

# **SUBTASK 7.2 – GLOBAL WARMING AND GREENHOUSE GASES**

Final Report

*(for the period April 1, 2001, through September 30, 2004)*

*Prepared for:*

AAD Document Control  
U.S. Department of Energy  
National Energy Technology Laboratory  
PO Box 10940, MS 921-143  
Pittsburgh, PA 15236-0940

Cooperative Agreement No.: DE-FC26-98FT40320  
Performance Monitor: Dr. Robert Patton  
UND Fund Nos. 4348, 4389, 4350 and 4245

*Task 7.2, initiated in 2001 under the title Global Warming and Greenhouse Gases, consisted of  
Activity 1 – Reconstruction of Paleohydrologic History of Devils Lake, North Dakota, and  
Activity 2 – Economic Source-Sited Long-Term Carbon Dioxide Sequestration.*

# **SUBTASK 7.2 – RECONSTRUCTION OF PALEOHYDROLOGIC HISTORY OF DEVILS LAKE, NORTH DAKOTA**

Final Report For Task 7.2, Activity 1

*(for the period April 1, 2003, through September 30, 2004)*

*Prepared for:*

AAD Document Control  
U.S. Department of Energy  
National Energy Technology Laboratory  
PO Box 10940, MS 921-143  
Pittsburgh, PA 15236-0940

Cooperative Agreement No.: DE-FC26-98FT40320  
Performance Monitor: Dr. Robert Patton  
UND Fund Nos. 4348, 4389, 4350 and 4245

*Prepared by:*

Jaroslav Solc  
Kurt Eylands  
Jaroslav Solc Jr.

Energy & Environmental Research Center  
15 North 23rd Street  
Grand Forks, ND 58202-9018

Sara Mueller  
Daniel Engstrom  
Mark Edlund

Saint Croix Watershed Research Station  
Science Museum of Minnesota  
310 Pillsbury Drive SE  
Minneapolis, MN 55455

January 2005

## **DOE DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

## **ACKNOWLEDGMENT**

This report was prepared with the support of the U.S. Department of Energy (DOE) National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-98FT40320. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors(s) and do not necessarily reflect the views of DOE.

## **EERC DISCLAIMER**

LEGAL NOTICE. This research report was prepared by the Energy & Environmental Research Center (EERC), an agency of the University of North Dakota, as an account of work sponsored by DOE. Because of the research nature of the work performed, neither the EERC nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement or recommendation by the EERC.

## **SUBTASK 7.2-ACTIVITY 1 – RECONSTRUCTION OF PALEOHYDROLOGIC HISTORY OF DEVILS LAKE, NORTH DAKOTA**

### **ABSTRACT**

Evaluation of current climatic trends and reconstruction of paleoclimatic conditions for Devils Lake have been conducted based on diatom-inferred salinity for the last 2000 years. The 3-year cross-disciplinary research, funded by the U.S. Department of Energy (DOE) was carried out by the Energy & Environmental Research Center (EERC) and St. Croix Watershed Research Station (SCWRS) at the Science Museum of Minnesota. The results indicate that frequent climatic fluctuations resulting in alternating periods of drought and wet conditions are typical for the northern Great Plains and suggest that the severity and length of extremes exceeded those on modern record. Devils Lake has experienced five fresh periods and two minor freshening periods in the last 2000 years. Transitions between fresh and saline periods have been relatively fast, representing lake level changes that have been similar to those observed in the last 150 years. From 0 to 1070 A.D., Devils Lake showed more variable behavior, with fresh phases centered at 200, 500, 700, and 1000 A.D. From 1070 A.D. to present, Devils Lake was generally saline, experiencing two minor freshening periods at 1305–1315 and 1800–1820 A.D and the major current freshening from 1960 A.D. to present.

## TABLE OF CONTENTS

LIST OF FIGURES .....	iii
LIST OF TABLES.....	iv
EXECUTIVE SUMMARY .....	v
1.0 INTRODUCTION .....	1
1.1 General Introduction.....	1
1.2 Scientific Background and Objectives.....	1
1.3 Project History and Partners .....	1
2.0 EXPERIMENTAL.....	2
3.0 RESULTS AND DISCUSSIONS.....	2
3.1 Devils Lake Characteristics .....	2
3.1.1 Lake Environment .....	2
3.1.2 Lake Level and Area/Volume Fluctuation.....	3
3.2 Regional Climatic Trends .....	4
3.2.1 Precipitation Records .....	4
3.2.2 Regional Climatic Trends .....	5
3.3 Reconstruction of Paleohydrologic History for Devils Lake.....	7
3.3.1 Lake Salinity and Paleoindicators .....	7
3.3.2 Sediment Recovery and Sampling Strategy.....	7
3.3.3 Core Characterization .....	8
3.3.4 Diatom Analyses .....	11
3.3.5 Reconstruction of Lake Salinity Record .....	13
3.3.6 Diatom Composition by SEM .....	14
3.4 Discussion.....	16
3.4.1 Lake Level and Inferred Salinity .....	16
3.4.2 Comparison to Other Systems .....	17
3.5 Socioeconomic Implications.....	19
4.0 CONCLUSIONS .....	20
5.0 REFERENCES .....	20
PRECIPITATION SUMMARIES.....	APPENDIX A
CONTOUR MAPS.....	APPENDIX A-1
PRECIPITATION DATABASE .....	APPENDIX A-2
A HIGH-RESOLUTION RECORD OF LATE HOLOCENE CLIMATE AND HYDROLOGIC CHANGE FROM DEVILS LAKE, NORTH DAKOTA, TEXT OF THESIS BY SARA MUELLER .....	APPENDIX B

Continued . . .

## TABLE OF CONTENTS (continued)

CORE CHARACTERIZATION DATA .....	APPENDIX C
CORE DESCRIPTION AND DOCUMENTATION.....	APPENDIX C-1
LOSS-ON-IGNITION DATA.....	APPENDIX C-2
C-14 DATA.....	APPENDIX C-3
PB-210 DATA .....	APPENDIX C-4
INFERRRED SALINITY DATA.....	APPENDIX C-5
DIATOM SEM ANALYSES .....	APPENDIX D
DIATOM COMPOSITION .....	APPENDIX D-1
SEM ANALYTICAL RESULTS.....	APPENDIX D-2
DIATOM MORPHOLOGY FOR SELECTED SAMPLES .....	APPENDIX D-3

## LIST OF FIGURES

1	Devils Lake and Red River Watershed.....	3
2	Devils Lake lake level fluctuation (1867–November 2004).....	4
3	Annual precipitation average for selected stations .....	6
4	Average annual precipitation for selected monitoring periods .....	6
5	Results of Pb <sup>210</sup> , pollen, and Cs <sup>137</sup> analyses .....	8
6	Abundance of major taxa of pollen .....	9
7	Age model .....	10
8	Results of loss-on-ignition analysis .....	10
9	Relative abundance of major diatom taxa .....	12
10	Inferred salinity 0–2000 A.D. .....	13
11	A diatom identified as <i>Cyclotella</i> from Devils Lake core Arch DLA-2 deposited at an estimated date of 394 A.D. when lake conditions were saline.....	15
12	Regional records of climate change .....	18
13	Population trend for Fargo and West Fargo combined.....	19

## LIST OF TABLES

1	Number of Stations Contributing to Precipitation Statistics .....	5
2	Calibrated Ages – Intercept Method .....	9
3	Radiocarbon Dates from the NSF–Arizona AMS Laboratory .....	9
4	Core Samples for SEM Analysis .....	14
5	Elemental Analyses for a Sample Representing Low Salinity .....	15
6	Elemental Analyses for a Sample Representing High Salinity .....	16

## **SUBTASK 7.2-ACTIVITY 1 – RECONSTRUCTION OF PALEOHYDROLOGIC HISTORY OF DEVILS LAKE, NORTH DAKOTA**

### **EXECUTIVE SUMMARY**

Evaluation of current precipitation trends and reconstruction of paleoclimatic conditions based on diatom-inferred salinity over the last 2000 years have been conducted in this 3-year cross-disciplinary research project, funded by the U.S. Department of Energy (DOE), carried out by the Energy & Environmental Research Center (EERC) and St. Croix Watershed Research Station (SCWRS) at the Science Museum of Minnesota.

The results of the research indicate that frequent climatic fluctuations resulting in alternating periods of drought and wet conditions are typical for the northern Great Plains and suggest that the severity and length of extremes exceeded those on modern record. Based on reconstruction of paleoclimatic conditions for the region, wet and dry conditions recur at intervals ranging between 100 and 300 years (with shorter reoccurrence intervals documented for smaller lakes), or at about a 150-year average recurrence interval. The hydrologic system is currently in the wet cycle.

Devils Lake has experienced five fresh periods and two minor freshening periods in the last 2000 years. Transitions between fresh and saline periods have been relatively fast, representing lake level changes that have been similar to those observed in the last 150 years. From 0 to 1070 A.D., Devils Lake showed more variable behavior, with fresh phases centered at 200, 500, 700, and 1000 A.D. From 1070 A.D. to present, Devils Lake was generally saline, experiencing two minor freshening periods at 1305–1315 and 1800–1820 A.D. and the major current freshening from 1960 A.D. to present.

Climate changes, duration of extremes, and transition between wet and dry periods control the distribution and availability of water resources and, in wider terms, economic and demographic sustainability. High water demand in the primary economic sectors (energy and agriculture) makes the regional economy extremely vulnerable to climatic extremes. Without conservation-based water management policies, long-term periods of droughts will limit socioeconomic development in the region and may threaten even the sustainability of current conditions.

## **SUBTASK 7.2-ACTIVITY 1 – RECONSTRUCTION OF PALEOHYDROLOGIC HISTORY OF DEVILS LAKE, NORTH DAKOTA**

### **1.0 INTRODUCTION**

#### **1.1 General Introduction**

Global atmospheric changes and a shift toward more frequent occurrence of climatic extremes observed in recent decades can be associated with general global-warming patterns that have a serious economic and social impact in areas sensitive to reoccurrence of natural disasters. Available historical records and monitoring data are, in general, insufficient to evaluate if the recently observed climatic changes represent a human-induced deviation from natural climatic and hydrologic cycles. It is obvious that at the current stage of the knowledge (or lack of), the answers for the future must be based on interpretation of events that occurred in the past.

Physical characteristics of sediments, microscale geophysical properties of the preserved soil profiles, and occurrence and distribution of paleoindicators in soil and water provide information critical for reconstruction of paleohydrologic response to climatic events that have dominated the hydrological cycle. Matching of the analogous past climatic patterns with those observed today allows for evaluation of the magnitude and periodic occurrence of these past events and extrapolation of these cyclic climatic and hydrologic patterns for the future.

#### **1.2 Scientific Background and Objectives**

The primary project objectives were reconstruction of the paleohydrologic history of Devils Lake for the last 2000 years and evaluation of climatic trends based on available modern-day records, with a focus on data extrapolation for prediction of climatic patterns that affect current and future conditions in the region. Paleo hydrologic reconstruction was based on relative abundance of diatom species in bottom lake sediment as primary indicators of fresh versus saline lake conditions. Precipitation trends for the region have been interpreted based on about 90 years of precipitation records from 110 stations.

The Devils Lake Watershed represents a unique setting of a closed basin with a hydrological budget driven entirely by climatic phenomena and their extremes. The hydrograph of the terminal Devils Lake written in its bottom sediments represents a long-term historical record undisturbed by erosional events typical for watersheds drained by rivers. In addition, most of the project findings correlate with records derived from lake sediments in a larger area, are applicable for the entire Red River Basin, and provide indices for regional climatic cyclicity in the upper Midwest.

#### **1.3 Project History and Partners**

Task 7.2, initiated in 2001 under the title Global Warming and Greenhouse Gases, consisted of Activity 1 – Reconstruction of Paleohydrologic History of Devils Lake, North Dakota, and Activity 2 – Economic Source-Sited Long-Term Carbon Dioxide Sequestration. This final report presents results for work performed under Activity 1 – Reconstruction of Paleohydrologic History of Devils Lake, North Dakota.

This report integrates the results of an extensive 3-year cross-disciplinary research project carried out by the Energy & Environmental Research Center (EERC) and St. Croix Watershed Research Station (SCWRS) at the Science Museum of Minnesota. The SCWRS team was led by Dr. Daniel Engstrom and Dr. Mark Edlund. Extensive sampling, analytical, and interpretive efforts to provide core value to the project was conducted by Ms. Sara Mueller at the Limnological Research Center in fulfillment of thesis requirements at the University of Minnesota.

## 2.0 EXPERIMENTAL

Evaluation of precipitation trends based on modern records is based on data compiled from over 100 reporting stations in the U.S. portion of the Red River Basin. Annual averages were then calculated for each station. The annual totals for each station were aggregated into a final summary to allow for construction of contour maps depicting lines of equal precipitation (isohyets) and interpretation on a decadal basis. A second-order polynomial function was used to generate the isohyetal lines to a degree that best fit the data.

A principal assumption for reconstruction of paleohydrologic history for Devils Lake is based on the inverse relationship between water elevation and inferred salinity. Diatoms were selected as a primary indicator for salinity reconstruction for their short generation times relative to environmental change and their species distribution related to brine composition and salinity in lakes (Fritz et al., 1999). After detailed core characterization and development of an age model using lead-210 ( $Pb^{210}$ ), cesium-137 ( $Cs^{137}$ ), carbon-14 ( $C^{14}$ ), and pollen dating, diatom slide analysis was completed for 378 samples from Devils Lake bottom sediment encompassing the last 2000 years. A diatom transfer function was developed using regression techniques in a software program C2 (Juggins, 2003). The transfer function defines for each diatom species the optimum and range of values for the measured limnological variable of interest. These optima and ranges are then applied to fossil diatom assemblages to reconstruct past changes in the limnological variable.

Salinity was reconstructed using a training set for the Great Plains developed by Fritz et al. (1993; 66 lakes) and applied to earlier studies of Devils Lake (Fritz, 1990; Fritz et al., 1991, 1994); the training set has been augmented and now contains data from 79 lakes (Fritz, unpublished).

## 3.0 RESULTS AND DISCUSSIONS

### 3.1 Devils Lake Characteristics

#### 3.1.1 *Lake Environment*

A watershed of about 8600 km<sup>2</sup> is a tributary to Devils Lake (Figure 1). Developed on till deposits of low permeability, Devils Lake represents a typical terminal lake setting with extremely limited potential for hydraulic communication with ambient sediments. Devils Lake is composed of several basins that may be connected or divided, depending on the water elevation.

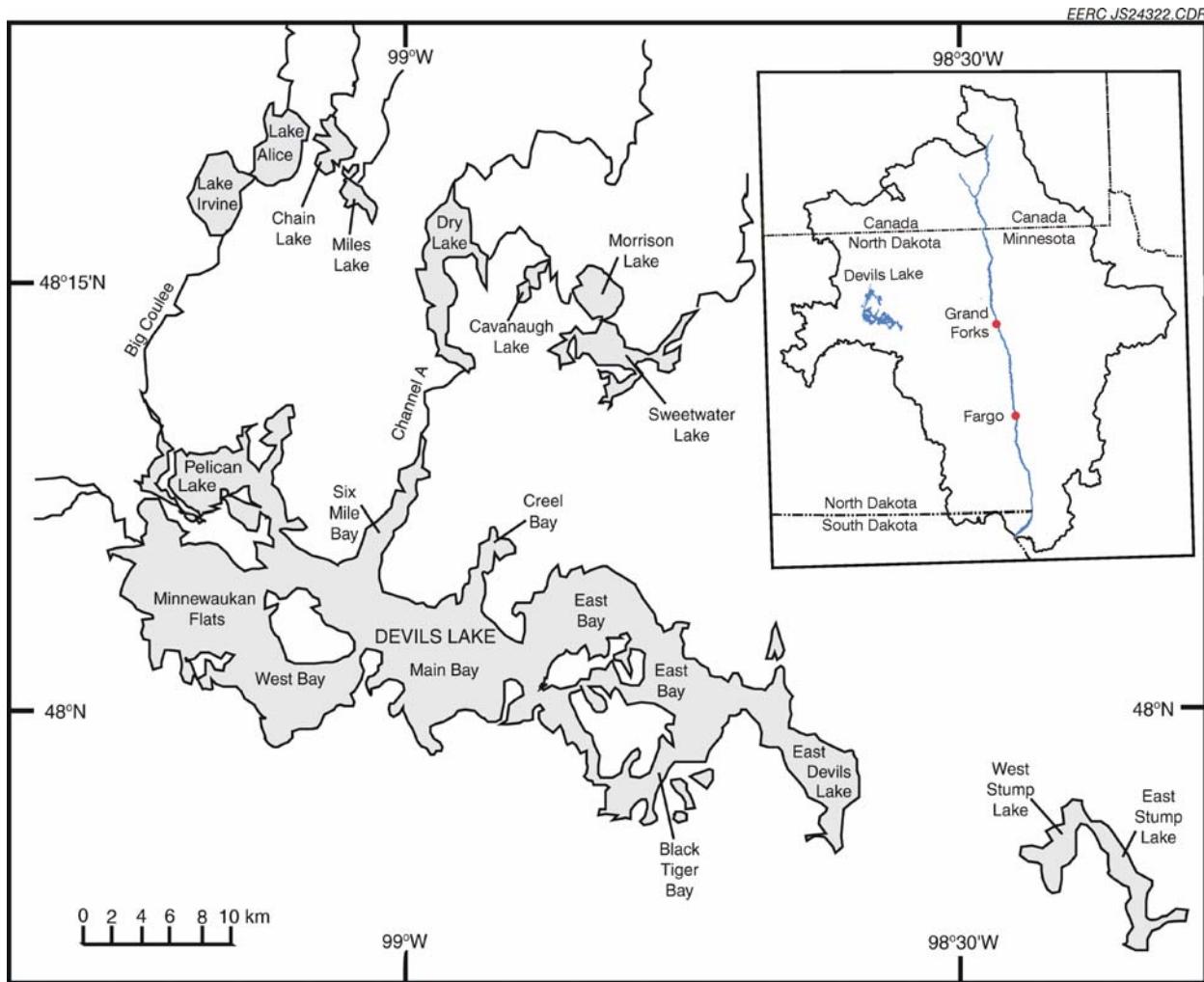


Figure 1. Devils Lake and Red River Watershed.

Lake recharge dominated by Big Coulee, Channel A, and local runoff depend on regional precipitation. Although Devils Lake overlies the significant Spiritwood Aquifer, the groundwater contribution of about 3.7 million  $m^3$  (3000 acre-ft) annually is negligible in the overall lake water budget (Pusc, 1993). Discharge is dominated entirely by evaporation estimated at 0.9 m (3 ft) per acre annually. Similarly to other terminal lakes, the lake water budget is very sensitive to climatic changes. The historical record of lake level fluctuation is discussed in Section 2.1.2.

### 3.1.2 Lake Level and Area/Volume Fluctuation

Intensity and magnitude of lake level and volume changes in the flat, semiarid setting of terminal Devils Lake are controlled by regional changes of hydrological cycle. Long-term climatic trends and the occurrence of floods and droughts resulted in dramatic changes of the lake level with attendant decline or increase of lake area. The historical record on Devils Lake levels provided in Figure 2 indicates that lake level fluctuated over 14 m in the period from 1867 to 2004, with the fastest documented increase between 1940 and 1998. The estimated lake area corresponding to water level was 363  $km^2$  in 1867 (lake level at 438.4 m above sea level), 26.4  $km^2$  (Wiche, 1994; Pusc, 1993) in 1940 (426.99 m), and 521  $km^2$  in November 2004 (over

441.3 m). Lake level fluctuation and ratio of watershed to lake area (Engstrom et al., 1994; Swain et al., 1992) were found to be important factors controlling salinity, chemistry, and sediment deposition patterns in the lake.

Relative to the entire Devils Lake, the area selected for sampling in Creel Bay originally represented a relatively low-energy system with only minor disturbance. Because samples were collected at a depth of approximately 14 m below the water near the axis of the respective bay, it is assumed that soil profiles represent a sedimentary environment uninterrupted by temporary drying resulting from significant lake level fluctuation observed in the past. It is assumed that the most dramatic changes in depositional environment are associated with new agricultural practices introduced late in the 19th century. It follows from Figure 2 that lake level records are insufficient for evaluation of long-term cyclicity; except for an historical low documented from 1930 to 1940, data for the complete period of high lake levels are unavailable prior to 1886 and past 2004. Also, the accuracy of data recorded before 1920 may be questionable.

### 3.2 Regional Climatic Trends

#### 3.2.1 *Precipitation Records*

Daily precipitation data were compiled from over 100 reporting stations in the U.S. portion of the Red River Basin. Annual averages were then calculated for each station. A year was considered valid for inclusion in the final summary if it had 11 or 12 complete months of data. A complete month was defined as having no more than 5 days of missing data. In the case of an entire month missing, values for the missing month were derived as an average from monthly totals for preceding and following monthly precipitation values. The annual totals for each data point were aggregated into final summary values representing an average from 10 consecutive

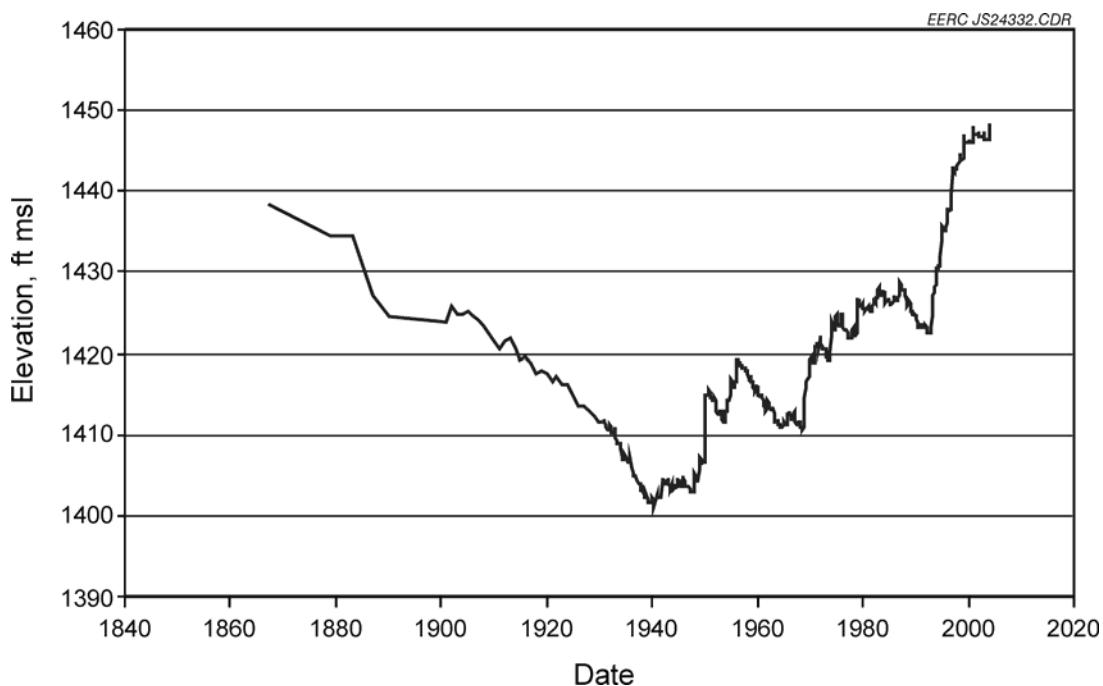


Figure 2. Devils lake level fluctuation (1867–November 2004).

years to allow for interpretation on a decadal basis. A summary of data including precipitation contour maps for periods evaluated is provided in Appendix A.

The large variability of data sets processed reflects the age of the gauging station and data collection method, incomplete records and the necessity to substitute missing data, irregular distribution throughout the watershed, varying periods of records from different stations, and difficulties with snow/water equivalent estimates for winter precipitation. Unlike interpretations based on monthly or annual averages with poorly discernible trends, evaluation based on decadal averages yields simplified but clearly apparent trends. An example for selected stations is provided in Figure 3.

Using the contouring software program Surfer®, contour maps depicting lines of equal precipitation (isohyets) were constructed using the data sets for the time periods mentioned above. A second-order polynomial function was used to generate the isohyetal lines to a degree that best fit the data. With respect to the variability noted among input data, we assume that limitations of using mathematical function for interpretation and increased distortion toward the margins of the area evaluated are negligible.

### **3.2.2 Regional Climatic Trends**

The regional weather patterns in the northern Great Plains including the Red River Watershed are influenced by the unstable interface between the eastern, wetter Atlantic climatic province; the western, drier Pacific province; and the cold Arctic province. The climate is continental, with low precipitation; large temperature extremes; short, hot summers, and long, cold winters (Hinckley, 1995).

The resulting configuration of isohyets in Figure 4 and Appendix A-1 illustrates both increased precipitation and a gradual shift of higher precipitation toward the northwest that may indicate the beginning of regional transition towards a wetter climatic cycle in recent decades. It follows from data that modern precipitation records (similarly to lake level records) are insufficient for evaluation of long-term climatic cyclicity; reliable data are not available prior to 1920–1930. With respect to cyclicity of fresh and saline conditions documented from bottom lake sediments and inferred fluctuation of water levels for terminal lakes, we assume that observed isohyetal shift follows similar cyclic pattern. The duration of transition period between wet and dry cycle and vice versa is relatively short and comparable to salinity changes documented for lake sediments.

**Table 1. Number of Stations Contributing to Precipitation Statistics**

Time Period	Number of Stations
Average all years	109
30–39	46
40–49	66
50–59	80
60–69	78
70–79	80
80–89	79
90–99	75
0–03	58

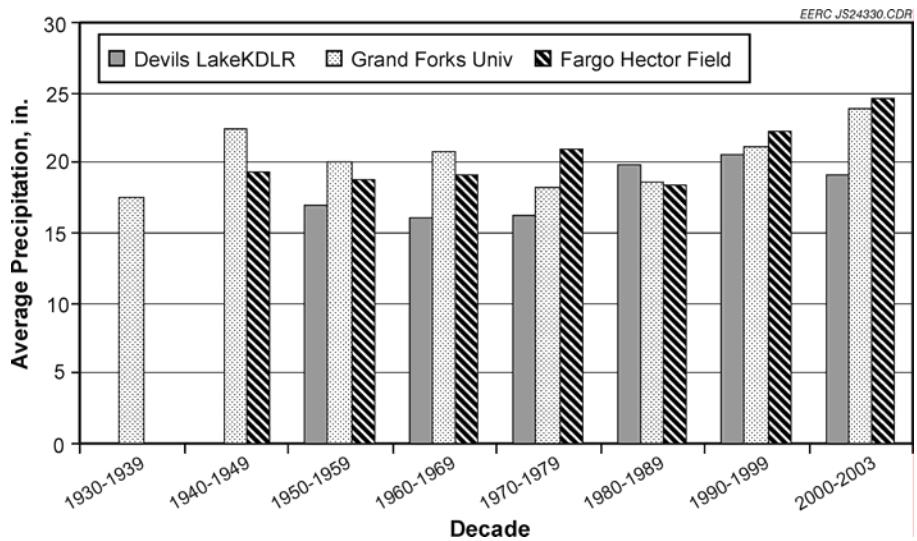


Figure 3. Annual precipitation average for selected stations.

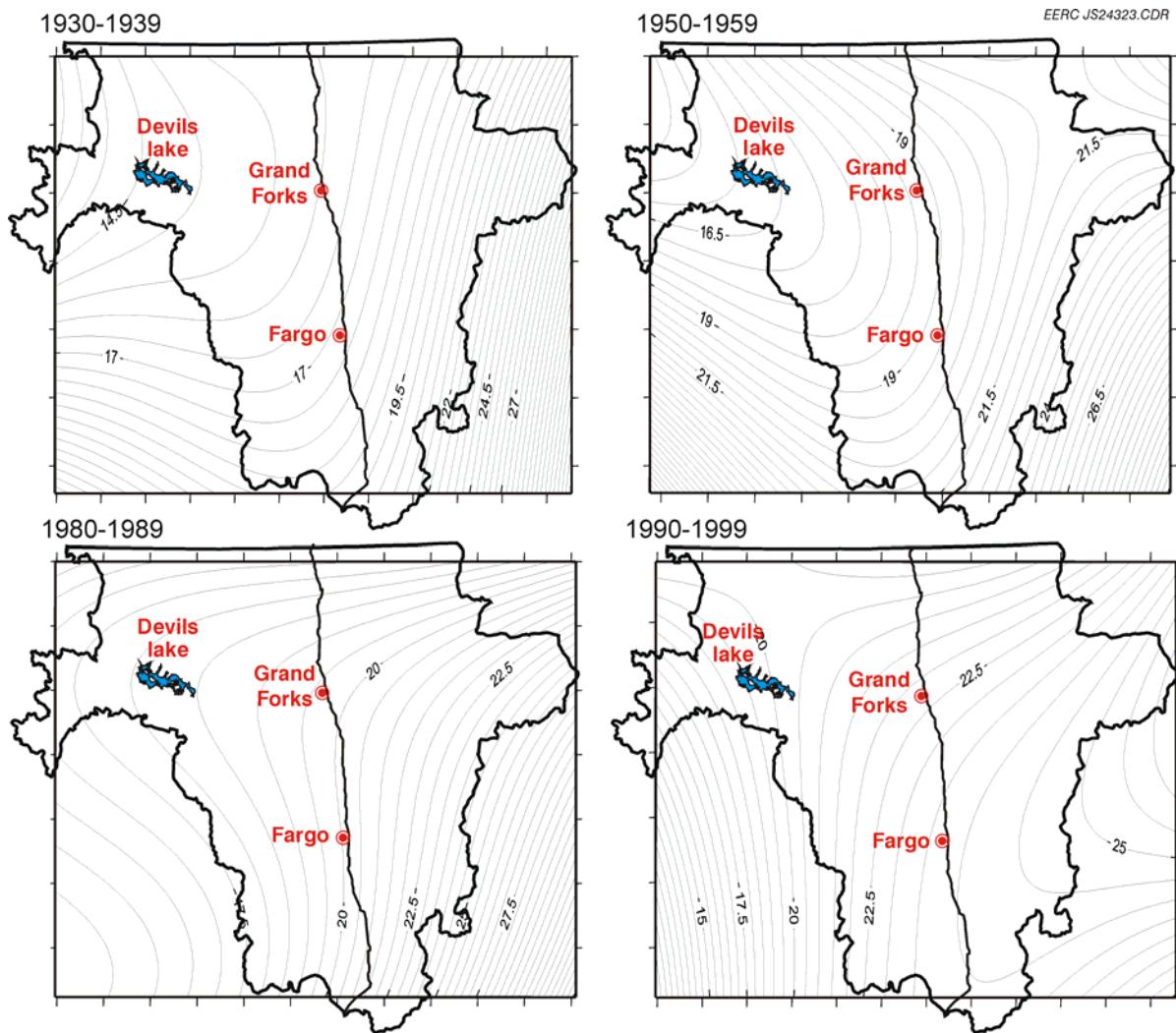


Figure 4. Average annual precipitation for selected monitoring periods.

### 3.3 Reconstruction of Paleohydrologic History for Devils Lake

#### 3.3.1 *Lake Salinity and Paleoindicators*

A principal assumption for reconstruction of lake history is based on the inverse relationship between water elevation and salinity, allowing inferences to be made about the history of lake level changes using diatom-inferred salinity (high or low lake water levels resulting in fresh or saline conditions, respectively). Diatoms were selected as a primary indicator for salinity reconstruction for their short generation times relative to environmental change and their species distribution related to brine composition and salinity in lakes (Fritz et al., 1999). Their hydrous silica frustules are resistant enough to be preserved in sediment and can be identified to species level centuries after the living tissue has expired. A transfer function is developed by using regression techniques in a software program such as C2 (Juggins, 2003). The transfer function defines for each diatom species the optimum and range of values for the measured limnological variable of interest. These optima and ranges are then applied to fossil diatom assemblages to reconstruct past changes in the limnological variable.

For this project, salinity was reconstructed using a training set for the Great Plains developed by Fritz et al. (1993; 66 lakes) and applied to earlier studies of Devils Lake (Fritz, 1990; Fritz et al., 1991, 1994); the training set has been augmented and now contains data from 79 lakes (Fritz, unpublished). A strong relationship between salinity and species composition has been identified for this training set.

#### 3.3.2 *Sediment Recovery and Sampling Strategy*

A set of sediment cores was recovered at 48°04.401'N, 98°56.345'W from Creel Bay, Devils Lake, North Dakota, on March 13, 2002. Creel Bay was chosen as the coring site because it is less prone to sediment transport and resuspension than Main Bay (Jacobson and Engstrom, 1989); in addition, comparison with previous paleolimnological studies from sediment cores in Creel Bay (Callender, 1968; Jacobson and Engstrom, 1989; Fritz, 1990; Engstrom and Nelson, 1991; Fritz et al., 1991; Fritz et al., 1993; Haskell et al., 1996) is made easier by using a similar location. The depth from the surface of the water to the sediment–water interface was 13.2 m, an increase of 5.7 m in water depth since the last long sediment core from Creel Bay was taken in 1985 (Haskell et al., 1996).

The surface sediment was retrieved from two locations using polycarbonate tubes. Deeper sediment was retrieved using a 5-cm-diameter aluminum Livingstone piston corer at two sites, A and B. Seven 1-meter drives were collected from A and B extending to 8.09 m and 7.73 m below the sediment–water interface, respectively. Core sequences A and B overlapped, so that the end of a 1-m core in one sequence overlapped with the middle of a 1-m core in the other sequence.

The surface core was sectioned into 2-cm increments; the first 30 cm was sectioned in the field, and the remaining 65 cm was sectioned in the lab. Each increment in the short core represents 1.8 to 18 years of sedimentation. The two long core sequences were aligned with each other using field measurements, magnetic susceptibility measurements, and visual observations. The long core was sectioned into 5-year increments for the last 2000 years using  $Pb^{210}$ ,  $C^{14}$ , and pollen dating. Each increment in the long core encompassed 0.6 to 1.0 cm in depth. Samples were taken from the middle 70 cm of the cores, moving between core sequences to avoid edge effects. The last 2000 years is represented by 378 increments.

### 3.3.3 Core Characterization

#### 3.3.3.1 Core Screening

The initial sediment core characterization consisted of visual description, photographic documentation, and magnetic susceptibility screening (Appendix C-1). Magnetic susceptibility profiles allow alignment and correlation among the surface and the two series of deep cores using magnetic features.

#### 3.3.3.2 Development of Age Model

An age model for the core was developed using  $\text{Pb}^{210}$ ,  $\text{Cs}^{137}$ ,  $\text{C}^{14}$ , and pollen dating before the core was sampled at 2-cm increments in the surface sediment core and 5-year increments in the long sediment cores, representing the past 2000 years. Core-dating techniques and age model derivation are described in more detail in Appendix B; a summary of data for  $\text{Pb}^{210}$ ,  $\text{Cs}^{137}$ , and  $\text{C}^{14}$  analyses is provided in Appendices C-3 and C-4.

Nineteen samples from the surface core were dated by  $\text{Pb}^{210}$  analyses, and 12 samples were analyzed for  $\text{Cs}^{137}$  activity at the St. Croix Watershed Research Station. While the  $\text{Pb}^{210}$  dating curve is fairly smooth (Figure 5), suggesting that the sediment is undisturbed and that the dating model is reliable, results of  $\text{Cs}^{137}$  dating were less reliable and may indicate possible  $\text{Cs}^{137}$  mobility in the sediments of Devils Lake.

Six sediment samples were prepared for pollen analysis. Pollen analysis identified the first occurrence of *Salsola iberica*, Russian thistle (which arrived in the Devils Lake area in 1894–1895; Jacobson and Engstrom, 1989) in the interval of 42–44 cm (Figure 6); this interval is dated as 1887.0 A.D.  $\pm$  6.74 years by  $\text{Pb}^{210}$  dating.

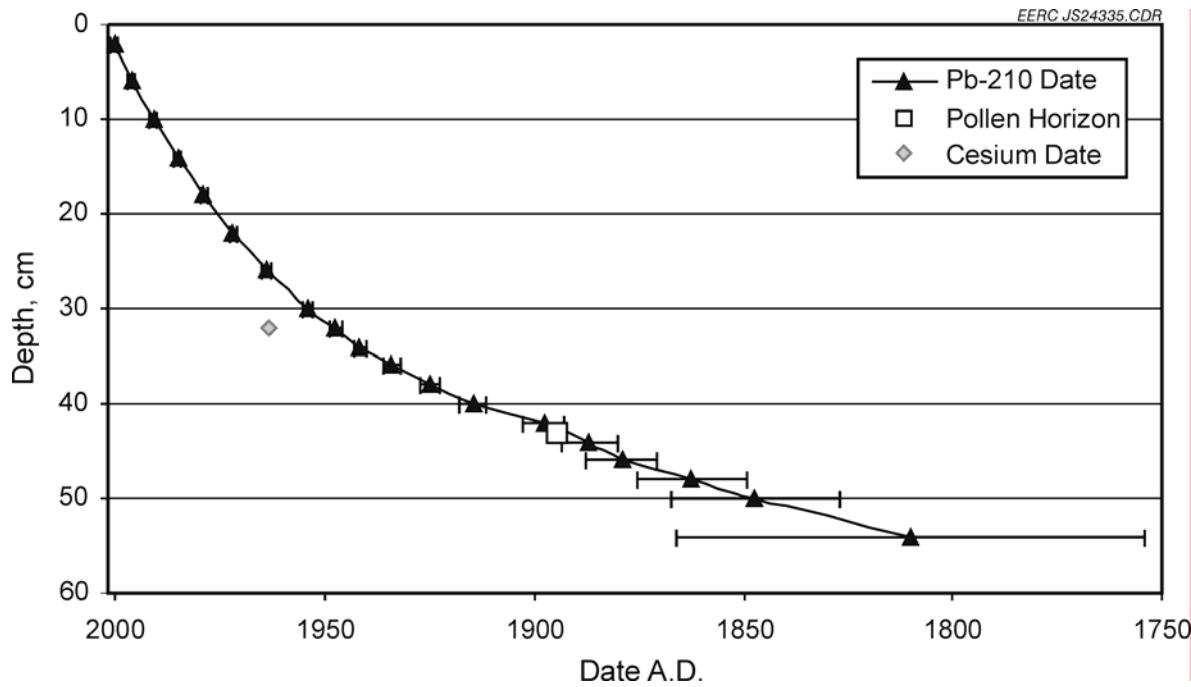


Figure 5. Results of  $\text{Pb}^{210}$ , pollen, and  $\text{Cs}^{137}$  analyses.

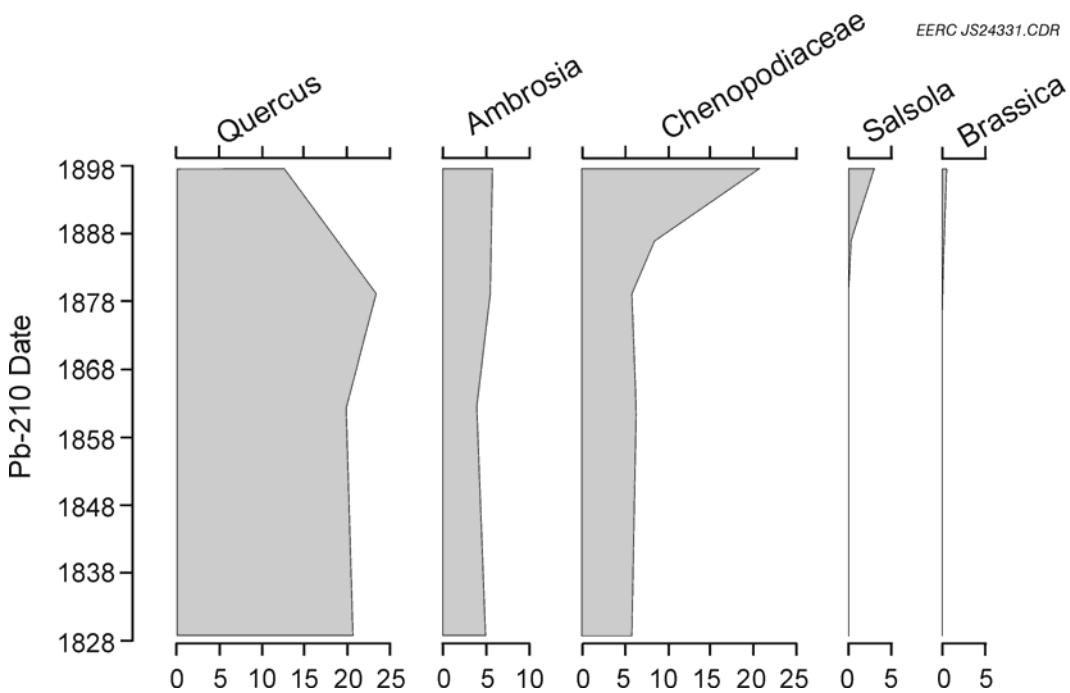


Figure 6. Abundance of major taxa of pollen.

Sediment samples from four depths (Table 2) were picked for grass charcoal to be analyzed by accelerator mass spectrometry (AMS)  $C^{14}$  analyses. Samples were analyzed at the NSF–Arizona AMS Laboratory (Table 3). The dates of the *Salsola iberica* pollen horizon and the  $C^{14}$  intercepts calibrated by the intercept method for the three most recent radiocarbon intervals were used to develop an age model (Figure 7) used to subsample sediment core in sections representing 5-year intervals.

