Hayes (1989) attribute the positive  $\delta$  N-15 compositions of organic matter in the Green River Formation to an extremely complex nitrogen cycle where nitrogen is not a limiting nutrient. If nitrogen is not limiting, every redox reaction

**N-15 COMPOSITION OF  
ORGANIC MATTER  
PER MIL**

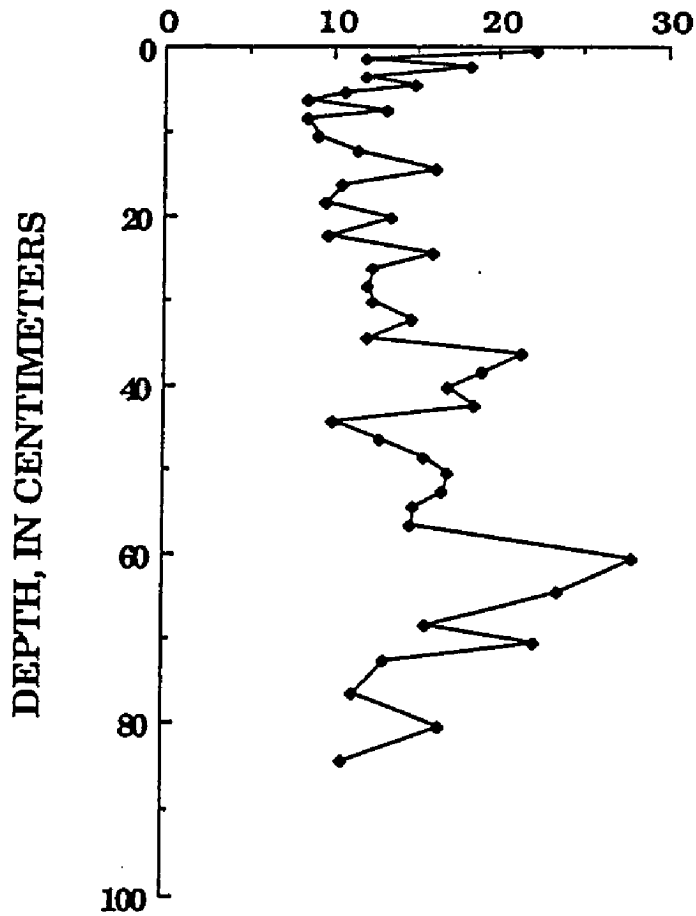


Figure 4.8. Down-core variations in the  $\delta^{15}\text{N}$  composition of sedimentary organic matter in Main Bay.

could fractionate the organic matter further, resulting in the highly positive  $\delta$  N-15 composition.



## STATISTICAL ANALYSIS OF THE DATA:

The statistical analyses performed on the data included factor analysis (Drever, 1988) and correspondence analysis following the methods outlined in Carr (1990) and Oleson and Carr (1990).

### Factor Analysis

The data used to construct the biogeochemical stratigraphies were treated statistically to help identify significant trends in the data. The calculations were restricted to the 39 samples where all of the variables were analyzed. Initially, a matrix of correlation was calculated for the seven variables; biogenic silica, TOC,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , C:N, sediment conductivity and sediment depth (Table 4.4). This involved the estimation of linear relationships between variable pairs. Unfortunately, there were no strong correlations between any of the variables with the exception of a reasonable correlation (0.89) between depth and sediment conductivity. The possibility of statistically valid relationships in the data was tested using factor analysis.

The technique and applications of factor analysis are explained in detail in Drever (1988). Briefly, factor analysis is used to identify a small number of factors that can explain the numerical variation of variables in a seemingly uncorrelated data set. After factor analysis identifies the number of factors necessary to explain the variance in the data, the loading of each variable is calculated. Loading is a measure of how closely a variable is associated with a factor and can range from +1 to -1.

If two loadings in the same factor have the same sign they are positively related. If two variables in the same factor have opposite signs they are negatively related (Drever, 1988). Lastly, the factors were adjusted using a varimax rotation.