**Table 2. Calibrated Ages – Intercept Method**

Depth (m)	Calibrated age(s) B.P.	Calibrated age - 1 $\sigma$	Calibrated age + 1 $\sigma$	Calibrated age - 2 $\sigma$	Calibrated age + 2 $\sigma$
1.01–1.05	686	668	729	657	759
2.20–2.22	1421, 1433, 1442, 1448, 1464, 1465, 1485, 1500, 1510	1395	1528	1334	1563
3.91–3.93	2729	2494	2747	2362	2762
6.30–6.32	3483, 3508, 3551	3469	3630	3409	3682

**Table 3. Radiocarbon Dates from the NSF–Arizona AMS Laboratory**

AMS Lab ID	Core	Depth (m)	Fraction modern	Radiocarbon age B.P.
AA51330	DL-B1	1.01-1.05	$0.9079 \pm 0.0045$	$776 \pm 40$
AA51327	DL-A2	2.20-2.22	$0.8221 \pm 0.0054$	$1,574 \pm 52$
AA51328	DL-A3	3.91-3.93	$0.7288 \pm 0.0052$	$2,541 \pm 57$
AA51329	DL-A6	6.30-6.32	$0.6623 \pm 0.0039$	$3,310 \pm 47$

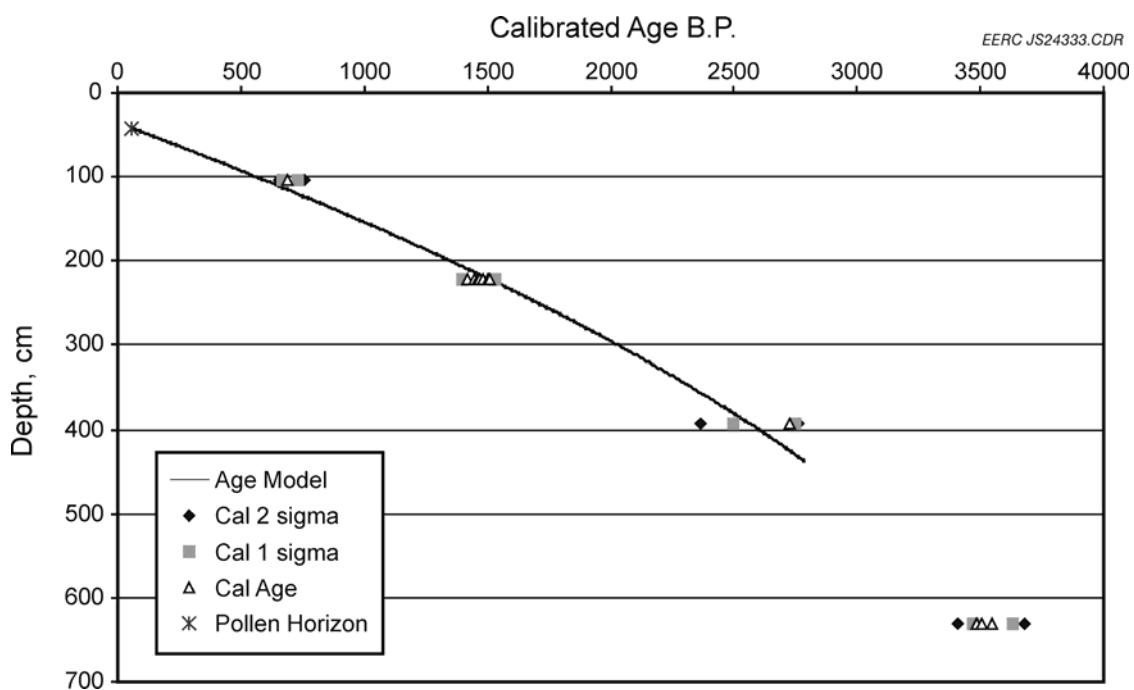


Figure 7. Age model.

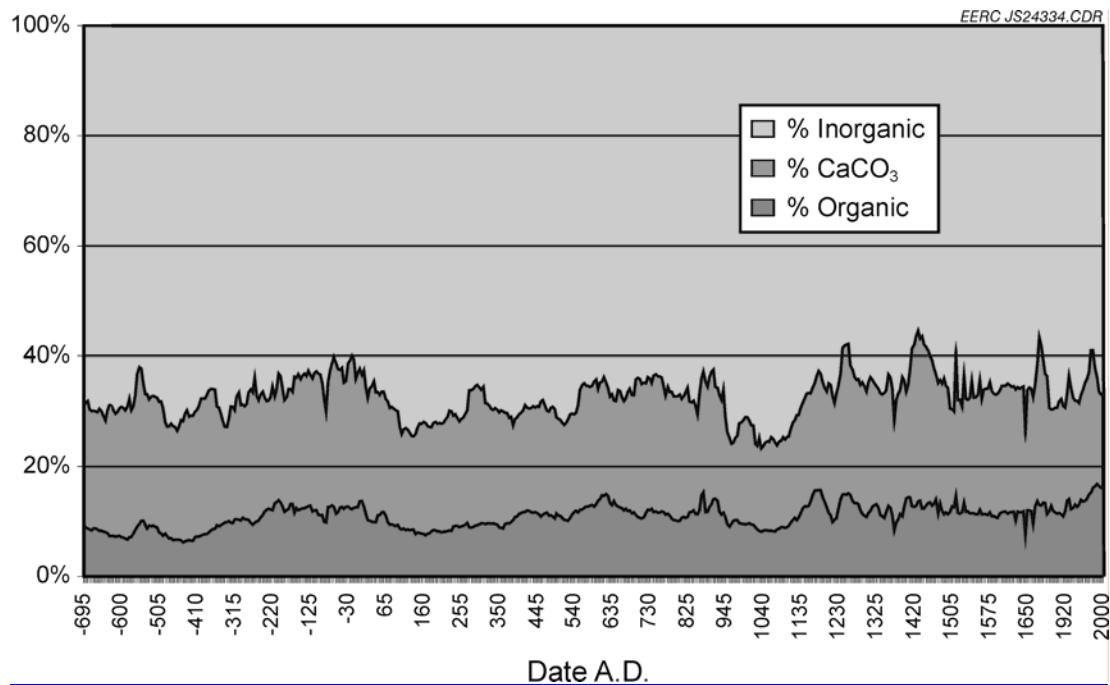


Figure 8. Results of loss-on-ignition analysis.

### 3.3.3.3 Loss in Ignition

Loss on ignition (LOI) has been completed on samples from the surface sediment core divided into 2-cm depth increments and from the long core divided into 5-year time increments, totaling 514 samples (Figure 8). The inorganic portion averages 67 wt%,  $\text{CaCO}_3$  averages 22 wt%, and the organic portion averages 11 wt% of the dry sediment. Correlation between inferred salinity and values determined through LOI is low. A period of high inorganic content coincides with a fresh period which occurred 940–1060 A.D.; this may be an erosional signal. LOI correlation and variability are further discussed in Appendix B, with data provided in Appendix C-2.

### 3.3.4 Diatom Analyses

Diatom slide preparation and analysis were completed for 378 samples encompassing the last 2000 years. For each slide with sufficient preservation for a representative sample, 250 diatom valves were identified and counted. Smaller valve counts were used for limited number of intervals with poor preservation (Appendix B).

Diatom diversity is low in Devils Lake. Thirty-five genera and 124 species were identified in the sediments of Devils Lake; of these, 22 genera and 44 species were present in a maximum relative abundance of at least 1%. Fifteen taxa were present with a maximum relative abundance of at least 10%; the relative abundance of taxa is provided in Figure 9. Generally, a lower number of species was identified in saline periods as compared to fresh periods. During saline periods, *Cyclotella quillensis* was the dominant diatom, with *Cyclotella choctawatcheeana*, *Cyclotella meneghiniana*, and *Chaetoceros muelleri/elmorei* present in lower abundances. During fresh periods, the dominant diatom was variable, alternating between *Stephanodiscus niagarae*, *Aulacoseira granulata*, *Stephanodiscus minutulus*, and *Fragilaria capucina* var. *mesolepta*.

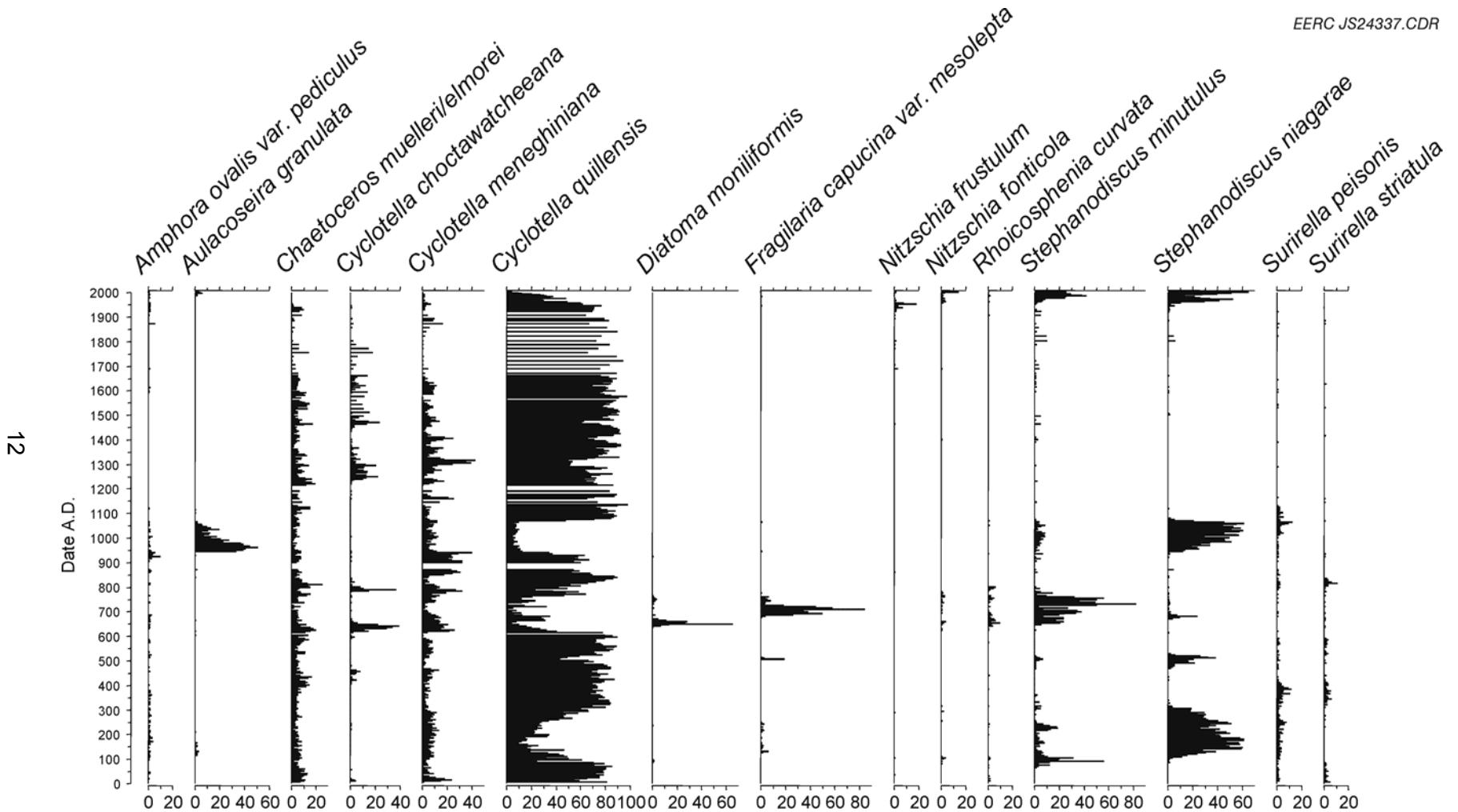


Figure 9. Relative abundance of major diatom taxa.

### 3.3.5 Reconstruction of Lake Salinity Record

Diatom counts were converted into paleosalinity values using a training set of diatoms and limnological variables from 79 northern Great Plains lakes (Fritz, unpublished). Eighteen environmental variables were measured or calculated for each lake (Fritz et al., 1993). A salinity transfer function based on regression techniques applied to the training set diatom and environmental variable data was calculated using a weighted averaging model with inverse deshrinking, and species optima and salinity ranges were determined. An inferred salinity curve was calculated using the fossil diatom counts from the last 2000 years (Figure 10). Detailed methodology is provided in Appendix B.

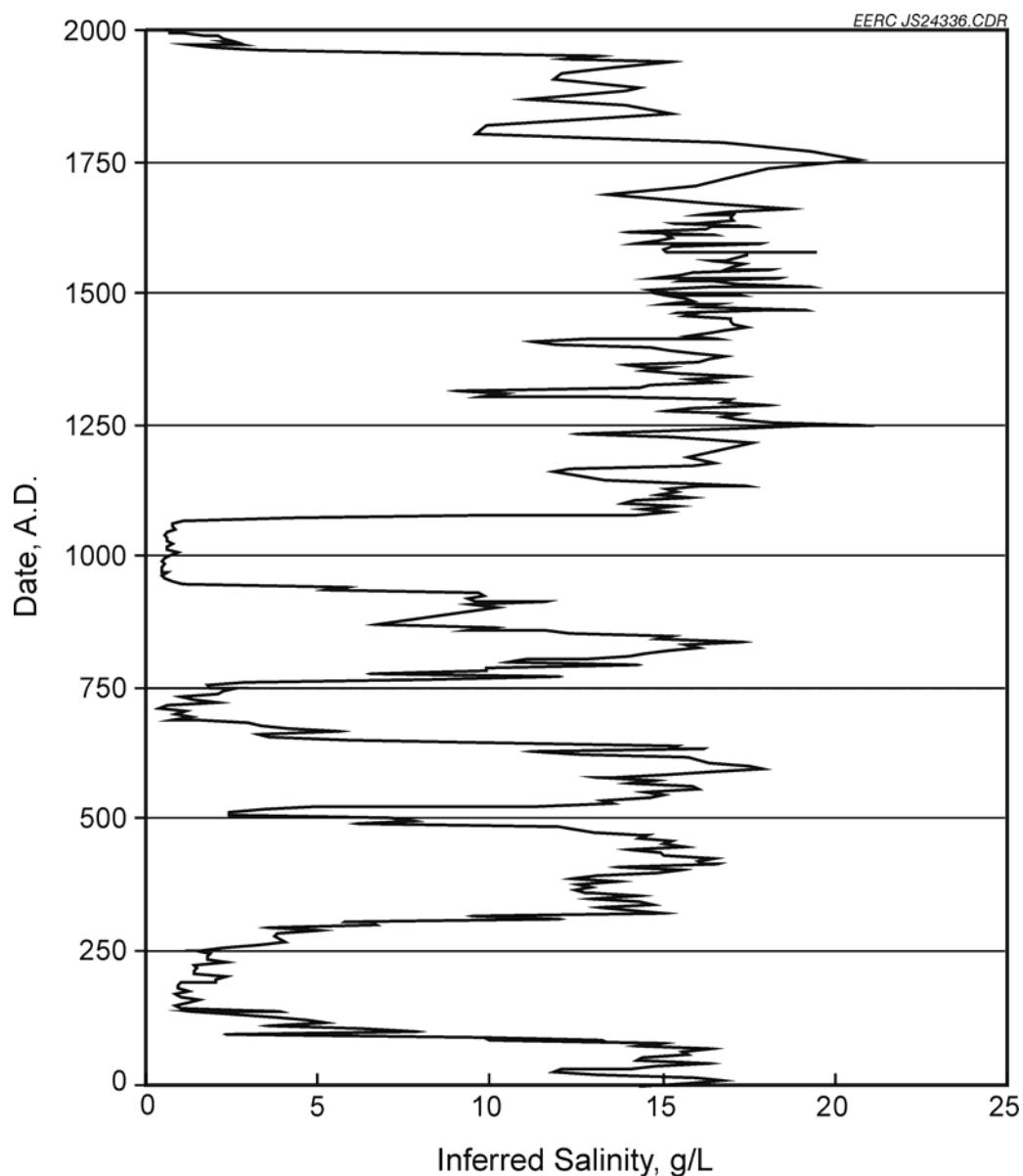


Figure 10. Inferred salinity 0–2000 A.D.

High-resolution diatom-inferred salinity curve for the last 2000 years in Devils Lake depicts a widely varying system, with salinity values ranging from <1 g/L to >20 g/L (Figure 10). The lake is saline for over three-fourths of this record; however, small fluctuations in salinity occur even in the long saline period from 1070 to 1960 A.D. The threshold between fresh and saline lakes has been previously defined as 3 g/L (Williams, 1981). Using this criterion, five fresh periods have occurred in the last 2000 years: 125–255 A.D., 505–510 A.D., 680–760 A.D., 945–1065 A.D. and 1966 A.D.–present. Accounting for entire excursions from high-salinity conditions, the first four fresh periods are centered roughly at 200, 500, 700, and 1000 A.D. Time-series analysis indicates that there may be a 95-year period to shifts in inferred salinity in Devils Lake. Transitions between fresh and saline phases have been relatively fast, occurring in less than 50 years. No abrupt shift in species richness was observed at 3 g/L salinity, nor was there any shift in dominant species, as is found between fresh (<3 g/L) lakes and saline (>3 g/L) lakes in the northern Great Plains (Fritz et al., 1999).

### 3.3.6 Diatom Composition by SEM

A relationship between salinity and diatom species has been determined and salinity reconstructions made based on species and relative abundance of diatoms recovered from the cores in Sections 2.3.4–2.3.5. The objective of scanning electron microscopy (SEM) analyses was to determine if the chemical composition of the diatom valves vary between high (freshwater) and low (more saline) lake level conditions. An additional objective was verification of a possibly faster quantitative method for diatom analyses. Six samples extracted from cores taken from Creel Bay on Devils Lake were analyzed at the EERC (Table 4).

**Table 4. Core Samples for SEM Analysis**

Core	Depth	Estimated Date	Fresh/Saline	Inferred Salinity
DLPA	1321–1323	1997	Fresh	2.4
DLPA	1403–1405	1525	Saline	18
Arch DLB-1	1466–1467	994	Fresh	2.5
Arch DLB-2	1490–1491	819	Saline	14.6
Arch DLA-2	1556–1557	394	Saline	17.2
Arch DLA-2	1588–1589	194	Fresh	8.8

Because of the significant amount of organic material associated with each of the samples, a procedure using hydrogen peroxide ( $H_2O_2$ ) to oxidize any organic matter and small amounts of hydrochloric acid (HCl) to neutralize the  $H_2O_2$  and dissolve any carbonates that may be present was used. Detailed sample preparation is described in Appendix D-1.

Several species of diatoms were found and analyzed. Because of its abundance, *Cyclotella quillensis* (Figures 9 and 11, Appendix D) was selected for detailed analyses of possible trace chemical variances. The objective of this work was not to identify the species, but to take a chemical analysis of the frustules found. It is very likely that some of the analyses are not of *Cyclotella quillensis* but are a species of *Cyclotella*.

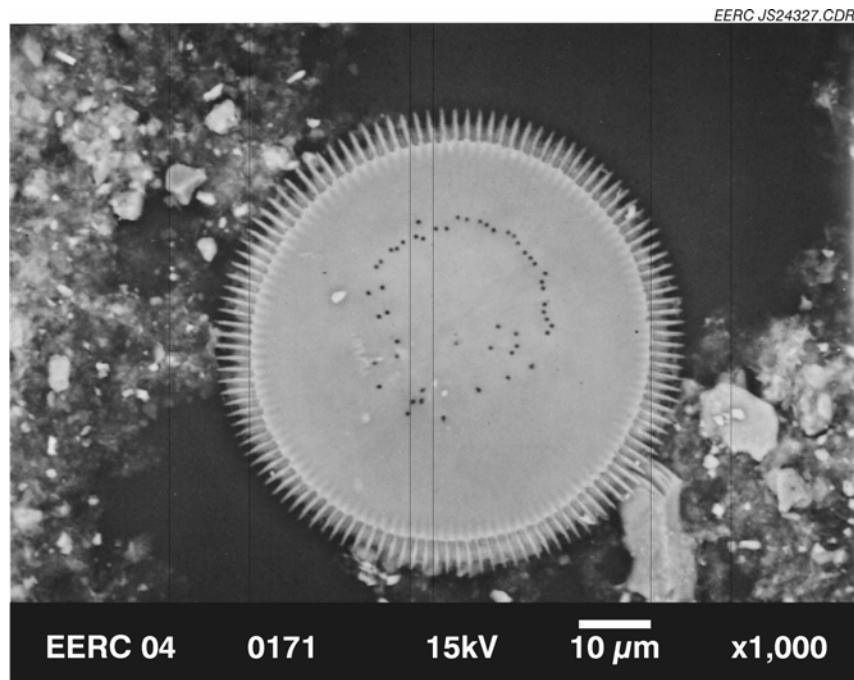


Figure 11. A diatom identified as *Cyclotella quillensis* from Devils Lake core Arch DLA-2 deposited at an estimated date of 394 A.D. when lake conditions were saline.

Examples of chemical analyses for individual diatoms presented in Tables 5 and 6 show a stable chemical composition from both high-water (low-salinity) and low-water (high-salinity) events.

**Table 5. Elemental Analyses for a Sample Representing Low Salinity**

Core DLPA	Depth 1321–1323	Corrected Depth 6 cm	Estimated Date 1997	Fresh/Saline Fresh
Inferred Salinity = 2.4				
	Average	Minimum	Maximum	Std Dev.
Na	0.49	0.00	1.80	0.52
Mg	0.87	0.00	2.45	0.74
Al	3.71	0.00	10.86	2.97
Si	88.02	68.40	98.77	8.61
P	0.34	0.00	1.94	0.50
S	0.12	0.00	1.47	0.29
Cl	0.15	0.00	1.52	0.30
K	1.63	0.00	5.66	1.46
Ca	0.46	0.00	1.63	0.47
Ti	0.27	0.00	1.98	0.46
Cr	0.40	0.00	4.13	0.85
Fe	2.95	0.00	6.88	2.19
Ba	0.59	0.00	5.97	1.23

**Table 6. Elemental Analyses for a Sample Representing High Salinity**

Core DLPA	Depth 1403–1405	Corrected Depth 88 cm	Estimated Date 1525	Fresh/Saline Saline
Inferred Salinity = 18				
	Average	Minimum	Maximum	Std Dev.
Na	0.94	0.00	2.99	0.70
Mg	2.49	0.03	8.87	1.95
Al	3.51	0.00	8.14	2.32
Si	76.57	25.00	98.43	15.70
P	0.26	0.00	1.20	0.39
S	2.38	0.00	37.21	6.64
Cl	0.39	0.00	2.32	0.54
K	1.69	0.00	4.30	1.19
Ca	7.29	0.00	31.61	6.92
Ti	0.19	0.00	1.57	0.42
Cr	0.37	0.00	2.33	0.62
Fe	3.30	0.00	12.48	3.17
Ba	0.62	0.00	3.22	0.82

The greatest variability is with silica, the main element along with oxygen that makes up the frustules. While the standard deviation for individual elements shows variability, they were not consistent between diatoms representing fresh and saline water conditions. The possible exception is Mg, which is consistently higher in the saline samples; the limited number of samples analysed, however, does not allow for evaluation of its statistical significance. The variability of the chemical analyses can be at least partially attributed to submicron particles attached to the surface of the diatom.

The diatoms were abundant and relatively easy to identify from the cores provided. Since this work was to focus mostly on *Cyclotella quillensis* because of its abundance and ability to tolerate a wide variety of salinities, there was a need to manually operate the SEM to find and analyze each individual. An effort to find a method for automated diatom identification and analysis did not yield reliable results because all particles of a certain size (10–50  $\mu\text{m}$ ) were analyzed whether they were of diatomaceous origin or not. Detailed discussion of SEM results including photographic documentation and complete chemical analyses are in Appendix D.

### 3.4 Discussion

#### 3.4.1 Lake Level and Inferred Salinity

A principal assumption for reconstruction of lake history is based on the inverse relationship between water elevation and salinity. The diatom-inferred salinity values correlate well with measured values (Mueller, 2004, Appendix B).

The inferred salinity curve (Figure 10) shows two apparently inconsistent patterns: Devils Lake significantly fluctuated several times before about 1070 A.D. followed by a long period of high salinity between 1070 and 1960 A.D. Although the noted period is saline relative to the entire record, less pronounced fluctuation of salinity is apparent and suggests a prolonged period of dry conditions, with maximum salinity levels in excess of those inferred for the recorded drought in the 1930s. While there is little doubt that salinity fluctuations are associated

with lake level changes, uncertainty persists on the magnitude of this change. In other words, was the lake level low during the saline period noted or could high lake levels also be associated with relatively high salinity?

Our reconstruction agrees relatively well with other reconstructions for the period from 0 to 1070 A.D., and we can infer that salinity and lake level had an inverse relationship for that period. From 1070–1960 A.D., fresh periods recorded in other records show as minor freshening events in our record (Murphy et al., 1997; Haskell et al., 1996). A disparity between sedimentary and salinity records may indicate that Devils Lake was a large saline lake after 1070 A.D. and two cooler, wetter phases were unable to trigger freshening sufficient to reverse lake salinity trend. In the late 1800s to early 1900s, the lake level dropped, and Devils Lake became a small saline lake until the lake level increase observed in recent decades.

The relatively fast transitions in salinity indicate that the lake is unresponsive to climate changes up to a certain threshold, after which it changes rapidly. This may be due to the multibasin nature of the system – as one basin reaches a physical threshold of lake level, it quickly overflows into another basin, creating a rapid freshening. As a basin becomes disconnected from the rest of the lake, evaporation associated with salinity increase exceeds input of fresh water. This interbasin flow offers a partial explanation for poor correlation between the lake elevation and precipitation within the Devils Lake Watershed conducted in initial stages of this project.

### ***3.4.2 Comparison to Other Systems***

Similar shifts in diatom-inferred salinity and ostracode shell magnesium:calcium ratios that are indicative of climate changes in the northern Great Plains were derived for Coldwater Lake, Moon Lake, and Rice Lake, North Dakota (Fritz et al., 2000), and Waubay Lake, South Dakota (Shapley et al., in press). Devils Lake records the same regional climate changes, but its response to climate change is unique in this group (Figure 12). The lake-specific characteristics and hydrology determine the differences in the sedimentary record: the small lakes are more sensitive to minor climate fluctuations.

All these records indicate a shift in climate conditions between the period of 0–1070 A.D. and the period of 1070 A.D. to present. This shift in climate conditions may have created the conditions that made it possible for Devils Lake to become large and saline. Wet and dry conditions recur at intervals ranging between 100 and 300 years, or at about a 150-year average recurrence interval. Wiche and others (1996) suggest that droughts and floods over the most recent 500 years occurred on an even more frequent basis.

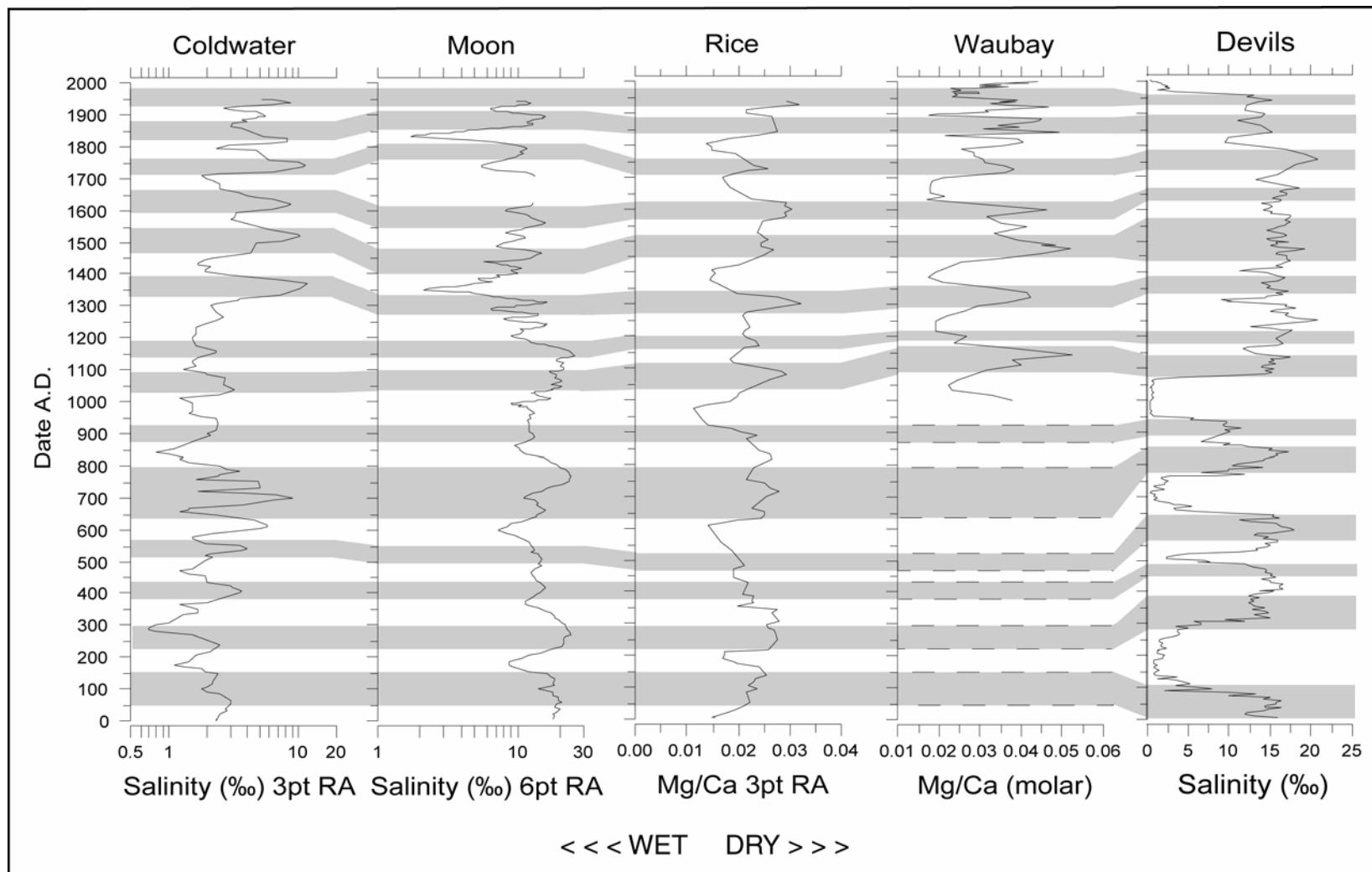


Figure 12. Regional records of climate change (project data integrated with data from Fritz et al., 2000, and Shapley et al., *in press*).

### 3.5 Socioeconomic Implications

Climate changes, duration of extremes, and transition between wet and dry periods control the distribution and availability of water resources and, in wider terms, economic and demographic sustainability. The Red River Watershed, the only watershed in United States draining to the north, sustained vast damage during the flood of 1997. In spite of the devastating effect of recurring floods, however, it is severity and duration of droughts that will have a more pronounced impact on the long-term socioeconomic development of the region regardless of its watershed boundaries.

The energy industry and agriculture are primary water users in United States, in North Dakota using 902 million gallons and 145 million gallons per day in 2000, respectively. Water usage in the energy sector, concentrated in western North Dakota, rose by only 2.5% between 1995 and 2000; for the same period, a 24% increase is reported for agriculture (USGS, 2000). While energy use is covered almost entirely by surface water, about 50% of water for irrigation comes from groundwater, a resource requiring a long period of wet conditions for replenished.

Population in North Dakota and western Minnesota remains relatively stable or exhibits a slow decline; population centers in eastern North Dakota, most notably Fargo and West Fargo, recorded substantial growth associated with increased demand for water supplies for municipal, industrial, and agriculture purposes (Figure 13). Raw water demand for the Red River Valley was estimated at 38.8 million m<sup>3</sup> (10.2 billion gallons) in 1994; water need projections for 2050 by the Bureau of Reclamation (USDI, 2000) ask for 105.4 million m<sup>3</sup>, i.e. (2.7 times more).

Groundwater resources were extensively used during 1930 to partially offset water shortage. With respect to noted economic and demographic growth, using the most populated area of Fargo as an example, this option becomes increasingly limited. For example, the water level in the originally confined Moorhead Aquifer dropped from 2 m (6 ft) below ground in 1913 to 58 m (190 ft) in 1948, and continuing withdrawals combined with water-table decline in larger areas do not allow for aquifer replenishment.

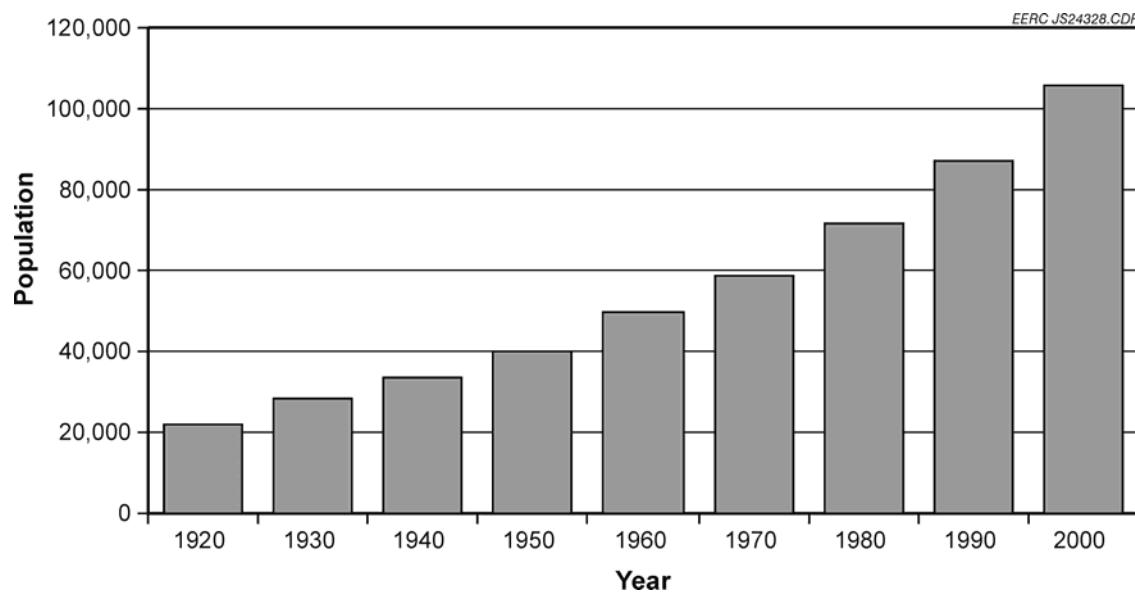


Figure 13. Population trend for Fargo and West Fargo combined.

The water levels in individual Aquifers of the West Fargo Aquifer system were close to or, locally, even above the ground surface in the early 1900s (Armstrong, 1985) and have declined dramatically since. Data on hydrology for the aquifers in the Fargo area provide evidence on continuous water-table decline in aquifers of up to 0.7 m (2.3 ft) per year during last 15 years (West Fargo South Aquifer, Ripley, 2000). Aside from reducing amounts of water in storage, water-table decline and the loss of aquifer pressure result in deterioration of water quality and, potentially, even irreversible changes to aquifer structural integrity. This trend is even more alarming with respect to the fact that the regional hydrologic system, as documented in our study, is currently at its wet stage and the aquifer usage will considerably increase once the system moves to the dry cycle.

High water demand in the primary economic sectors makes the regional economy extremely sensitive to climatic extremes. Without conservation-based water management policies, long-term periods of drought will limit socioeconomic development in the region and may threaten even sustainability of current conditions.

#### 4.0 CONCLUSIONS

Evaluation of current precipitation trends and high-resolution reconstruction of paleoclimatic conditions based on diatom-inferred salinity have been conducted in our project. Devils Lake has experienced five fresh periods and two minor freshening periods in the last 2000 years. Transitions between fresh and saline periods have been relatively fast, representing lake level changes that have been similar to those observed in the last 150 years. From 0 to 1070 A.D., Devils Lake showed more variable behavior, with fresh phases centered at 200, 500, 700, and 1000 A.D. From 1070 A.D. to present, Devils Lake was generally saline, experiencing two minor freshening periods at 1305–1315 and 1800–1820 A.D and the major current freshening from 1960 A.D. to present.

The results indicate that frequent climatic fluctuations resulting in alternating periods of drought and wet conditions are typical for the northern Great Plains and suggest that the severity and length of extremes exceeded those on modern record. Based on reconstruction of paleoclimatic conditions for the region, wet and dry conditions recur at intervals ranging between 100 and 300 years (with shorter reoccurrence intervals documented for smaller lakes), or at about a 150-year average recurrence interval. The hydrologic system is currently in the wet cycle.

Climate changes, duration of extremes, and transition between wet and dry periods control the distribution and availability of water resources and, in wider terms, economic and demographic sustainability. High water demand in the primary economic sectors in the region makes the regional economy extremely vulnerable to climatic extremes.

#### 5.0 REFERENCES

Armstrong, C.A., 1985, Hydrologic Effects of Withdrawal of Ground Water on the West Fargo Aquifer System, Eastern Cass County, North Dakota, USGS Water Resources Investigation Report 83-4279, Bismarck.

Callender, E., 1968, The Postglacial Sedimentology of Devils Lake, North Dakota. Unpublished Ph.D. dissertation, University of North Dakota.

Engstrom, D.R., Swain, E.B., Henning, T.A., Bingham, M.E., and Brezonik, P.L., 1994, Atmospheric mercury deposition to lakes and watersheds, a quantitative reconstruction from multiple sediment cores, *in* Baker, L.A., ed., Environmental chemistry of lakes and reservoirs: Washington D.C., American Chemical Society, p. 33.

Engstrom, D.R., and Nelson, S.R., 1991, Paleosalinity from trace metals in fossil ostracodes compared with observational records at Devils Lake, North Dakota, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology* 83: 295-312.

Fritz, S.C., 1990, Twentieth-century salinity and water-level fluctuations in Devils Lake, North Dakota: Test of a diatom-based transfer function. *Limnology & Oceanography* 35(8): 1771-1781.

Fritz, S.C., Juggins, S., Battarbee, R.W., and Engstrom, D.R., 1991, Reconstruction of past changes in salinity and climate using a diatom-based transfer function. *Nature* 352: 706-708.

Fritz, S.C., Juggins, S., and Battarbee, R.W., 1993, Diatom assemblages and ionic characterization of lakes of the Northern Great Plains, North America: A tool for reconstructing past salinity and climate fluctuations. *Canadian Journal of Fisheries and Aquatic Sciences* 50: 1844-1856.

Fritz, S.C., Engstrom, D.R., and Haskell, B.J., 1994, 'Little Ice Age' aridity in the North American Great Plains: a high-resolution reconstruction of salinity fluctuations from Devils Lake, North Dakota, U.S.A. *The Holocene* 4(1): 69-73.

Fritz, S.C., Engstrom, D.R., and Haskell, B.J., 1996, Nineteenth-century climate in the Devils Lake region as reconstructed from paleolimnological proxies: a reply to Wiche, Lent and Rannie. *The Holocene* 6: 490-493.

Fritz, S.C., Cumming, B.F. Gasse, F., and Laird, K., 1999, Diatoms as indicators of hydrologic and climatic change in saline lakes. In E.F. Stoermer & J.P. Smol (eds.), *The Diatoms: Applications for the Environmental and Earth Sciences*. Cambridge University Press, Cambridge & New York: 41-72.

Fritz, S.C., Ito, E., Yu, Z., Laird, K.R., and Engstrom, D.R., 2000, Hydrologic variation in the Northern Great Plains during the last two millennia. *Quaternary Research* 53:175-184.

Haskell, B.J., Engstrom, D.R., and Fritz, S.C., 1996, Late Quaternary paleohydrology in the North American Great Plains inferred from the geochemistry of endogenic carbonate and fossil ostracodes from Devils Lake, North Dakota, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology* 124: 179-193.

Hinckley, D., 1995, Great Plains climates and biota: past, present, and future. In Stanley R. Johnson & Aziz Bouzaher (eds.), *Conservation of Great Plains Ecosystems*. Kluwer Academic Publishers: 149-159.

Jacobson, H.A., and Engstrom, D.R., 1989, Resolving the chronology of recent lake sediments: an example from Devils Lake, North Dakota. *Journal of Paleolimnology* 2: 81-97.

Juggins, S., 2003, C2 Data Analysis, Version 1.3. Software for ecological and palaeoecological data analysis and visualisation. University of Newcastle, Newcastle upon Tyne, UK.

Lent, R.M., and Alexander, C.R., 1997, Mercury accumulation in Devils Lake, North Dakota—effects of environmental variation in closed-basin lakes on mercury chronologies: Water, Air, and Soil Pollution, v. 98, p. 275-296.

Murphy, E.C., Fritz, A.M.K., and Fleming, R.F., 1997 (revised 2002), *The Jerusalem and Tolna Outlets in the Devils Lake Basin, North Dakota*. Report of Investigation Number 100. North Dakota Geological Survey.

Mueller S.B., 2004, A two Thousand Year Diatom-Inferred Salinity Record from Devils Lake, North Dakota. A thesis, University of Minnesota.

Population of ND's top 20 Cities: [www.business.und.edu/bber](http://www.business.und.edu/bber)

Pusc, S.W., 1993, The interaction between ground water and a large terminal lake – Devils Lake, North Dakota: Hydrogeology of the Devils Lake area. North Dakota State Water Commission Water Resources Investigation 13.

Ripley, D.P., 2000, The Water Resource Characteristics of the West Fargo Aquifer System, ND Ground-Water Studies No. 106, Part II. NDSWC, Bismarck.

Shapley, M.D., Johnson, W.C., Engstrom, D.R., and Osterkamp, W.R. Late Holocene flooding and drought in the Northern Great Plains, reconstructed from tree rings, lake sediments and ancient shorelines. *The Holocene: In press.*

Swain, E.B., Engstrom, D.R., Brigham, M.E., Henning, T.A., and Brezonik, P.L., 1992, Increasing rates of atmospheric mercury deposition in midcontinental North America: *Science*, no. 257, p. 784–787.

Timpe, R.C., and Aulich T.R., 2001, Aulich Economic Source-Sited Long-Term Carbon Dioxide Sequestration. EERC Final Report.

USDI, Bureau of Reclamation, 2000, Red River Valley Water Needs Assessment, Phase II: Appraisal of Alternatives to Meet Projected Shortages.

USGS, 2004, Period of Record for Station 05056500 Devils Lake near Devils Lake, North Dakota. <http://nd.water.usgs.gov/devilstake/dvlakepor.html>.

USGS, Estimated Use of Water in United States in 1995. [www.water.usgs.gov/watuse/pdf1995](http://www.water.usgs.gov/watuse/pdf1995)

USGS, Estimated Use of Water in United States in 2000, (Draft) [www.water.usgs.gov/pubs/circ/2004/circ1268](http://www.water.usgs.gov/pubs/circ/2004/circ1268).

Wiche, G.J., 1992, Hydrology and water-level fluctuations of Devils Lake, North Dakota. In S. Subitzky (ed.), *Selected papers in the hydrologic sciences, 1988-1992*. U.S. Geological Survey Water-Supply Paper, W 2340: 75-87.

Wiche, G.J., 1994, Hydrology of Devils Lake Area, North Dakota, NDSWC Water Resources Investigation 22, Bismarck, North Dakota.

Wiche, G.J., Lent, R.M., and Rannie, W.F., 1996, 'Little Ice Age' aridity in the North American Great Plains – a high-resolution reconstruction of salinity fluctuations from Devils Lake, North Dakota, USA: a comment on Fritz, Engstrom and Haskell. *The Holocene* 6: 489-490.

Wiche, G.J., and Vecchia, A.V., 1996, Lake-level frequency analysis for Devils Lake, North Dakota. U.S. Geological Survey Water-Supply Paper 2469.

Williams, W.D., 1981, Inland salt lakes: an introduction. *Hydrobiologia* 81: 1-14.

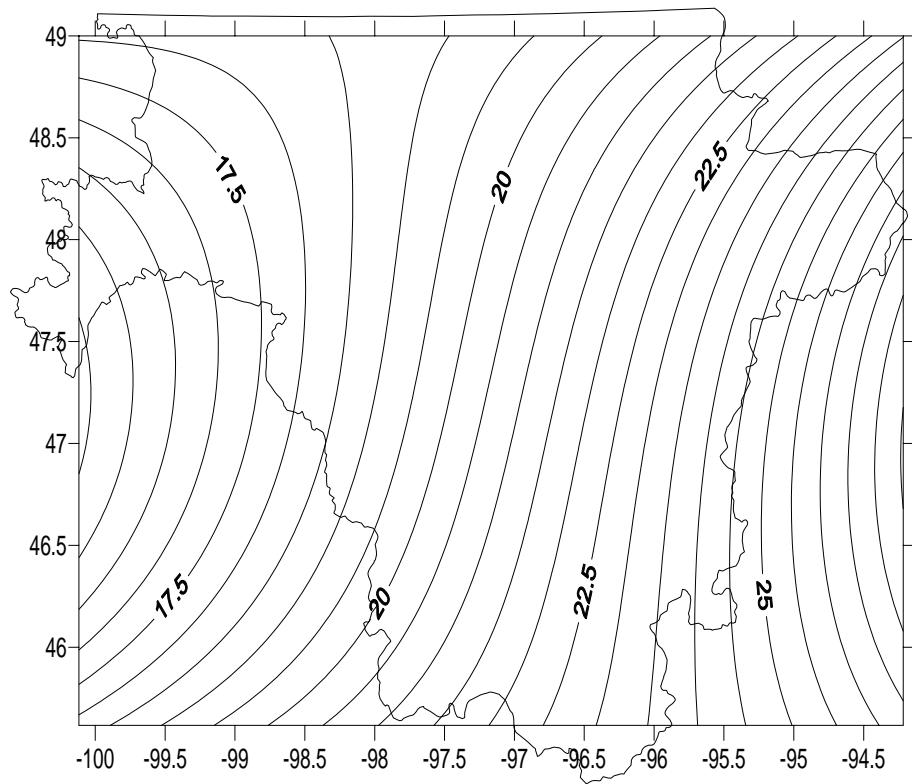
# **APPENDIX A**

## **PRECIPITATION SUMMARIES**

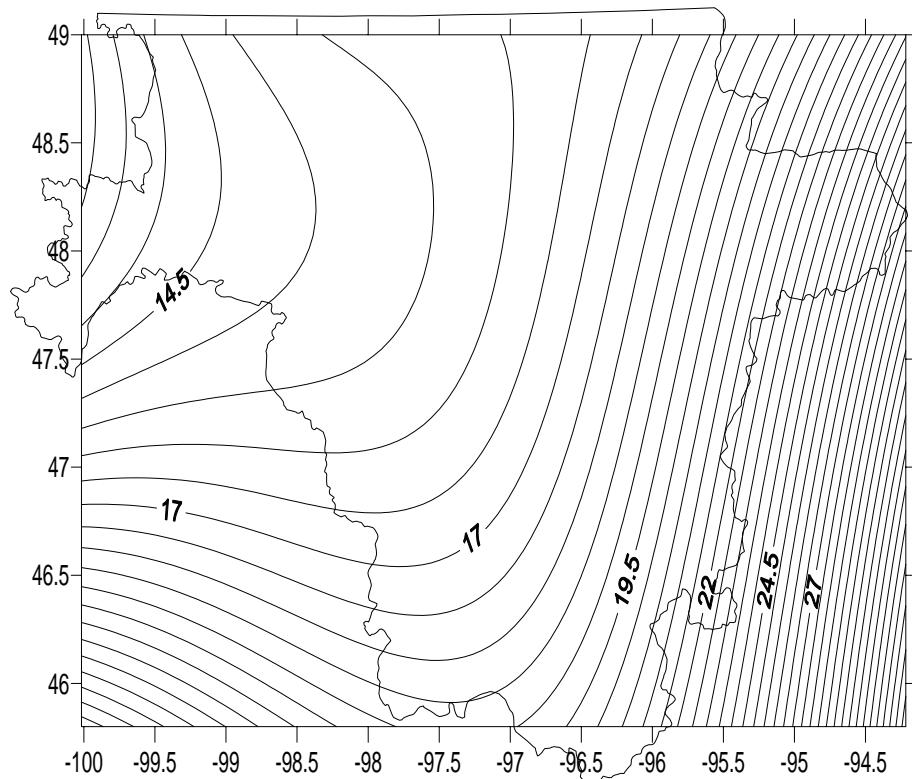
**APPENDIX A-1**

**CONTOUR MAPS**

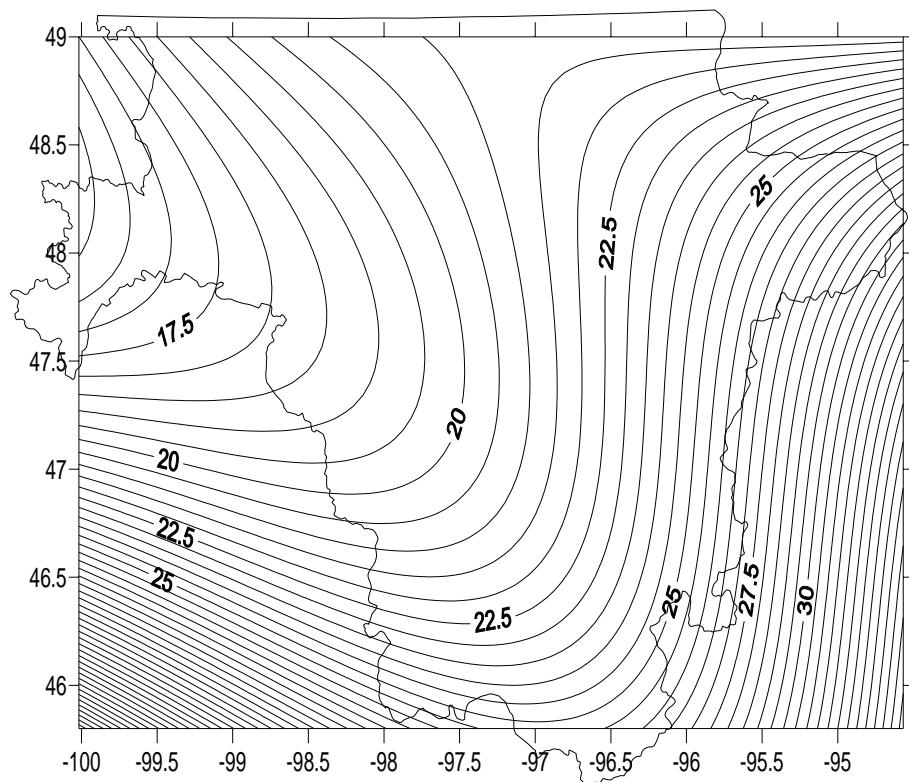
Average precipitation for all years



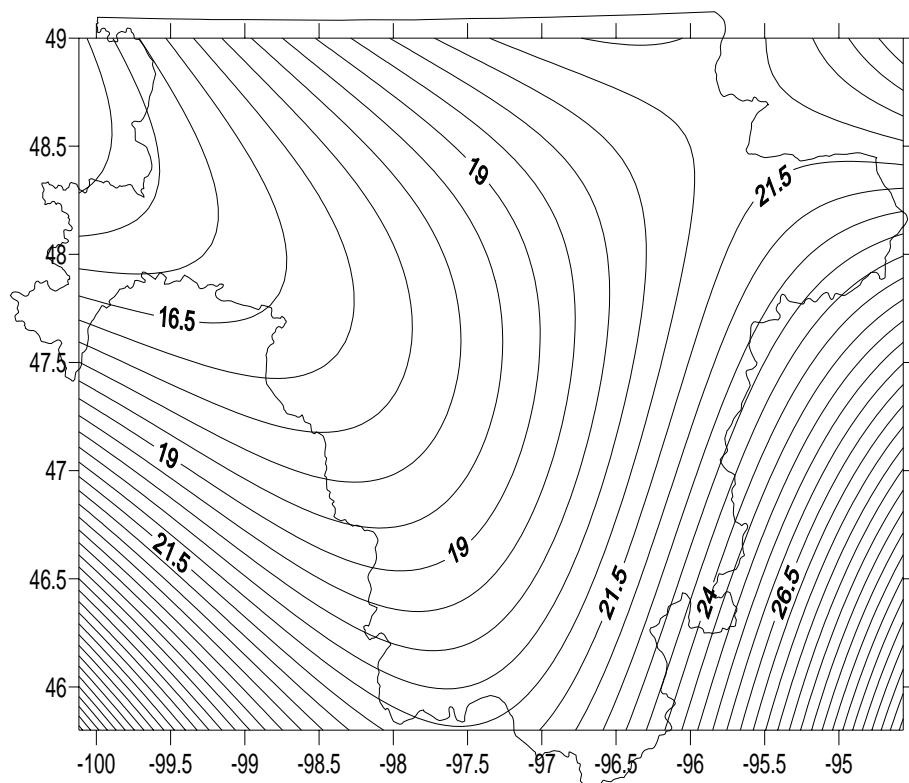
Average Annual Precipitation 1930-1939



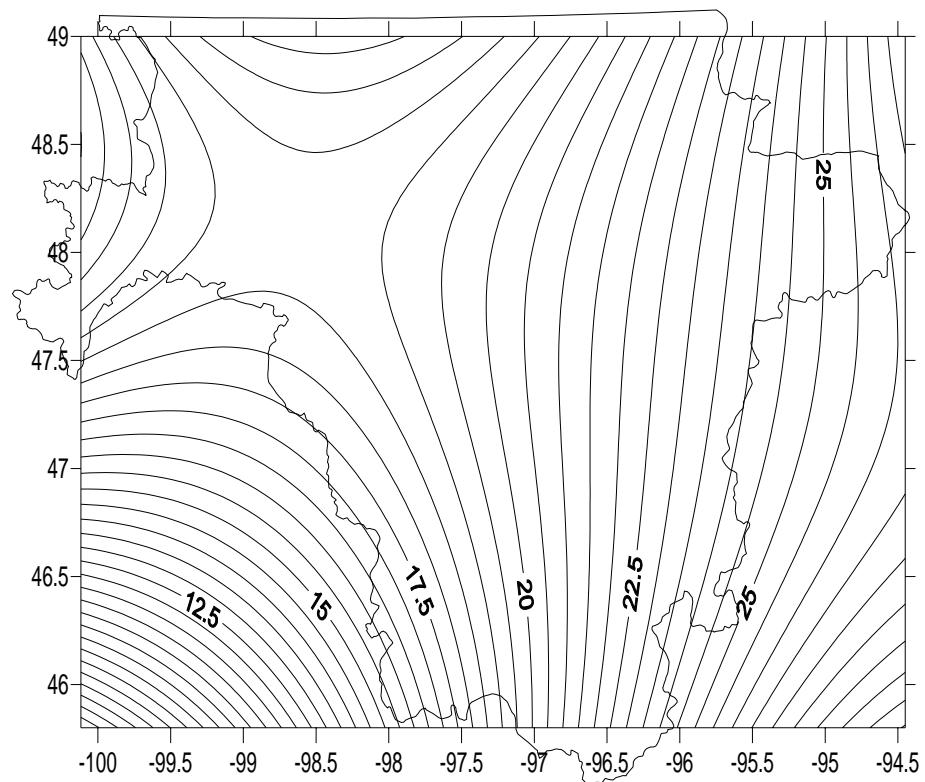
Average Annual Precipitation 1940-1949



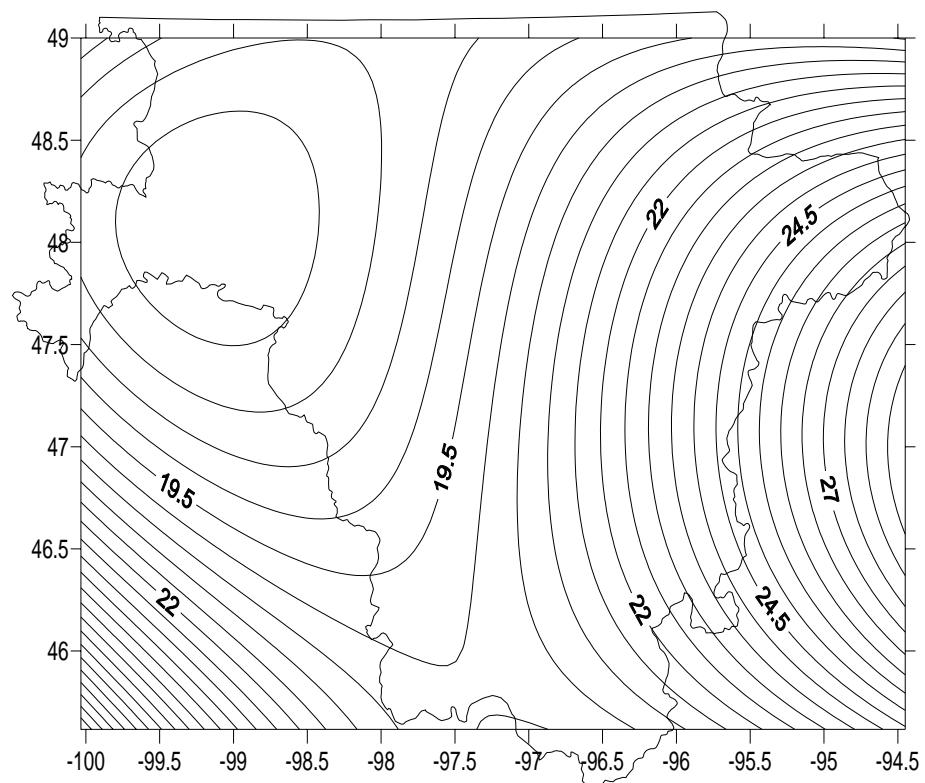
Average Annual Precipitation 1950-1959



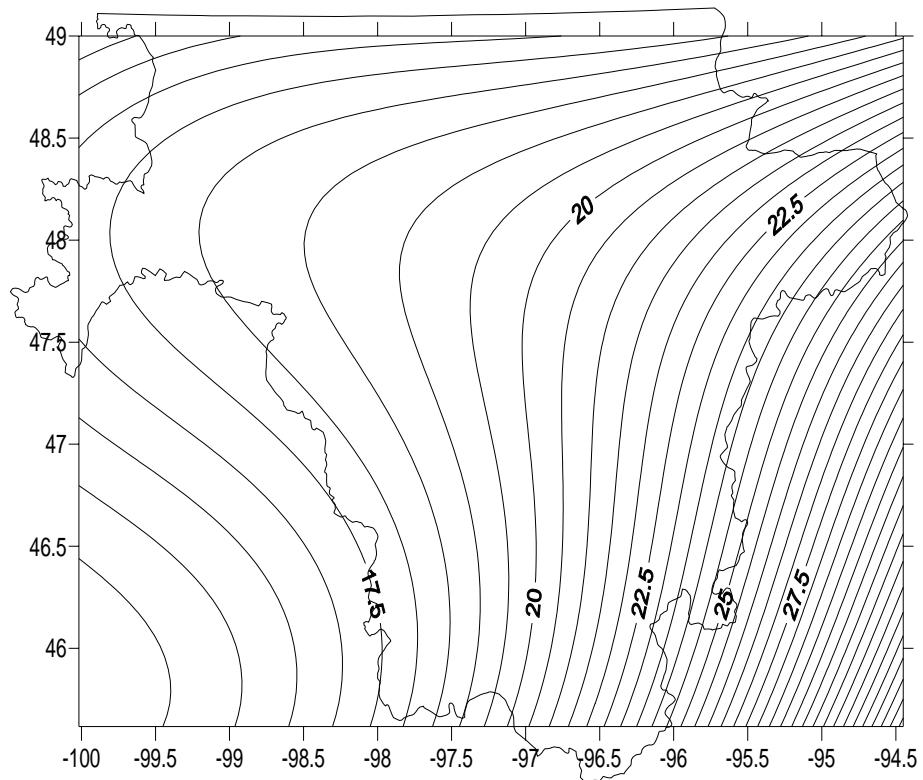
Average Annual Precipitation 1960-1969



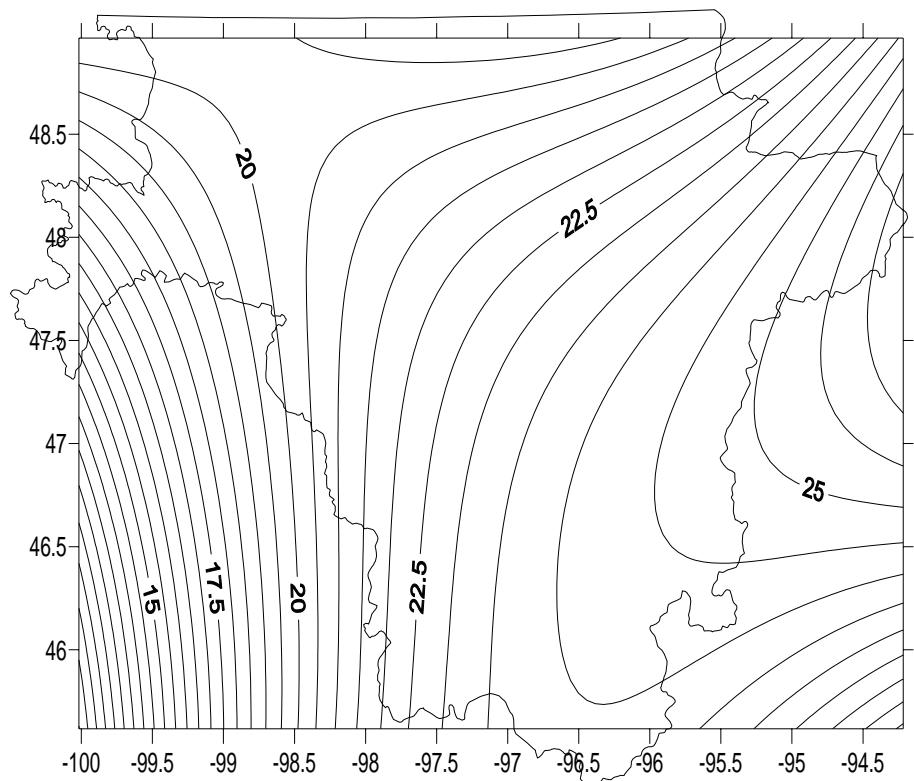
Average Annual Precipitation 1970-1979



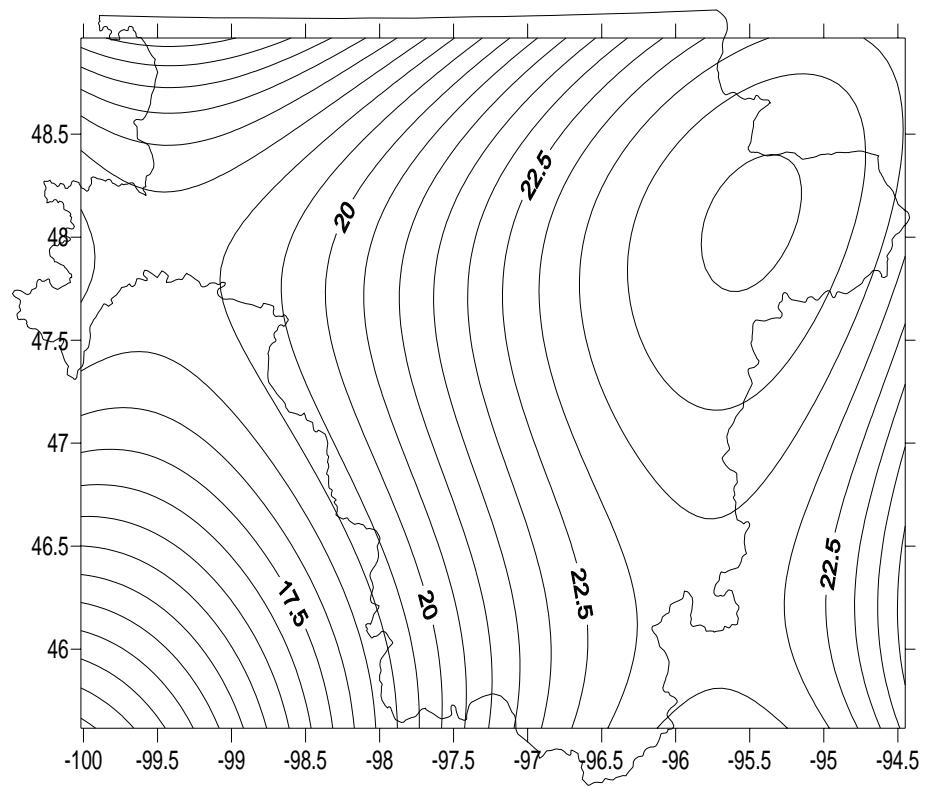
Average Annual Precipitation 1980-1989



Average Annual Precipitation 1990-1999



Average Annual Precipitation 2000-2003



**APPENDIX A-2**

**PRECIPITATION DATABASE**



NUMBER	LOCATION	STATE	Latitude (deg)	Longitude (deg)	Avg precip for all yrs	Avg1900-1909	Avg1910-1919	Avg1920-1929	Avg1930-1939	Avg1940-1949	Avg1950-1959	Avg1960-1969	Avg1970-1979	Avg1980-1989	Avg1990-1999	Avg2000-2003	
215589	MOORHEAD ST TEACHERS	MN	46.87	-96.75	18.15				15.41	21.47	16.29						
215902	NEW YORK MILLS	MN	46.52	-95.38	24.82										24.34	25.55	
216148	OKLEE	MN	47.83	-95.85	22.78					28.63	21.7	22.76	23.78	21.84	23.4		
216228	ORWELL DAM	MN	46.20	-96.17	21.79										21.7	22.01	
216405	PELICAN RAPIDS	MN	46.57	-96.08	24.04						24.78	24.04	22.54	22.18	25.9	24.58	
216787	RED LAKE FALLS	MN	47.90	-96.27	22.12				17.32	24.9	19.81	22.41	21.6	23.56	22.94	25.07	
216795	RED LAKE IND AGENCY	MN	47.87	-95.03	22.82	26.13	21.97	21.02	22.51	23.94	21.96	22.62	23.4	23.29	22.49	27.13	
217087	ROSEAU 1E	MN	48.85	-95.73	20.34				17.93	21	20.45	21.46	20.27	20.46	20.38	22.93	
217149	ROTHSAY	MN	46.48	-96.27	23.26							24.53	23.2	22.8	23.34	20.92	
217594	SHELLY 4SE	MN	47.42	-96.77	24.54										24.54		
218191	TAMARAC WILDLIFE REF	MN	46.97	-95.65	23.56									23.43	23.14	25.32	18.62
218235	THIEF LAKE REF	MN	48.48	-95.95	24.81						24.81						
218243	THIEF RIVER FALLS AP	MN	48.07	-96.18	23.07								22.96	20.37	23.4		
218247	THIEF RIVER FALLS 2	MN	48.18	-96.17	22.37				17.76	21.56	19.83	25.77	28.49				
218254	THORHULT 1S	MN	48.23	-95.25	23.98					26.99	22.71	24.18	25.35	20.92	26.95	23.91	
218332	TRAIL 11N	MN	47.95	-95.65	22.22						21.32			25.36			
218411	TWIN VALLEY 3SW	MN	47.23	-96.28	22.71				24.54	20.51							
218656	WANNASKA 1S	MN	48.65	-95.75	22.94						26.31	22.67	19.35				
218700	WASKISH 4NE	MN	48.17	-94.52	24.69						26.34	23.46	24.25	25.32	24.28		
218907	WHEATON	MN	45.80	-96.48	22.37				20.39	25.53	20.28	22.81	20.46	21.5	25.06	22.29	
218947	WHITE ROCK DAM	MN	45.90	-96.57	21.14						26.25					18.59	
320005	ABERCROMBIE	ND	46.45	-96.73	20.93						23.65	21.64	20.37	20.08	19.15		
320022	ADAMS 7 SSW	ND	48.33	-98.12	18.38					18.67	17.5	17.63	18.18	17.82	19.99	20.06	
320196	AMENIA	ND	47.00	-97.22	19.47				16.32		19.37	20.58	20.98				
320369	ARVILLA STATE PARK	ND	47.93	-97.50	19.32					18.29	18.6	21.57					
320450	BALDHILL DAM	ND	47.03	-98.08	14.95						14.95						
320500	BALTA	ND	48.17	-100.03	16.79						16.66	16.81	16.94				
320796	BISBEE 6 NE	ND	48.62	-99.37	18.09				11.87	18.93	16.93	18.87	20.04				
321288	CANDO 2E	ND	48.50	-99.20	17.54						9.29			17.08	19.38	15.15	
321400	CASSELTON	ND	46.90	-97.22	21.73				21.73								
321408	CASSELTON AGRONOMY F	ND	46.88	-97.23	23.45									20.14	24.49	25.83	

321435	CAVALIER 7NW	ND	48.80	-97.63	19.1				16.22	21.7	21.35	19.13	18.56	16.99	19.04	19.57	
321477	CHAFFEE 5 NE	ND	46.80	-97.27	20.23							19.22	19.83	18.01	22.45	23.04	
321500	CHURCHS FERRY 5 NW	ND	48.33	-99.25	20.21										20.21		
NUMBER	LOCATION	STATE	Latitude (deg)	Longitude (deg)	Avg precip for all yrs	Avg1900-1909	Avg1910-1919	Avg1920-1929	Avg1930-1939	Avg1940-1949	Avg1950-1959	Avg1960-1969	Avg1970-1979	Avg1980-1989	Avg1990-1999	Avg2000-2003	
321686	COLGATE	ND	47.23	-97.65	18.17					18.47	16.33	19.12	17.62	16.76	20.16	19.81	
321766	COOPERSTOWN	ND	47.45	-98.12	19.56				16.02	20.1	18.13	20.67	19.33	19.49	22.08	20.52	
321816	COURTENAY 1NW	ND	47.22	-98.57	18.22				15.53	18.37	18.43	18.68	19.51	17.44	19.21	17.76	
322158	DEVILS LAKE KDLR	ND	48.12	-98.87	18.06					17.04	16.16	16.3	19.9	20.52	19.24		
322312	DRAYTON	ND	48.58	-97.18	19.21						18.72	17.85	18.43	21.84			
322525	EDMORE 1 NW	ND	48.42	-98.47	17.2			15.04	18.32	16.82	15.99	17.01	16.27	19.82	20.2		
322695	ENDERLIN 2W	ND	46.62	-97.60	20.93					21.39	21.08	21.39	18.5	22.95	19.41		
322697	ENDERLIN 1E	ND	46.62	-97.57	13.89								13.89				
322767	ESMOND	ND	48.03	-99.77	11.95					11.95							
322859	FARGO HECTOR FIELD	ND	46.90	-96.80	20.25					19.29	18.82	19.18	20.99	18.44	22.31	24.56	
323117	FORMAN 5 SSE	ND	46.10	-97.65	20.34				17.27	22.19	20.03	21.35	18.99	19.06	23.09	20.94	
323594	GRAFTON	ND	48.42	-97.42	18.74				16.38	21.83	19.2	18.6	17.21	18.6	18.68	20.94	
323616	GRAND FORKS INTL AP	ND	47.95	-97.18	19.43					20.88	18.44	18.53	18.3	18.37	21.47	21.46	
323621	GRAND FORKS UNIV	ND	47.92	-97.08	20.05				17.54	22.47	20.13	20.76	18.31	18.59	21.12	23.92	
323908	HANKINSON	ND	46.07	-96.90	20.69				18.14	20.18	20.78	21.29	20.45	22.77	22.37		
323936	HANNAH 2 N	ND	49.00	-98.68	17.58				14.45	22.3	17.92	17.3	17.49	15.76			
323963	HANSBORO 4NNE	ND	48.95	-99.38	16.95				16.1	16.16	14.93	16.27	18.77	16.45	20.4	15.51	
324013	HARVEY	ND	47.70	-100.02	16.31				14.17	16.29	17.87	18.2	18.08	15.35	13.61	19.7	
324203	HILLSBORO 3N	ND	47.40	-97.07	20.34				17.64	22.21	20.05	20.4	19.48	18.7	22.19	29.04	
324958	LANGDON EXPERIMENT F	ND	48.75	-98.33	18.28				15.49	19.65	20.35	18.66	17.38	16.56	20.21	16.72	
325013	LARIMORE	ND	47.90	-97.63	19.17				16.2	18.66	19.2	19.43	19.77	15.93	21.67	21.15	
325078	LEEDS	ND	48.28	-99.43	17.74					16.5	17.73	17.34	16.93	17.27	19.94	19.75	
325186	LIDGERWOOD 1SSW	ND	46.07	-97.17	20.77								18.96	19.21	23.37	19.95	
325220	LISBON	ND	46.43	-97.67	20.06			18.52	20.88	20.41	20.68	20.41	17.39	23.31	18.78		
325230	LITCHVILLE 2NW	ND	46.65	-98.18	20.10					17.8	20.39	19.45	20.52	22.3	19.2		
325434	MADDOCK	ND	47.97	-99.50	17.10				14.54	17.03	17.83	16.6	18.37	17.27	19.53		
325610	MARTIN	ND	47.83	-100.12	15.40					15.4							
325660	MAYVILLE	ND	47.50	-97.32	19.26				15.68	20.48	17.84	19.17	20.43	21.34		27.21	
325730	MC HENRY 3W	ND	47.58	-98.60	18.65				14.15	19.15	16.33	18.01	17.91	19.67	21.38	20.86	
325754	MC LEOD 3 E	ND	46.40	-97.23	19.67				17.76	20.67	18.96	19.53	19.33	19.22	22.14	19.47	
325764	MC VILLE	ND	47.77	-98.17	19.03					19.23	17.12	19.92	18.3	17.93	23.52		

NUMBER	LOCATION	STATE	Latitude (deg)	Longitude (deg)	Avg precip for all yrs	Avg1900-1909	Avg1910-1919	Avg1920-1929	Avg1930-1939	Avg1940-1949	Avg1950-1959	Avg1960-1969	Avg1970-1979	Avg1980-1989	Avg1990-1999	Avg2000-2003
325848	MINNEWAUKAN	ND	48.07	-99.25	19.44										19.86	18.71
325933	MILNOR	ND	46.27	-97.47	29.14					29.14						
326195	MUNICH 1 SSW	ND	48.60	-98.88	16.72					16.64	17.52	16.81	15.15	17.97		
326857	PARK RIVER	ND	48.38	-97.75	18.33				14.59	18.85	18.29	17.65	19.33	20.39	19.92	
326947	PEMBINA	ND	48.95	-97.25	18.69				15.52	21.21	18.71	18.11	18.57	16.68	20.31	22.51
327027	PETERSBURG 2 N	ND	48.03	-98.00	18.26				14.42	18.9	17.19	17.35	19.07	20.21	19.87	19.03
327664	ROLLA 3 NW	ND	48.90	-99.67	18.31				13.8	20.08	18.75	17.2	18.29	17.34	19.66	16.96
327986	SHARON	ND	47.60	-97.90	20.10				17.1	21.21	18.47	20.12	21.16	21.4	21.52	15.59
328057	SHEYENNE	ND	47.83	-99.12	17.23							18.71	16.1	19.23		
328937	VALLEY CITY 3 NNW	ND	46.92	-98.00	18.80				15.77	20.33	17.92	20.25	17.48	17.67	21.31	19.9
	WAHPETON POWER															
329095	PLANT	ND	46.28	-96.60	24.37					24.37						
329100	WAHPETON 3 N	ND	46.27	-96.60	21.41				18.45	21.72	21.14	23.06	21.08	21.49	22.76	
329155	WALHALLA 1 SW	ND	48.92	-97.92	20.05				19.59	20.17	19.31	21.14	18.86	21.52		
329185	WARWICK	ND	47.85	-98.70	17.41					18.53	17.5	15.5	21.16			

## **APPENDIX B**

# **A HIGH-RESOLUTION RECORD OF LATE HOLOCENE CLIMATE AND HYDROLOGIC CHANGE FROM DEVILS LAKE, NORTH DAKOTA, TEXT OF THESIS BY SARA MUELLER**

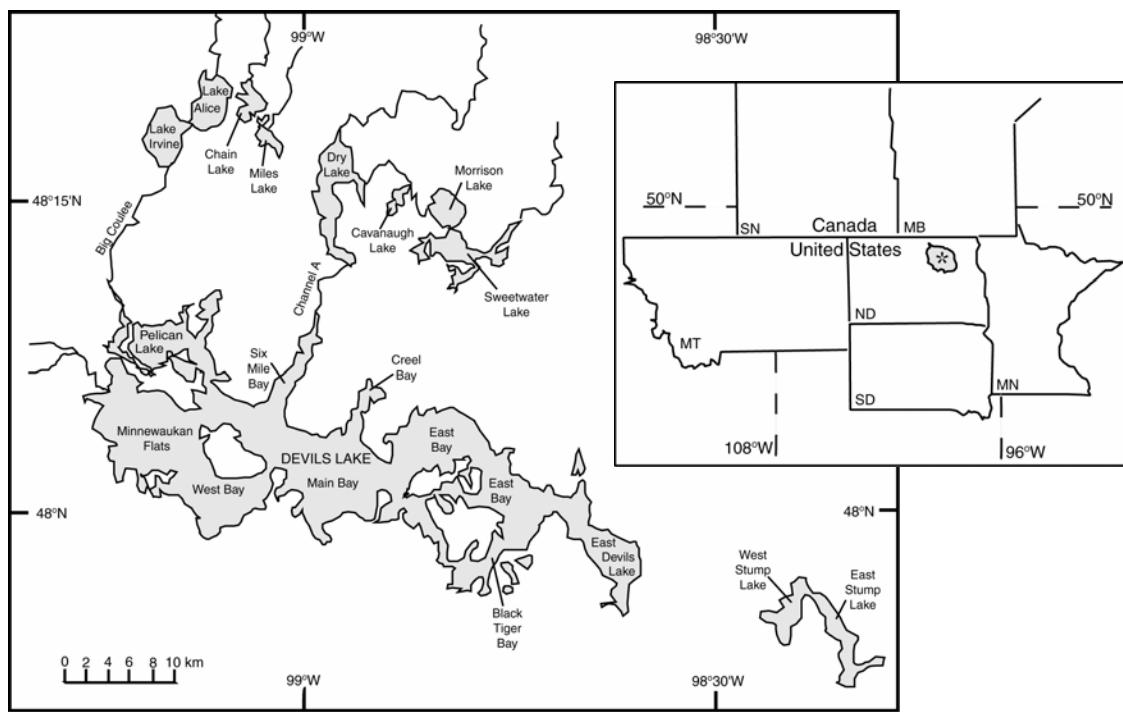
## **Abstract**

Changing water levels have brought Devils Lake a lot of scientific attention in the last century, and several studies of lake level and salinity fluctuations have been completed. However, no previous study was high-resolution and encompassed more than the last 500 years. This new study uses a diatom-inferred paleosalinity reconstruction, calculated with a 74-lake training set for the Northern Great Plains, to investigate lake level change at 5-year intervals for the past 2000 years. In addition to the recent fresh period, four fresh periods have occurred in that time period, peaking at 200, 500, 700 and 1000 A.D. Fluctuations between fresh and saline conditions have consistently been rapid, occurring in less than 60 years, and were likely accompanied by lake level shifts similar to those observed in the last 150 years. The period from 1070 – 1960 A.D. was saline, coinciding with a regional shift in climate, as compared to the conditions from 0 – 1070 A.D. During at least part of this prolonged saline period, Devils Lake had high water levels. As compared to other lakes in the region with high-resolution records, Devils Lake is less sensitive to small climate fluctuations, but clearly records climate changes that are large enough to trigger large salinity and lake level changes.

## **Introduction**

Devils Lake, North Dakota (Figure 1), has been the subject of numerous scientific investigations, spurred recently by a rapidly rising lake level and the resulting inundation of roads and houses. Early observations of lake level go back to 1867; early water quality observations go back to 1899 (Swenson & Colby, 1955). State and federal government agencies have focused several research projects on Devils Lake: Bluemle (1988) reconstructed lake level history from sedimentary changes and radiocarbon dating

**Figure 1: Study Site.** After Wiche et al., 2000 and Shapley et al., *in press*.



of old beach strandlines; Pusc (1993) completed an extensive study of groundwater and lake level; Wiche & Vecchia (1996) modeled lake level change frequency in order to predict what future lake levels might be; Murphy et al. (1997) examined the fluvial sediments between basins to identify past periods of overflow. In addition, the US Army Corps of Engineers has been investigating methods to limit lake level, mainly through the installation of an artificial outlet (USACE, 2003a).

Callender (1968) completed the first sediment core work on the lake, employing sedimentological analyses to reconstruct lake level changes at 10 to 30 cm intervals for the past 6500 years. Stoermer et al. (1971) completed the first diatom study of Devils Lake sediment; several shifts were recorded between saline and fresh conditions in an undated sediment core. Subsequent sediment cores collected from Devils Lake in 1985 and 1986 were analyzed for pollen, ostracodes and diatoms to reconstruct salinity and the settlement history of the lake and its basin. Pollen was sampled at 1 to 2 cm intervals for the last ~200 years to study changes in flora at the time of European settlement (Jacobson & Engstrom, 1989). Ostracodes were sampled at 1 to 2 cm intervals for the last ~100 years to infer salinity values from Mg/Ca and Sr/Ca values and compare them with the historical record (Engstrom & Nelson, 1991). In addition, ostracodes were sampled in 8-cm sections for the last ~12 ka for a long-term inferred salinity record (Haskell et al., 1996). Diatoms were sampled at 1 to 2 cm intervals for the past ~500 years (Fritz, 1990; Fritz et al., 1991; 1994) and from spot samples at 10 cm intervals for 500 to ~11 ka BP (Fritz et al., 1991) to infer salinity.

In all of this research, no high-resolution study had been undertaken which encompassed more than 500 years of the record. Since Devils Lake is a system that has

undergone dramatic changes, a longer-term high-resolution study was necessary to understand the true variability of the system. Thus, this study investigates the lake level changes in Devils Lake, ND at ~5 year intervals for the last 2000 years, inferred by using diatoms to reconstruct paleosalinity values. From the paleosalinity reconstruction, it is possible to investigate long-term lake-level and lake volume variability, determine whether the recent rapid freshening is unique, and elucidate how variability in salinity may be related to climate change.

### **Diatoms as paleoindicators**

Diatoms are good candidates for lacustrine environmental reconstruction because they have short generation times relative to environmental change and their species distribution is related to brine composition and salinity in lakes (Fritz et al., 1999). Furthermore, their hydrous silica frustules are resistant enough to be preserved in sediment, and can be identified to species level centuries after the living tissue has expired. To infer environmental conditions from a diatom assemblage, researchers collect surface sediment samples from a suite of regional lakes and simultaneously measure limnological variables (e.g. ionic composition, pH, salinity) in those lakes. Ordination techniques, such as Canonical Correspondence Analysis (CCA), are used to determine which limnological variables independently explain the variance in the species data, using software programs such as CANOCO (ter Braak, 1997). A transfer function is developed by using regression techniques in a software program such as C2 (Juggins, 2003). The transfer function defines for each diatom species the optimum and range of values for the measured limnological variable of interest. These optima and ranges are

then applied to fossil diatom assemblages to reconstruct past changes in the limnological variable.

Diatom training sets have been used to reconstruct environmental variables around the world: in Africa (Gasse et al., 1995), Europe (Reed, 1998; Bennion et al., 1996), Asia (Kashima, 2003), Australia (Gell, 1997, 1998), North America (Wilson et al. 1996; Fritz 1990; Fritz et al., 1991, 1993), South America (Roux et al., 1991), the Arctic (Ryves et al., 2002) and the Antarctic (Roberts & McMinn, 1996).

For this study, salinity was reconstructed using a training set for the Great Plains developed by Fritz et al. (1993; 66 lakes) and applied to earlier studies of Devils Lake (Fritz, 1990; Fritz et al., 1991, 1994); the training set has been augmented, and now contains data from 79 lakes (Fritz, unpublished). A strong relationship between salinity and species composition has been identified for this training set.

## **Study Site**

Devils Lake is located in northeastern North Dakota, in the northern Great Plains of the United States. In the Cretaceous, the Pierre Shale was laid down in this area beneath an epeiric sea (Clayton et al., 1980). The Cannonball River cut into this shale in the Paleocene, creating a river valley that lies directly beneath the present location of Devils Lake (Clayton et al., 1980; Pusc, 1993). In the Pleistocene, glaciers pushed over the river valley, depositing till; the Spiritwood aquifer formed in the buried river channel sediments (Pusc, 1993). Glaciers last stopped at this site around 12 ka, forming the basins of the lake as ice-thrust features facilitated by the high pore pressure in the underlying aquifer (Bluemle, 1981, 1999). End moraines were deposited south of the lake. Water from the Spiritwood aquifer flooded the area, creating glacial Lake

Minnewaukan, an open system that flowed to the Sheyenne River. As the glaciers receded and water level fell, the modern closed-basin system, Devils Lake, was born (Bluemle, 1981).

In the early Holocene, climate was cool and wet in the northern Great Plains; a transition to warmer, drier conditions occurred around 9.5 ka - < 8 ka at various sites in the area, manifested in a shift in the diatom record from freshwater to saline species and a shift in the pollen record from forest to prairie species in several regional lakes (Fritz et al. 1999). This shift probably occurred around 8 ka in Devils Lake (Haskell et al. 1996).