Table 4.4. Correlation Matrix for Devils Lake sediment data

	Depth	C:N	Silica	del N-15	del C-13	TOC	Cond
Depth	1	-0.419	0.374	0.267	0.537	-0.138	0.890
C:N	---	1	0.043	-0.588	-0.262	0.384	-0.542
Silica	---	---	1	-0.041	0.159	0.189	0.329
del N-15	---	---	---	1	-0.133	-0.222	0.305
del C-13	---	---	---	---	1	-0.295	0.606
TOC	---	---	---	---	---	1	-0.362
Cond.	---	---	---	---	---	---	1

The factor analysis was performed using all seven variables; biogenic silica, TOC, del C-13, del N-15, C:N, sediment conductivity and sediment depth (Table 4.5). The variations in the data can be explained by three factors. The first factor showed a strong positive loadings for sediment conductivity, depth, del C-13 , a weak positive loading for silica, and weak negative loadings for TOC and C:N. The only variable that did not have significant loading in the first factor was del N-15. The large number of variables with significant loading suggests that there may be long term variability related to sediment depth and more importantly sediment conductivity. This is probably the result of climatic variability. The increase of sediment conductivity with time (i.e. depth)

Table 4.5. Solutions to Factor Analyses for Devils Lake sediment data  
(Orthogonal Transformation Solution-Varimax)

Factor Analysis 1:

<u>Variable</u>	<u>Factor 1</u>	<u>Factor 2</u>	<u>Factor 3</u>
C:N	-0.382	-0.741	0.262
Silca	0.406	-0.022	0.757
del N-15	-0.008	0.940	-0.027
del C-13	0.855	-0.222	-0.210
TOC	-0.365	-0.205	0.735
Conductivity	0.889	0.353	0.041
Depth	0.834	0.311	0.241

Factor Analysis 2:

<u>Variable</u>	<u>Factor 1</u>	<u>Factor 2</u>	<u>Factor 3</u>
C:N	-0.800	-0.365	0.108
Silca	0.011	0.204	0.904
del N-15	0.933	-0.114	-0.018
del C-13	-0.109	0.910	0.058
TOC	-0.292	-0.554	0.552
Conductivity	0.437	0.768	0.267

Factor Analysis 3:

<u>Variable</u>	<u>Factor 1</u>	<u>Factor 2</u>	<u>Factor 3</u>
C:N	-0.800	-0.365	0.023
Silca	-0.012	-0.079	0.947
del N-15	-0.926	0.161	-0.024
del C-13	0.059	-0.901	0.206
TOC	0.342	0.636	0.433

indicates that during the Little Ice Age the general climate in the Great Plains was indeed different than at the present. This conclusion is supported by forest fire produced charcoal obtained in lake sediments of northwest Minnesota (Clark, 1988).

The second factor was primarily a C:N-( $\delta$  N-15) factor which is probably related to the source of the organic material. The C:N ratio is strongly negative while  $\delta$  N-15 is strongly positive, indicating that the relationship between increased N (decrease in C:N) and more positive  $\delta$  N-15 exists. This is in agreement with the earlier observation that the episodes of extremely positive  $\delta$  N-15 are related to periods of decreased nitrogen limitation. This factor also may be a diagenetic factor. Aquatic organic matter that has undergone bacterial decomposition should be more positive with respect to  $\delta$  N-15 and the C:N ratio. The last factor was primarily a biogenic silica-TOC factor which is related to primary productivity.

The overall trend of increasing sediment conductivity with depth resulting from diffusion away from the high salt episode at 63-64 cm may have resulted in misleading interpretations based upon the initial factor analysis. The increase in sediment conductivity with depth along with the inclusion of depth as a variable may have biased the first factor. Therefore, the factor analysis was repeated after removing depth (Table 4.5, Factor Analysis 2), and then again after removing depth and sediment conductivity as variables (Table 4.5, Factor Analysis 3).

The second factor analysis (Table 4.5, Factor Analysis 2) also used three factors to explain the data. The first factor showed strong positive  $\delta$  N-15 loading and weaker positive sediment conductivity loading. The first factor also showed weak negative C:N and TOC loadings. In general

this factor appears to be similar to the second factor in the initial analysis. The second factor showed strong positive  $\delta^{13}\text{C}$  and sediment conductivity loading, and weak negative TOC and C:N loadings. The last factor showed strong positive biogenic silica loading and weaker TOC loading.

The final factor analysis, without depth and sediment conductivity as variables, examines how the strictly biogeochemical variables behave with respect to one another. In the final factor analysis the data was described by three factors (Table 4.5, Factor Analysis 3). The first factor is primarily a strong negative C:N and a strong negative  $\delta^{15}\text{N}$  factor once again demonstrating the strong inverse relationship between the two stratigraphies. The second factor generally showed strong negative  $\delta^{13}\text{C}$  loading and weaker positive TOC loading. As TOC increases the  $\delta^{13}\text{C}$  composition of the organic matter decreases. The last factor showed strong positive biogenic silica loading and weak positive TOC loading.