Long-term paleoenvironmental reconstructions (Callender, 1968; Stoermer et al., 1971; Bluemle, 1988; Fritz et al., 1991, 1994; Haskell et al., 1996; Murphy et al., 1997) indicate that multiple salinity and lake-level fluctuations have occurred over the history of the lake. Since 1867, when the first permanent settlement was established on Devils Lake at Fort Totten, the lake has displayed its potential for variability. Water level declined from 1867 to 1940, when the lake level reached a historical low level of 427 m (USGS, 2003). In the 1950's the low lake level and lack of fish in Devils Lake led to plans to channel water from the Missouri River into the lake; these plans were eventually abandoned (Swenson & Colby, 1955). In the 1960's, water level was beginning to rise, but it was generally low. Callender (1968) noted that salt loss was occurring through aeolian transport from West Bay and Six Mile Bay during high winds, and Jones & Van Denburgh (1966) described East Bay as a nearly dry lakebed with only a few pools of water and some marsh area. Lake level has generally been rising since the 1940 low level, for a total rise of ~14 m to an elevation of over 441 m above mean sea level in 2003 (USGS, 2003). The increase in lake level since 1940 has caused a >16-fold

increase in the area of the lake and a ~260-fold increase in the capacity of the lake (raw data from Swenson & Colby, 1955; USGS, 2003); > \$350 million in Federal emergency response funding has been used to move or repair houses, roads and dikes (USACE, 2003b).

Devils Lake is located in the prairie of the Northern Great Plains, in the rain shadow of the Rocky Mountains. Effective precipitation (P-E) is annually negative in this region (Fritz et al., 1993). Tornadoes, blizzards, thunderstorms and droughts can all influence the water balance in the area (Hinckley, 1995); historical records show that the 1930's Dust Bowl had a great effect on Devils Lake (Swenson & Colby, 1955). The climate of the region is influenced by three air masses: the Atlantic airstream, bringing moisture from the Gulf of Mexico, the Jet Stream, bringing dry Pacific Ocean air from the west, and the Arctic Airstream, bringing cold dry air from the north (Anderson et al., 1993). The climate is continental, with low precipitation, large temperature extremes, short hot summers and long cold winters (Hinckley, 1995).

Devils Lake is composed of several basins that may be connected or divided, depending on the water elevation. Generally, water flows from northwest to southeast basins (Manous, 2000). The lake has a natural outlet only when the water level exceeds 444.7 m and water can flow to the Sheyenne River; this has not occurred in recorded history. Water may be stored in upper basins and only be transferred to lower basins after reaching a threshold level (Swenson & Colby, 1955). Regionally, groundwater flows toward the lake (Pusc, 1993). The lake is underlain by till and bordered to the south by end moraines and outwash sands (Pusc, 1993). Centuries of sedimentation have added meters of clay and silt to the lake bottom, which, combined with the till, create a low-

transmissivity boundary between Devils Lake and the Spiritwood aquifer below (Pusc, 1993). Using Darcy equations, the maximum theoretical groundwater discharge into the lake is  $3.70 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$  (Pusc 1993). Compared with the capacity of the lake in 2002, which was  $2.99 \times 10^9 \text{ m}^3$  (USGS, 2003), the maximum theoretical groundwater input is 0.12% of the lake capacity. Thus, due to low transmissivity, groundwater input into the lake is insignificant except during dry periods. Precipitation and water level have both increased in the historical period, but the two records are poorly correlated, indicating a complex short-term relationship. Swenson & Colby (1955) found that either a decrease in precipitation or an increase in temperature can decrease the amount of runoff, which ultimately affects lake level. Under current conditions, the water elevation in a given basin is determined by precipitation, evaporation, runoff and the input from upflow basins (Wiche, 1992).

## Methods

### *Core Retrieval*

Sediment cores were taken at  $48^{\circ}04.401' \text{N}$ ,  $98^{\circ}56.345' \text{W}$  from Creel Bay, Devils Lake, N.D., U.S.A. on March 13, 2002, using the frozen lake surface as a coring platform. Creel Bay was chosen as the coring site because it is less prone to sediment transport and resuspension than Main Bay (Jacobson & Engstrom, 1989); in addition, comparison with previous paleolimnological studies from sediment cores in Creel Bay (Callender, 1968; Jacobson & Engstrom, 1989; Fritz, 1990; Engstrom & Nelson, 1991; Fritz et al., 1991; Fritz et al., 1993; Haskell et al., 1996) is made easier by using a similar location. The depth from the surface of the water to the sediment-water interface was 13.2 m, an increase of 5.7 m in water depth since the last long sediment core from Creel

Bay was taken in 1985 (Haskell et al., 1996). The surface sediment was retrieved from two locations using polycarbonate tubes. Sediment recovery was 0.95 m for piston core A (PA) and 0.96 m for piston core B (PB). Deeper sediment was retrieved using a 5 cm diameter aluminum Livingstone piston corer at two sites, A & B. Seven one-meter drives were collected from A & B extending to 8.09 m and 7.73 m below the sediment-water interface, respectively. Core sequences A and B overlapped, so that the end of a 1-m core in one sequence overlapped with the middle of a 1-m core in the other sequence.

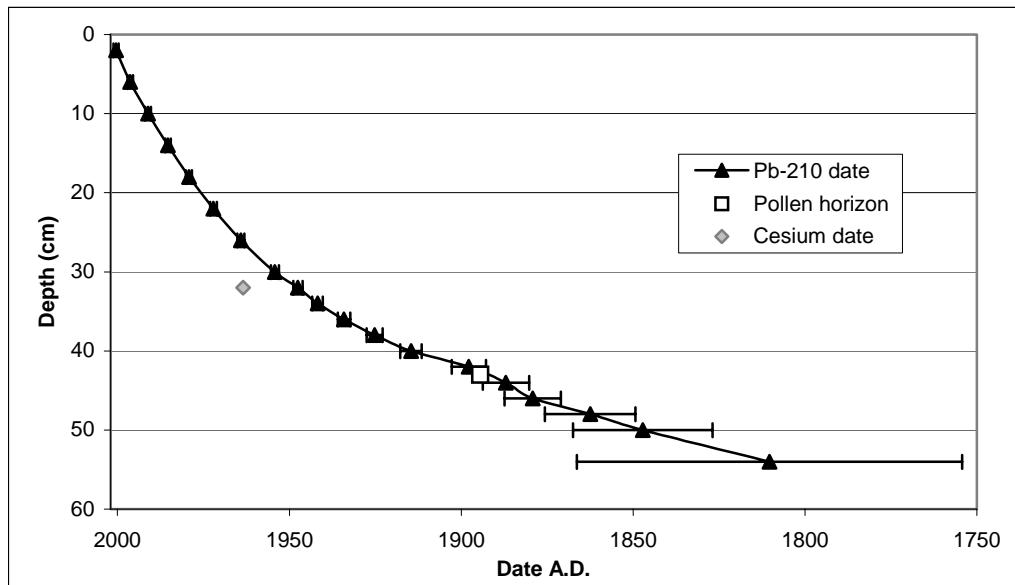
#### *Sampling strategy*

Surface core PA was sectioned into 2-cm increments; the first 30 cm was sectioned in the field, and the remaining 65 cm was sectioned in the lab. Each increment in the short core represents 1.8 to 18 years of sedimentation. The two long core sequences were aligned with each other using field measurements, magnetic susceptibility measurements and visual observations. The long core was sectioned into 5-year increments for the last 2000 years, based on Pb-210, C-14 and pollen dating. Each increment in the long core encompassed 0.6 to 1.0 cm in depth. Samples were taken from the middle 70 cm of the cores, moving between core sequences to avoid edge effects. The last 2000 years are represented by 378 increments.

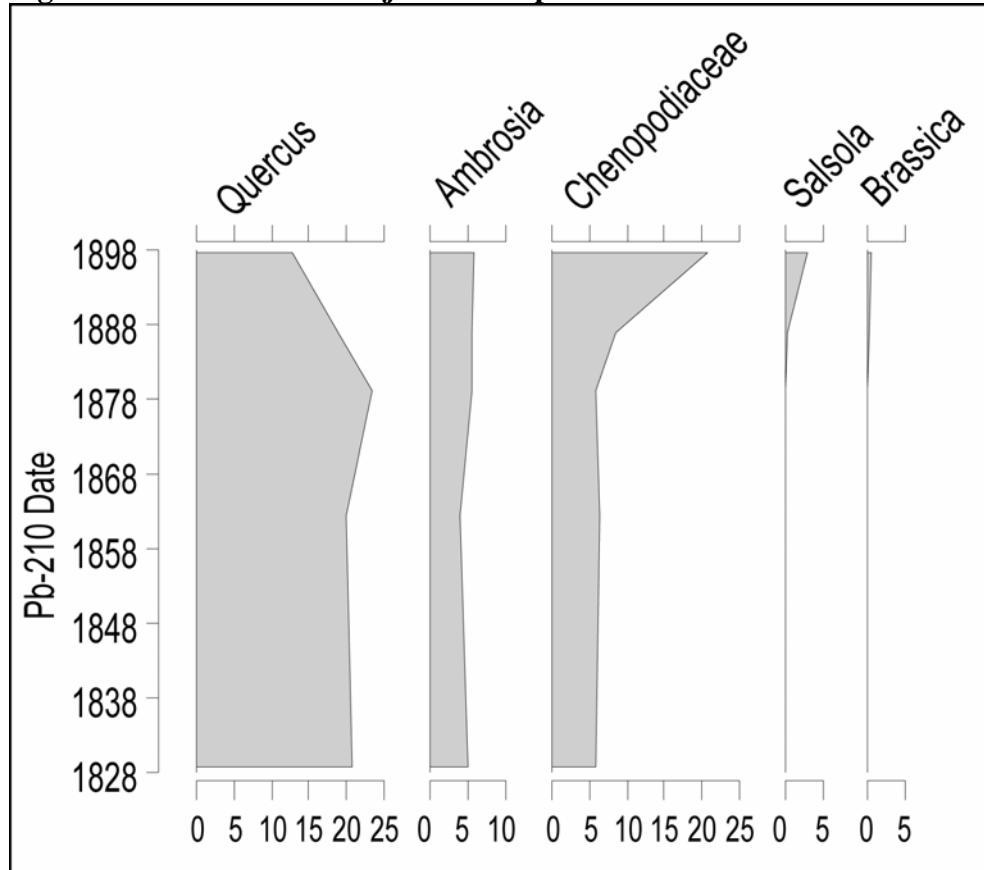
#### *Dating Techniques*

Four analytical methods were used to date the sediment core sequence: Lead-210, pollen, Cesium-137 and Carbon-14. These tools were used to develop an age model (Figure 4).

**Figure 2: Results of Lead-210, Pollen and Cesium analyses**



**Figure 3: Abundance of major taxa of pollen**



### Lead-210 Dating

Nineteen increments from the surface core were dated by Lead-210 analyses at St. Croix Watershed Research Station using a procedure based on Eakins & Morrison (1978). Sediment was freeze-dried, homogenized, and subsamples of ~1 g dry sediment were taken from each interval. After pretreatment with hydrochloric acid, a spike of Polonium-209 of known activity was added to each subsample and volatile radioisotopes were extracted from the sediment, including Po-209, Pb-210 and Po-210. Lead-210 activity was measured through its granddaughter, Polonium-210, using an Ortec Octet-PC alpha spectrometer. A dating curve was calculated from the relative amount of unsupported Lead-210 activity in the sediment using a constant rate of supply model (Appleby & Oldfield, 1978). The Lead-210 dating curve is fairly smooth, suggesting that the sediment is undisturbed, and that the dating model is reliable.

### Pollen

Six sediment samples of approximately 1 cm<sup>3</sup> from the surface core (40-42 cm, 42-44 cm, 44-46 cm, 46-48 cm, 48-50 cm and 50-52 cm) were prepared for pollen analysis at the Limnological Research Center. Pollen analysis by B.C.S. Hansen identified the rise in *Salsola iberica*, Russian thistle, which arrived in the Devils Lake area in 1894-1895 (Jacobson & Engstrom, 1989). The first occurrence of *Salsola iberica* was detected in the interval of 42 – 44 cm; this interval is dated as 1887.0 A.D. ± 6.74 years by Lead-210 dating. The rise in *Brassica* occurs at the same time as the rise in *Salsola iberica*, confirming the signal for European settlement (Figure 3).

### Cesium-137 Dating

Twelve samples were analyzed for Cesium-137 activity at the St. Croix Watershed Research Station. A peak in Cesium-137 in the sediment is expected to mark the 1963-1964 peak in deposition from atmospheric nuclear testing. Figure 2 illustrates that the depth identified as 1963-1964 A.D. by cesium dating is identified as 1947.9 A.D. by Lead-210 dating. This could indicate a problem with the Lead-210 dating model. However, surface sediments date near 0 years with Lead-210, and the *Salsola iberica* pollen rise in 1894-1895 agrees with the Lead-210 date, providing confirmation of the Lead-210 model above and below the cesium peak (Figure 2). Thus, we infer that there is a problem using cesium dating in this sediment core. It is possible that the Cs-137 is mobile in the sediments of Devils Lake.

### Radiocarbon dating

Sediment samples from four depths (Table 1) were picked for grass charcoal to be analyzed by Accelerator Mass Spectrometry (AMS) Carbon-14 analyses. Samples were acidified with 10% HCl and sieved with water through 250 and 125 micron sieves to isolate the coarser fractions. Charcoal samples were picked from the fraction larger than 125 microns under a dissecting microscope for each of the four depths. The charcoal was graphitized by B. Haskell at the Limnological Research Center and analyzed at the NSF-Arizona AMS Laboratory. B. Haskell calibrated radiocarbon dates (Table 2) using the University of Washington Quaternary Isotope Lab Radiocarbon Calibration Program Rev. 4.3 (based on Stuiver & Reimer, 1993).

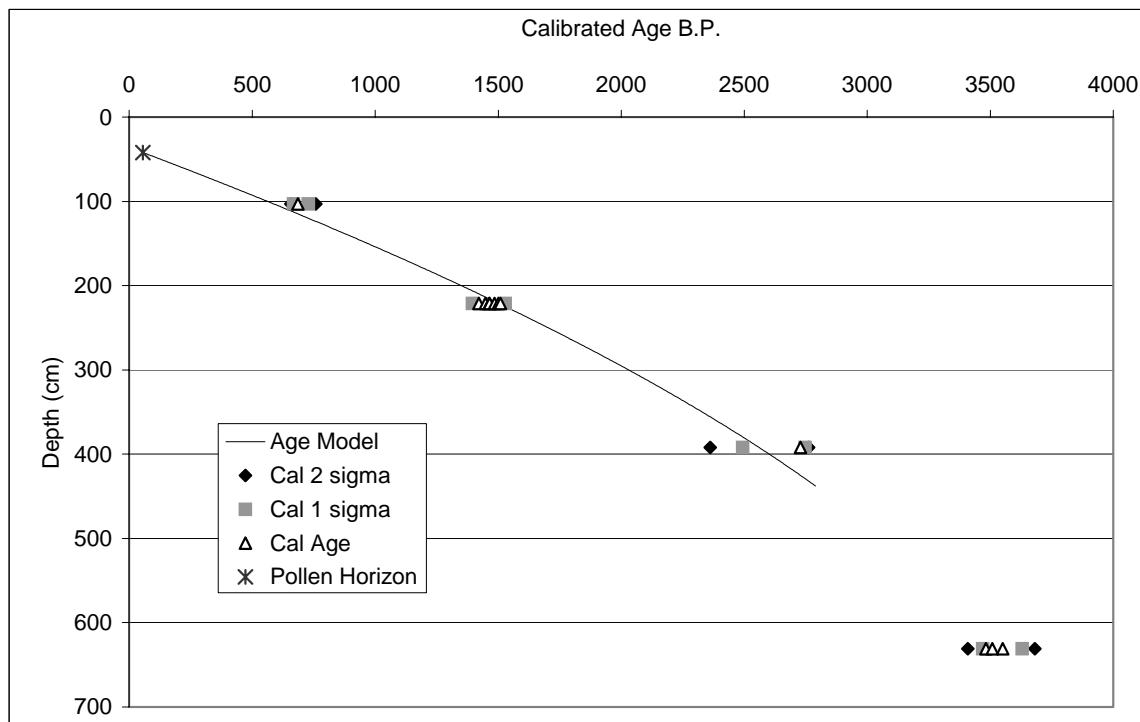
The dates of the *Salsola iberica* pollen horizon (n=1) and the C-14 intercepts calibrated by the intercept method for the three most recent radiocarbon intervals (n=11)

**Table 1: Radiocarbon Dates from the NSF-Arizona AMS Laboratory**

AMS Lab ID	Core	Depth (m)	Fraction modern	Radiocarbon age B.P.
AA51330	DL-B1	1.01-1.05	0.9079 $\pm$ 0.0045	776 $\pm$ 40
AA51327	DL-A2	2.20-2.22	0.8221 $\pm$ 0.0054	1,574 $\pm$ 52
AA51328	DL-A3	3.91-3.93	0.7288 $\pm$ 0.0052	2,541 $\pm$ 57
AA51329	DL-A6	6.30-6.32	0.6623 $\pm$ 0.0039	3,310 $\pm$ 47

**Table 2: Calibrated Ages – Intercept Method**

Depth (m)	Calibrated age(s) B.P.	Calibrated age - 1 $\sigma$	Calibrated age + 1 $\sigma$	Calibrated age - 2 $\sigma$	Calibrated age + 2 $\sigma$
1.01-1.05	686	668	729	657	759
2.20-2.22	1421, 1433, 1442, 1448, 1464, 1465, 1485, 1500, 1510	1395	1528	1334	1563
3.91-3.93	2729	2494	2747	2362	2762
6.30-6.32	3483, 3508, 3551	3469	3630	3409	3682

**Figure 4: Age Model**

were used to calculate an age model for the core. A second-order polynomial ( $r^2 = 0.98$ ) was fit to these twelve points; this age model (Figure 4) was used to section the long core into 5-year intervals.

#### *Loss on ignition*

Each 2-cm increment from the surface core and each 5-year increment from the long core underwent loss on ignition analyses (Dean, 1974). Efforts were made to use consistent sample size and prevent the effects of moisture adhesion in order to avoid potential errors (Heiri et al., 2001). A subsample of homogenized sediment from each interval was massed (mean = 2.38 g, standard deviation = 0.48 g). Samples were heated at 105°C overnight in a drying oven, and then placed in a desiccator. Samples were heated for 1 hour at 550°C, and for 1 hour at 1000°C in a Fisher Scientific Isotemp Muffle Furnace. After each heating in the muffle furnace, samples were placed in a drying oven overnight, and then placed in a desiccator to remove any water that may have adhered to the samples or the crucibles during the drying period. Samples were massed after each heating (105°C, 550°C, 1000°C); the loss of mass between burns was used to determine water, organic, carbonate, and inorganic contents, respectively.

#### *Diatom slide preparation*

Sediments were prepared for diatom analysis following the technique of Renberg (1990). Each of 378 increments (see Sampling Strategy) encompassing the last 2000 years was homogenized before slide preparation. Small (~0.1 cm<sup>3</sup>) sediment subsamples were placed in test tubes and treated with 10% hydrochloric acid to remove carbonate and 30% hydrogen peroxide to remove organic matter. The samples were then heated in an 85°C water bath for 3 hours. The test tubes were filled with distilled water and rinsed

daily for five days. Cover slips were prepared from the rinsed samples; the cover slips were mounted to microscope slides using Naphrax mountant.

#### *Diatom counts*

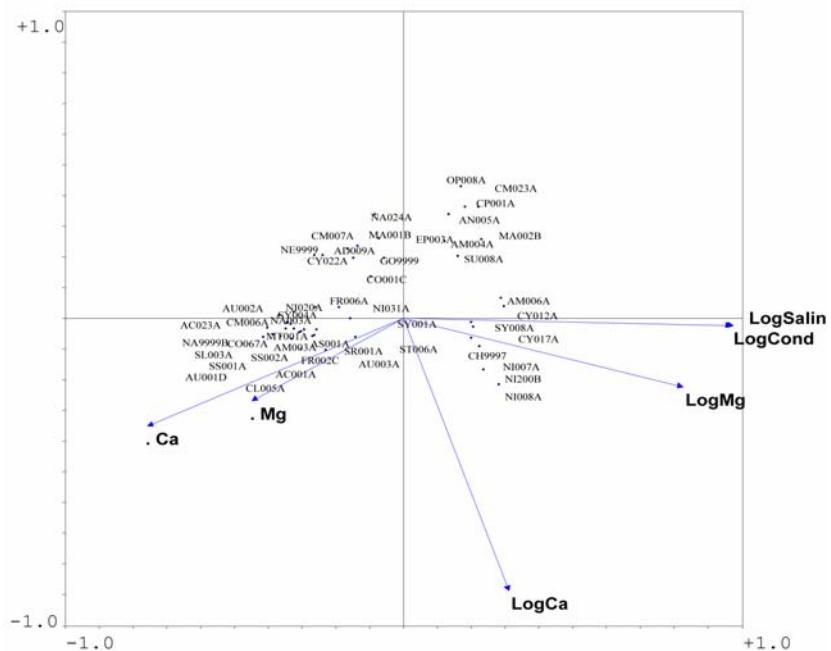
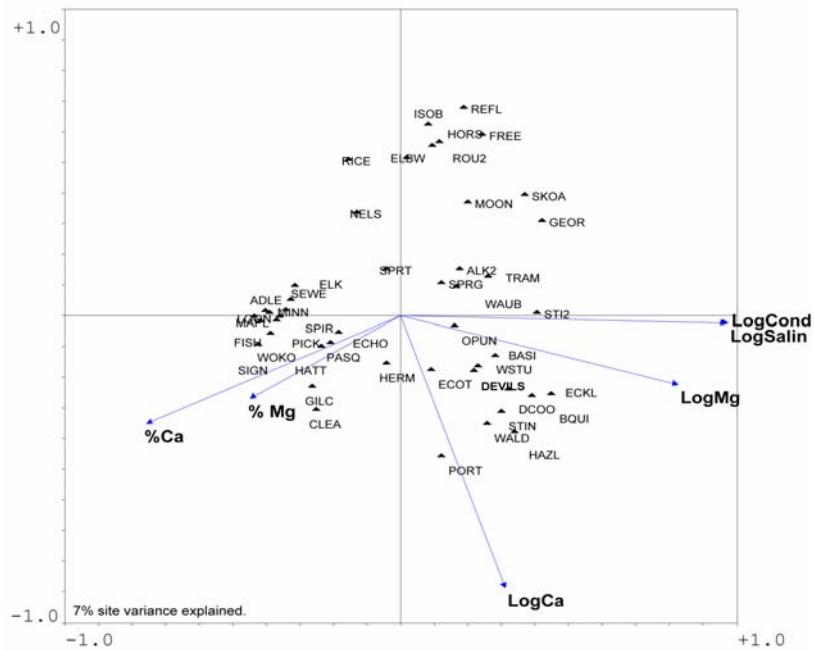
Diatoms were counted on an Olympus BX50 microscope at 600x magnification. Before counting, test slides were examined to calculate efficiency (Pappas & Stoermer, 1996) to determine an adequate number of valves to count; for the relatively low diversity of the Devils Lake system, 250 counts were sufficient for a representative sample. Thus, 250 diatom valves were identified and counted in each slide with sufficient preservation (359 slides). On 8 slides (DL19, DL21, DL22, DL24, DL25, DL67, DL104, DL207), the concentration of diatoms was low (due to poor preservation, low productivity and/or high influx of other sediment), and 100 valves were counted; on 11 slides (DL20, DL91, DL92, DL93, DL94, DL96, DL97, DL102, DL103, DL105, DL206), the concentration of diatoms was very low, and 0 valves were counted. Individual valves were counted if they contained at least half of a valve or contained the central area of a valve. Spores of *Chaetoceros muelleri/elmorei* were each counted as one valve.

Each diatom valve was designated as “pristine” or “not pristine” to record a rough index of preservation for each slide. This does not allow for a distinction between slightly damaged and very corroded valves; rather, it is a more objective measure of preservation. The number of pristine valves was divided by the total number of valves in each slide to calculate percent pristine.

#### *Inferred salinity*

Diatom counts were converted into paleosalinity values using a training set of diatoms and limnological variables from 79 Northern Great Plains lakes (Fritz

**Figure 5: Canonical Correspondence Analysis plots**



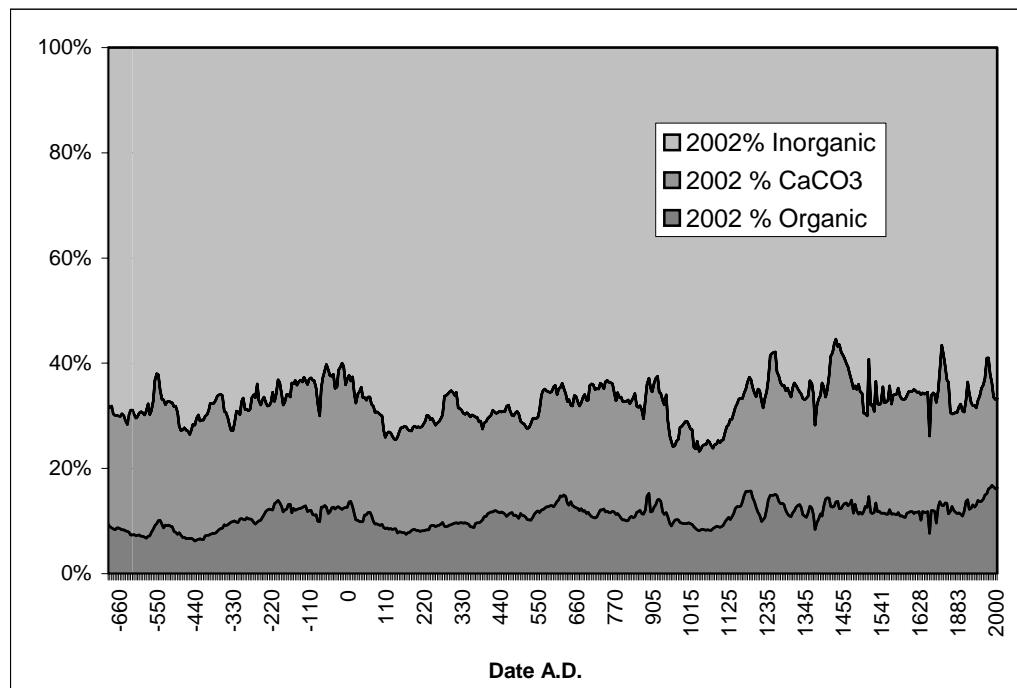
unpublished). Sediment samples were collected from the top 3 cm of sediment, and water chemistry data was determined from a single sample taken in midsummer; 18 environmental variables were measured or calculated for each lake (Fritz et al., 1993). CANOCO (ter Braak, 1997) was used to perform Canonical Correspondence Analysis (CCA), a statistical ordination technique that helps to determine which environmental variables explain the most variability in the diatom species composition of the training set lakes (Figure 5). The six variables that explained most of the diatom variability were (1) log salinity, (2) log Calcium, (3) log Magnesium, (4) log conductivity, (5) % Magnesium, and (6) % Calcium. A salinity transfer function based on regression techniques applied to the training set diatom and environmental variable data was calculated in C2 (Juggins, 2003), using a weighted averaging model with inverse deshrinking; cross-validation was performed using bootstrapping. Species optima and ranges for salinity were determined in C2 (Juggins, 2003). Additionally, and an inferred salinity curve was calculated using the fossil diatom counts from the last 2 ka. Fossil species were included in the reconstruction if their maximum abundance was greater than 1%.

## Results

### *Loss on ignition*

The inorganic portion averaged 66.5 weight percent (standard deviation = 4.6), calcium carbonate averaged 21.7 weight percent (standard deviation = 3.5), and the organic portion averaged 11.8 weight percent (standard deviation = 1.84) of the dry sediment.

**Figure 6: Results of loss on ignition analysis**

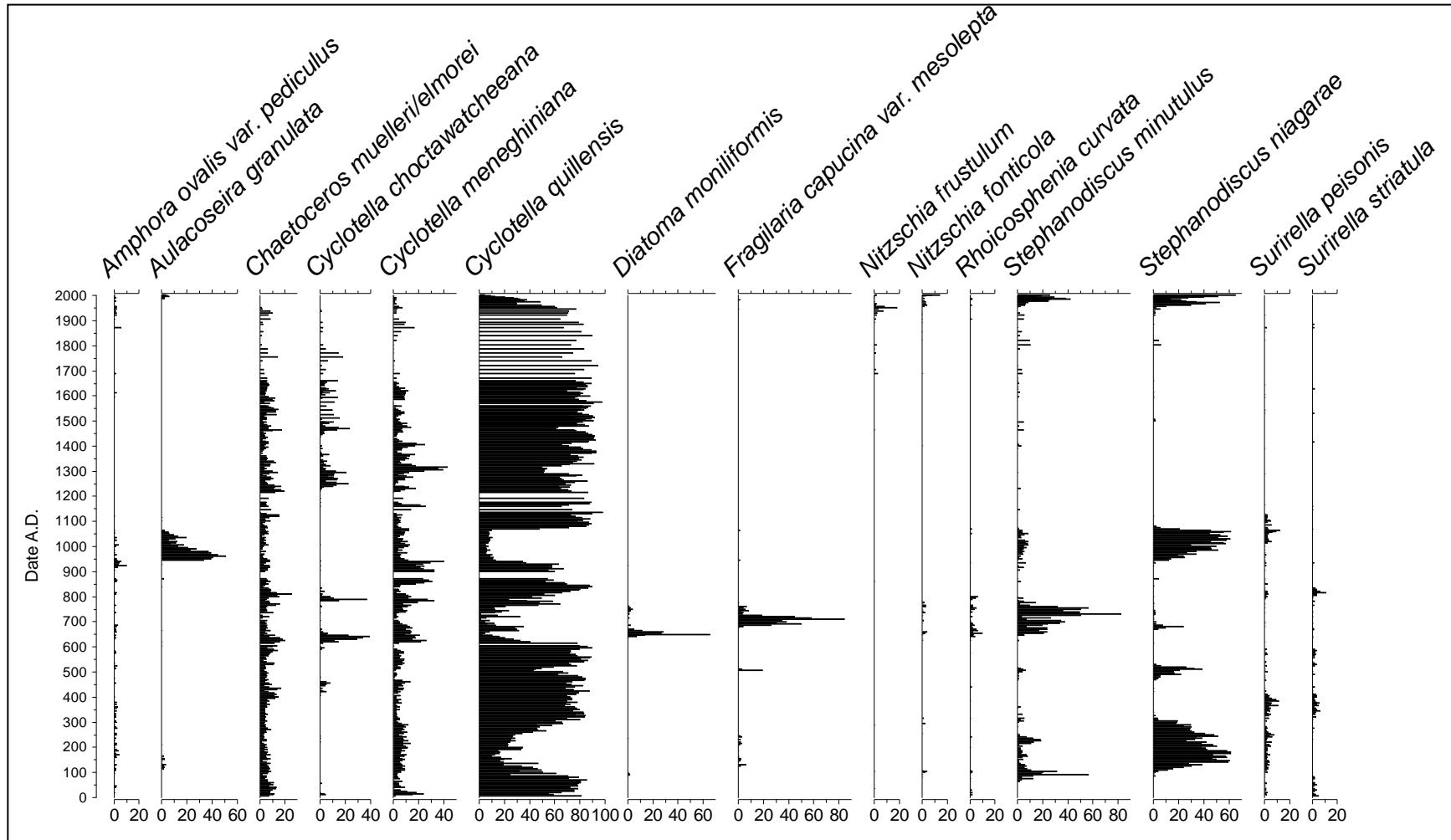


### *Diatom analyses*

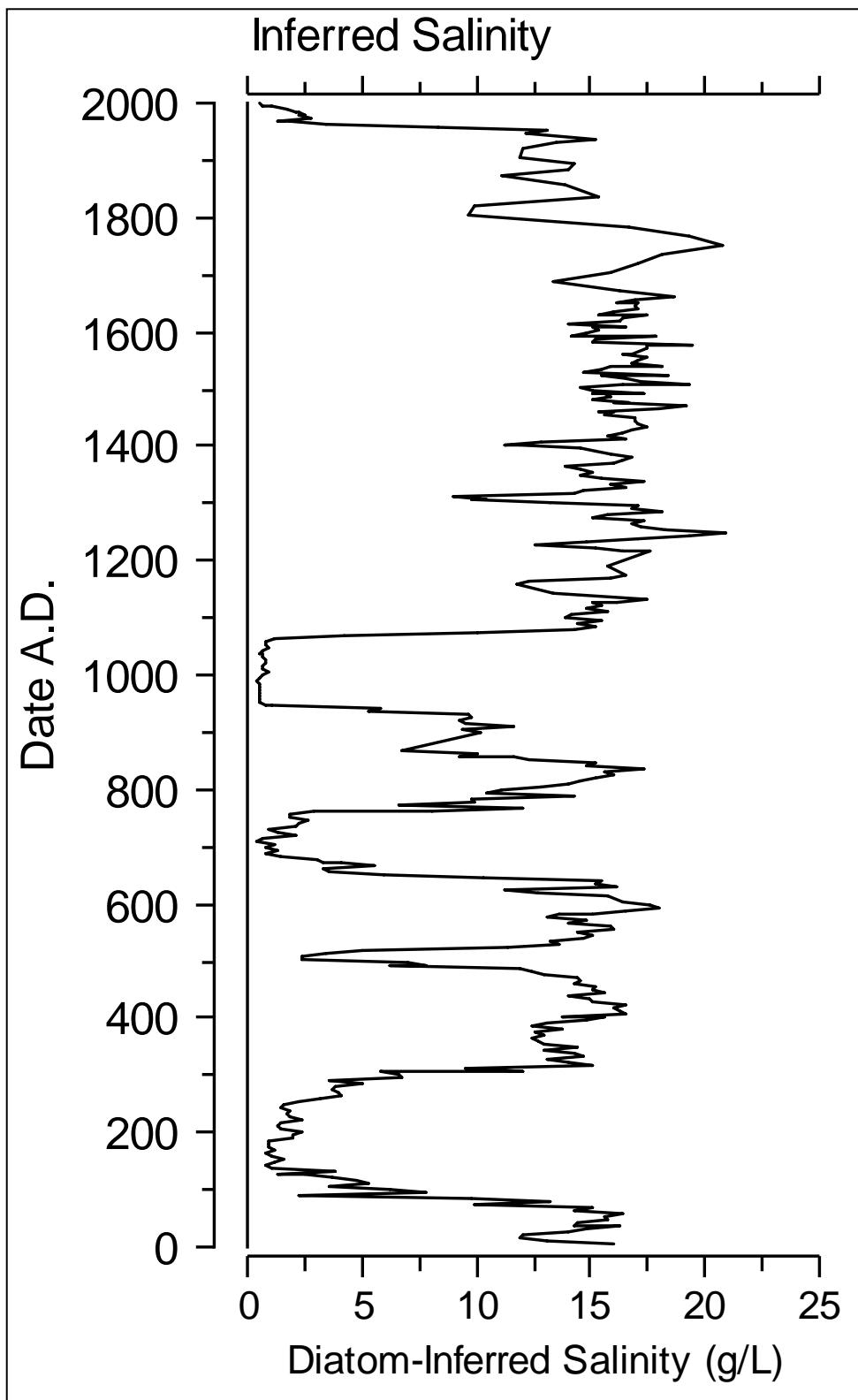
Diatom diversity is low in Devils Lake. Thirty-five genera and 124 species were identified in the sediments of Devils Lake; of these, 22 genera and 44 species were present in a maximum relative abundance of at least 1%. Only fifteen taxa were present with a maximum relative abundance of at least 10%. On average, 10 species were identified in each slide; the minimum was 3 species and the maximum was 24 species. Generally, a lower number of species was identified in saline periods as compared to fresh periods. During saline periods, *Cyclotella quillensis* was the dominant diatom, with *Cyclotella choctawatcheeana*, *Cyclotella meneghiniana* and *Chaetoceros muelleri/elmorei* present in lower abundances. During fresh periods, the dominant diatom was variable, alternating between *Stephanodiscus niagarae*, *Aulacoseira granulata*, *Stephanodiscus minutulus*, and *Fragilaria capucina* var. *mesolepta*.

In five periods, diatoms were sparse: 600-610, 1135-1215, 1330, 1530-1590 and 1855-1895 A.D. These periods include the slides in which zero (11 slides) or 100 (8 slides) were counted. Overall, the average percent pristine was 16.0 %, with a minimum of 0.4 % and a maximum of 84.8 % pristine. For the five periods of sparse diatoms, the average percent pristine was 7.3%, 6.3%, 2.7%, 7.8%, and 3.9%, respectively, for those slides that could be counted – consistently below average. The number of slide transects is also an indicator of sparseness; the average number of transects was 3. For the four periods of sparse diatoms, the average number of transects was 17, 13, 10, 10 and 11, respectively, for those slides with 100 – 250 diatoms counted – consistently above average. These periods could represent (1) low diatom productivity, (2) poor preservation, or (3) an influx of silicates from another source, making diatoms relatively

**Figure 7: Abundance of major diatom taxa.**



**Figure 8: Inferred Salinity**



less abundant. Only the brief sparse period in 1330 A.D. corresponds with an increase in percent inorganic in loss on ignition; an influx of non-diatom silicates can probably be ruled out for the four other sparse periods.

#### *Inferred Salinity*

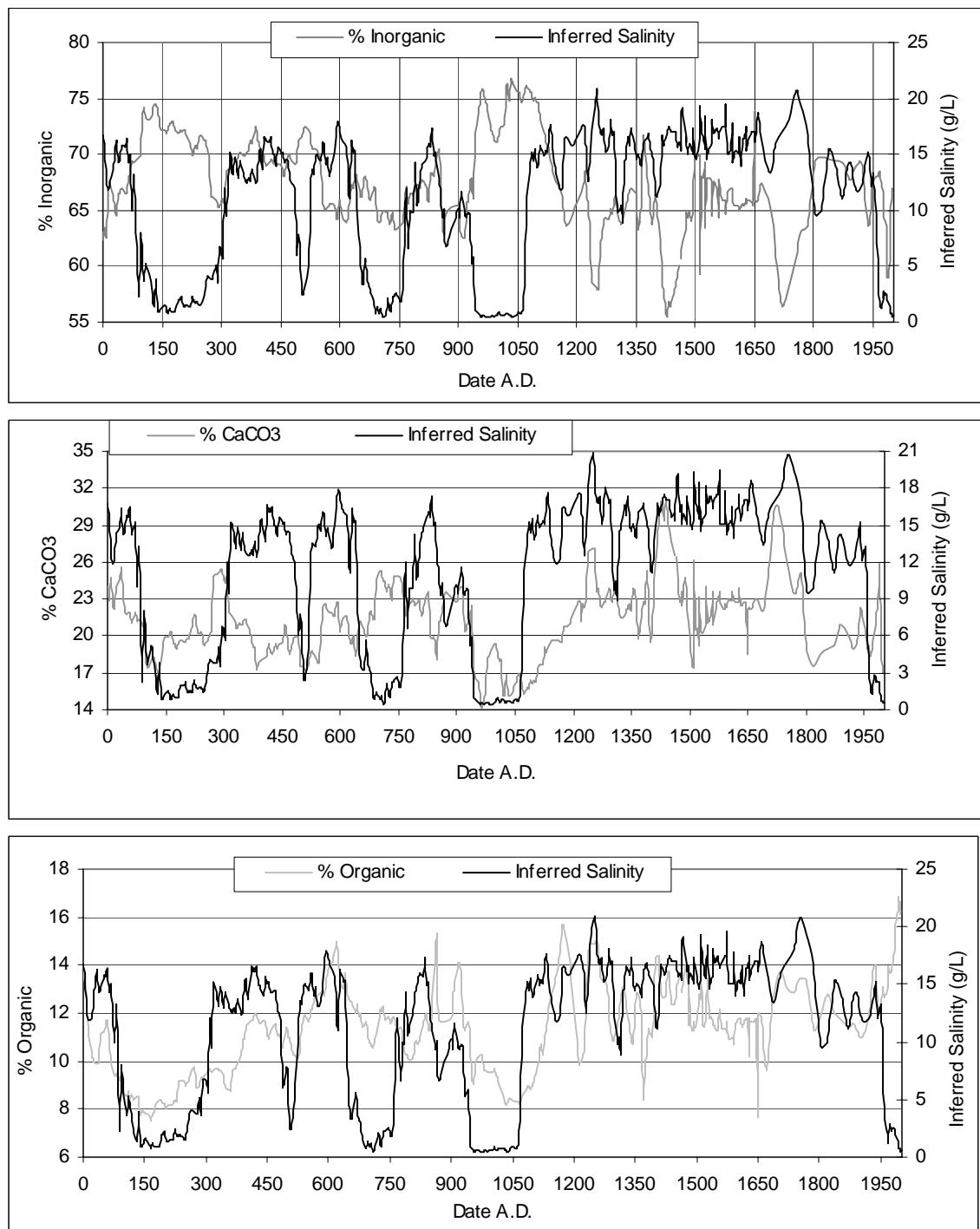
Our diatom-inferred salinity curve for the last 2000 years in Devils Lake depicts a widely-varying system, with salinity values ranging from  $< 1$  g/L to  $> 20$  g/L. The lake is saline for over three-fourths of this record; however, small fluctuations in salinity occur even in the long saline period from 1070 – 1960 A.D. The threshold between fresh and saline lakes has been previously defined as 3 g/L (Williams, 1981). Using this criterion, five fresh periods have occurred in the last 2000 years: 125 – 255 AD, 505 – 510 AD, 680 – 760 AD, 945 – 1065 AD and 1966 AD – present. Accounting for entire excursions from high salinity conditions, the first four fresh periods are centered roughly at 200, 500, 700 and 1000 A.D. Time-series analysis indicates that there may be a 95-year period to shifts in inferred salinity in Devils Lake. Transitions between fresh and saline phases have been rapid, occurring in less than 50 years. No abrupt shift in species richness was observed at 3 g/L salinity, nor was there any shift in dominant species, as is found between fresh ( $< 3$  g/L) lakes and saline ( $> 3$  g/L) lakes in the Northern Great Plains (Fritz et al. 1999). During the five sparse periods, inferred salinity was consistently high (17.0, 15.1, 16.6, 16.6, and 13.3 ‰).

## **Discussion**

### *Loss on ignition*

Loss on ignition was performed on the sediments of each increment that was analyzed for diatoms, so the data can be easily compared. Overall, correlation between

Figure 9: Loss on ignition and inferred salinity



inferred salinity and values determined through loss on ignition is low. Visually, inferred salinity and percent inorganic carbon appear to be inversely related in some periods, and unrelated in other periods (Figure 9). This is probably due to the interplay between percent inorganic carbon, percent organic carbon and percent calcium carbonate: a relative increase in one value will cause a relative decrease in the other two values. For instance, an increase in percent inorganic carbon with a decrease in salinity may indicate that the water level has risen and more erosion is occurring. However, if productivity in the lake rises at the same time, then percent organic carbon will increase, and the relative increase in percent inorganic carbon will be diminished.

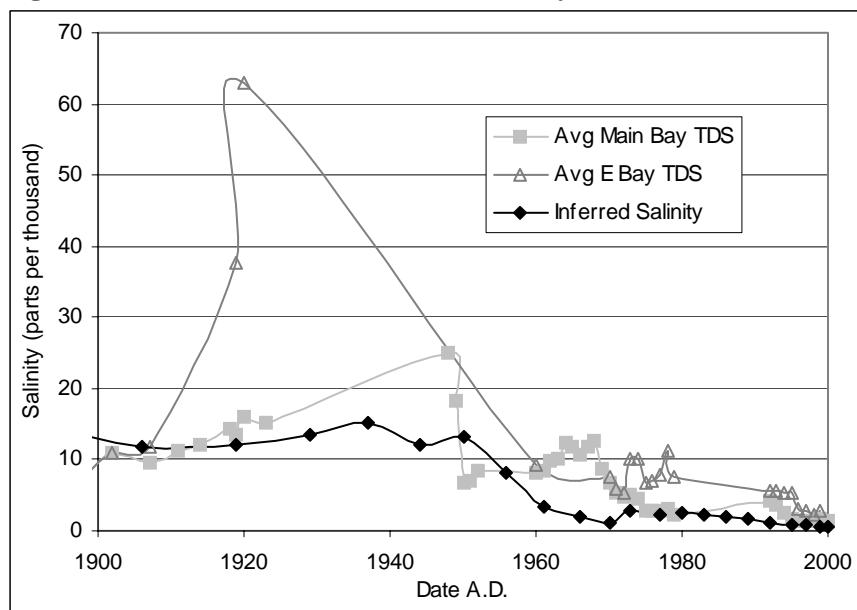
#### *Diatom analyses*

Diversity is low in Devils Lake, both in the recent sediments used in the transfer function (Fritz, unpublished) and in the older sediments. As Fritz (1993) noted, the results of diatom analyses may be skewed because of diatom preservation problems, including dissolution at high salinities and high erosion rates making diatoms relatively less abundant in the sediment, bias toward better-preserved highly-silicified diatom valves in the diatom species distribution, and bias toward species with distinctive central areas, which are easier to identify when broken than other taxa. Species richness and the proportion of pristine valves are positively correlated ( $r = 0.73$ ;  $r^2 = 0.54$ ); this is most likely because more lightly silicified species are preserved when valves are not corroded.

#### *Inferred salinity*

The inferred salinity curve (Figure 8) displays different behavior in the first part of the record, as compared to the second part. From 0 – 1070 A.D., Devils Lake fluctuated several times between fresh and saline conditions. However, between 1070

**Figure 10: Measured and inferred salinity**



and 1960 A.D., Devils Lake remained saline. This is not to say that climate or lake level remained constant for 900 years. Small climate perturbations, recorded by fluctuations in the paleoecological records of other regional lakes, are recorded by fluctuations within the saline realm in Devils Lake.

For the historical record, the diatom-inferred salinity values correlate well with measured values (Figure 10). Long-term records of salinity exist for Main Bay (1899–2002) and East Bay (1899 – 2001), Devils Lake – nearby basins, which should have similar salinity values to Creel Bay. Reconstructed salinity values from Creel Bay correlate well with these measured values;  $r^2= 0.39$  with Main Bay and  $r^2=0.99$  with East Bay. The correlation between the two measured salinity records from Main Bay and East Bay ( $r^2=0.66$ ) is midway between the correlation of each with inferred salinity values. Inferred salinity and water elevation are negatively correlated;  $r = -0.54$  and  $r^2 = 0.30$ .

The rapid transitions in salinity indicate that the lake is unresponsive to climate changes up to a certain threshold, after which it changes rapidly. This may be due to the multi-basin nature of the system – as one basin reaches a physical threshold of lake level, it quickly overflows into another basin, creating a rapid freshening. As a basin becomes disconnected from the rest of the lake, evaporation can exceed input of water, and solutes become more concentrated. The rapidity of these changes may indicate that basin-to-basin flow is more important than precipitation or evaporation in determining lake level and salinity in Devils Lake.

#### *Lake level and capacity changes*

Large, rapid changes in salinity imply large, rapid changes in lake level. Inferred lake level and inferred lake volume were calculated from our inferred salinity values in

order to determine the changes in lake size that are represented by rapid shifts in our inferred salinity curve. In reality, a single value for salinity does not match with a single value for lake level; the calculations were made for the purpose of a conceptual model, rather than to precisely reconstruct lake level history. For the purpose of these calculations, it is necessary to assume that lake level and volume are always inversely related to salinity.

The USGS has developed a model of lake level-volume relationships in Devils Lake based on the bathymetry of the lake basins (Vecchia, 2002). A fifth order polynomial ( $r^2=1$ ) was fit to this table of data in order to calculate lake volume from lake level, and a sixth order polynomial ( $r^2=0.99$ ) was fit to this table of data in order to calculate lake level from lake volume. Inferred lake level and inferred lake volume were calculated by using the relationship between inferred salinity and measured lake level and volume. A linear relationship was assumed between the logarithm of inferred salinity and the logarithm of lake size (level or volume, Figure 11). On a linear scale, this means that at low salinity and high lake size, salinity changes very little with changes in lake size. At high salinity and low lake size, salinity changes more quickly with changes in lake size. This mathematical model makes physical sense: as lake size becomes large, a dilution limit is approached because salinity will never reach zero. As lake size shrinks, increases in salinity are only limited by the amount of dissolved solids in the lake.

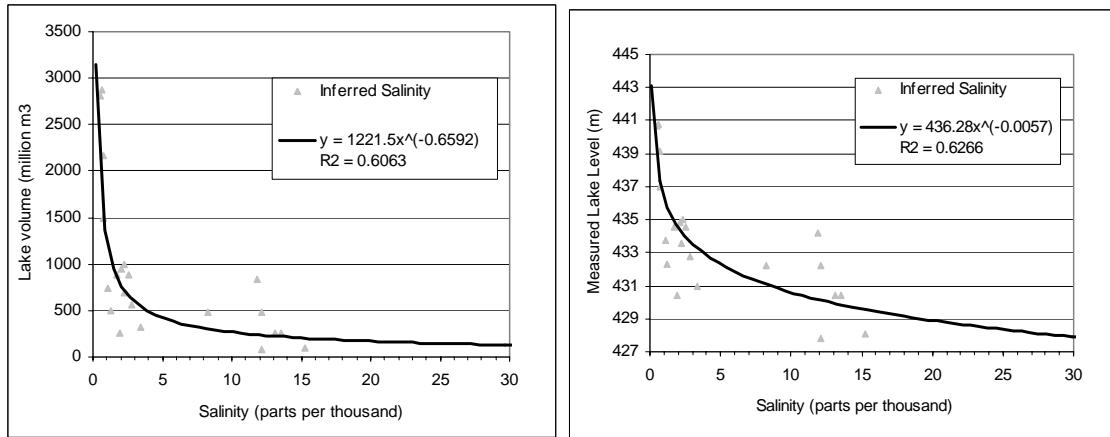
Values for inferred lake level and inferred lake volume were compared to measured values for lake level (USGS, 2003) and calculated volume (Vecchia, 2002). A positive linear relationship exists between measured and inferred values. Reconstructed lake levels range between 428 and 439 m. In recorded history, the lake has ranged from

427 to 441 m. Sedimentary history (Murphy et al., 1997) indicates that lake level exceeded 444.7 m, the elevation of the outlet to the Sheyenne River, twice in the last 2 ka. Thus, our reconstructions underestimate the lake level variability of the system by a few meters. Inferred values were compared to annual averages from the period of record (1867-2003; USGS, 2003), (Table 3). Inferred values match measured values within a few meters for lake level and within an order of magnitude for volume (Table 3). Change per year is calculated by dividing change in elevation or volume over change in time. For the inferred values, the average change in time is 5 years; for measured annual values, the average change in time is 1 year.

To test the feasibility of rapid salinity shifts, changes in inferred lake level and volume were determined for transitions between saline and fresh periods; these values were compared to transitions in the period of record (Table 4). The most dramatic transitions in the reconstruction occurred around the fresh period centered at 1000 A.D. From 910 to 960 A.D., inferred salinity decreased from 11.59 ‰ to 0.49 ‰. According to our models, Devils Lake gained over 7 m in elevation and on the order of  $1.5 \times 10^9 \text{ m}^3$  in volume in that 50-year period, a change of 0.15 m/yr and  $3.0 \times 10^7 \text{ m}^3/\text{yr}$ . This compares well with measured changes (Table 4). From 1992 to 2002, lake level rose by 7.2 m and gained  $2.2 \times 10^9 \text{ m}^3$  in lake volume, an increase of 0.65 m/yr and  $2.0 \times 10^8 \text{ m}^3/\text{yr}$  (USGS, 2003).

From 1045-1085, inferred salinity increased from 0.65 ‰ to 15.2 ‰. Our calculations indicate that lake level dropped over 8 m, and lake volume dropped by  $1.5 \times 10^9 \text{ m}^3$ . For the 40-year period, lake level dropped by 0.2 m/yr and lake volume dropped

**Figure 11: Inferred salinity – lake size relationships**



**Table 3: Statistics for inferred and measured lake level and volume**

	LAKE LEVEL			VOLUME		
	Inferred		Measured	Inferred		Measured
	Model #1	Model #2	Annual	Model #1	Model #2	Annual
<b>max</b>	438.6	438.9	441.1	1995.8	2227.7	3032.8
<b>min</b>	428.8	429.0	427.2	126.2	200.0	56.4
<b>average</b>	431.4	431.4	432.4	461.5	495.9	642.6
<b>st dev</b>	2.7	2.8	3.1	465.3	448.2	623.9
change per year			change per year			
<b>max</b>	0.8	0.9	1.9	163.9	219.5	421.7
<b>min</b>	-1.5	-1.1	-0.5	-148.1	-172.6	-86.4
<b>average</b>	0.0	0.0	0.1	0.4	0.5	21.9
<b>st dev</b>	0.2	0.2	0.5	32.7	35.0	96.0

**Table 4: Transitions between fresh and saline phases**

	To	Date	# Years	Lake level change	Lake level change/yr	Volume change	Volume change/yr
Measured	Fresh	1992 - 2002	11	7.2 m	0.65 m/yr	$2.2 \times 10^9 \text{ m}^3$	$2.0 \times 10^8 \text{ m}^3/\text{yr}$
Inferred #1	Fresh	910-960	50	7.3 m	0.15 m/yr	$1.5 \times 10^9 \text{ m}^3$	$3.0 \times 10^7 \text{ m}^3/\text{yr}$
Inferred #2	Fresh	910-960	50	7.6 m	0.15 m/yr	$1.6 \times 10^9 \text{ m}^3$	$3.2 \times 10^7 \text{ m}^3/\text{yr}$
Measured	Saline	1902 - 1940	38	-7.0 m	-0.18 m/yr	$-7.4 \times 10^8 \text{ m}^3$	$-1.9 \times 10^7 \text{ m}^3/\text{yr}$
Inferred #1	Saline	1045-1085	40	-8.4 m	-0.21 m/yr	$-1.6 \times 10^9 \text{ m}^3$	$-4.0 \times 10^7 \text{ m}^3/\text{yr}$
Inferred #2	Saline	1045-1085	40	-8.6 m	-0.21 m/yr	$-1.6 \times 10^9 \text{ m}^3$	$-4.1 \times 10^7 \text{ m}^3/\text{yr}$

by  $4.0 \times 10^7 \text{ m}^3/\text{yr}$ . This compares well to measured changes (Table 4). In the period of record (1867-2003; USGS, 2003), a large drop in lake level occurred from 1902 to 1940. In this 38-year period, lake level dropped 7.0 m and lake volume dropped by  $7.4 \times 10^8 \text{ m}^3$ , a loss of  $0.18 \text{ m/yr}$  and  $1.9 \times 10^7 \text{ m}^3/\text{yr}$ .

The good agreement between measured and inferred values of lake level and volume indicate that the rapid salinity changes of our inferred salinity model are reasonable.

Another way to estimate the lake level and volume changes represented by our inferred salinity changes is by calculating what the effective precipitation (P-E) would have been for a transition period. Assuming that lake level started at the threshold level to Stump Lake and maintained a constant amount of dissolved solids, we can examine the changes that took place from 1045-1085 A.D. Inferred salinity dropped from 15.18 to 0.65 ‰, indicating a drop of 13 m in lake level and  $2.8 \times 10^9 \text{ m}^3$  in lake volume, which averages to a loss of 0.33 m per year in lake level and 70 million  $\text{m}^3$  per year in volume. The lake level calculated for the end of this salinization period is 427.8 m, less than a meter above the low lake level recorded in 1940.

#### *Comparison to other Devils Lake records*

Several studies (Callender, 1968; Stoermer et al., 1971; Bluemle, 1988; Fritz et al., 1991, 1994; Haskell et al., 1996; Murphy et al., 1997) have reconstructed lake level or salinity changes in Devils Lake. In our new reconstruction of Devils Lake, five fresh periods have occurred in the last 2000 years, centered roughly at 200 A.D., 500 A.D., 700 A.D., 1000 A.D., and the recent fresh period. Two minor freshening events at 1305 – 1315 and 1800 – 1820 A.D. also occurred within the saline realm. The former minor

freshening period may be extended from 1295 – 1410, if one includes one other proximate freshening. These five fresh periods and two minor freshenings match well with other reconstructions of Devils Lake, if differences in dating and sampling strategy are taken into account. All of the reconstructions show a system with large variability, and all show some similarities to our new diatom-inferred salinity record. Data for Callender (1968), Bluemle (1988) and Murphy et al. (1997) was obtained graphically, which may introduce additional discrepancies.

A series of studies (Callender, 1968; Bluemle, 1988; Murphy et al., 1997) have focused on the sedimentary history of the lake. Murphy et al. (1997) produced the most recent interpretation, building on Callender's (1968) sedimentological analysis of lake sediment cores and Bluemle's (1988) radiocarbon dating and analysis of old beach strandlines. Murphy et al. (1997) added more data to the reconstruction by using analyses of fluvial sediments in the natural outlets between basins. Sedimentological assessment of the Jerusalem Outlet (between East Devils Lake and Stump Lake) and the Tolna Outlet (between Stump Lake and the Sheyenne River) was achieved by drilling auger holes and digging trenches in the outlet areas and examining the cross-sections. Their reconstruction showed fourteen fresh periods in the last 10 ka, five of which were in the last 2 ka: 100 A.D., 750 A.D., 1150 A.D., 1650 A.D. and the recent period. The first three may correspond with fresh periods in our reconstruction at 200, 700 and 1000 A.D., while the fourth may correspond with our minor freshening period at 1800-1820. Water levels were assigned qualitative values, on a scale going from dry land to overflow.

Reconstructions of Devils Lake's salinity have been based on paleoecological studies of diatoms and ostracodes (Stoermer et al., 1971; Fritz et al., 1991, 1994; Haskell et al., 1996. Stoermer et al. (1971) completed the first diatom study of Devils Lake sediments; several shifts between saline and fresh conditions were identified in this undated core.

Diatoms were analyzed from point samples at 10 cm intervals for the last ~11 ka in a 24 m long sediment core collected from Creel Bay in 1985 (Fritz et al., 1991; Haskell et al., 1996). Salinity was reconstructed from the diatom assemblage using a transfer function developed for the Great Plains (Fritz et al., 1993); at least seven oscillations of fresh and saline periods were identified in the last ~11 ka, including five fresher periods in the last 2 ka at 40, 425-615, 1150 and 1490-1655 A.D. (Fritz et al., 1991). The first three fresh periods may correspond with fresh periods in our record at 200, 500 and/or 700, and 1000 A.D., while the fourth may correspond with our minor freshening events. Salinity ranged from 1.0 g/L to 38.2 g/L in the entire core (Fritz et al., 1991). For the last 2000 years, salinity ranged from 1.4 g/L to 18.0 g/L for the reconstruction of Fritz et al. (1991) and from 0.4 g/L to 20.9 g/L for our reconstruction. The diatom assemblage represented by point samples displays the potential for variability in taxa and salinity in Devils Lake, but it is not a reliable reconstruction of long-term salinity changes.

Diatom, ostracode, and bulk carbonate values from a short core collected in 1986 from Creel Bay were compared to reconstruct the past 500 years of climate change in the Devils Lake area (Fritz et al., 1994). The ostracode Mg/Ca ratio and diatom-inferred salinity values had similar trends (reflecting lake chemistry changes), while the Sr/Ca

ratio of bulk carbonate samples showed less variability (reflecting the aragonite/calcite ratio, and affected by a threshold response in their precipitation; Fritz et al., 1994). From the 1500's until 1850, all three proxies indicated that Devils Lake was very saline (> 20 ‰); Fritz et al. (1994) interpreted this high salinity as aridity in the Great Plains during the Little Ice Age, which coincided with this time period. Diatom and ostracode data indicate that after 1850 a shift to less saline conditions began. Wiche et al. (1996) argued against the findings of Fritz et al. (1994). Historical records of lake level and floods in the 1800's, a strong commercial fishing industry in the 1880's and tree ring data of higher moisture were given as evidence against high salinity in the 1800's (Wiche et al., 1996). Fritz et al. (1996) argued that their data represented averages for decadal to subdecadal periods, and were intrinsically difficult to compare to pulse events like floods, which may not be representative of average annual conditions. Furthermore, they cited historical evidence of higher fire frequency in the early 19<sup>th</sup> century, commercial fisheries in the 1830's thriving in saline conditions, and an alternate interpretation of tree ring data to support their paleolimnological interpretation (Fritz et al., 1996). Fritz et al. (1996) point out that salinity values above 10 ‰ have a great deal of uncertainty in their salinity model, so they assert that this period of high salinity had values of at least 10 ‰. Our new paleosalinity reconstruction displays lower salinity values (0.5 g/L to 20.7 g/L) than the Fritz et al. (1994) reconstruction (1.2 g/L to 37.8 g/L). However, our reconstruction does show a prolonged saline interval during the Little Ice Age, with salinity values generally above 15 g/L from 1500 – 1800. The transition toward fresher values begins around 1800 in our reconstruction. A minor freshening period, where salinity briefly dips below 10 ‰, occurs around 1850 in the Fritz et al. (1994) reconstruction, and from 1800

– 1820 in our reconstruction. After 1850, and particularly after 1940, both reconstructions become fresher, and salinity values match more closely.

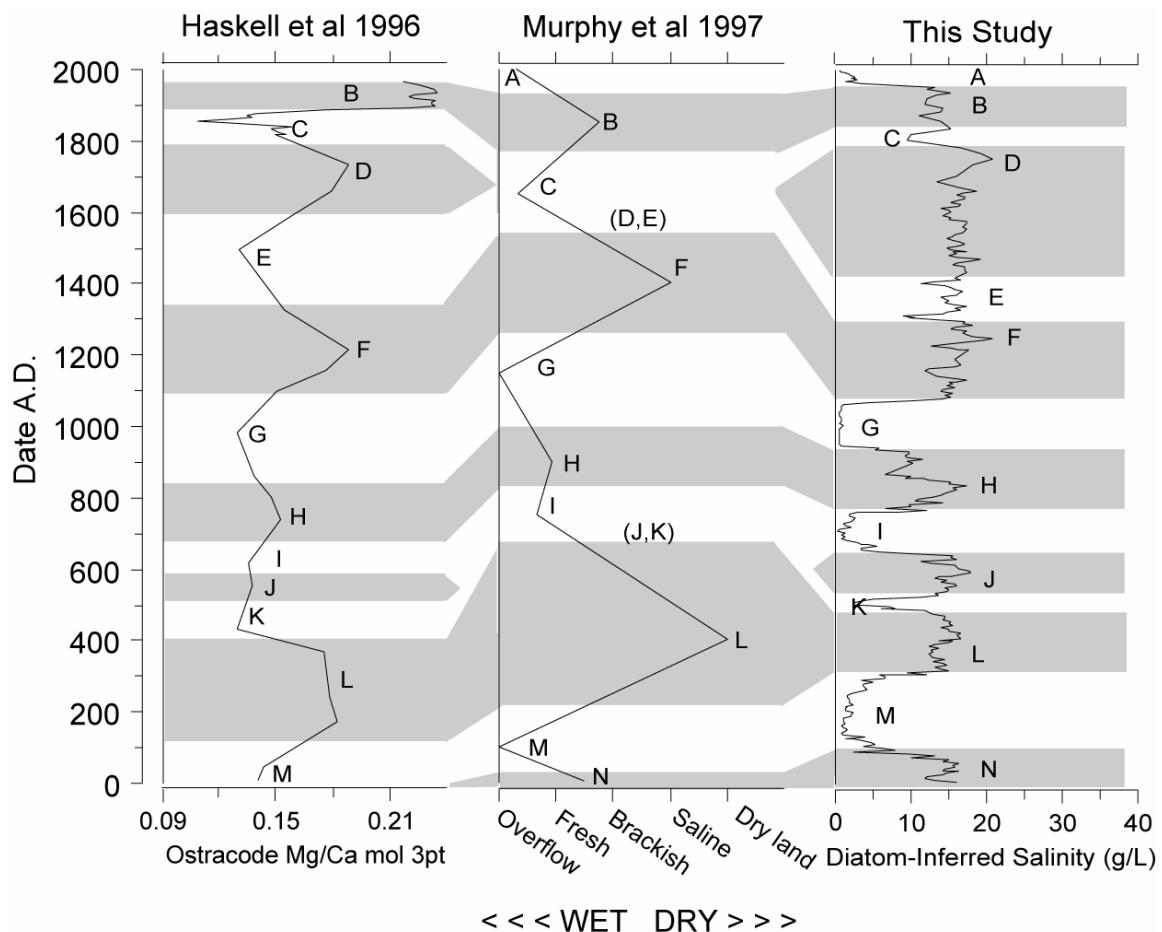
Ostracodes were sampled in 1 to 2-cm sections for the last 150 years in a 1 m core collected from Creel Bay in 1986 (Engstrom & Nelson, 1991). This data was added to ostracode data from a 24 m long sediment core collected from Creel Bay in 1985, where ostracodes were sampled in 8-cm sections for the last ~12 ka (Haskell et al., 1996). Many fresh-saline fluctuations were inferred from the ostracode and bulk carbonate data, including five fresh periods in the last 2 ka centered at 450, 600, 1000, 1500 and 1850 A.D. The first three may correspond to fresh periods in our reconstruction dated at 500, 700 and 1000 A.D., and the last two may correspond to our minor freshening periods. Additionally, a peak in salinity that occurs at 1650 in the ostracode record may match a saline peak at 1750 in our record. The more extreme values in the last 150 years of the ostracode record reflect finer-resolution sampling; the lower-resolution sampling of the rest of the core could dampen the extreme values, because more ostracode shells may be included and because a longer time period is more likely to contain high and low values that would average toward the middle.

Our study gives a clearer picture of the last 2000 years than the earlier reconstructions of Devils Lake because there is significantly more data at high resolution. The paucity of data in other records makes it difficult to compare them and to identify the same event in several records. Uncertainty in radiocarbon dating adds to the difficulty. Still, all of the fresh periods from our reconstruction were also identified in other reconstructions, and all of the reconstructions show that Devils Lake has broad natural variability. However, in low-resolution records, data points are found at high and low

lake level or salinity, and a smooth curve is fit between the data points. Our high-resolution study shows that changes in Devils Lake's salinity appear to occur in rapid phase shifts rather than slow undulations.

Comparing our record to other records (Figure 12) allows us to distinguish between lake level changes that are tied to salinity changes and those that are not. In the period from 0 to 1070 A.D., our reconstruction agrees relatively well with other reconstructions, and we can infer that salinity and lake level had an inverse relationship for that period. From 1070 – 1960 A.D., fresh periods recorded in other records are recorded as minor freshening events in our record. Specifically, the sedimentary record (Murphy et al., 1997) shows high lake level at 1650, and the ostracode record (Haskell et al., 1996) shows low Mg/Ca at 1500 and 1850. These high-water periods may correspond with our two minor freshening periods, at 1305 – 1315 (1295-1410) and 1800-1820 A.D. A disparity between sedimentary and salinity records may indicate that Devils Lake was a large saline lake during these periods, so that an inflow of water into the lake could only decrease salinity slightly. For the 1800's, historical evidence suggests that lake level and salinity were both high (Fritz et al., 1996). The stronger response of ostracodes as compared to diatoms in these two events may be due differences in the way that each organism records change; diatoms in Devils Lake respond to salinity changes, whereas ostracodes may respond to changes in chemistry and/or temperature. Because the Mg/Ca ratio of *Candona rawsoni* has been found to be positively correlated with temperature (Xia et al., 1997), periods of low Mg/Ca may indicate cooler, wetter conditions, rather than low salinity. In addition to cooler climate,

**Figure 12: Ostracode, sediment and diatom records from Devils Lake**



the water temperature rise would be seasonally slower at high water levels, because more energy input is required to raise the temperature of a larger volume of water; the timing of ostracode shell formation would determine what effect this would have on Mg/Ca ratios. *Candona rawsoni* (used in ostracode studies of Devils Lake) lives on the substrate (Haskell et al., 1996). When lake level is high, thermal stratification is more likely, and the temperature in the ostracode habitat would be lower.

By comparing different records of Devils Lake (Figure 12), we can reconstruct its history. From 0 – 1070 A.D., the ostracode record (Haskell et al., 1996; Engstrom & Nelson, 1991), the sedimentary record (Murphy et al., 1997) and this study record similar changes, because high-water periods were also fresh periods. Sometime after 1070 A.D., Devils Lake became a large, saline lake. Two cooler, wetter phases raised the water level, but were unable to trigger an extreme freshening of the lake, because the mass of dissolved solids was too great. In the late 1800's to early 1900's, the lake level dropped, and Devils Lake became a small saline lake. Thus, the recent increase in precipitation changed both the water level and salinity level drastically.

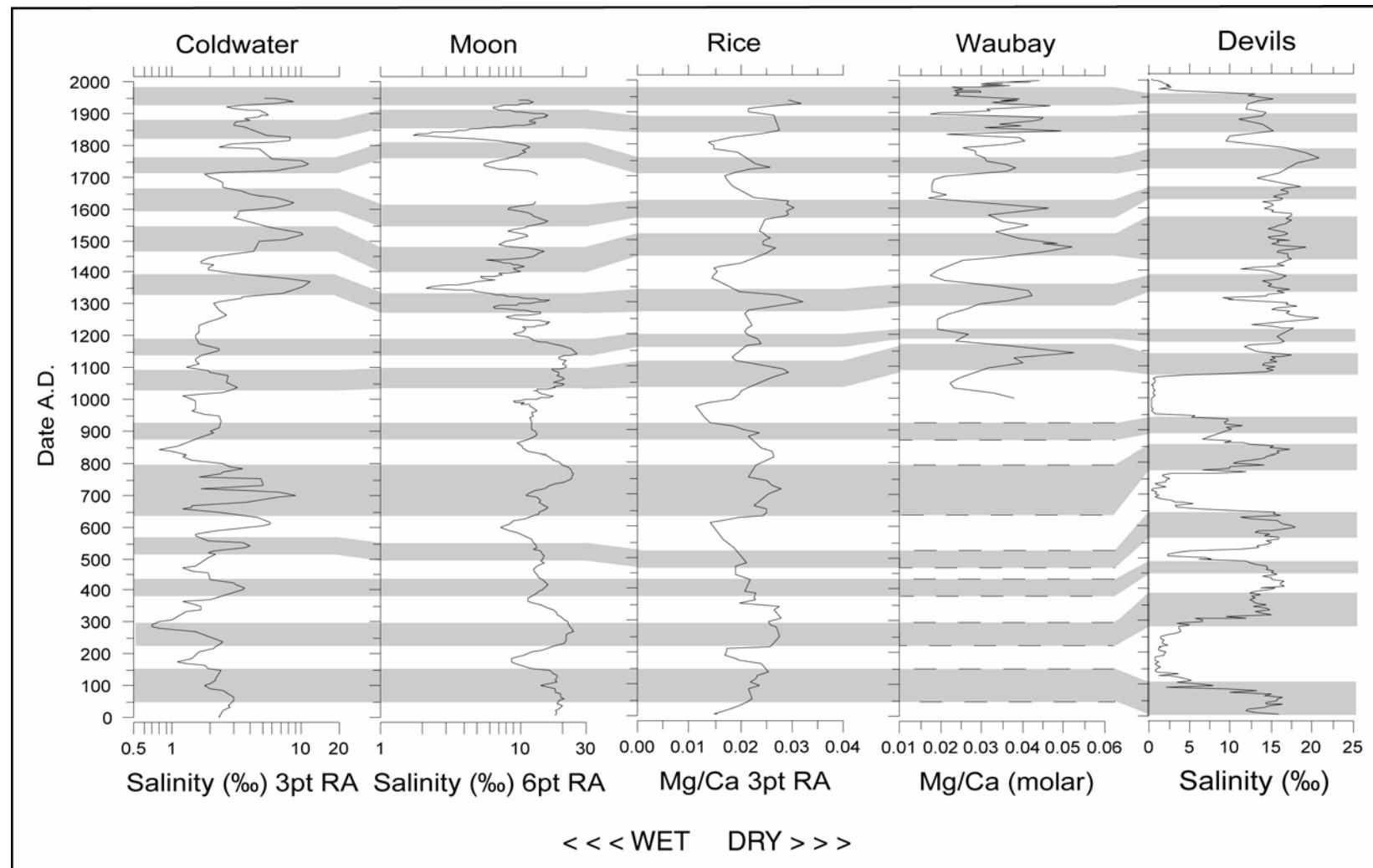
### **Comparison to other systems**

Paleoecological records from Coldwater Lake, Moon Lake, and Rice Lake, N.D. (Fritz et al., 2000), and Waubay Lake, S.D. (Shapley et al., *in press*) have revealed similar shifts in diatom-inferred salinity and ostracode shell magnesium-calcium ratios, which tell a fairly cohesive story of regional climate change in the Northern Great Plains of the United States over the last 2000 years. Devils Lake records the same regional climate changes, but its response to climate change is unique in this group (Figure 13).

Coldwater, Moon and Rice are all small ( $<1 \text{ km}^2$ ), topographically closed lakes; lake level is controlled by precipitation, evapotranspiration and groundwater flow (Fritz et al., 2000). Devils Lake, in contrast, is a large (30  $\text{km}^2$  in 1940 and 500  $\text{km}^2$  in 2002; USGS, 2003) multibasin system, where lake level is controlled by precipitation, evaporation, surface runoff and inter-basin flow (Wiche, 1992). Groundwater input is a minor component of the Devils Lake water budget, except during dry periods (Pusc, 1993). The differences in size and hydrology determine the differences found in the sedimentary record of the lakes: the small lakes are more sensitive to small climate fluctuations. Thus, the trio of small lakes record more frequent moderate salinity shifts, while Devils Lake records less frequent broad salinity shifts.

The Waubay Lake system is more like Devils Lake in that it is larger than the first three lakes and it is composed of several basins that may connect or separate depending on water level. However, Waubay appears to record climate changes in the same way that Coldwater, Moon and Rice Lakes do. Why? The sediment core was collected from Spring Lake, one basin of Waubay Lake that behaves like a small lake while it is separated from the other basins. The whole Waubay Lake system is smaller than Devils Lake at high stand (134  $\text{km}^2$  vs. 437  $\text{km}^2$ , respectively, in 1998) and appears to have a smaller range of size variability: its lowest lake stand (1939, 37  $\text{km}^2$ ) was 3.5 times smaller than the modern, while Devils Lake's low stand (1940, 30  $\text{km}^2$ ) was 16 times smaller than the modern. Furthermore, the thresholds between basins in Waubay are all within 2 m in elevation (Shapley et al, *in press*), while in Devils Lake, the thresholds between basins have a range in elevation of over 15 m. Thus, a smaller precipitation input is required to see dramatic changes in the size of Waubay Lake, as

**Figure 13: Region records of climate change.** After Fritz et al., 2000 and Shapley et al., *in press*.



compared to Devils Lake. In addition, the lake level of Spring Lake is controlled partly by groundwater flow (Shapley et al., *in press*), which connects the basins even when they have not coalesced on the surface. This groundwater input limits the extremity and sustainability of wet and dry periods, as compared to Devils Lake. At a low stand, Spring Lake remains fresher because of groundwater input, and at a high stand, groundwater outflow will limit the water elevation (Shapley et al., *in press*). All of these factors support the idea that dramatically more precipitation input is required to make Devils Lake fresh, as compared to Waubay Lake. This makes Devils Lake less sensitive to small changes in climate that are recorded in Waubay Lake.

These regional records indicate a shift in climate conditions between the period from 0-1070 AD and the period from 1070 AD to present. Coldwater, Moon, Rice and Devils Lakes show a shift in average salinity and Mg/Ca from one period to the other. Coldwater, Rice and Devils Lakes show higher average values for the second period, while Moon Lake shows lower average values. This shift in climate conditions may have created the conditions that made it possible for Devils Lake to become large and saline, preventing pluvial events from quickly freshening the lake. It is also possible that climate was more stable during this period as compared to the first millennium, and the pluvial events that occurred were not as large.

## **Conclusions**

In addition to the recent fresh period, Devils Lake has experienced four fresh periods and two minor freshening periods in the last 2000 years. Transitions between fresh and saline periods have been rapid, representing lake level changes that have been similar to those observed in the last 150 years. From 0 – 1070 A.D., Devils Lake showed

more variable behavior, with fresh phases centered at 200, 500, 700 and 1000 A.D. From 1070 to 1960 A.D., Devils Lake was saline, experiencing two minor freshening periods at 1305-1315 and 1800-1820 A.D. Other records from Devils Lake indicate that water level was high during at least part of this prolonged saline period, from which we infer that the lake became large and saline. Any large pluvial events that occurred could not dilute the lake enough to become fresh. Other regional records indicate a shift in climate between the two periods, 0-1070 A.D. and 1070-present, which may have caused the shift in lake behavior. In the late 1800's and early 1900's, the lake began to shrink, and Devils Lake became small and saline. The recent increase in precipitation was able to change both lake level and salinity drastically, similar to the behavior of Devils Lake in the first millennium.

## References

Anderson, R.Y., W.E. Dean & J.P. Bradbury, 1993. Elk Lake in perspective. In J.P. Bradbury and W.E. Dean (eds.), *Elk Lake, Minnesota: Evidence for Rapid Climate Change in the North-Central United States*. Boulder, Colorado, Geological Society of America Special Paper 276: 1-6.

Appleby, P.G. & F. Oldfield, 1978. The calculation of lead-210 dates assuming a constant rate of supply of the unsupported  $^{210}\text{Pb}$  to the sediment. *Catena* 5:1-8.

Bennion, H., S. Juggins & N.J. Anderson, 1996. Predicting epilimnetic phosphorous concentrations using an improved diatom-based transfer function and its application to lake eutrophication management. *Environmental Science and Technology* 30: 2004-2007.

Bluemle, J.P., 1981. The origin of Devils Lake. *North Dakota Geological Survey Newsletter* 8(2): 7-9.

Bluemle, J.P., 1988, Radiocarbon dates on Devils Lake beaches: *North Dakota Geological Survey Newsletter* 15(1): 39-45.

Bluemle, J.P., 1999. The origin and behavior of Devils Lake. *North Dakota Geological Survey website*. [http://www.state.nd.us/ndgs/Devils\\_Lake/Orgin\\_Devils\\_Lake.htm](http://www.state.nd.us/ndgs/Devils_Lake/Orgin_Devils_Lake.htm).

Callender, E., 1968. *The Postglacial Sedimentology of Devils Lake*, North Dakota. Unpublished Ph.D. dissertation, University of North Dakota.

Clayton, L., S.R. Moran, J.P. Bluemle & C.G. Carlson, 1980. Geologic map of North Dakota. *North Dakota Geological Survey*, Grand Forks, North Dakota.

Dean, W.E., 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. *Journal of Sedimentary Petrology* 44: 242-248.

Eakins, J.D. & R.T. Morrison, 1978. A new procedure for the determination of Lead-210 in lake and marine sediments. *International Journal of Applied Radiation and Isotopes* 29:531-536.

Engstrom, D.R. & S.R. Nelson, 1991. Paleosalinity from trace metals in fossil ostracodes compared with observational records at Devils Lake, North Dakota, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology* 83: 295-312.

Fritz, S.C., 1990. Twentieth-century salinity and water-level fluctuations in Devils Lake, North Dakota: Test of a diatom-based transfer function. *Limnology & Oceanography* 35(8): 1771-1781.

Fritz, S.C., S. Juggins, R.W. Battarbee, & D.R. Engstrom, 1991. Reconstruction of past changes in salinity and climate using a diatom-based transfer function. *Nature* 352: 706-708.

Fritz, S.C., S. Juggins & R.W. Battarbee , 1993. Diatom assemblages and ionic characterization of lakes of the Northern Great Plains, North America: A tool for reconstructing past salinity and climate fluctuations. *Canadian Journal of Fisheries and Aquatic Sciences* 50: 1844-1856.

Fritz, S.C., D.R. Engstrom & B.J. Haskell, 1994. 'Little Ice Age' aridity in the North American Great Plains: a high-resolution reconstruction of salinity fluctuations from Devils Lake, North Dakota, U.S.A. *The Holocene* 4(1): 69-73.

Fritz, S.C., D.R. Engstrom & B.J. Haskell, 1996. Nineteenth-century climate in the Devils Lake region as reconstructed from palaeolimnological proxies: a reply to Wiche, Lent and Rannie. *The Holocene* 6: 490-493.

Fritz, S.C., B.F. Cumming, F. Gasse & K. Laird, 1999. Diatoms as indicators of hydrologic and climatic change in saline lakes. In E.F. Stoermer & J.P. Smol (eds.), *The Diatoms: Applications for the Environmental and Earth Sciences*. Cambridge University Press, Cambridge & New York: 41-72.

Fritz, S.C., E. Ito, Z. Yu, K.R. Laird & D.R. Engstrom, 2000. Hydrologic variation in the Northern Great Plains during the last two millennia. *Quaternary Research* 53:175-184.

Gasse, F., S. Juggins & L. Ben Khelifa, 1995. Diatom-based transfer functions for inferring hydrochemical characteristics of African palaeolakes. *Palaeogeography, Palaeoclimatology, Palaeoecology* 117: 31-54.

Gell, P.A., 1997. The development of a diatom database for inferring lake salinity, Western Victoria, Australia: towards a quantitative approach for reconstructing past climates. *Australian Journal of Botany* 45: 389-423.

Gell, P.A., 1998. Quantitative reconstructions of the Holocene palaeosalinity of paired crater lakes based on a diatom transfer function. *Palaeoclimates* 31: 83-96.

Haskell, B.J., D.R. Engstrom, & S.C. Fritz, 1996. Late Quaternary paleohydrology in the North American Great Plains inferred from the geochemistry of endogenic carbonate and fossil ostracodes from Devils Lake, North Dakota, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology* 124: 179-193.

Heiri, O., A.F. Lotter & G. Lemcke, 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology* 25: 101-110.

Hinckley, D., 1995. Great Plains climates and biota: past, present, and future. In Stanley R. Johnson & Aziz Bouzaher (eds.), *Conservation of Great Plains Ecosystems*. Kluwer Academic Publishers: 149-159.

Jacobson, H.A. & D.R. Engstrom, 1989. Resolving the chronology of recent lake sediments: an example from Devils Lake, North Dakota. *Journal of Paleolimnology* 2: 81-97.

Jones, B.F. & A.S. Van Denburgh, 1966. Geochemical influences on the chemical character of closed lakes. In *Symposium of Garda, Hydrology of Lakes and Reservoirs, Proceedings of the International Association of Scientific Hydrology Publication* 70: 438-446.

Juggins, S., 2003. C2 Data Analysis, Version 1.3. Software for ecological and palaeoecological data analysis and visualisation. University of Newcastle, Newcastle upon Tyne, UK.

Kashima, K., 2003. The quantitative reconstruction of salinity changes using diatom assemblages in inland saline lakes in the central part of Turkey during the Lake Quaternary. *Quaternary International* 105: 13-19.

Manous, J.D., 2000. Sulfate distribution within Devils Lake, ND : movement of dissolved solids by gravity, buoyancy, and wind induced advection. Unpublished Ph.D. Dissertation. University of Minnesota.

Murphy, E.C., A.M.K. Fritz & R.F. Fleming, 1997 (revised 2002). The Jerusalem and Tolna Outlets in the Devils Lake Basin, North Dakota. Report of Investigation Number 100. North Dakota Geological Survey.

Pappas, J.L. & E.F. Stoermer, 1996. Quantitative method for determining a representative algal sample count. *Journal of Phycology* 32: 693-696.

Pusc, S.W., 1993. The interaction between ground water and a large terminal lake – Devils Lake, North Dakota: Hydrogeology of the Devils Lake area. North Dakota State Water Commission Water Resources Investigation 13.

Reed, J.M., 1998. A diatom-conductivity transfer function for Spanish salt lakes. *Journal of Paleolimnology* 19: 399-416.

Renberg, I., 1990. A procedure for preparing large sets of diatom slides from sediment cores. *Journal of Paleolimnology* 4: 87-90.

Roberts, D. & A. McMinn, 1998. A weighted-averaging regression and calibration model for inferring lakewater salinity from fossil diatom assemblages in saline lakes of the Vestfold Hills: a new tool for interpreting Holocene lake histories in Antarctica. *Journal of Paleolimnology* 19: 99-113.

Roux, M., S. Servant-Vildary & M. Servant, 1991. Inferred ionic composition and salinity of a Bolivian Quaternary lake, as estimated from fossil diatoms in the sediments. *Hydrobiologia* 210: 3-18.

Ryves, D.B., S. McGowan & N.J. Anderson, 2002. Development and evaluation of a diatom-conductivity model from lakes in West Greenland. *Freshwater Biology* 47: 995-1014.