In summary, the results of the factor analyses suggest that: (1) the variations in total organic carbon are related to variations in the input of detrital plant material into the lake; (2) high organic  $\delta^{15}\text{N}$  compositions are associated with organic matter produced in-situ, probably during periods of increased N input into the lake; and (3) as the primary production increased (reflected by increasing TOC) biogenic silica production increased. This information will later be related to the paleohydrology.

## CLIMATIC INTERPRETATIONS

Reconstructions of prehistoric lake level fluctuations in Devils Lake, based primarily upon sediment cores and ancient shorelines, have been compiled by Callender (1968) and Hutchenson and Klausing (1980). These studies, along with similar studies in Stump Lake (Aronow, 1955; 1957) describe the general paleohydrology of Devils Lake. During the past 1000 years there have been at least two significant periods of decreased lake level and increased salinity. The more recent event occurred in the 1940's and is documented by historical records (Wiche, 1986; Wiche et al, 1988). The earlier drying event occurred between 400 and 500 y.b.p. (Aronow, 1957; Callender, 1968). During the same 1000 year period Devils Lake experienced at least three episodes of extremely high lake level. The most recent high lake level events occurred in 1986 and during the 1930's (Wiche, 1986; Wiche and others, 1986).

Based upon the inferences from the statistical analyses, it is possible to identify episodes of high and low lake level. The downcore variations in biogenic silica appear to be an excellent proxy for prehistoric lake level. Specifically, episodes of high biogenic silica correspond to wet periods (high lake level) in the basins history. These high stands can be characterized as having: increased biogenic silica, increased primary production (as seen by high TOC); increased input of detrital organic matter (High C:N ratios and more negative  $\delta^{13}\text{C}$ ); and in many cases, nitrogen unlimiting conditions (extremely positive  $\delta^{15}\text{N}$ ). In contrast, periods of low lake level can be characterized by low

biogenic silica, with an apparent decrease in primary productivity (low TOC), where algal matter is the dominant source of organic matter to the lake bottom (low C:N and more negative  $\delta^{13}\text{C}$ ).

### Biogenic Silica Data

The biogenic silica data demonstrate two significant periods of increased concentration. Based on the Pb-210 data the more recent period occurred between ~1830 A.D. and ~1870 A.D. The period was a time of documented global climate deterioration (Bradley and others, 1987; Crowley and Howard, 1990). The annual precipitation index for North America was at its lowest value in 125 years (Bradley and others, 1987) and numerous climatic indicators in China including winter temperatures and drought indices suggest abnormally cold and dry conditions. In addition, the historic lake level records for Devils Lake and the Great Salt Lake (Figure 12.1) show decreasing trends during this time. During this period not only was total precipitation lower but the major loss of precipitation was in the fall and winter months (Bradley and others, 1987). It is more difficult to assign an age to the earlier period of increased biogenic silica concentrations. Based on Pb-210 data this period occurred from ~1600 A.D. to ~1700 A.D. In contrast, the C-14 data indicate that the period of maximum biogenic silica concentrations occurred approximately 900 years ago. The period between 1600 A.D. and 1700 A.D. was a period of colder than normal conditions in China (Crowley and Howard, 1990) and northern Greenland (Johnsen and others, 1970).

During periods of lowering lake levels (based on the decrease in biogenic silica) the C:N ratios are also decreasing from their maximum levels of ~11.5 to 7-9. In addition, the C:N ratio first decreases during the onset of the drying phase then increases at the end of the drying (Figure 8). This must mean that as the lake level is lowered and the terrestrial input of nutrients decreases, primary productivity in the lake decreases. However, at some later time the biogeochemistry of the lake "reequilibrates" and primary productivity increases. The source of this late, dry stage productivity cannot be due to diatoms, the major primary producer during "wet" periods. Stoermer and others (1971) have shown that in Devils Lake at times of increased salinity (i.e., "dry" periods) the total number of diatoms do decrease and primary productivity probably decreases in the lake.

#### Other Climatic Signals

A power spectra analysis was run on the biogenic silica, C:N and TOC data using the Pb-210 based sedimentation rate. The TOC and C:N spectra yielded maximum relative power at ~11 year frequency, while the biogenic silica yielded maximum relative power at ~5 and ~6 years. The C:N spectra yielded much higher power at the 11 year harmonic than the TOC. Due to the limited amount of data available, both in number of data points as well as length of record, the spectral analysis could not resolve any significant power above a frequency of ~15 years.