Shapley, M.D., W.C. Johnson, D.R. Engstrom & W.R. Osterkamp. Late Holocene flooding and drought in the Northern Great Plains, reconstructed from tree rings, lake sediments and ancient shorelines. *The Holocene: In press*.

Stoermer, E.F., S.M. Taylor & E. Callender, 1971. Paleoecological Interpretation of the Holocene diatom succession in Devils Lake, North Dakota. *Transactions of the American Microscope Society* 90 (2): 195-206.

Stuiver, M. and P.J. Reimer, 1993. Extended 14C database and revised CALIB 3.0 14C Age calibration program. *Radiocarbon* 35: 215-230.

Swenson, H.A., and Colby, B.R., 1955, Chemical quality of surface waters in Devils Lake basin, North Dakota: U.S. Geological Survey Water-Supply Paper 1295, 82 p.

ter Braak, C.J.F. & P. Šmilauer, 1997-1999. CANOCO for Windows Version 4.02: Software for Canonical Community Ordination. Centre for Biometry Wageningen, Wageningen, The Netherlands.

US Army Corps of Engineers (USACE), 2003a. Final integrated planning report and environmental impact statement for Devils Lake, ND.

US Army Corps of Engineers (USACE), 2003b. Devils Lake Basin project website. <http://www.mvp.usace.army.mil/finder/display.asp?pageid=14>.

USGS, 2003. Period of Record for Station 05056500 Devils Lake near Devils Lake, North Dakota. <http://nd.water.usgs.gov/devilstake/dvlakepor.html>

Vecchia, A.V., 2002. Simulation of a Proposed Emergency Outlet from Devils Lake, North Dakota: USGS Water-Resources Investigations Report 02-4042.

Xia, J., D.R. Engstrom & E. Ito, 1997. Geochemistry of ostracode calcite: Part 2. The effects of water chemistry and seasonal temperature variation on *Candona rawsoni*. *Geochimica et Cosmochimica Acta* 61: 383-391.

Wiche, G.J., 1992. Hydrology and water-level fluctuations of Devils Lake, North Dakota. In S. Subitzky (ed.), Selected papers in the hydrologic sciences, 1988-1992. U.S. Geological Survey Water-Supply Paper, W 2340: 75-87.

Wiche, G.J., R.M. Lent & W.F. Rannie, 1996. 'Little Ice Age' aridity in the North American Great Plains – a high-resolution reconstruction of salinity fluctuations from Devils Lake, North Dakota, USA: a comment on Fritz, Engstrom and Haskell. *The Holocene* 6: 489-490.

Wiche, G.J. & A.V. Vecchia, 1996. Lake-level frequency analysis for Devils Lake, North Dakota. U.S. Geological Survey Water-Supply Paper 2469.

Wiche, G.J., A.V. Vecchia, L. Osborne & J.T. Fay, 2000. Climatology and potential effects of an emergency outlet, Devils Lake Basin, North Dakota. USGS Fact Sheet FS-089-00.

Williams, W.D., 1981. Inland salt lakes: an introduction. *Hydrobiologia* 81: 1-14.

Wilson, S.E., B.F. Cumming & J.P. Smol, 1996. Assessing the reliability of salinity inference models from diatom assemblages: an examination of a 219-lake data set from western North America. *Canadian Journal of Fisheries and Aquatic Sciences* 53: 1580-1594.

## **APPENDIX C**

## **CORE CHARACTERIZATION DATA**

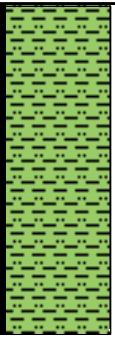
## **APPENDIX C-1**

### **CORE DESCRIPTION AND DOCUMENTATION**

## Devils Lake, ND 2002, DL02-PA

Date: March 29, 2002

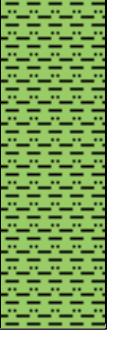
Described by: Brian Haskell

METERS	CORE	GRAPHIC LITH.	STRUCTURE	ACCESSORIES	FOSSILS	DISTURB.	SAMPLE	COLOR	DESCRIPTION
1								BK OL .. OL	Core starts 0.30 mblf (0.30 m extruded and placed in cups)  DL02-PA, 14.5-15 cm Distinct darker band not observed in DL02-PB

## Devils Lake, ND 2002, DL02-PB

Date: March 29, 2002

Described by: Brian Haskell

METERS	CORE	GRAPHIC LITH.	STRUCTURE	ACCESSORIES	FOSSILS	DISTURB.	SAMPLE	COLOR	DESCRIPTION
1								BK OL .. OL	Core starts 0.30 mblf (0.30 m extruded and placed in cups)  0-15 cm with smooth surface to sediment. Clumping sediment below 54 cm.

## Devils Lake, ND 2002, Site A, DL02-LA

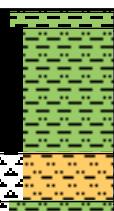
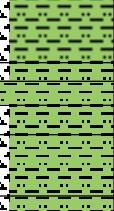
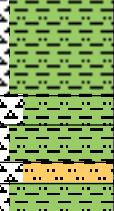
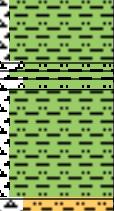
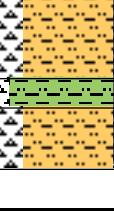
Date: March 18, 2002

Described by: Brian Haskell

# Devils Lake, ND 2002, Livingstone Core B, DL02-LB

Date: March 20, 2002

Described by: Brian Haskell

METERS	CORE	GRAPHIC LITH.	STRUCTURE	ACCESSORIES	FOSSILS	DISTURB.	SAMPLE	COLOR	DESCRIPTION
1								.. BK ol GY dk ol GY .. .. dk GY .. OL ol GY OL ol GY .. OL .. .. ..	Top of core starts 0.66 mblf DL02-LB-1, 0-10 Olive gray (5Y4/1) SILTY CLAY WITH ORGANICS Other units as described for DL02-LA and in Core Description.
2								OL	
3								dk ol GY dk GY .. OL .. .. ..	
4								OL dk GY	
5								.. OL .. .. OL .. dk GY .. OL .. .. OL .. dk GY	
6								.. OL .. .. OL .. dk GY .. dk ol GY .. OL .. dk ol GY	
6.5								.. OL .. dk ol GY	

# Description of Devils Lake 2002 Cores

## Explanatory Notes

The Devils Lake sediments consist primarily (>60%) of non-biogenic components and are therefore given clastic primary lithology names (silty clay, clayey silt). Major modifying components (~20%) are placed in front of the primary lithology name; those comprising 10-20% are placed after the name ("with"). Lithologies were determined for specific depths by smear-slide (labeled "SS" in the sample column on the barrel sheet) analysis and then assigned to depth intervals on the basis of visual characteristics, specifically color.

Core and intervals are identified by: core location (Devils Lake, DL) year (02) - core type (L=Livingstone, P = surface piston corer) and site (A, B, etc.) - section, depth or depth interval (in cm in section)

## Lithologies

DL02-LB-1, 0-10; DL02-PA-1, 0-65; DL02-PB-1, 0-66.5  
Olive gray (5Y4/1) SILTY CLAY WITH ORGANICS

DL02-LA-1, 0-31 and DL02-LB-1, 10-70

Dark yellowish brown (10YR4/2) ORGANIC SILTY CLAY. This is transitional from the overlying silty clay with organics and probably overlaps with the base of DL02-PA and DL02-PB, but the transition point is not clear.

DL02-LA-1, 31 to DL02-LA-7, 95 and DL02-LB-1, 31 to DL02-LB-7, 92

Most of the hole is alternating dm-scale zones of olive (5Y5/3, 5Y5/2), gray, dark gray (5Y5/1), and olive gray (5Y4/1) SILTY CLAY WITH DIATOMS and SILTY CLAY; and dark olive gray (5Y3/2), greenish black (5GY2/1) and very dark gray (5Y3/1) DIATOMACEOUS SILTY CLAY, DIATOMACEOUS CLAYEY SILT and SILTY CLAY WITH DIATOMS. In some cases the lighter zones darken downwards gradually, whereas the darker zones may change to lighter zones over a shorter distance, though rarely are the boundaries very distinct. Most color transitions are gradual, with some mottling and indistinct wispy lamination.

The lightest zones have fewer diatoms (<5-15%); ~40% total sediment is silt evenly split between carb. and non-carb., to 40µm; <2% organics and Fe/Mn oxides. The diatoms are salinity tolerant genera (Cyclotella, Surirella, some Chaetoceras).

Darker zones have 1-2% Fe/Mn (e.g. pyrite) and stained grains. Slightly greater amounts of silt (~60%) though still split evenly between carbonate and non-carbonate. Diatoms are more common (15-20%) and can consist of both saline and fresh (e.g. Stephanodiscus) genera.

The carbonate grains are mostly anhedral and in some cases are fairly large (40 µm) suggesting at least some input from detrital sources. A few of the smaller grains are subhedral and show some signs of original crystal shape more indicative of an endogenic origin. Quartz and feldspars comprise most of the non-carbonate lithogenic fraction. It was not possible to determine how much of the <4µm fraction was carbonate, though a few aragonite needles were observed in some samples. There are also rare white lenses that largely consist of aragonite.

## Legend and Abbreviations Used

Black = organics

Triangles on white = diatoms

Dashes with stippling on green = silty clay

Stipples with dashes on tan = clayey silt

Leaf = plant material

=Arag= = Aragonite lens

SS = smear slide

## **Smear Slide Descriptions**

DL02-LA-1, 20 cm

**ORGANIC SILTY CLAY**

No diatoms. ~20% organics. ~20% of non-organics is  $>4\text{ }\mu\text{m}$  of which half is anhedral carbonate, remainder quartz/feldspar. Some aragonite in  $<4\text{ }\mu\text{m}$ . From cultural horizon.

DL02-LA-1, 44 cm

**DIATOMACEOUS CLAYEY SILT**

~15-20% diatoms, some Stephanodiscus (fresh). Coarser silt than at 20 cm and 63 cm in this section, also more non-carbonate. 2-3% organics and Fe-Mn oxides. From a very dark layer.

DL02-LA-1, 63 cm

**SILTY CLAY WITH DIATOMS**

5-10% diverse diatoms.  $<5\text{ }\mu\text{m}$  organics. 60% non-organics  $<4\text{ }\mu\text{m}$ , of which about half are carbonate grains, some aragonite. From a lighter layer.

DL02-LA-3, 19 cm

**DIATOMACEOUS CLAYEY SILT**

15-20% diatoms (Cyclotella). Stained grains and pyrite. Many carbonate grains 4-40 $\mu\text{m}$ . From a very dark gray layer.

DL02-LA-3, 54 cm

Much aragonite in fine fraction. Surirella and Cyclotella diatoms. From a white lens.

DL02-LA-3, 83 cm

**SILTY CLAY**

2-5% diatoms.  $<5\text{ }\mu\text{m}$  organics. Trace pyrite. Non-organic fraction with even amounts of silt and clay, 50% of silt size is carbonate.

DL02-LA-5, 14 cm

**ORGANIC SILTY CLAY WITH DIATOMS**

15% diatoms (Cyclotella, Surirella). 20% organics. Silt to 150 $\mu\text{m}$ . This is a thin (1 mm) layer.

DL02-LA-6, 26 cm

**SILTY CLAY WITH DIATOMS**

Cyclotella, Surirella. Lighter layer.

DL02-LA-6, 89 cm

**DIATOMACEOUS CLAYEY SILT**

15% Stephanodiscus. 1-2% stained grains. Carbonate grains to 50 $\mu\text{m}$ . Darker layer.

DL02-LB-1, 6 cm

**CLAYEY SILT WITH ORGANICS**

2-5% diatoms, Cyclotella. 5-10% organics. 20% silt size non-biogenic, mixture of carbonate and

non-carbonate.

DL02-LB-1, 15 cm

**ORGANIC SILTY CLAY**

1% diatoms (Cyclotella). 20% organics. Slightly more silt than clay. Silt has carbonate and non-carbonate.

DL02-LB-2, 34 cm

**SILTY CLAY WITH DIATOMS**

Diatoms < 15%, at least four genera including Surirella, Cyclotella. Organics 5%. Many stained grains. Silty clay matrix. From a darker layer

DL02-LB-2, 42 cm

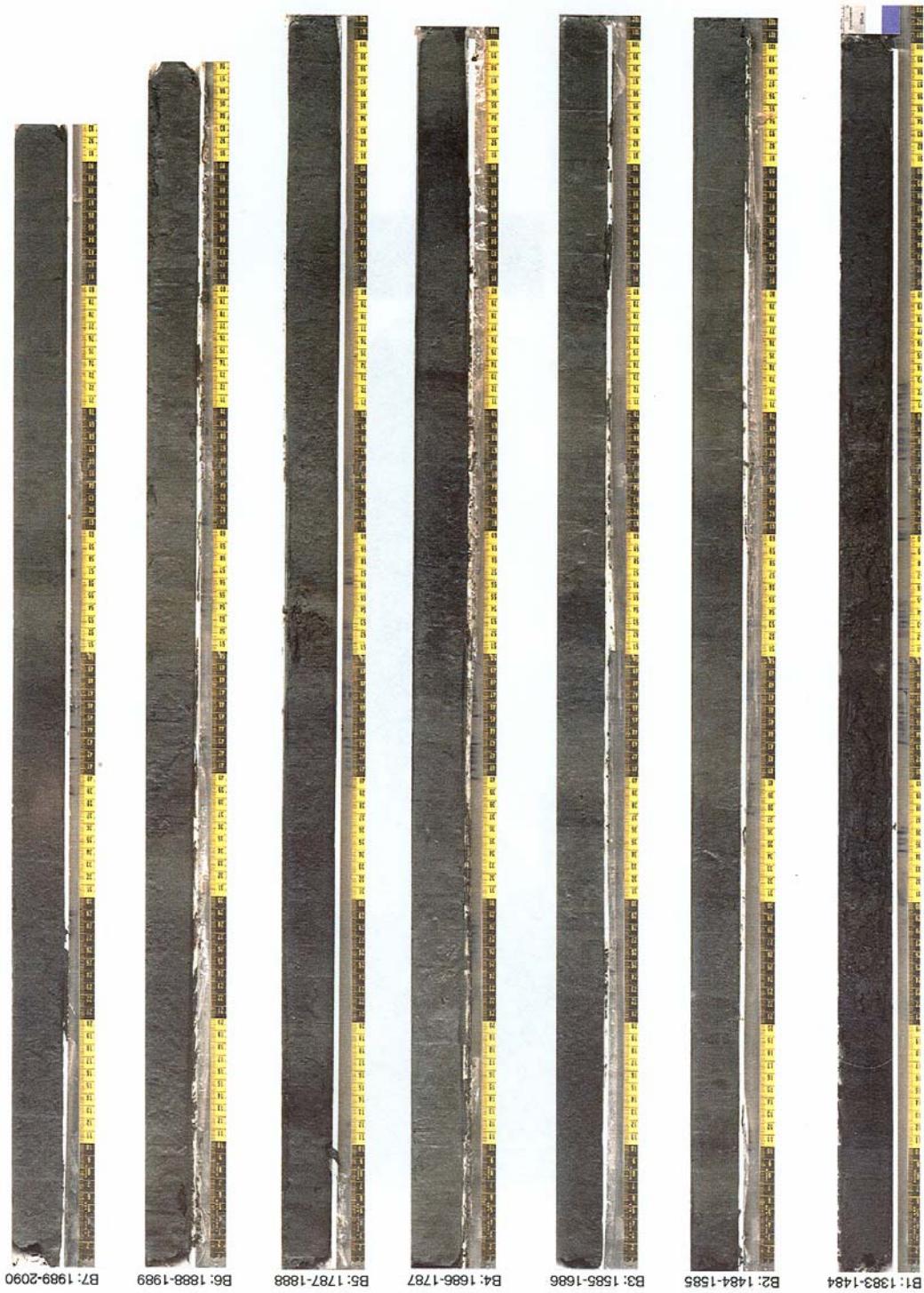
**SILTY CLAY**

Diatoms ~1%, only Cyclotella. 5-10% organics and stained grains. Silty clay matrix. From a lighter layer.

Brian Haskell

March 28, 2002

Core B, Creel Bay, Devils Lake, ND, March 13 2002



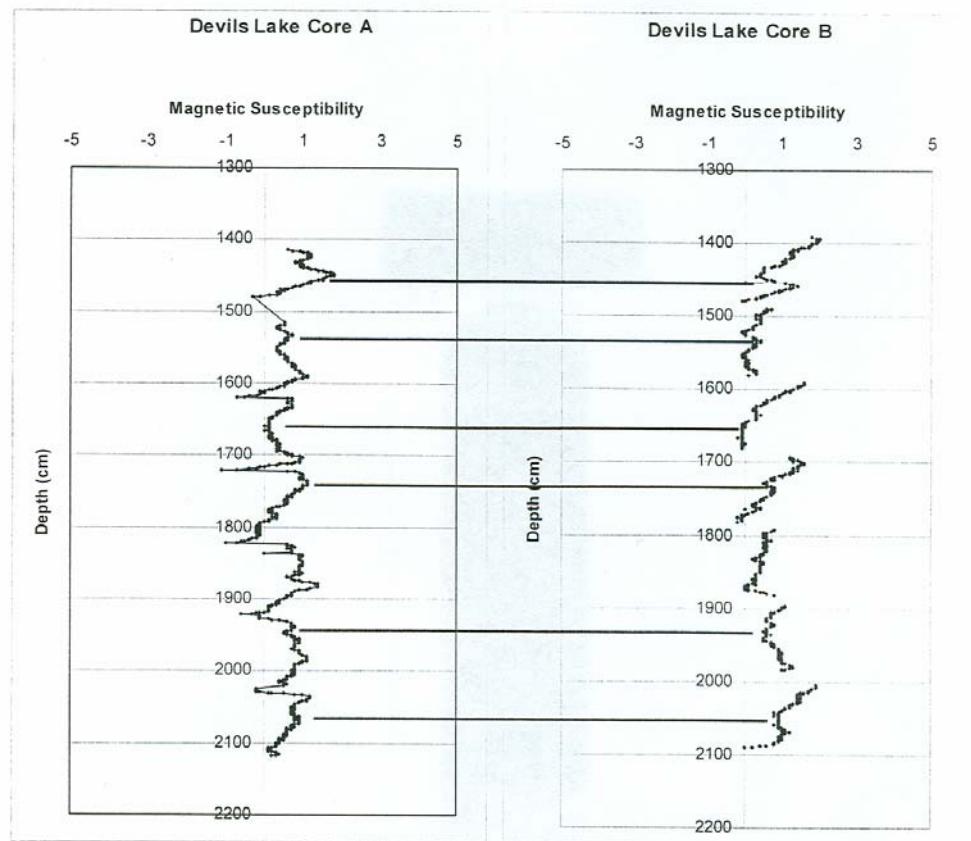
Core A, Creel Bay, Devils Lake, ND, March 13 2002



## Surface Cores, Creel Bay, Devils Lake, ND, March 13 2002



Top 30 cm  
extruded  
from each  
core prior  
to imaging.



**APPENDIX C-2**

**LOSS-ON-IGNITION DATA**

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
1.79	0	2	1.0566487	0.100045	0.094681	0.015433	16.299955	16.95034	66.74970813
3.84	2	4	1.0586845	0.104042	0.098275	0.015824	16.101416	16.99697	66.90161343
5.89	4	6	1.0622433	0.110494	0.10402	0.017146	16.483138	17.05891	66.45794907
8.54	6	8	1.0669492	0.118686	0.111239	0.018705	16.815423	19.3221	63.86247769
11.19	8	10	1.0724743	0.127997	0.119347	0.019479	16.32107	21.67525	62.00367893
14.09	10	12	1.0746595	0.131971	0.122803	0.019778	16.105378	24.88924	59.00537751
16.99	12	14	1.0806512	0.141643	0.131072	0.019942	15.214536	25.7866	58.99886165
20.09	14	16	1.0823074	0.14477	0.13376	0.020006	14.956884	22.17877	62.86434731
23.19	16	18	1.0858678	0.150478	0.138578	0.01965	14.179894	21.7173	64.10280423
26.79	18	20	1.0904815	0.157596	0.14452	0.019853	13.737565	21.49043	64.77200379
30.39	20	22	1.0932752	0.162765	0.148878	0.020333	13.65723	20.1824	66.16036725
34.49	22	24	1.0929519	0.16238	0.14857	0.020728	13.951522	18.97136	67.07711387
38.59	24	26	1.1088612	0.189218	0.170642	0.022303	13.069801	18.42361	68.50658832
43.64	26	28	1.1225067	0.212419	0.189236	0.023931	12.646159	19.26703	68.08681418
48.69	28	30	1.1223126	0.212602	0.189432	0.02475	13.065647	18.88961	68.04474187
54.29	30	32	1.1462909	0.253253	0.220933	0.027513	12.452954	20.01983	67.52721322
59.89	32	34	1.1578895	0.272922	0.235706	0.028888	12.256064	22.06398	65.67995623
67.49	34	36	1.1414854	0.247312	0.216658	0.030412	14.036834	22.37402	63.58914883
75.09	36	38	1.1406589	0.245619	0.215331	0.029583	13.738208	19.37459	66.88720519
89.09	38	40	1.1819336	0.314307	0.265926	0.03148	11.837813	18.86463	69.29756098
103.09	40	42	1.2348739	0.403782	0.326982	0.035824	10.95585	20.01201	69.03213914
107.5	42	44	1.3080808	0.530006	0.405178	0.045832	11.311659	20.90448	67.7838565
125.5698	44	46	1.3054348	0.526594	0.403386	0.046517	11.531581	20.24602	68.22240264
143.5964	46	48	1.3143364	0.541337	0.411871	0.047138	11.444881	19.216	69.3391166
161.5798	48	50	1.2976074	0.51354	0.395759	0.046222	11.679373	18.95	69.37062685
179.52	50	52	1.3099861	0.535691	0.408929	0.048985	11.978942	18.44792	69.57314231
197.417	52	54	1.2973354	0.516614	0.398212	0.050985	12.803398	17.54715	69.64945388
215.2708	54	56	1.3034647	0.523913	0.401939	0.047793	11.89056	18.75342	69.3560166
233.0814	56	58	1.3269366	0.562676	0.424041	0.048251	11.378807	24.99787	63.62332082
250.8488	58	60	1.2970503	0.516599	0.398288	0.053242	13.367667	23.49868	63.13365428
268.573	60	62	1.2941875	0.511313	0.395084	0.053074	13.433566	25.90598	60.66045716
286.254	62	64	1.3091573	0.536045	0.409458	0.052684	12.866879	28.94933	58.18378919
303.8918	64	66	1.3265705	0.566553	0.427081	0.055545	13.005694	30.42676	56.5675457
321.4864	66	68	1.3130658	0.545517	0.415453	0.056972	13.713212	24.883	61.40378835
339.0378	68	70	1.3125428	0.541535	0.412585	0.05248	12.719909	22.04637	65.23371725

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
356.546	70	72	1.3856964	0.65665	0.473877	0.045455	9.5920512	22.96377	67.44417694
374.011	72	74	1.4330172	0.730113	0.509493	0.039049	7.6642039	18.51767	73.8181213
391.4328	74	76	1.3585976	0.612256	0.450653	0.045869	10.178269	23.80215	66.01957972
408.8114	76	78	1.3364529	0.579434	0.433561	0.049581	11.435693	23.57886	64.98544367
426.1468	78	80	1.3391065	0.581031	0.433894	0.046346	10.681334	22.54095	66.77771469
443.439	80	82	1.3228513	0.55648	0.420667	0.048987	11.645011	23.63756	64.71743074
460.688	82	84	1.3249412	0.561118	0.423504	0.051412	12.139637	23.57675	64.28361463
477.8938	84	86	1.3305073	0.568558	0.427324	0.049069	11.482917	24.05629	64.46079605
495.0564	86	88	1.2914209	0.507038	0.39262	0.05273	13.430271	23.11574	63.45398546
512.1758	88	90	1.285848	0.500468	0.389212	0.057077	14.664641	26.09334	59.24201916
529.252	90	92	1.3042008	0.524495	0.402158	0.04685	11.649678	22.94342	65.40690659
546.285	92	94	1.301843	0.519798	0.399278	0.045897	11.49491	23.64253	64.86256434
323.2435	66.2	66.8	1.3160035	0.545069	0.414185	0.049168	11.871132	22.19505	65.93382003
328.5121	66.8	67.4	1.3154901	0.544454	0.413945	0.04961	11.984704	22.354	65.66129453
333.7769	67.4	68	1.3192629	0.551302	0.417887	0.050136	11.997504	21.85018	66.15231304
339.0378	68	68.6	1.3234282	0.55771	0.421413	0.049807	11.819153	22.69413	65.48672125
344.2948	68.6	69.2	1.3276491	0.564268	0.425013	0.049447	11.634204	22.70226	65.66353393
349.5479	69.2	69.8	1.3341073	0.576161	0.43187	0.050396	11.669353	22.44267	65.88798137
354.7971	69.8	70.4	1.3259107	0.56234	0.424116	0.050035	11.797445	22.57401	65.62854015
360.0425	70.4	71	1.3269637	0.564009	0.425038	0.050093	11.785492	22.78254	65.43196841
365.2839	71	71.6	1.3256142	0.561265	0.4234	0.049529	11.697867	22.74635	65.55577908
370.5215	71.6	72.2	1.3252261	0.560452	0.422911	0.049371	11.673989	23.12128	65.20473415
375.7551	72.2	72.8	1.3369297	0.581416	0.434889	0.051228	11.779613	22.88314	65.3372517
380.9849	72.8	73.4	1.3373747	0.581713	0.434967	0.051247	11.781931	22.81638	65.40168805
386.2108	73.4	74	1.3417105	0.588963	0.438964	0.051065	11.633001	23.0038	65.36320273
391.4328	74	74.6	1.3352198	0.577059	0.432183	0.04969	11.497373	22.32184	66.18078809
396.6509	74.6	75.2	1.3457892	0.592959	0.440603	0.047394	10.756694	22.30761	66.93569267
401.8651	75.2	75.8	1.3639255	0.624807	0.458095	0.0504	11.002036	22.19101	66.80695172
407.0755	75.8	76.4	1.3723609	0.639378	0.465896	0.050908	10.926903	22.77583	66.29726656
412.2819	76.4	77	1.3704041	0.636426	0.464407	0.051873	11.169737	22.97997	65.85029512
417.4845	77	77.6	1.3663002	0.629797	0.46095	0.052187	11.321578	22.76779	65.91063198
422.6832	77.6	78.2	1.357554	0.615168	0.453144	0.051537	11.373161	22.53833	66.08850989
427.878	78.2	78.8	1.3600434	0.619725	0.455666	0.051639	11.332634	20.91857	67.74879328
433.0689	78.8	79.4	1.3605756	0.620013	0.455699	0.051459	11.292238	21.67702	67.03074598
438.2559	79.4	80	1.353151	0.607907	0.449253	0.050747	11.295844	21.28331	67.42085086

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
443.439	80	80.6	1.3535229	0.608985	0.449926	0.051626	11.474366	21.02382	67.50181509
448.6182	80.6	81.2	1.3566327	0.613994	0.452587	0.051899	11.467236	20.97457	67.55819088
453.7936	81.2	81.8	1.3559173	0.614089	0.452896	0.053662	11.84868	20.2427	67.90861629
458.965	81.8	82.4	1.3609939	0.623145	0.45786	0.053919	11.776273	20.49432	67.72940791
464.1326	82.4	83	1.3755102	0.647431	0.470685	0.05505	11.695652	19.15598	69.14836957
469.2963	83	83.6	1.3712046	0.639416	0.466317	0.053332	11.436852	20.68425	67.87889867
474.4561	83.6	84.2	1.3706633	0.639711	0.466716	0.05416	11.604413	20.43366	67.96193008
479.612	84.2	84.8	1.3557075	0.617225	0.455279	0.057225	12.569214	17.40126	70.02952381
484.764	84.8	85.4	1.3517487	0.610816	0.451871	0.057831	12.798219	17.60174	69.60004241
489.9122	85.4	86	1.3545996	0.612244	0.451974	0.053205	11.7717	18.7554	69.47290023
495.0564	86	86.6	1.3690526	0.635298	0.464042	0.052386	11.289075	23.00877	65.70215398
500.1968	86.6	87.2	1.3595292	0.617844	0.454454	0.051382	11.306378	24.67669	64.01693499
505.3332	87.2	87.8	1.353973	0.611169	0.45139	0.053981	11.958788	23.09422	64.94698884
510.4658	87.8	88.4	1.3244579	0.564527	0.426233	0.056381	13.227838	22.464	64.30815794
515.5945	88.4	89	1.3048758	0.532659	0.408206	0.057177	14.006908	22.74	63.25309154
520.7193	89	89.6	1.3193878	0.55471	0.42043	0.055625	13.230508	24.58378	62.18570822
525.8402	89.6	90.2	1.3207424	0.556332	0.421227	0.054224	12.872841	26.4467	60.68045526
530.9572	90.2	90.8	1.3231979	0.562254	0.424921	0.057151	13.449883	26.5035	60.04662005
536.0704	90.8	91.4	1.3265505	0.568084	0.428241	0.057102	13.334151	27.61605	59.04980373
541.1796	91.4	92	1.3360253	0.583006	0.436373	0.056452	12.936642	28.59619	58.46716454
546.285	92	92.6	1.3515411	0.607021	0.449132	0.055619	12.383639	29.69992	57.9164457
551.3865	92.6	93.2	1.3544268	0.612302	0.452075	0.055873	12.359209	31.21991	56.4208828
556.4841	93.2	93.8	1.3501092	0.610342	0.452069	0.062254	13.770883	29.38833	56.84078759
561.5778	93.8	94.4	1.3666381	0.637238	0.466369	0.063637	13.645195	30.92722	55.4275893
566.6676	94.4	95	1.3588364	0.621309	0.457236	0.05882	12.864333	30.79735	56.33831207
571.7535	95	95.6	1.3582235	0.619431	0.45606	0.057582	12.626036	29.39946	57.97450146
576.8355	95.6	96.2	1.34137	0.590799	0.440445	0.056326	12.788451	28.48639	58.7251563
581.9137	96.2	96.8	1.3289166	0.575214	0.432845	0.062229	14.376694	23.29463	62.32867209
586.9879	96.8	97.4	1.324593	0.567952	0.428775	0.06178	14.40857	20.44816	65.14327097
592.0583	97.4	98	1.317147	0.554971	0.421343	0.059621	14.150331	19.45432	66.39535246
597.1248	98	98.6	1.340625	0.591016	0.440851	0.055944	12.69002	22.84521	64.46477198
602.1874	98.6	99.2	1.3671875	0.629474	0.460416	0.050442	10.955658	25.27237	63.77197337
607.2461	99.2	99.8	1.3805042	0.655378	0.474738	0.053871	11.347609	22.53881	66.11357866
612.3009	99.8	100.4	1.3922222	0.670476	0.481587	0.049937	10.369318	22.79922	66.83146307
617.3519	100.4	101	1.3907407	0.666111	0.478961	0.046738	9.7581318	22.2216	68.02026689
622.3989	101	101.6	1.4302222	0.728356	0.50926	0.042884	8.4207957	19.78719	71.79201855

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
627.4421	101.6	102.2	1.3764497	0.647929	0.470725	0.05279	11.214612	22.9269	65.85848402
632.4813	102.2	102.8	1.3485744	0.603801	0.447733	0.055908	12.486884	23.66264	63.85047219
637.5167	102.8	103.4	1.3432222	0.595444	0.443296	0.056911	12.838216	23.84751	63.31427505
642.5482	103.4	104	1.3424535	0.590007	0.439499	0.051389	11.692559	22.09985	66.20759257
647.5758	104	104.6	1.3603163	0.617997	0.454304	0.048547	10.686	22.66519	66.64881199
652.5995	104.6	105.2	1.34882	0.598719	0.443883	0.048643	10.958441	22.1279	66.91366145
657.6193	105.2	105.8	1.3364677	0.578005	0.432487	0.048333	11.175555	22.09984	66.72460037
662.6353	105.8	106.4	1.3195421	0.553393	0.419383	0.052485	12.514775	21.60434	65.88088061
667.6473	106.4	107	1.3121837	0.543393	0.414113	0.054353	13.125216	21.41435	65.46043463
672.6555	107	107.6	1.3117604	0.541782	0.413019	0.053458	12.943239	22.19733	64.85943104
677.6598	107.6	108.2	1.3231873	0.560423	0.42354	0.053713	12.681941	23.07712	64.2409434
682.6602	108.2	108.8	1.332542	0.573422	0.430322	0.051275	11.915581	24.31754	63.76687872
687.6567	108.8	109.4	1.3436133	0.591179	0.439992	0.05079	11.543512	23.72539	64.73109705
692.6493	109.4	110	1.3507909	0.602109	0.445746	0.048183	10.809496	22.78867	66.40182915
697.638	110	110.6	1.3470037	0.595755	0.442282	0.048658	11.001676	23.49292	65.50540654
702.6228	110.6	111.2	1.3289474	0.565718	0.425689	0.048542	11.403068	23.87214	64.72479256
707.6038	111.2	111.8	1.3114465	0.538554	0.410656	0.049633	12.086285	22.72317	65.19054668
712.5808	111.8	112.4	1.2957386	0.514489	0.397062	0.052138	13.130867	22.70233	64.16680287
717.554	112.4	113	1.2915823	0.507975	0.393296	0.052629	13.38151	22.32634	64.29215051
722.5233	113	113.6	1.2909091	0.505882	0.391881	0.052288	13.34273	22.94299	63.71428236
727.4887	113.6	114.2	1.2794274	0.48735	0.380913	0.052297	13.729508	23.79623	62.4742623
732.4502	114.2	114.8	1.2764514	0.485062	0.380008	0.056368	14.833244	23.54734	61.61941904
737.4078	114.8	115.4	1.2825641	0.496044	0.38676	0.058434	15.108551	27.03545	57.85600354
742.3616	115.4	116	1.2788171	0.48934	0.38265	0.056954	14.884048	27.13459	57.98136332
747.3114	116	116.6	1.285459	0.500162	0.389093	0.058013	14.909859	26.92457	58.16556765
752.2574	116.6	117.2	1.2851142	0.499926	0.389013	0.057916	14.887972	26.51436	58.59767099
757.1994	117.2	117.8	1.2845703	0.497591	0.38736	0.054533	14.078242	22.82033	63.10142614
762.1376	117.8	118.4	1.2860544	0.494898	0.384819	0.047395	12.316151	22.28676	65.39708591
767.0719	118.4	119	1.3063927	0.525266	0.402074	0.042701	10.62011	22.66752	66.71237323
772.0023	119	119.6	1.3154034	0.539364	0.410037	0.042193	10.290118	21.235	68.47488667
776.9288	119.6	120.2	1.3169591	0.540936	0.410746	0.040742	9.9189189	22.86292	67.21816216
781.8514	120.2	120.8	1.2844379	0.488817	0.380568	0.042337	11.124561	23.64564	65.22980269
786.7702	120.8	121.4	1.2777981	0.478041	0.374113	0.043366	11.591806	23.4952	64.91299147
791.685	121.4	122	1.2713419	0.470061	0.369736	0.046515	12.580691	21.07307	66.3462344
796.596	122	122.7	1.2607123	0.454551	0.360551	0.049144	13.630146	20.70101	65.66884716
802.3205	122.7	123.4	1.2488916	0.436549	0.349549	0.050566	14.466099	20.91106	64.62283832

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
808.0398	123.4	124.1	1.2406011	0.424985	0.342564	0.053817	15.709928	21.12562	63.16444814
813.7538	124.1	124.8	1.2407035	0.425063	0.342598	0.053767	15.693808	21.64114	62.66505098
819.4624	124.8	125.5	1.2446286	0.431737	0.34688	0.054303	15.65477	20.7903	63.55492677
825.1658	125.5	126.2	1.2414305	0.426113	0.343244	0.053756	15.661124	19.48114	64.85773555
830.8639	126.2	126.9	1.2442393	0.42909	0.344861	0.051005	14.79009	19.43071	65.7792019
836.5567	126.9	127.6	1.2559783	0.44606	0.355149	0.048464	13.646055	19.63689	66.71705757
842.2442	127.6	128.3	1.2561468	0.445076	0.354319	0.045379	12.807476	20.53069	66.66183867
847.9264	128.3	129	1.2466929	0.427832	0.343174	0.043704	12.735344	20.46704	66.79761212
853.6033	129	129.7	1.2391277	0.414981	0.334898	0.0428	12.779893	19.60524	67.61486672
859.2749	129.7	130.4	1.2433596	0.421528	0.339024	0.042043	12.401093	19.20354	68.39536757
864.9413	130.4	131.1	1.2740343	0.471888	0.370389	0.042446	11.459754	19.10512	69.4351296
870.6023	131.1	131.8	1.2968695	0.509451	0.392831	0.042221	10.747826	18.58748	70.66469565
876.258	131.8	132.5	1.3026221	0.517892	0.397577	0.040811	10.265065	19.03089	70.7040405
881.9085	132.5	133.2	1.3063814	0.525375	0.402161	0.042986	10.688768	17.67728	71.63395256
887.5537	133.2	133.9	1.3107456	0.531944	0.405833	0.041715	10.278961	17.65576	72.06527415
893.1935	133.9	134.6	1.3142857	0.536876	0.408492	0.040253	9.8539751	17.02118	73.12484586
898.8281	134.6	135.3	1.3308026	0.563015	0.423064	0.038794	9.1697168	16.27415	74.55613562
904.4574	135.3	136	1.3457325	0.588025	0.436956	0.039048	8.9363085	16.42935	74.63433709
910.0814	136	136.7	1.3631181	0.617161	0.452757	0.039945	8.8226977	16.07597	75.10132906
915.7001	136.7	137.4	1.3694358	0.62827	0.45878	0.041061	8.9500691	16.33582	74.71411091
921.3135	137.4	138.1	1.3740968	0.635719	0.462645	0.041572	8.9856316	15.65417	75.3601973
926.9216	138.1	138.8	1.3812728	0.647626	0.468862	0.040938	8.7313733	15.78887	75.47975836
932.5245	138.8	139.5	1.391558	0.664246	0.47734	0.04086	8.5599477	15.279	76.16105037
938.122	139.5	140.2	1.3935032	0.666115	0.478014	0.039217	8.2042456	16.17762	75.61812966
943.7142	140.2	140.9	1.3842885	0.65132	0.470509	0.03898	8.2847257	16.70373	75.01154721
949.3012	140.9	141.6	1.3859275	0.654371	0.472154	0.039385	8.3414793	16.99264	74.66588465
954.8829	141.6	142.3	1.3839506	0.650617	0.470116	0.039028	8.3017078	16.20818	75.49010911
960.4592	142.3	143	1.3861494	0.65475	0.472352	0.039445	8.3508694	16.1691	75.48003101
966.0303	143	143.7	1.384635	0.651698	0.470664	0.039666	8.4277713	15.84721	75.7250228
971.5961	143.7	144.4	1.3867245	0.655771	0.472892	0.039303	8.311292	15.33736	76.351353
977.1566	144.4	145.1	1.3976271	0.672712	0.481324	0.039292	8.1632653	15.06833	76.76840514
982.7118	145.1	145.8	1.3906198	0.662228	0.476211	0.039629	8.3217402	16.88173	74.79653472
988.2617	145.8	146.5	1.3799841	0.645215	0.467553	0.040104	8.5774317	15.14876	76.27381041
993.8063	146.5	147.2	1.3743881	0.636538	0.463143	0.041468	8.9535842	15.1142	75.93221642
999.3456	147.2	147.9	1.3602689	0.613667	0.451136	0.042165	9.3464768	18.04367	72.60985761
1004.88	147.9	148.6	1.3463057	0.590382	0.43852	0.041586	9.4832236	17.98298	72.53380084

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
1010.408	148.6	149.3	1.3513753	0.599911	0.443926	0.042876	9.6583346	18.66691	71.67475226
1015.932	149.3	150	1.3586739	0.611025	0.449722	0.042844	9.5268139	19.39715	71.07603785
1021.45	150	150.7	1.3559478	0.606063	0.446966	0.042506	9.5099405	19.40833	71.08172724
1026.963	150.7	151.4	1.3537954	0.602475	0.445027	0.042479	9.54533	18.841	71.61366749
1032.47	151.4	152.1	1.3529452	0.602055	0.444996	0.042677	9.5904437	18.39379	72.01576792
1037.973	152.1	152.8	1.3513768	0.599731	0.443793	0.043137	9.7200448	18.10542	72.17453527
1043.47	152.8	153.5	1.3476636	0.596168	0.442372	0.045284	10.236714	15.29309	74.47019909
1048.961	153.5	154.2	1.3482065	0.596588	0.442505	0.04549	10.2801	14.90656	74.81334507
1054.448	154.2	154.9	1.348172	0.596129	0.442176	0.044824	10.137085	14.19199	75.67092352
1059.929	154.9	155.6	1.3597525	0.614119	0.451641	0.043462	9.6231334	14.52579	75.85107845
1065.405	155.6	156.3	1.3631774	0.617372	0.452892	0.041009	9.0548341	16.07879	74.86637807
1070.875	156.3	157	1.3489627	0.59527	0.44128	0.042264	9.5775826	16.64366	73.77875366
1076.34	157	157.7	1.3168486	0.543929	0.413054	0.044652	10.810133	18.25132	70.93855029
1081.8	157.7	158.4	1.308844	0.53266	0.40697	0.0473	11.622434	22.35649	66.02107465
1087.255	158.4	159.1	1.3056604	0.526415	0.403179	0.045455	11.274031	20.85797	67.86800261
1092.704	159.1	159.8	1.2921852	0.504559	0.390469	0.045918	11.759644	21.16486	67.07549118
1098.149	159.8	160.5	1.2590604	0.452685	0.359542	0.04944	13.750927	20.52331	65.72575982
1103.587	160.5	161.2	1.2516715	0.440334	0.351797	0.049701	14.127744	20.34177	65.53048358
1109.021	161.2	161.9	1.2514793	0.439053	0.350827	0.049375	14.073931	23.46677	62.45929919
1114.449	161.9	162.6	1.2614012	0.45466	0.36044	0.04721	13.097834	24.03253	62.86963221
1119.872	162.6	163.3	1.2614417	0.453227	0.359293	0.045452	12.650268	23.55169	63.79803958
1125.289	163.3	164	1.2801738	0.483017	0.377306	0.044425	11.774325	22.75859	65.46708095
1157.684	167.5	168.2	1.2938073	0.506346	0.391361	0.045914	11.731844	23.62241	64.64574966
1163.065	168.2	168.9	1.2347768	0.413591	0.334952	0.051203	15.286727	21.90483	62.80844072
1168.44	168.9	169.6	1.2366575	0.415887	0.336299	0.049552	14.734579	21.24706	64.01835621
1173.81	169.6	170.3	1.241349	0.416911	0.335853	0.040594	12.086753	21.06049	66.85275498
1179.175	170.3	171	1.2196835	0.377785	0.30974	0.035027	11.308427	18.13409	70.55748031
1184.534	171	171.7	1.2154729	0.37135	0.305519	0.034681	11.35159	19.65309	68.99531802
1189.888	171.7	172.4	1.2076136	0.359205	0.29745	0.035758	12.021512	19.89121	68.08728251
1195.237	172.4	173.1	1.2120361	0.366331	0.302244	0.035653	11.796208	19.8469	68.3568968
1200.58	173.1	173.8	1.2155618	0.371807	0.305873	0.035651	11.655405	20.14505	68.19954955
1205.919	173.8	174.5	1.2160897	0.370502	0.304667	0.032956	10.817213	23.43127	65.75151994
1211.251	174.5	175.2	1.2145424	0.367322	0.302436	0.032269	10.66952	22.76781	66.56267197
1216.579	175.2	175.9	1.2158258	0.370214	0.304496	0.033081	10.86429	21.90375	67.23195819
1221.901	175.9	176.6	1.2161153	0.370224	0.304432	0.032383	10.637071	21.63217	67.73075814
1227.219	176.6	177.3	1.2251947	0.384705	0.313995	0.031776	10.119994	22.91424	66.96576551