The power in the 5-6 year frequency in the biogenic silica spectra is similar to the 6.5 year frequency reported in paleotemperature records



from ice cores all over Greenland (Hilber and Johnson, 1979). Although the ENSO (El Nino-Southern Oscillation) phenomenon is typically aperiodic, it does have a range of frequency between 4 to 7 years. Whether or not there is a connection between ENSO events and lake levels in North America is currently a topic of some conjecture. However, there is some evidence that water levels in the Great Salt Lake can be correlated to the ENSO phenomenon (D. Stephens, personal communication).

The 11 year frequency in the TOC and C:N data is similar to the sunspot cycle. To our knowledge this is the first reported record of the 11 year cycle from lacustrine sediments. Clark (1988) has also observed an 11 year harmonic for forest fire occurrence just east of Devils Lake in Minnesota. A ~20 year frequency of climatic oscillation has been observed in numerous climatic data sets from very different milieu including, ice cores, temperature records, tree-rings, and drought indices (Roberts and Olson, 1975; Hilber and Johnson, 1979; Currie, 1984). Estimated precipitation and tree-ring records from areas in the prairie regions to the south and southeast of Devils Lake (i.e., Iowa and Illinois) indicate a roughly 20 year drought cycle since at least 1700 A.D. (Blasing and Durick, 1984).

While the data presented in this paper demonstrate the value of high-resolution geochemical chronologies of sediment cores from closed-basin lakes it also highlights the need of longer cores to resolve any possible correlations between Devils Lake and other climatic records. A deeper core from Devils Lake is necessary to substantiate the correlations proposed in this study. In addition, a longer core should detect any periodicities in the basin related to the climatic cycles discussed above,

and to lunar nodal cycle of 18.6 years and/or the double sunspot cycle of 22-23 years.

## CONCLUSIONS

General Circulation Models predict that the northern Great Plains of North America may be greatly affected by climate change as a result of anthropogenic influences on atmospheric composition. These predicted changes include; increased temperature, decreased precipitation, and a concurrent decrease in soil moisture. In addition, the predicted changes in regional climatic conditions may result in significant alteration of existing agricultural zones in the region (e.g. wheat growing zone).

Interpretation of geochemical stratigraphies from lacustrine sediments provides a method for determining past climatic conditions. Because the Devils Lake drainage basin is large, and there is a long record of lake-level and precipitation data, Devils Lake has the potential of providing an accurate, high resolution, long-term history of climate change for the north Great Plains.

Detailed radioisotopic measurements are necessary for accurate age determinations in short term sedimentation rates (<100 years). An examination of the activity of Cs-137 and excess Pb-210 in the upper 25 centimeters of the sediment core from Devils Lake result in a short-term sedimentation rate of ~0.22 cm/yr. Longer-term sedimentation rate calculations using C-14 analysis from other studies in Devils Lake result in significantly lower sedimentation rates (approximately 0.1 cm/yr). The discrepancy is undoubtedly related to increased compaction with depth, and may be compounded by short-term hiatuses in sedimentation.

Fluctuations in salinity and lake level can be delineated using sediment core data from Devils Lake as variations in sediment conductivity and biogenic silica. Sediment conductivity exhibits a general increase to about 64 cm depth. This horizon of high sediment conductivity is related to a period of extremely low, to no water in the basin. Biogenic silica is strongly correlated to lake level in Devils Lake. Periods of high lake level (identified by low sediment conductivity) correspond to increased biogenic silica content. In contrast, periods of low lake level (identified by high sediment conductivity) have extremely low biogenic silica. The variations in biogenic silica are likely related to variations in diatom productivity in the lake. The strong correlation between biogenic silica and lake level in Devils Lake can be demonstrated by direct comparison of biogenic silica in the upper part of the sediment core with historic records of lake level.

Based on the sediment conductivity, biogenic silica content and the composition of organic matter in the sediment (i.e. total organic carbon, carbon:nitrogen ratio and the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  composition of total organic matter), the paleobiologic conditions of Devils Lake can be described. In general, high lake level stands are characterized by; increased primary productivity, increased input of detrital organic matter, and nitrogen unlimiting conditions. In contrast, low lake level stands can be characterized by; decreased primary productivity, and decreased input of detrital organic matter where algal matter dominates the sedimentary organic matter.

The results of this study demonstrate the potential for high resolution paleobiologic studies that utilize multiple geochemical stratigraphies in the delineation of regional climatic histories.

Unfortunately, the sediment core used in this study was too short for conclusive spectral analysis of the data. However, many of the geochemical stratigraphies (i.e., biogenic silica, C:N, and TOC) exhibit short frequency variations on the order of 5-11 years. In addition, visual examination of the biogenic silica and sediment conductivity records suggest much longer (~100 and ~500 years respectively) frequency variations. Therefore, this study should be repeated using longer sediment cores.

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