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
1232.53	177.3	178	1.2236308	0.38215	0.312308	0.031413	10.058386	22.69172	67.24989384
1237.837	178	178.7	1.2208929	0.377503	0.309203	0.031669	10.242278	22.53372	67.22399816
1243.138	178.7	179.4	1.2220696	0.379941	0.3109	0.031824	10.23622	22.51398	67.24979992
1248.434	179.4	180.1	1.2230707	0.381994	0.312323	0.032862	10.521886	23.0654	66.41271044
1253.724	180.1	180.8	1.2163591	0.371854	0.305711	0.033795	11.05471	22.47066	66.47463057
1259.01	180.8	181.5	1.2209602	0.380072	0.31129	0.03556	11.423526	23.01182	65.56465634
1264.29	181.5	182.2	1.198435	0.34177	0.28518	0.032107	11.258487	21.61611	67.1254066
1269.565	182.2	182.9	1.2081843	0.358945	0.297094	0.034795	11.711936	22.83633	65.45173187
1274.834	182.9	183.6	1.215664	0.372412	0.306344	0.036292	11.846893	24.29218	63.86092272
1280.098	183.6	184.3	1.2179091	0.375342	0.308185	0.035784	11.611235	24.7203	63.66846868
1285.357	184.3	185	1.2177368	0.374679	0.307685	0.035655	11.588305	24.7931	63.6185927
1290.61	185	185.7	1.2145487	0.369915	0.30457	0.036121	11.859675	24.89862	63.24170915
1295.859	185.7	186.4	1.2160108	0.372453	0.306291	0.035909	11.723838	24.78393	63.49222753
1301.102	186.4	187.1	1.2102721	0.363742	0.300546	0.036932	12.2882	22.87538	64.83642192
1306.339	187.1	187.8	1.2176986	0.376168	0.308917	0.037367	12.096273	23.86994	64.03378882
1311.572	187.8	188.5	1.2252451	0.389412	0.317824	0.038488	12.109768	24.10257	63.78766365
1316.799	188.5	189.2	1.2142923	0.36921	0.304053	0.035045	11.526014	23.54951	64.924471
1322.021	189.2	189.9	1.2349856	0.402421	0.325851	0.035143	10.784875	24.4271	64.78802635
1327.237	189.9	190.6	1.2364072	0.40515	0.327683	0.034628	10.567544	24.4339	64.99855158
1332.448	190.6	191.3	1.2505295	0.428795	0.342891	0.036616	10.678584	25.21912	64.10229331
1337.654	191.3	192	1.2546036	0.436125	0.34762	0.037713	10.848849	25.23703	63.91411816
1342.855	192	192.8	1.2478337	0.425644	0.341106	0.038146	11.182944	24.58547	64.23158184
1348.792	192.8	193.6	1.2507402	0.432481	0.34578	0.040281	11.649378	21.32465	67.0259751
1354.722	193.6	194.4	1.2509769	0.432682	0.345875	0.039614	11.453202	21.50156	67.0452381
1360.646	194.4	195.2	1.2330626	0.402784	0.326653	0.039185	11.995968	22.07195	65.93208525
1366.562	195.2	196	1.2222784	0.383326	0.313616	0.037205	11.863391	21.66363	66.47297783
1372.471	196	196.8	1.2082219	0.361029	0.298811	0.036846	12.33105	20.08328	67.58566932
1378.374	196.8	197.6	1.2150323	0.371983	0.306151	0.036717	11.993048	19.89421	68.11274623
1384.27	197.6	198.4	1.21875	0.378713	0.310739	0.038588	12.418301	20.17618	67.40552288
1390.158	198.4	199.2	1.2210816	0.382924	0.313594	0.039327	12.540866	21.14311	66.31601935
1396.04	199.2	200	1.2114989	0.367162	0.303065	0.038438	12.683079	21.1881	66.12882518
1401.915	200	200.8	1.2056915	0.357414	0.296439	0.038468	12.976673	18.86794	68.15538483
1407.783	200.8	201.6	1.1970374	0.343665	0.287096	0.039295	13.687003	18.3066	68.00639257
1413.644	201.6	202.4	1.1964946	0.341237	0.285197	0.037069	12.997575	20.11528	66.8871451
1419.498	202.4	203.2	1.190437	0.332021	0.278907	0.037258	13.35853	19.35256	67.28890916
1425.345	203.2	204	1.1701745	0.298152	0.254793	0.037289	14.634986	19.57645	65.78856749

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
1431.186	204	204.8	1.1617982	0.284297	0.244704	0.03666	14.98144	20.22459	64.79397179
1437.019	204.8	205.6	1.1630809	0.286145	0.246023	0.035997	14.631579	21.54316	63.82526316
1442.846	205.6	206.4	1.1609712	0.282374	0.243222	0.035902	14.761146	20.6036	64.63525478
1448.665	206.4	207.2	1.1662367	0.290614	0.249189	0.035015	14.051737	21.12839	64.81986836
1454.478	207.2	208	1.1723197	0.301072	0.256817	0.035376	13.774684	20.31803	65.90728391
1460.284	208	208.8	1.1813644	0.315225	0.266831	0.035	13.116917	22.68599	64.19709686
1466.083	208.8	209.6	1.1902168	0.329854	0.277138	0.035294	12.735056	22.70176	64.56318606
1471.875	209.6	210.4	1.1934813	0.33587	0.281421	0.036521	12.977339	21.66169	65.36097356
1477.66	210.4	211.2	1.2010667	0.348907	0.290497	0.037433	12.885968	21.55121	65.56282482
1483.438	211.2	212	1.2005985	0.34756	0.289489	0.036852	12.730163	21.86944	65.4003974
1489.209	212	212.8	1.2034806	0.352744	0.293103	0.037301	12.726123	21.97769	65.29619228
1494.973	212.8	213.6	1.2085246	0.360703	0.298465	0.037168	12.452928	22.64846	64.89861057
1500.731	213.6	214.4	1.2153916	0.371933	0.306019	0.037209	12.159202	22.61268	65.22811587
1506.481	214.4	215.2	1.2160402	0.373077	0.306797	0.037128	12.101687	21.84489	66.05342081
1512.225	215.2	216	1.2204201	0.380557	0.311825	0.036266	11.630295	19.47058	68.89912709
1517.961	216	216.8	1.224901	0.38901	0.317585	0.03791	11.93688	17.79728	70.26584373
1523.691	216.8	217.6	1.2320485	0.400991	0.325467	0.038169	11.727547	17.76855	70.50390003
1529.414	217.6	218.4	1.2324643	0.400689	0.325112	0.036718	11.293887	18.28468	70.42143383
1535.13	218.4	219.2	1.2456713	0.421255	0.338175	0.036165	10.694068	18.77743	70.52850111
1540.839	219.2	220	1.253869	0.434286	0.346357	0.035177	10.15625	18.35781	71.4859375
1546.541	220	220.8	1.2474053	0.42389	0.339817	0.034817	10.245947	17.63121	72.12284107
1552.236	220.8	221.6	1.2481712	0.424747	0.340296	0.035071	10.305973	17.2279	72.46612312
1557.924	221.6	222.4	1.2433486	0.417775	0.336008	0.035879	10.678013	17.25943	72.06255833
1563.606	222.4	223.2	1.241595	0.415605	0.334735	0.036828	11.002209	17.45367	71.54411927
1569.28	223.2	224	1.2355673	0.405409	0.328115	0.036304	11.064385	17.57602	71.35959977
1574.948	224	224.8	1.2265317	0.390755	0.318585	0.036484	11.451771	17.50945	71.03877922
1580.608	224.8	225.6	1.2287452	0.392261	0.319237	0.033606	10.527057	19.86866	69.6042841
1586.262	225.6	226.4	1.2195859	0.377143	0.309238	0.033647	10.880545	19.94868	69.17077295
1591.909	226.4	227.2	1.2159566	0.371021	0.305127	0.033881	11.103889	19.51043	69.38567869
1597.549	227.2	228	1.2194977	0.377778	0.309781	0.03435	11.088573	18.91156	69.99986477
1603.182	228	228.8	1.210756	0.363673	0.300369	0.034822	11.593192	18.49528	69.91152344
1608.808	228.8	229.6	1.2090995	0.360066	0.297797	0.034276	11.509755	19.47356	69.01668194
1614.427	229.6	230.4	1.2140344	0.367951	0.303082	0.034163	11.271775	20.76452	67.96370261
1620.039	230.4	231.2	1.2152404	0.36956	0.304104	0.033096	10.883229	20.93715	68.17962289
1625.645	231.2	232	1.2107208	0.363184	0.299974	0.033988	11.330235	19.50938	69.16038186
1631.243	232	232.8	1.2006504	0.34626	0.288394	0.033315	11.552008	19.3549	69.09309697

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
1636.835	232.8	233.6	1.2006158	0.346281	0.28842	0.033853	11.737346	18.97592	69.28673051
1642.419	233.6	234.4	1.1996839	0.344362	0.287044	0.03326	11.587107	19.32111	69.09177887
1647.997	234.4	235.2	1.2004363	0.346291	0.288471	0.033874	11.742472	18.85211	69.40541766
1653.568	235.2	236	1.198492	0.342956	0.286156	0.034152	11.934673	18.5691	69.49623116
1659.131	236	236.8	1.2001646	0.34572	0.288061	0.034563	11.998572	18.70413	69.29729794
1664.688	236.8	237.6	1.1978116	0.341532	0.28513	0.033402	11.714723	19.38554	68.89973534
1670.238	237.6	238.4	1.193948	0.334515	0.280176	0.032908	11.745583	18.41699	69.83742756
1675.781	238.4	239.2	1.2006454	0.345906	0.2881	0.033228	11.533528	18.24504	70.2214344
1681.318	239.2	240	1.2016906	0.347337	0.289041	0.032815	11.353127	18.12448	70.52238988
1686.847	240	240.8	1.2101538	0.361363	0.298609	0.032545	10.898917	18.00723	71.09385719
1692.369	240.8	241.6	1.2115532	0.363279	0.299846	0.032485	10.833993	17.7947	71.37131169
1697.885	241.6	242.4	1.2234218	0.382496	0.312645	0.031986	10.230683	17.27251	72.4968117
1703.393	242.4	243.2	1.2340354	0.399569	0.323791	0.032003	9.8837906	19.12481	70.99139811
1708.895	243.2	244	1.2350362	0.400845	0.324561	0.03143	9.6838936	19.12305	71.19305569
1714.39	244	244.8	1.238552	0.407099	0.32869	0.031772	9.6662432	20.06393	70.26982331
1719.878	244.8	245.6	1.246454	0.420311	0.337205	0.032253	9.5646965	20.20627	70.22903355
1725.359	245.6	246.4	1.2584019	0.437966	0.348034	0.030439	8.74613	21.27161	69.98226448
1730.833	246.4	247.2	1.2493	0.42305	0.33863	0.029977	8.8523815	21.31287	69.83474767
1736.3	247.2	248	1.2467985	0.419313	0.336312	0.029978	8.9137182	20.89088	70.19540658
1741.76	248	248.8	1.2462758	0.419125	0.336302	0.031695	9.4244439	20.8576	69.7179546
1747.213	248.8	249.6	1.2456593	0.418254	0.335769	0.032096	9.559071	21.04847	69.39246045
1752.659	249.6	250.4	1.2461727	0.419725	0.336811	0.032484	9.6446107	20.62923	69.7261632
1758.099	250.4	251.2	1.2518422	0.428999	0.342694	0.032999	9.6291806	20.81685	69.55396585
1763.531	251.2	252	1.2507606	0.427637	0.341901	0.033124	9.68813	21.35667	68.95519981
1768.957	252	252.8	1.2551789	0.434557	0.346212	0.033383	9.6424702	21.75452	68.60301192
1774.376	252.8	253.6	1.2556133	0.435239	0.346635	0.033115	9.5533795	21.96878	68.47783616
1779.787	253.6	254.4	1.2541772	0.432658	0.344974	0.033407	9.6840257	24.78248	65.53349912
1785.192	254.4	255.2	1.2633089	0.448959	0.355383	0.034255	9.6390073	24.25638	66.10461268
1790.59	255.2	256	1.2683698	0.456886	0.360215	0.034145	9.4791778	24.92221	65.5986154
1795.981	256	256.8	1.2715648	0.461526	0.362959	0.03383	9.3206951	25.45089	65.22841171
1801.366	256.8	257.6	1.2774237	0.47139	0.369016	0.034126	9.2478067	25.31391	65.43828563
1806.743	257.6	258.4	1.2811308	0.477055	0.37237	0.033511	8.9994487	25.103	65.89754686
1812.113	258.4	259.2	1.2886757	0.489356	0.379736	0.033854	8.9150228	24.93118	66.15379363
1817.477	259.2	260	1.2807298	0.476056	0.371707	0.033392	8.9833244	24.80116	66.2155191
1822.833	260	260.8	1.2875285	0.490547	0.380999	0.037153	9.7515672	20.40634	69.84209427
1828.183	260.8	261.6	1.2902408	0.49455	0.383301	0.036198	9.4438749	20.0767	70.47942081

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
1833.525	261.6	262.4	1.2834903	0.482548	0.375966	0.034618	9.2078071	19.65927	71.13292767
1838.861	262.4	263.2	1.2879467	0.48934	0.379938	0.034612	9.1100384	19.5622	71.32776334
1844.19	263.2	264	1.2891059	0.490929	0.380829	0.034073	8.9470427	19.25994	71.79301565
1849.512	264	264.8	1.2872064	0.488806	0.379741	0.034903	9.1912892	19.62229	71.18642266
1854.827	264.8	265.6	1.2823281	0.479976	0.3743	0.034335	9.1731591	20.31684	70.51000251
1860.135	265.6	266.4	1.3015598	0.512421	0.393697	0.035775	9.0868095	20.15067	70.76252537
1865.436	266.4	267.2	1.2960305	0.501323	0.386814	0.032277	8.3443305	21.62966	70.02600751
1870.73	267.2	268	1.297469	0.503339	0.387939	0.032415	8.3556221	21.77415	69.87022574
1876.018	268	268.8	1.3	0.507329	0.390253	0.032206	8.2525233	20.74637	71.00110825
1881.298	268.8	269.6	1.3142407	0.531002	0.404037	0.032891	8.1405008	20.31947	71.54002611
1886.572	269.6	270.4	1.3129424	0.529054	0.402953	0.032792	8.1377933	19.75417	72.10803794
1891.838	270.4	271.2	1.3165693	0.534732	0.406155	0.032633	8.0345615	19.76115	72.2042904
1897.098	271.2	272	1.3110823	0.526183	0.401335	0.032971	8.2152975	19.68989	72.09481463
1902.351	272	272.9	1.3246214	0.549047	0.414494	0.034114	8.2302696	19.56542	72.20430643
1908.252	272.9	273.8	1.3107796	0.526131	0.401388	0.033629	8.3783042	19.67625	71.94544956
1914.145	273.8	274.7	1.3078317	0.521625	0.398847	0.033561	8.4145658	19.46595	72.11948459
1920.028	274.7	275.6	1.3164634	0.535671	0.406901	0.033441	8.2185544	18.89607	72.88537279
1925.903	275.6	276.5	1.3065027	0.51765	0.396211	0.031202	7.8750132	19.30007	72.82491291
1931.769	276.5	277.4	1.3066745	0.517838	0.396302	0.030965	7.8133911	19.53145	72.6551614
1937.627	277.4	278.3	1.3229677	0.544258	0.411392	0.03082	7.4917022	20.40562	72.10267899
1943.475	278.3	279.2	1.3144281	0.530693	0.403744	0.031334	7.7607514	20.30076	71.93848739
1949.315	279.2	280.1	1.3219487	0.543128	0.410854	0.032004	7.7896327	19.98956	72.22081012
1955.146	280.1	281	1.3191604	0.53859	0.408282	0.032273	7.9044669	19.86086	72.23467573
1960.969	281	281.9	1.3019171	0.510466	0.392088	0.031201	7.9577751	19.06541	72.97681689
1966.783	281.9	282.8	1.3101998	0.523607	0.399639	0.030979	7.7517823	18.15273	74.09549152
1972.588	282.8	283.7	1.3092744	0.524604	0.400683	0.034097	8.5096638	16.97637	74.51396904
1978.384	283.7	284.6	1.3140124	0.532921	0.405567	0.034561	8.5216473	17.049	74.42935586
1984.171	284.6	285.5	1.3187905	0.539903	0.409392	0.034474	8.4208421	17.71623	73.86292629
1989.95	285.5	286.4	1.3083004	0.522727	0.399547	0.034252	8.5727788	18.16191	73.26531191
1995.72	286.4	287.3	1.3076763	0.52111	0.398501	0.033714	8.4602369	18.5143	73.02546034
2001.481	287.3	288.2	1.3122659	0.529728	0.403674	0.035178	8.7144975	18.0011	73.28440744
2007.233	288.2	289.1	1.3114545	0.528727	0.403161	0.034521	8.562586	17.33391	74.10350757
2012.977	289.1	290	1.2964875	0.503406	0.388285	0.033907	8.7324241	18.51126	72.75631674
2018.712	290	290.9	1.2808264	0.478402	0.373511	0.035058	9.3861569	20.58464	70.0292065
2024.438	290.9	291.8	1.2814346	0.478762	0.373614	0.034391	9.204857	21.02092	69.7742264
2030.156	291.8	292.7	1.2716449	0.462221	0.363483	0.03391	9.3292072	21.21462	69.45617548

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
2035.864	292.7	293.6	1.2656877	0.452863	0.3578	0.033955	9.48984	21.30953	69.20062689
2041.564	293.6	294.5	1.2713102	0.461602	0.363092	0.034208	9.4212191	21.22944	69.34933744
2047.255	294.5	295.4	1.2565844	0.438117	0.348657	0.034591	9.9213338	21.86692	68.21174122
2052.938	295.4	296.3	1.2473791	0.42499	0.340706	0.037755	11.081365	21.11152	67.80711349
2058.612	296.3	297.2	1.234811	0.40452	0.327597	0.038292	11.68887	21.86538	66.4457456
2064.277	297.2	298.1	1.2390137	0.412438	0.332876	0.03874	11.638103	21.93336	66.42853727
2069.933	298.1	299	1.2426449	0.417236	0.335765	0.037586	11.194207	21.7844	67.02139126
2075.58	299	299.9	1.245818	0.422702	0.339297	0.037847	11.154599	22.3741	66.47129811
2081.219	299.9	300.8	1.2554067	0.43555	0.34694	0.03434	9.8978359	23.58185	66.52031199
2086.849	300.8	301.7	1.2549738	0.43438	0.346127	0.034209	9.8834873	25.58136	64.53515468
2092.47	301.7	302.6	1.258159	0.439928	0.34966	0.034728	9.9320652	24.5938	65.47413043
2098.083	302.6	303.5	1.260479	0.44496	0.353009	0.035788	10.137939	23.99724	65.86482001
2103.686	303.5	304.4	1.2551629	0.436334	0.347631	0.035546	10.225259	22.21625	67.55849152
2109.281	304.4	305.3	1.2344394	0.403661	0.327	0.037307	11.40873	22.97849	65.61278345
2114.868	305.3	306.2	1.2145084	0.371343	0.305756	0.038799	12.6897	24.74453	62.56577333
2120.445	306.2	307.1	1.2020073	0.351962	0.292812	0.040193	13.726507	22.87264	63.40085548
2126.014	307.1	308	1.2019807	0.352319	0.293115	0.03999	13.64322	24.07141	62.28536953
2131.574	308	308.9	1.2155606	0.373112	0.306947	0.038686	12.603496	24.37176	63.02474701
2137.125	308.9	309.8	1.2212689	0.3829	0.313527	0.039481	12.592709	23.32492	64.08237336
2142.668	309.8	310.7	1.2331763	0.403297	0.327039	0.040737	12.456209	26.96816	60.57563254
2148.201	310.7	311.6	1.2383733	0.411228	0.332071	0.040577	12.219391	27.78689	59.99371436
2153.726	311.6	312.5	1.2439549	0.421816	0.339093	0.04203	12.394904	26.88245	60.72264968
2159.242	312.5	313.4	1.2385562	0.41343	0.3338	0.042425	12.7098	25.97802	61.31218192
2164.75	313.4	314.3	1.2365557	0.41046	0.331938	0.041994	12.651223	22.79853	64.55024453
2170.249	314.3	315.2	1.2464204	0.426357	0.342065	0.041999	12.278075	22.93457	64.78735829
2175.739	315.2	316.1	1.2464005	0.427029	0.34261	0.043318	12.643678	25.23182	62.12450575
2181.22	316.1	317	1.2510809	0.434775	0.347519	0.043495	12.515982	25.03694	62.44708055
2186.692	317	317.9	1.2730136	0.469936	0.369152	0.043354	11.744097	25.9094	62.34650419
2192.156	317.9	318.8	1.2785262	0.478987	0.37464	0.042822	11.430288	27.3044	61.2653125
2197.611	318.8	319.7	1.2566397	0.443995	0.35332	0.044705	12.652796	27.14606	60.20114434
2203.058	319.7	320.6	1.2391026	0.414789	0.33475	0.043345	12.948449	25.70456	61.34699194
2208.495	320.6	321.5	1.2416957	0.41928	0.337667	0.042793	12.67313	24.59825	62.72861496
2213.924	321.5	322.4	1.2359943	0.409211	0.331078	0.041925	12.66305	22.62713	64.70982339
2219.344	322.4	323.3	1.2804803	0.47905	0.374117	0.036793	9.8346667	20.18099	69.98434133
2224.755	323.3	324.2	1.2725576	0.465203	0.365565	0.036401	9.9575271	22.40196	67.64051439
2230.158	324.2	325.1	1.2246545	0.386358	0.315483	0.035385	11.216247	24.01004	64.77371336

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
2235.551	325.1	326	1.2324683	0.398904	0.323663	0.035983	11.117537	25.54428	63.33818129
2240.936	326	326.9	1.2315527	0.397953	0.323131	0.036403	11.265839	25.56146	63.17270104
2246.313	326.9	327.8	1.2337529	0.40345	0.32701	0.03945	12.063786	25.17324	62.76297666
2251.68	327.8	328.7	1.2305215	0.398057	0.323487	0.038764	11.983046	24.97136	63.04559466
2257.039	328.7	329.6	1.2231158	0.384972	0.314747	0.037159	11.806136	24.15972	64.0341411
2262.389	329.6	330.5	1.1988367	0.345091	0.287855	0.037069	12.877562	23.79482	63.32761597
2267.73	330.5	331.4	1.1991334	0.345017	0.287722	0.036711	12.75901	24.58764	62.65334673
2273.063	331.4	332.3	1.2042395	0.353895	0.293874	0.037053	12.608565	23.83648	63.55495657
2278.387	332.3	333.2	1.2205369	0.381745	0.312768	0.038821	12.412096	24.41378	63.17412096
2283.702	333.2	334.1	1.2259564	0.391348	0.319218	0.039416	12.347721	24.14565	63.50663258
2289.008	334.1	335	1.2007214	0.347295	0.289239	0.035333	12.21602	23.61677	64.16720758
2294.305	335	335.9	1.1968989	0.339992	0.284061	0.034288	12.070599	24.64712	63.28227908
2299.594	335.9	336.8	1.203125	0.351375	0.292052	0.03619	12.391794	23.6757	63.93250326
2304.874	336.8	337.7	1.2141526	0.368988	0.303906	0.035188	11.578694	24.66211	63.75919202
2310.146	337.7	338.6	1.2256091	0.392483	0.320235	0.042213	13.181878	20.39421	66.42390701
2315.408	338.6	339.5	1.2230427	0.388167	0.317378	0.041791	13.167545	20.84804	65.98441439
2320.662	339.5	340.4	1.2290171	0.396197	0.322369	0.03964	12.296408	21.75642	65.94716859
2325.907	340.4	341.3	1.2311342	0.399592	0.324572	0.039198	12.076802	20.52316	67.4000371
2331.143	341.3	342.2	1.2379092	0.410379	0.33151	0.038978	11.757774	20.2848	67.95742906
2336.371	342.2	343.1	1.2526169	0.438363	0.349958	0.044717	12.777848	21.40269	65.81945891
2341.59	343.1	344	1.2456681	0.428132	0.343696	0.046382	13.495063	22.87029	63.63464586
2346.8	344	344.9	1.2417964	0.422143	0.339946	0.047264	13.903518	22.94599	63.15049505
2352.001	344.9	345.8	1.2287312	0.398495	0.324314	0.043895	13.534808	20.61695	65.84824609
2357.194	345.8	346.7	1.2229612	0.388495	0.317668	0.042234	13.295014	19.43541	67.26957391
2362.378	346.7	347.6	1.2225967	0.385028	0.314926	0.03805	12.082078	22.41696	65.5009614
2367.553	347.6	348.5	1.2115917	0.366205	0.302251	0.036841	12.188976	20.41228	67.39874016
2372.719	348.5	349.4	1.2055446	0.356115	0.295397	0.036272	12.279152	19.68657	68.03427562
2377.876	349.4	350.3	1.2143322	0.370467	0.305079	0.037017	12.133646	19.76087	68.10548066
2383.025	350.3	351.2	1.2197351	0.379294	0.310964	0.036812	11.83797	20.64626	67.51577232
2388.165	351.2	352.1	1.2151177	0.370178	0.304643	0.034129	11.202857	22.35432	66.44282526
2393.297	352.1	353	1.2255443	0.386352	0.315249	0.033713	10.694158	22.34928	66.95656357
2398.419	353	353.9	1.2304591	0.393733	0.319988	0.032476	10.149042	21.88002	67.9709419
2403.533	353.9	354.8	1.23125	0.395025	0.320832	0.03216	10.023941	22.86545	67.11060685
2408.638	354.8	355.7	1.2399901	0.409046	0.329878	0.03233	9.8006042	26.29871	63.90068882
2413.735	355.7	356.6	1.2427088	0.412686	0.332086	0.031389	9.4519199	24.00624	66.54184444
2418.822	356.6	357.5	1.2390392	0.407731	0.32907	0.032042	9.7372698	24.2675	65.99523294

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
2423.901	357.5	358.4	1.2396996	0.409979	0.330708	0.034014	10.285266	23.1804	66.53433656
2428.971	358.4	359.3	1.230303	0.394021	0.320264	0.033251	10.382457	20.96277	68.65477032
2434.032	359.3	360.2	1.2371124	0.406406	0.328512	0.034191	10.407806	20.53825	69.05394046
2439.085	360.2	361.1	1.2369356	0.405987	0.32822	0.034906	10.634841	20.60297	68.76218445
2444.129	361.1	362	1.2461573	0.420968	0.337813	0.034509	10.215281	20.97379	68.81093288
2449.164	362	363	1.2367462	0.404859	0.327358	0.033781	10.319331	23.05191	66.62876125
2454.748	363	364	1.234938	0.402084	0.325591	0.034038	10.454209	22.25725	67.28854604
2460.322	364	365	1.2370549	0.40567	0.327932	0.034076	10.391158	19.81034	69.79850471
2465.884	365	366	1.2570997	0.438066	0.348474	0.033846	9.7126437	21.09331	69.19404598
2471.436	366	367	1.245842	0.419283	0.336546	0.033	9.8053799	21.08531	69.10930953
2476.977	367	368	1.2417569	0.413072	0.332652	0.033426	10.048377	18.58712	71.36450312
2482.508	368	369	1.2415567	0.413061	0.332696	0.032976	9.9116363	17.2856	72.80276802
2488.027	369	370	1.2369575	0.404853	0.327297	0.032104	9.8086676	17.45602	72.73531581
2493.536	370	371	1.2417221	0.412368	0.332094	0.031677	9.5387244	18.73417	71.72710706
2499.034	371	372	1.2560583	0.435698	0.346877	0.032328	9.3197219	20.33252	70.34776027
2504.521	372	373	1.2586264	0.439636	0.349298	0.031853	9.1191417	21.55014	69.33071711
2509.997	373	374	1.2546145	0.433422	0.345462	0.032088	9.2884683	21.58028	69.13124781
2515.463	374	375	1.2498839	0.423519	0.338847	0.029317	8.6521322	25.25627	66.09159468
2520.917	375	376	1.2420892	0.410091	0.330162	0.028374	8.5940398	25.44788	65.95808087
2526.361	376	377	1.2500784	0.422531	0.338004	0.028274	8.365019	25.66501	65.96997125
2531.794	377	378	1.2529252	0.426815	0.340655	0.027282	8.0086305	25.77335	66.21802259
2537.217	378	379	1.254014	0.428185	0.341452	0.026373	7.7236601	25.25637	67.01997147
2542.628	379	380	1.2603399	0.438244	0.347719	0.026673	7.6707606	24.67052	67.65871579
2548.029	380	381	1.2652209	0.446386	0.352812	0.02679	7.5933423	24.73474	67.67192083
2553.419	381	382	1.2720369	0.457682	0.359803	0.026814	7.4525225	24.908	67.63947823
2558.798	382	383	1.2792469	0.469665	0.367142	0.026689	7.2694878	23.68201	69.04849889
2564.166	383	384	1.2900524	0.487784	0.378111	0.027496	7.2719141	22.9434	69.78468694
2569.524	384	385	1.2954198	0.496679	0.383412	0.02749	7.1697533	22.75223	70.07801429
2574.87	385	386	1.3393042	0.568077	0.424158	0.027521	6.4884549	22.71553	70.79601092
2580.206	386	387	1.3381079	0.566313	0.423219	0.027554	6.5105386	22.7045	70.78496487
2585.531	387	388	1.3347069	0.56096	0.420287	0.027818	6.618705	22.42142	70.95987883
2590.846	388	389	1.3309985	0.55385	0.416116	0.027171	6.5297336	23.63948	69.83078303
2596.149	389	390	1.3420676	0.572207	0.426362	0.027316	6.406782	23.11766	70.47556111
2601.442	390	391	1.3357749	0.561372	0.42026	0.026032	6.1942041	22.04977	71.75602252
2606.724	391	392	1.3422271	0.573144	0.42701	0.028012	6.56	21.8304	71.6096
2611.995	392	393	1.3349625	0.561827	0.420856	0.028168	6.6929134	20.60578	72.7013081

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
2617.255	393	394	1.3344677	0.56082	0.420258	0.028019	6.6671853	19.79622	73.53659561
2622.505	394	395	1.3349057	0.562075	0.42106	0.028198	6.6968781	20.4576	72.84551863
2627.743	395	396	1.3341411	0.560335	0.419997	0.027754	6.6081537	20.66747	72.7243783
2632.971	396	397	1.3102133	0.52096	0.397615	0.027674	6.9600819	20.78666	72.25325565
2638.188	397	398	1.3108345	0.521899	0.398143	0.027434	6.8904594	20.40975	72.69978799
2643.395	398	399	1.3006984	0.506067	0.389073	0.028558	7.3400035	19.88818	72.77181301
2648.59	399	400	1.2959222	0.499478	0.385423	0.029929	7.7653313	20.24883	71.98583634
2653.775	400	401	1.2926399	0.492508	0.381009	0.028435	7.4630872	23.1775	69.3594094
2658.949	401	402	1.2927972	0.49408	0.382179	0.030071	7.8681977	23.93206	68.19974039
2664.112	402	403	1.2962791	0.499958	0.385687	0.031021	8.0429635	23.73237	68.22466171
2669.264	403	404	1.2903882	0.493022	0.382073	0.034093	8.9230481	23.55207	67.52488518
2674.406	404	405	1.2878175	0.488993	0.379707	0.034223	9.013082	23.60183	67.38509042
2679.536	405	406	1.2910794	0.494692	0.383162	0.03548	9.2597602	23.51707	67.22317194
2684.656	406	407	1.2793162	0.474359	0.370791	0.033872	9.1351351	23.53897	67.32589189
2689.765	407	408	1.2807879	0.47701	0.372435	0.034509	9.265754	22.87121	67.86303881
2694.864	408	409	1.2785588	0.472281	0.369386	0.032157	8.7054198	24.37265	66.92193204
2699.951	409	410	1.2678883	0.455788	0.359486	0.033999	9.4575622	23.71229	66.83014678
2705.028	410	411	1.2481155	0.424082	0.339778	0.034511	10.156971	24.93421	64.9088181
2710.094	411	412	1.2538682	0.433238	0.345521	0.034925	10.108025	27.64795	62.24402557
2715.149	412	413	1.2717716	0.462392	0.363581	0.034701	9.544341	28.45564	62.0000196
2720.193	413	414	1.2732673	0.463366	0.363919	0.033141	9.1066341	27.62674	63.26662597
2725.227	414	415	1.2706919	0.457628	0.360141	0.03037	8.4327167	24.40776	67.15952672
2730.249	415	416	1.2747527	0.463354	0.363485	0.028415	7.817424	23.13992	69.04265528
2735.261	416	417	1.2913644	0.489472	0.379034	0.027299	7.2021268	23.02762	69.77025699
2740.262	417	418	1.2975898	0.499545	0.384979	0.027406	7.1187984	25.17236	67.70883933
2745.253	418	419	1.3162568	0.530013	0.402666	0.02714	6.7400708	24.14392	69.11600472
2750.232	419	420	1.3174133	0.532528	0.404223	0.027973	6.9202634	23.22241	69.8573226
2755.201	420	421	1.3121667	0.524611	0.399805	0.028367	7.0952028	23.52746	69.37733771
2760.159	421	422	1.3155662	0.530052	0.402908	0.028775	7.1417787	23.65674	69.20147969
2765.106	422	423	1.317098	0.533569	0.405109	0.029834	7.3643981	23.18123	69.45437307
2770.042	423	424	1.3327742	0.559441	0.419757	0.030723	7.3191358	22.55293	70.12793111
2774.968	424	425	1.3362028	0.565094	0.422911	0.030712	7.2621035	22.30342	70.43447412
2779.882	425	426	1.3394121	0.5714	0.426605	0.031545	7.394489	22.88277	69.72274154
2784.786	426	427	1.3289692	0.553249	0.416299	0.03062	7.3554084	23.75401	68.89057837
2789.679	427	428	1.3409286	0.573345	0.427573	0.031549	7.3785243	23.70171	68.91976605
2794.562	428	429	1.3387991	0.571478	0.426859	0.033638	7.8803799	22.28511	69.83451202

## Appendix C-2: Loss on Ignition Data

Age	Top (cm)	Base (cm)	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	% Organic	% CaCO <sub>3</sub>	% Inorganic
2799.433	429	430	1.3332703	0.562713	0.422054	0.033815	8.0120937	20.33938	71.64852608
2804.294	430	431	1.3151356	0.532765	0.405102	0.032963	8.1369571	20.96808	70.89496675
2809.144	431	432	1.3186945	0.539121	0.408829	0.033976	8.3106828	21.72671	69.96260605
2813.983	432	433	1.3122705	0.528309	0.402592	0.033574	8.3394294	22.10371	69.55685808
2818.811	433	434	1.3040493	0.515009	0.39493	0.033718	8.5377318	21.35823	70.10404239
2823.629	434	435	1.3054089	0.517802	0.396659	0.034518	8.7020892	21.28485	70.01306136
2828.435	435	436	1.3002244	0.508975	0.391452	0.034083	8.7068332	21.38663	69.90653931
2833.231	436	437	1.3	0.50797	0.390746	0.032667	8.3601046	21.71216	69.92774001
2838.016	437	438	1.2935175	0.497507	0.384615	0.032827	8.535081	21.8283	69.63662298
2842.791	438	439	1.2962025	0.502215	0.387451	0.033761	8.7136556	23.17191	68.11442974
2847.554	439	440	1.2932986	0.498027	0.385083	0.034372	8.9257681	22.57511	68.49912536
2852.307	440	441	1.2835149	0.48252	0.375937	0.035394	9.4148832	22.57033	68.014785
			1.4330172	0.730113	0.509493	0.063637	16.815423	31.21991	76.76840514
			1.0566487	0.100045	0.094681	0.015433	6.1942041	14.19199	55.4275893
			1.2733992	0.468817	0.364668	0.03919	10.923258	21.66043	67.41631633
			0.0645117	0.108902	0.06947	0.009005	2.1223632	2.865652	3.854667187

max  
min  
avg  
sd

## **APPENDIX C-3**

### **C-14 DATA**

## Appendix C-3: C-14 Data

Sample depths	age by initial model	Age by new model	increments	$\delta$ age: init-new
42	107.69	55.5		52.19
42.5055	112.69	60.07122149	4.571221487	52.61877851
43.012	117.69	64.64871802	4.577496536	53.04128198
43.5195	122.69	69.2324732	4.583755174	53.4575268
44.028	127.69	73.82247057	4.58999737	53.86752943
44.5375	132.69	78.41869366	4.59622309	54.27130634
45.048	137.69	83.02112596	4.602432302	54.66887404
45.5595	142.69	87.62975093	4.608624974	55.06024907
46.072	147.69	92.24455201	4.614801074	55.44544799
46.5855	152.69	96.86551257	4.620960568	55.82448743
47.1	157.69	101.492616	4.627103425	56.197384
47.6155	162.69	106.1258456	4.633229613	56.56415439
48.132	167.69	110.7651847	4.639339098	56.92481529
48.6495	172.69	115.4106166	4.645431848	57.27938344
49.168	177.69	120.0621244	4.651507832	57.62787561
49.6875	182.69	124.7196914	4.657567016	57.97030859
50.208	187.69	129.3833008	4.663609368	58.30669923
50.7295	192.69	134.0529356	4.669634856	58.63706437
51.252	197.69	138.7285791	4.675643448	58.96142092
51.7755	202.69	143.4102142	4.68163511	59.27978581
52.3	207.69	148.097824	4.687609811	59.592176
52.8255	212.69	152.7913915	4.693567519	59.89860848
53.352	217.69	157.4908997	4.6995082	60.19910028
53.8795	222.69	162.1963315	4.705431822	60.49366846
54.408	227.69	166.9076699	4.711338354	60.78233011
54.9375	232.69	171.6248977	4.717227762	61.06510234
55.468	237.69	176.3479977	4.723100014	61.34200233
55.9995	242.69	181.0769527	4.728955078	61.61304725
56.532	247.69	185.8117457	4.734792922	61.87825433
57.0655	252.69	190.5523592	4.740613512	62.13764082
57.6	257.69	195.298776	4.746416817	62.391224
58.1355	262.69	200.0509788	4.752202805	62.6390212
58.672	267.69	204.8089502	4.757971442	62.88104975
59.2095	272.69	209.5726729	4.763722696	63.11732706
59.748	277.69	214.3421295	4.769456536	63.34787052
60.2875	282.69	219.1173024	4.775172928	63.57269759
60.828	287.69	223.8981742	4.78087184	63.79182575
61.3695	292.69	228.6847275	4.78655324	64.00527251
61.912	297.69	233.4769446	4.792217096	64.21305542
62.4555	302.69	238.274808	4.797863374	64.41519204
63	307.69	243.0783	4.803492043	64.6117
63.5455	312.69	247.8874031	4.809103071	64.80259693
64.092	317.69	252.7020995	4.814696424	64.98790051
64.6395	322.69	257.5223716	4.82027207	65.16762844
65.188	327.69	262.3482015	4.825829978	65.34179846
65.7375	332.69	267.1795717	4.831370114	65.51042834
66.288	337.69	272.0164641	4.836892446	65.6735359
66.8395	342.69	276.858861	4.842396942	65.83113896
67.392	347.69	281.7067446	4.84788357	65.98325539
67.9455	352.69	286.5600969	4.853352296	66.12990309
68.5	357.69	291.4189	4.858803089	66.2711

## Appendix C-3: C-14 Data

Sample depths	age by initial model	Age by new model	increments	$\delta$ age: init-new
69.0555	362.69	296.2831359	4.864235917	66.40686408
69.612	367.69	301.1527867	4.869650746	66.53721334
70.1695	372.69	306.0278342	4.875047544	66.66216579
70.728	377.69	310.9082605	4.88042628	66.78173951
71.2875	382.69	315.7940474	4.88578692	66.89595259
71.848	387.69	320.6851768	4.891129432	67.00482316
72.4095	392.69	325.5816306	4.896453784	67.10836938
72.972	397.69	330.4833906	4.901759944	67.20660943
73.5355	402.69	335.3904384	4.907047878	67.29956156
74.1	407.69	340.302756	4.912317555	67.387244
74.6655	412.69	345.2203249	4.917568943	67.46967506
75.232	417.69	350.143127	4.922802008	67.54687305
75.7995	422.69	355.0711437	4.928016718	67.61885633
76.368	427.69	360.0043567	4.933213042	67.68564329
76.9375	432.69	364.9427477	4.938390946	67.74725234
77.508	437.69	369.8862981	4.943550398	67.80370195
78.0795	442.69	374.8349894	4.948691366	67.85501058
78.652	447.69	379.7888032	4.953813818	67.90119676
79.2255	452.69	384.747721	4.95891772	67.94227904
79.8	457.69	389.711724	4.964003041	67.978276
80.3755	462.69	394.6807937	4.969069749	68.00920625
80.952	467.69	399.6549116	4.97411781	68.03508844
81.5295	472.69	404.6340588	4.979147192	68.05594125
82.108	477.69	409.6182166	4.984157864	68.07178339
82.6875	482.69	414.6073664	4.989149792	68.08263359
83.268	487.69	419.6014894	4.994122944	68.08851065
83.8495	492.69	424.6005666	4.999077288	68.08943336
84.432	497.69	429.6045794	5.004012792	68.08542057
85.0155	502.69	434.6135089	5.008929422	68.07649115
85.6	507.69	439.627336	5.013827147	68.062664
86.1855	512.69	444.6460419	5.018705935	68.04395807
86.772	517.69	449.6696077	5.023565752	68.02039231
87.3595	522.69	454.6980143	5.028406566	67.99198575
87.948	527.69	459.7312426	5.033228346	67.9587574
88.5375	532.69	464.7692737	5.038031058	67.92072634
89.128	537.69	469.8120883	5.04281467	67.87791167
89.7195	542.69	474.8596675	5.04757915	67.83033252
90.312	547.69	479.9119919	5.052324466	67.77800806
90.9055	552.69	484.9690425	5.057050584	67.72095747
91.5	557.69	490.0308	5.061757473	67.6592
92.0955	562.69	495.0972451	5.066445101	67.5927549
92.692	567.69	500.1683585	5.071113434	67.52164147
93.2895	572.69	505.244121	5.07576244	67.44587903
93.888	577.69	510.3245131	5.080392088	67.36548694
94.4875	582.69	515.4095154	5.085002344	67.28048459
95.088	587.69	520.4991086	5.089593176	67.19089142
95.6895	592.69	525.5932731	5.094164552	67.09672687
96.292	597.69	530.6919896	5.09871644	66.99801043
96.8955	602.69	535.7952384	5.103248806	66.89476162
97.5	607.69	540.903	5.107761619	66.787
98.1055	612.69	546.0152548	5.112254847	66.67474515

## Appendix C-3: C-14 Data

Sample depths	age by initial model	Age by new model	increments	$\delta$ age: init-new
98.712	617.69	551.1319833	5.116728456	66.5580167
99.3195	622.69	556.2531657	5.121182414	66.43683428
99.928	627.69	561.3787824	5.12561669	66.31121759
100.5375	632.69	566.5088137	5.13003125	66.18118634
101.148	637.69	571.6432397	5.134426062	66.04676028
101.7595	642.69	576.7820408	5.138801094	65.90795919
102.372	647.69	581.9251971	5.143156314	65.76480287
102.9855	652.69	587.0726888	5.147491688	65.61731119
103.6	657.69	592.224496	5.151807185	65.465504
104.2155	662.69	597.3805988	5.156102773	65.30940123
104.832	667.69	602.5409772	5.160378418	65.14902281
105.4495	672.69	607.7056113	5.164634088	64.98438872
106.068	677.69	612.874481	5.168869752	64.81551897
106.6875	682.69	618.0475664	5.173085376	64.64243359
107.308	687.69	623.2248473	5.177280928	64.46515267
107.9295	692.69	628.4063037	5.181456376	64.28369629
108.552	697.69	633.5919154	5.185611688	64.0980846
109.1755	702.69	638.7816622	5.18974683	63.90833777
109.8	707.69	643.975524	5.193861771	63.714476
110.4255	712.69	649.1734805	5.197956479	63.51651952
111.052	717.69	654.3755114	5.20203092	63.3144886
111.6795	722.69	659.5815965	5.206085062	63.10840354
112.308	727.69	664.7917153	5.210118874	62.89828467
112.9375	732.69	670.0058477	5.214132322	62.68415234
113.568	737.69	675.223973	5.218125374	62.46602697
114.1995	742.69	680.446071	5.222097998	62.24392897
114.832	747.69	685.6721212	5.226050162	62.01787881
115.4655	752.69	690.902103	5.229981832	61.78789698
116.1	757.69	696.135996	5.233892977	61.554004
116.7355	762.69	701.3737796	5.237783565	61.31622044
117.372	767.69	706.6154331	5.241653562	61.07456687
118.0095	772.69	711.8609361	5.245502936	60.82906394
118.648	777.69	717.1102677	5.249331656	60.57973228
119.2875	782.69	722.3634074	5.253139688	60.32659259
119.928	787.69	727.6203344	5.256927	60.06966559
120.5695	792.69	732.881028	5.26069356	59.80897203
121.212	797.69	738.1454673	5.264439336	59.5445327
121.8555	802.69	743.4136316	5.268164294	59.2763684
122.5	807.69	748.6855	5.271868403	59.0045
123.1455	812.69	753.9610516	5.275551631	58.72894837
123.792	817.69	759.2402656	5.279213944	58.44973443
124.4395	822.69	764.5231209	5.28285531	58.16687912
125.088	827.69	769.8095966	5.286475698	57.88040342
125.7375	832.69	775.0996717	5.290075074	57.59032834
126.388	837.69	780.3933251	5.293653406	57.29667494
127.0395	842.69	785.6905357	5.297210662	56.99946428
127.692	847.69	790.9912825	5.30074681	56.69871747
128.3455	852.69	796.2955444	5.304261816	56.39445565
129	857.69	801.6033	5.307755649	56.0867
129.6555	862.69	806.9145283	5.311228277	55.77547172
130.312	867.69	812.2292079	5.314679666	55.46079206

## Appendix C-3: C-14 Data

Sample depths	age by initial model	Age by new model	increments	$\delta$ age: init-new
130.9695	872.69	817.5473177	5.318109784	55.14268227
131.628	877.69	822.8688363	5.3215186	54.82116367
132.2875	882.69	828.1937424	5.32490608	54.49625759
132.948	887.69	833.5220146	5.328272192	54.1679854
133.6095	892.69	838.8536315	5.331616904	53.8363685
134.272	897.69	844.1885717	5.334940184	53.50142831
134.9355	902.69	849.5268137	5.338241998	53.16318632
135.6	907.69	854.868336	5.341522315	52.821664
136.2655	912.69	860.2131171	5.344781103	52.4768829
136.932	917.69	865.5611354	5.348018328	52.12886457
137.5995	922.69	870.9123694	5.351233958	51.77763061
138.268	927.69	876.2667974	5.354427962	51.42320265
138.9375	932.69	881.6243977	5.357600306	51.06560234
139.608	937.69	886.9851486	5.360750958	50.70485139
140.2795	942.69	892.3490285	5.363879886	50.3409715
140.952	947.69	897.7160156	5.366987058	49.97398444
141.6255	952.69	903.086088	5.37007244	49.603912
142.3	957.69	908.459224	5.373136001	49.230776
142.9755	962.69	913.8354017	5.376177709	48.85459829
143.652	967.69	919.2145992	5.37919753	48.47540076
144.3295	972.69	924.5967947	5.382195432	48.09320533
145.008	977.69	929.9819661	5.385171384	47.70803395
145.6875	982.69	935.3700914	5.388125352	47.31990859
146.368	987.69	940.7611487	5.391057304	46.92885129
147.0495	992.69	946.1551159	5.393967208	46.53488408
147.732	997.69	951.551971	5.396855032	46.13802905
148.4155	1002.69	956.9516917	5.399720742	45.73830831
149.1	1007.69	962.354256	5.402564307	45.335744
149.7855	1012.69	967.7596417	5.405385695	44.93035831
150.472	1017.69	973.1678266	5.408184872	44.52217343
151.1595	1022.69	978.5787884	5.410961806	44.11121163
151.848	1027.69	983.9925048	5.413716466	43.69749516
152.5375	1032.69	989.4089537	5.416448818	43.28104634
153.228	1037.69	994.8281125	5.41915883	42.86188751
153.9195	1042.69	1000.249959	5.42184647	42.44004104
154.612	1047.69	1005.674471	5.424511706	42.01552934
155.3055	1052.69	1011.101625	5.427154504	41.58837483
156	1057.69	1016.5314	5.429774833	41.1586
156.6955	1062.69	1021.963773	5.432372661	40.72622734
157.392	1067.69	1027.398721	5.434947954	40.29127939
158.0895	1072.69	1032.836221	5.43750068	39.85377871
158.788	1077.69	1038.276252	5.440030808	39.4137479
159.4875	1082.69	1043.71879	5.442538304	38.97120959
160.188	1087.69	1049.163814	5.445023136	38.52618646
160.8895	1092.69	1054.611299	5.447485272	38.07870119
161.592	1097.69	1060.061223	5.44992468	37.62877651
162.2955	1102.69	1065.513565	5.452341326	37.17643518
163	1107.69	1070.9683	5.454735179	36.7217
163.7055	1112.69	1076.425406	5.457106207	36.26459379
164.412	1117.69	1081.884861	5.459454376	35.80513942
165.1195	1122.69	1087.34664	5.461779654	35.34335976

## Appendix C-3: C-14 Data

Sample depths	age by initial model	Age by new model	increments	$\delta$ age: init-new
166.5375	1132.69	1098.277084	5.46636141	34.41291634
167.248	1137.69	1103.745701	5.468617822	33.94429852
167.9595	1142.69	1109.216553	5.470851214	33.47344731
168.672	1147.69	1114.689614	5.473061554	33.00038575
169.3855	1152.69	1120.164863	5.475248808	32.52513695
170.1	1157.69	1125.642276	5.477412945	32.047724
170.8155	1162.69	1131.12183	5.479553933	31.56817007
171.532	1167.69	1136.603502	5.481671738	31.08649833
172.2495	1172.69	1142.087268	5.483766328	30.602732
172.968	1177.69	1147.573106	5.485837672	30.11689433
173.6875	1182.69	1153.060991	5.487885736	29.62900859
174.408	1187.69	1158.550902	5.489910488	29.13909811
175.1295	1192.69	1164.042814	5.491911896	28.64718621
175.852	1197.69	1169.536704	5.493889928	28.15329628
176.5755	1202.69	1175.032548	5.49584455	27.65745173
177.3	1207.69	1180.530324	5.497775731	27.159676
178.0255	1212.69	1186.030007	5.499683439	26.65999256
178.752	1217.69	1191.531575	5.50156764	26.15842492
179.4795	1222.69	1197.035003	5.503428302	25.65499662
180.208	1227.69	1202.540269	5.505265394	25.14973123
180.9375	1232.69	1208.047348	5.507078882	24.64265234
181.668	1237.69	1213.556216	5.508868734	24.13378361
182.3995	1242.69	1219.066851	5.510634918	23.62314869
183.132	1247.69	1224.579229	5.512377402	23.11077129
183.8655	1252.69	1230.093325	5.514096152	22.59667514
184.6	1257.69	1235.609116	5.515791137	22.080884
185.3355	1262.69	1241.126578	5.517462325	21.56342168
186.072	1267.69	1246.645688	5.519109682	21.04431199
186.8095	1272.69	1252.166421	5.520733176	20.52357882
187.548	1277.69	1257.688754	5.522332776	20.00124604
188.2875	1282.69	1263.212662	5.523908448	19.47733759
189.028	1287.69	1268.738123	5.52546016	18.95187743
189.7695	1292.69	1274.26511	5.52698788	18.42488955
190.512	1297.69	1279.793602	5.528491576	17.89639798
191.2555	1302.69	1285.323573	5.529971214	17.36642676
192	1307.69	1290.855	5.531426763	16.835
192.7455	1312.69	1296.387858	5.532858191	16.30214181
193.492	1317.69	1301.922124	5.534265464	15.76787635
194.2395	1322.69	1307.457772	5.53564855	15.2322278
194.988	1327.69	1312.99478	5.537007418	14.69522038
195.7375	1332.69	1318.533122	5.538342034	14.15687834
196.488	1337.69	1324.072774	5.539652366	13.61722598
197.2395	1342.69	1329.613712	5.540938382	13.0762876
197.992	1347.69	1335.155912	5.54220005	12.53408755
198.7455	1352.69	1340.69935	5.543437336	11.99065021
199.5	1357.69	1346.244	5.544650209	11.446
200.2555	1362.69	1351.789839	5.545838637	10.90016136
201.012	1367.69	1357.336841	5.547002586	10.35315878
201.7695	1372.69	1362.884983	5.548142024	9.805016753
202.528	1377.69	1368.43424	5.54925692	9.255759834
203.2875	1382.69	1373.984587	5.55034724	8.705412594

## Appendix C-3: C-14 Data

Sample depths	age by initial model	Age by new model	increments	δ age: init-new
204.048	1387.69	1379.536	5.551412952	8.153999642
204.8095	1392.69	1385.088454	5.552454024	7.601545617
205.572	1397.69	1390.641925	5.553470424	7.048075194
206.3355	1402.69	1396.196387	5.554462118	6.493613075
207.1	1407.69	1401.751816	5.555429075	5.938184
207.8655	1412.69	1407.308187	5.556371263	5.381812737
208.632	1417.69	1412.865476	5.557288648	4.82452409
209.3995	1422.69	1418.423657	5.558181198	4.266342891
210.168	1427.69	1423.982706	5.559048882	3.70729401
210.9375	1432.69	1429.542598	5.559891666	3.147402344
211.708	1437.69	1435.103307	5.560709518	2.586692826
212.4795	1442.69	1440.66481	5.561502406	2.025190419
213.252	1447.69	1446.22708	5.562270298	1.462920122
214.0255	1452.69	1451.790093	5.56301316	0.899906961
214.8	1457.69	1457.353824	5.563730961	0.336176
215.5755	1462.69	1462.918248	5.564423669	-0.228247669
216.352	1467.69	1468.483339	5.56509125	-0.793338918
217.1295	1472.69	1474.049073	5.565733672	-1.359072591
217.908	1477.69	1479.615423	5.566350904	-1.925423494
218.6875	1482.69	1485.182366	5.566942912	-2.492366406
219.468	1487.69	1490.749876	5.567509664	-3.05987607
220.2495	1492.69	1496.317927	5.568051128	-3.627927199
221.032	1497.69	1501.886494	5.568567272	-4.19649447
221.8155	1502.69	1507.455553	5.569058062	-4.765552533
222.6	1507.69	1513.025076	5.569523467	-5.335076
223.3855	1512.69	1518.595039	5.569963455	-5.905039455
224.172	1517.69	1524.165417	5.570377992	-6.475417446
224.9595	1522.69	1529.736184	5.570767046	-7.046184493
225.748	1527.69	1535.307315	5.571130586	-7.617315078
226.5375	1532.69	1540.878784	5.571468578	-8.188783656
227.328	1537.69	1546.450565	5.57178099	-8.760564646
228.1195	1542.69	1552.022632	5.57206779	-9.332632437
228.912	1547.69	1557.594961	5.572328946	-9.904961382
229.7055	1552.69	1563.167526	5.572564424	-10.47752581
230.5	1557.69	1568.7403	5.572774193	-11.0503
231.2955	1562.69	1574.313258	5.572958221	-11.62325822
232.092	1567.69	1579.886375	5.573116474	-12.19637469
232.8895	1572.69	1585.459624	5.57324892	-12.76962361
233.688	1577.69	1591.032979	5.573355528	-13.34297914
234.4875	1582.69	1596.606415	5.573436264	-13.91641541
235.288	1587.69	1602.179907	5.573491096	-14.4899065
236.0895	1592.69	1607.753426	5.573519992	-15.06342649
236.892	1597.69	1613.326949	5.57352292	-15.63694941
237.6955	1602.69	1618.900449	5.573499846	-16.21044926
238.5	1607.69	1624.4739	5.573450739	-16.7839
239.3055	1612.69	1630.047276	5.573375567	-17.35727557
240.112	1617.69	1635.62055	5.573274296	-17.93054986
240.9195	1622.69	1641.193697	5.573146894	-18.50369676
241.728	1627.69	1646.76669	5.57299333	-19.07669009
242.5375	1632.69	1652.339504	5.57281357	-19.64950366
243.348	1637.69	1657.912111	5.572607582	-20.22211124

## Appendix C-3: C-14 Data

Sample depths	age by initial model	Age by new model	increments	$\delta$ age: init-new
244.1595	1642.69	1663.484487	5.572375334	-20.79448657
244.972	1647.69	1669.056603	5.572116794	-21.36660337
245.7855	1652.69	1674.628435	5.571831928	-21.93843529
246.6	1657.69	1680.199956	5.571520705	-22.509956
247.4155	1662.69	1685.771139	5.571183093	-23.08113909
248.232	1667.69	1691.341958	5.570819058	-23.65195815
249.0495	1672.69	1696.912387	5.570428568	-24.22238672
249.868	1677.69	1702.482398	5.570011592	-24.79239831
250.6875	1682.69	1708.051966	5.569568096	-25.36196641
251.508	1687.69	1713.621064	5.569098048	-25.93106445
252.3295	1692.69	1719.189666	5.568601416	-26.49966587
253.152	1697.69	1724.757744	5.568078168	-27.06774404
253.9755	1702.69	1730.325272	5.56752827	-27.63527231
254.8	1707.69	1735.892224	5.566951691	-28.202224
255.6255	1712.69	1741.458572	5.566348399	-28.7685724
256.452	1717.69	1747.024291	5.56571836	-29.33429076
257.2795	1722.69	1752.589352	5.565061542	-29.8993523
258.108	1727.69	1758.15373	5.564377914	-30.46373021
258.9375	1732.69	1763.717398	5.563667442	-31.02739766
259.768	1737.69	1769.280328	5.562930094	-31.59032775
260.5995	1742.69	1774.842494	5.562165838	-32.15249359
261.432	1747.69	1780.403868	5.561374642	-32.71386823
262.2655	1752.69	1785.964425	5.560556472	-33.2744247
263.1	1757.69	1791.524136	5.559711297	-33.834136
263.9355	1762.69	1797.082975	5.558839085	-34.39297508
264.772	1767.69	1802.640915	5.557939802	-34.95091489
265.6095	1772.69	1808.197928	5.557013416	-35.5079283
266.448	1777.69	1813.753988	5.556059896	-36.0639882
267.2875	1782.69	1819.309067	5.555079208	-36.61906741
268.128	1787.69	1824.863139	5.55407132	-37.17313873
268.9695	1792.69	1830.416175	5.5530362	-37.72617493
269.812	1797.69	1835.968149	5.551973816	-38.27814874
270.6555	1802.69	1841.519033	5.550884134	-38.82903288
271.5	1807.69	1847.0688	5.549767123	-39.3788
272.3455	1812.69	1852.617423	5.548622751	-39.92742275
273.192	1817.69	1858.164874	5.547450984	-40.47487373
274.0395	1822.69	1863.711126	5.54625179	-41.02112552
274.888	1827.69	1869.256151	5.545025138	-41.56615066
275.7375	1832.69	1874.799922	5.543770994	-42.10992166
276.588	1837.69	1880.342411	5.542489326	-42.65241098
277.4395	1842.69	1885.883591	5.541180102	-43.19359108
278.292	1847.69	1891.423434	5.53984329	-43.73343437
279.1455	1852.69	1896.961913	5.538478856	-44.27191323
280	1857.69	1902.499	5.537086769	-44.809
280.8555	1862.69	1908.034667	5.535666997	-45.344667
281.712	1867.69	1913.568887	5.534219506	-45.8788865
282.5695	1872.69	1919.101631	5.532744264	-46.41163077
283.428	1877.69	1924.632872	5.53124124	-46.94287201
284.2875	1882.69	1930.162582	5.5297104	-47.47258241
285.148	1887.69	1935.690734	5.528151712	-48.00073412
286.0095	1892.69	1941.217299	5.526565144	-48.52729926

## Appendix C-3: C-14 Data

Sample depths	age by initial model	Age by new model	increments	δ age: init-new
286.872	1897.69	1946.74225	5.524950664	-49.05224993
287.7355	1902.69	1952.265558	5.523308238	-49.57555816
288.6	1907.69	1957.787196	5.521637835	-50.097196
289.4655	1912.69	1963.307135	5.519939423	-50.61713542
290.332	1917.69	1968.825348	5.518212968	-51.13534839
291.1995	1922.69	1974.341807	5.516458438	-51.65180683
292.068	1927.69	1979.856483	5.514675802	-52.16648263
292.9375	1932.69	1985.369348	5.512865026	-52.67934766
293.808	1937.69	1990.880374	5.511026078	-53.19037373
294.6795	1942.69	1996.389533	5.509158926	-53.69953266
295.552	1947.69	2001.896796	5.507263538	-54.2067962
296.4255	1952.69	2007.402136	5.50533988	-54.71213608
297.3	1957.69	2012.905524	5.503387921	-55.215524
298.1755	1962.69	2018.406932	5.501407629	-55.71693163
299.052	1967.69	2023.906331	5.49939897	-56.2163306
299.9295	1972.69	2029.403693	5.497361912	-56.71369251
300.808	1977.69	2034.898989	5.495296424	-57.20898893
301.6875	1982.69	2040.392191	5.493202472	-57.70219141
302.568	1987.69	2045.883271	5.491080024	-58.19327143
303.4495	1992.69	2051.3722	5.488929048	-58.68220048
304.332	1997.69	2056.85895	5.486749512	-59.16894999
305.2155	2002.69	2062.343491	5.484541382	-59.65349137
306.1	2007.69	2067.825796	5.482304627	-60.135796
306.9855	2012.69	2073.305835	5.480039215	-60.61583521
307.872	2017.69	2078.78358	5.477745112	-61.09358033
308.7595	2022.69	2084.259003	5.475422286	-61.56900261
309.648	2027.69	2089.732073	5.473070706	-62.04207332
310.5375	2032.69	2095.202764	5.470690338	-62.51276366
311.428	2037.69	2100.671045	5.46828115	-62.98104481
312.3195	2042.69	2106.136888	5.46584311	-63.44688792
313.212	2047.69	2111.600264	5.463376186	-63.9102641
314.1055	2052.69	2117.061144	5.460880344	-64.37114445
315	2057.69	2122.5195	5.458355553	-64.8295
315.8955	2062.69	2127.975302	5.455801781	-65.28530178
316.792	2067.69	2133.428521	5.453218994	-65.73852077
317.6895	2072.69	2138.879128	5.45060716	-66.18912793
318.588	2077.69	2144.327094	5.447966248	-66.63709418
319.4875	2082.69	2149.77239	5.445296224	-67.08239041
320.388	2087.69	2155.214987	5.442597056	-67.52498746
321.2895	2092.69	2160.654856	5.439868712	-67.96485617
322.192	2097.69	2166.091967	5.43711116	-68.40196733
323.0955	2102.69	2171.526292	5.434324366	-68.8362917
324	2107.69	2176.9578	5.431508299	-69.2678
324.9055	2112.69	2182.386463	5.428662927	-69.69646293
325.812	2117.69	2187.812251	5.425788216	-70.12225114
326.7195	2122.69	2193.235135	5.422884134	-70.54513528
327.628	2127.69	2198.655086	5.41995065	-70.96508593
328.5375	2132.69	2204.072074	5.41698773	-71.38207366
329.448	2137.69	2209.486069	5.413995342	-71.796069
330.3595	2142.69	2214.897042	5.410973454	-72.20704245
331.272	2147.69	2220.304964	5.407922034	-72.61496449

## Appendix C-3: C-14 Data

Sample depths	age by initial model	Age by new model	increments	δ age: init-new
332.1855	2152.69	2225.709806	5.404841048	-73.01980553
333.1	2157.69	2231.111536	5.401730465	-73.421536
334.0155	2162.69	2236.510126	5.398590253	-73.82012625
334.932	2167.69	2241.905547	5.395420378	-74.21554663
335.8495	2172.69	2247.297767	5.392220808	-74.60776744
336.768	2177.69	2252.686759	5.388991512	-74.99675895
337.6875	2182.69	2258.072491	5.385732456	-75.38249141
338.608	2187.69	2263.454935	5.382443608	-75.76493501
339.5295	2192.69	2268.83406	5.379124936	-76.14405995
340.452	2197.69	2274.209836	5.375776408	-76.51983636
341.3755	2202.69	2279.582234	5.37239799	-76.89223435
342.3	2207.69	2284.951224	5.368989651	-77.261224
343.2255	2212.69	2290.316775	5.365551359	-77.62677536
344.152	2217.69	2295.678858	5.36208308	-77.98885844
345.0795	2222.69	2301.037443	5.358584782	-78.34744322
346.008	2227.69	2306.3925	5.355056434	-78.70249965
346.9375	2232.69	2311.743998	5.351498002	-79.05399766
347.868	2237.69	2317.091907	5.347909454	-79.40190711
348.7995	2242.69	2322.436198	5.344290758	-79.74619787
349.732	2247.69	2327.77684	5.340641882	-80.08683975
350.6655	2252.69	2333.113803	5.336962792	-80.42380254
351.6	2257.69	2338.447056	5.333253457	-80.757056
352.5355	2262.69	2343.77657	5.329513845	-81.08656984
353.472	2267.69	2349.102314	5.325743922	-81.41231377
354.4095	2272.69	2354.424257	5.321943656	-81.73425742
355.348	2277.69	2359.74237	5.318113016	-82.05237044
356.2875	2282.69	2365.056622	5.314251968	-82.36662241
357.228	2287.69	2370.366983	5.31036048	-82.67698289
358.1695	2292.69	2375.673421	5.30643852	-82.98342141
359.112	2297.69	2380.975907	5.302486056	-83.28590746
360.0555	2302.69	2386.274411	5.298503054	-83.58441052
361	2307.69	2391.5689	5.294489483	-83.8789
361.9455	2312.69	2396.859345	5.290445311	-84.16934531
362.892	2317.69	2402.145716	5.286370504	-84.45571581
363.8395	2322.69	2407.427981	5.28226503	-84.73798084
364.788	2327.69	2412.70611	5.278128858	-85.0161097
365.7375	2332.69	2417.980072	5.273961954	-85.29007166
366.688	2337.69	2423.249836	5.269764286	-85.55983594
367.6395	2342.69	2428.515372	5.265535822	-85.82537176
368.592	2347.69	2433.776648	5.26127653	-86.08664829
369.5455	2352.69	2439.033635	5.256986376	-86.34363467
370.5	2357.69	2444.2863	5.252665329	-86.5963
371.4555	2362.69	2449.534613	5.248313357	-86.84461336
372.412	2367.69	2454.778544	5.243930426	-87.08854378
373.3695	2372.69	2460.01806	5.239516504	-87.32806029
374.328	2377.69	2465.253132	5.23507156	-87.56313185
375.2875	2382.69	2470.483727	5.23059556	-87.79372741
376.248	2387.69	2475.709816	5.226088472	-88.01981588
377.2095	2392.69	2480.931366	5.221550264	-88.24136614
378.172	2397.69	2486.148347	5.216980904	-88.45834705
379.1355	2402.69	2491.360727	5.212380358	-88.6707274

## Appendix C-3: C-14 Data

Sample depths	age by initial model	Age by new model	increments	δ age: init-new
380.1	2407.69	2496.568476	5.207748595	-88.878476
381.0655	2412.69	2501.771562	5.203085583	-89.08156158
382.032	2417.69	2506.969953	5.198391288	-89.27995287
382.9995	2422.69	2512.163619	5.193665678	-89.47361855
383.968	2427.69	2517.352527	5.188908722	-89.66252727
384.9375	2432.69	2522.536648	5.184120386	-89.84664766
385.908	2437.69	2527.715948	5.179300638	-90.02594829
386.8795	2442.69	2532.890398	5.174449446	-90.20039774
387.852	2447.69	2538.059965	5.169566778	-90.36996452
388.8255	2452.69	2543.224617	5.1646526	-90.53461712
389.8	2457.69	2548.384324	5.159706881	-90.694324
390.7755	2462.69	2553.539054	5.154729589	-90.84905359
391.752	2467.69	2558.688774	5.14972069	-90.99877428
392.7295	2472.69	2563.833454	5.144680152	-91.14345443
393.708	2477.69	2568.973062	5.139607944	-91.28306237
394.6875	2482.69	2574.107566	5.134504032	-91.41756641
395.668	2487.69	2579.236935	5.129368384	-91.54693479
396.6495	2492.69	2584.361136	5.124200968	-91.67113576
397.632	2497.69	2589.480138	5.119001752	-91.79013751
398.6155	2502.69	2594.593908	5.113770702	-91.90390821
399.6	2507.69	2599.702416	5.108507787	-92.012416
400.5855	2512.69	2604.805629	5.103212975	-92.11562897
401.572	2517.69	2609.903515	5.097886232	-92.21351521
402.5595	2522.69	2614.996043	5.092527526	-92.30604273
403.548	2527.69	2620.08318	5.087136826	-92.39317956
404.5375	2532.69	2625.164894	5.081714098	-92.47489366
405.528	2537.69	2630.241153	5.07625931	-92.55115297
406.5195	2542.69	2635.311925	5.07077243	-92.6219254
407.512	2547.69	2640.377179	5.065253426	-92.68717882
408.5055	2552.69	2645.436881	5.059702264	-92.74688109
409.5	2557.69	2650.491	5.054118913	-92.801
410.4955	2562.69	2655.539503	5.048503341	-92.84950334
411.492	2567.69	2660.582359	5.042855514	-92.89235885
412.4895	2572.69	2665.619534	5.0371754	-92.92953425
413.488	2577.69	2670.650997	5.031462968	-92.96099722
414.4875	2582.69	2675.676715	5.025718184	-92.98671541
415.488	2587.69	2680.696656	5.019941016	-93.00665642
416.4895	2592.69	2685.710788	5.014131432	-93.02078785
417.492	2597.69	2690.719077	5.0082894	-93.02907725
418.4955	2602.69	2695.721492	5.002414886	-93.03149214
419.5	2607.69	2700.718	4.996507859	-93.028
420.5055	2612.69	2705.708568	4.990568287	-93.01856829
421.512	2617.69	2710.693164	4.984596136	-93.00316442
422.5195	2622.69	2715.671756	4.978591374	-92.9817558
423.528	2627.69	2720.64431	4.97255397	-92.95430977
424.5375	2632.69	2725.610794	4.96648389	-92.92079366
425.548	2637.69	2730.571175	4.960381102	-92.88117476
426.5595	2642.69	2735.52542	4.954245574	-92.83542033
427.572	2647.69	2740.473498	4.948077274	-92.78349761
428.5855	2652.69	2745.415374	4.941876168	-92.72537377
429.6	2657.69	2750.351016	4.935642225	-92.661016

## Appendix C-3: C-14 Data

Sample depths	age by initial model	Age by new model	increments	$\delta$ age: init-new
430.6155	2662.69	2755.280391	4.929375413	-92.59039141
431.632	2667.69	2760.203467	4.923075698	-92.51346711
432.6495	2672.69	2765.12021	4.916743048	-92.43021016
433.668	2677.69	2770.030588	4.910377432	-92.34058759
434.6875	2682.69	2774.934566	4.903978816	-92.24456641
435.708	2687.69	2779.832114	4.897547168	-92.14211357
436.7295	2692.69	2784.723196	4.891082456	-92.03319603
437.752	2697.69	2789.607781	4.884584648	-91.91778068

C-14 Dates: Calibrated Age before 1950

Depth	Cal age	Cal age 1s	Cal age 2 s	(pollen)
42	55.5			
103	686	668	657	
103		729	759	
221	1421	1395		
221	1448			
221	1464			
221	1465			
221	1485			
221	1500			
221	1510			
221		1528		
392	2729	2494	2362	
392		2747	2762	
631	3483	3469	3409	
631	3508			
631	3551			
631		3630	3682	

## **APPENDIX C-4**

### **PB-210 DATA**

## Appendix C-4: Pb-210 and Cs-137 Data

2002 Depth	Top	Base	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	2002 % Organic	2002 % CaCO <sub>3</sub>	2002% Inorg.	Date(2002)
2	0	2	1.056649	0.100045	0.094681	0.015433	16.29996	16.95034	66.74971	2000.4
4	2	4	1.058684	0.104042	0.098275	0.015824	16.10142	16.99697	66.90161	
6	4	6	1.062243	0.110494	0.10402	0.017146	16.48314	17.05891	66.45795	1996.3
8	6	8	1.066949	0.118686	0.111239	0.018705	16.81542	19.3221	63.86248	
10	8	10	1.072474	0.127997	0.119347	0.019479	16.32107	21.67525	62.00368	1991
12	10	12	1.074659	0.131971	0.122803	0.019778	16.10538	24.88924	59.00538	
14	12	14	1.080651	0.141643	0.131072	0.019942	15.21454	25.7866	58.99886	1985.2
16	14	16	1.082307	0.14477	0.13376	0.020006	14.95688	22.17877	62.86435	
18	16	18	1.085868	0.150478	0.138578	0.01965	14.17989	21.7173	64.1028	1979
20	18	20	1.090482	0.157596	0.14452	0.019853	13.73757	21.49043	64.772	
22	20	22	1.093275	0.162765	0.148878	0.020333	13.65723	20.1824	66.16037	1971.8
24	22	24	1.092952	0.16238	0.14857	0.020728	13.95152	18.97136	67.07711	
26	24	26	1.108861	0.189218	0.170642	0.022303	13.0698	18.42361	68.50659	1963.6
28	26	28	1.122507	0.212419	0.189236	0.023931	12.64616	19.26703	68.08681	
30	28	30	1.122313	0.212602	0.189432	0.02475	13.06565	18.88961	68.04474	1953.5
32	30	32	1.146291	0.253253	0.220933	0.027513	12.45295	20.01983	67.52721	
34	32	34	1.157889	0.272922	0.235706	0.028888	12.25606	22.06398	65.67996	1942.3
36	34	36	1.141485	0.247312	0.216658	0.030412	14.03683	22.37402	63.58915	
38	36	38	1.140659	0.245619	0.215331	0.029583	13.73821	19.37459	66.88721	1927.1
40	38	40	1.181934	0.314307	0.265926	0.03148	11.83781	18.86463	69.29756	
42	40	42	1.234874	0.403782	0.326982	0.035824	10.95585	20.01201	69.03214	1899.1
44	42	44	1.308081	0.530006	0.405178	0.045832	11.31166	20.90448	67.78386	
46	44	46	1.305435	0.526594	0.403386	0.046517	11.53158	20.24602	68.2224	1873.5
48	46	48	1.314336	0.541337	0.411871	0.047138	11.44488	19.216	69.33912	
50	48	50	1.297607	0.51354	0.395759	0.046222	11.67937	18.95	69.37063	1846.5
52	50	52	1.309986	0.535691	0.408929	0.048985	11.97894	18.44792	69.57314	
54	52	54	1.297335	0.516614	0.398212	0.050985	12.8034	17.54715	69.64945	1807.2
56	54	56	1.303465	0.523913	0.401939	0.047793	11.89056	18.75342	69.35602	
58	56	58	1.326937	0.562676	0.424041	0.048251	11.37881	24.99787	63.62332	
60	58	60	1.29705	0.516599	0.398288	0.053242	13.36767	23.49868	63.13365	
62	60	62	1.294188	0.511313	0.395084	0.053074	13.43357	25.90598	60.66046	
64	62	64	1.309157	0.536045	0.409458	0.052684	12.86688	28.94933	58.18379	
66	64	66	1.32657	0.566553	0.427081	0.055545	13.00569	30.42676	56.56755	
68	66	68	1.313066	0.545517	0.415453	0.056972	13.71321	24.883	61.40379	
70	68	70	1.312543	0.541535	0.412585	0.05248	12.71991	22.04637	65.23372	

## Appendix C-4: Pb-210 and Cs-137 Data

2002 Depth	Top	Base	Wet (g/cc)	Dry (g/cc)	Dry/Wet	Org/Wet	2002 % Organic	2002 % CaCO <sub>3</sub>	2002% Inorg.	Date(2002)
72	70	72	1.385696	0.65665	0.473877	0.045455	9.592051	22.96377	67.44418	
74	72	74	1.433017	0.730113	0.509493	0.039049	7.664204	18.51767	73.81812	
76	74	76	1.358598	0.612256	0.450653	0.045869	10.17827	23.80215	66.01958	
78	76	78	1.336453	0.579434	0.433561	0.049581	11.43569	23.57886	64.98544	
80	78	80	1.339107	0.581031	0.433894	0.046346	10.68133	22.54095	66.77771	
82	80	82	1.322851	0.55648	0.420667	0.048987	11.64501	23.63756	64.71743	
84	82	84	1.324941	0.561118	0.423504	0.051412	12.13964	23.57675	64.28361	
86	84	86	1.330507	0.568558	0.427324	0.049069	11.48292	24.05629	64.4608	
88	86	88	1.291421	0.507038	0.39262	0.05273	13.43027	23.11574	63.45399	
90	88	90	1.285848	0.500468	0.389212	0.057077	14.66464	26.09334	59.24202	
92	90	92	1.304201	0.524495	0.402158	0.04685	11.64968	22.94342	65.40691	
94	92	94	1.301843	0.519798	0.399278	0.045897	11.49491	23.64253	64.86256	

Depth (cm)	Cs-137 (pCi/g)	sd Cs-137 (pCi/g)	Pb-210 Date
18	2.205	0.0974	1979
20	2.465	0.0858	1975.4
22	2.46	0.0759	1971.8
24	2.384	0.0995	1967.7
26	2.768	0.125	1963.6
28	2.927	0.0717	1958.55
30	3.706	0.1209	1953.5
32	3.890	0.094	1947.9
34	3.650	0.090	1942.3
36	2.490	0.077	1934.7
38	1.669	0.057	1927.1
40	0.660	0.031	1913.1
42			1899.1

**APPENDIX C-5**

**INFERRRED SALINITY DATA**

## Appendix C-5: Inferred Salinity Data

Slide	Depth (base)	Age	Date	Inferred Salinity	Slide	Depth (base)	Age	Date	Inferred Salinity
DLPA2A	2.0	1.8	2000.4	0.6	DL1	66.2	342.7	1659.5	18.7
DLPA4A	4.0	2.8	1999.4	0.5	DL2	66.8	347.7	1654.5	16.9
DLPA6A	6.0	4.9	1997.3	0.7	DL3	67.4	352.7	1649.5	16.2
DLPA8A	8.0	7.2	1995.0	0.7	DLPA74A	74.0	353.6	1648.6	17.1
DLPA10A	10.0	9.8	1992.4	1.1	DL4	68.0	357.7	1644.5	17.0
DLPA12A	12.0	12.5	1989.7	1.7	DL5	68.6	362.7	1639.5	17.1
DLPA14A	14.0	15.4	1986.8	2.1	DL6	69.2	367.7	1634.5	16.0
DLPA16A	16.0	18.4	1983.8	2.3	DL7	69.8	372.7	1629.5	15.3
DLPA18A	18.0	21.5	1980.7	2.6	DLPA76A	76.0	373.9	1628.3	17.5
DLPA20A	20.0	24.8	1977.4	2.2	DL8	70.4	377.7	1624.5	16.5
DLPA22A	22.0	28.3	1973.9	2.8	DL9	71.0	382.7	1619.5	16.2
DLPA24A	24.0	32.1	1970.1	1.3	DL10	71.6	387.7	1614.5	14.0
DLPA26A	26.0	36.1	1966.1	1.9	DLPA78A	78.0	392.0	1610.2	16.5
DLPA28A	28.0	40.6	1961.6	3.4	DL11	72.2	392.7	1609.5	15.1
DLPA30A	30.0	45.5	1956.7	8.3	DL12	72.8	397.7	1604.5	15.3
DLPA32A	32.0	51.3	1950.9	13.2	DL13	73.4	402.7	1599.5	14.8
DLPA34A	34.0	57.5	1944.7	12.1	DL14	74.0	407.7	1594.5	14.2
DLPA36A	36.0	64.2	1938.0	15.2	DLPA80A	80.0	409.6	1592.6	17.8
DLPA38A	38.0	72.5	1929.7	13.5	DL15	74.6	412.7	1589.5	15.3
DLPA40A	40.0	82.3	1919.9	12.1	DL16	75.2	417.7	1584.5	15.0
DLPA42A	42.0	96.0	1906.2	11.9	DL17	75.8	422.7	1579.5	15.1
DLPA44A	44.0	109.8	1892.4	14.3	DLPA82A	82.0	426.8	1575.4	19.5
DLPA46A	46.0	119.1	1883.1	14.0	DL18	76.4	427.7	1574.5	17.5
DLPA48A	48.0	131.3	1870.9	11.1	DL19	77.0	432.7	1569.5	17.5
DLPA50A	50.0	147.3	1854.9	14.0	DL21	78.2	442.7	1559.5	16.8
DLPA52A	52.0	164.2	1838.0	15.3	DLPA84A	84.0	443.7	1558.5	16.4
DLPA54A	54.0	182.7	1819.5	9.9	DL22	78.8	447.7	1554.5	17.4
DLPA56A	56.0	200.0	1802.2	9.6	DL23	79.4	452.7	1549.5	17.1
DLPA58A	58.0	216.6	1785.6	16.7	DL24	80.0	457.7	1544.5	16.8
DLPA60A	60.0	233.0	1769.2	19.3	DLPA86A	86.0	460.8	1541.3	18.1
DLPA62A	62.0	248.5	1753.7	20.7	DL25	80.6	462.7	1539.5	15.9
DLPA64A	64.0	264.4	1737.8	18.1	DL26	81.2	467.7	1534.5	15.5
DLPA66A	66.0	281.1	1721.1	17.0	DL27	81.8	472.7	1529.5	14.7
DLPA68A	68.0	298.0	1704.2	15.9	DLPA88A	88.0	477.1	1525.1	18.4
DLPA70A	70.0	314.4	1687.8	13.4	DL28	82.4	477.7	1524.5	15.5
DLPA72A	72.0	332.6	1669.6	16.3	DL29	83.0	482.7	1519.5	16.5

## Appendix C-5: Inferred Salinity Data

Slide	Depth (base)	Age	Date	Inferred Salinity	Slide	Depth (base)	Age	Date	Inferred Salinity
DL30	83.6	487.7	1514.5	17.1	DL62	102.8	647.7	1354.5	15.1
DLPA90A	90.0	492.4	1509.8	19.4	DL63	103.4	652.7	1349.5	14.5
DL31	84.2	492.7	1509.5	16.4	DL64	104.0	657.7	1344.5	15.5
DL32	84.8	497.7	1504.5	14.6	DL65	104.6	662.7	1339.5	17.3
DL33	85.4	502.7	1499.5	15.1	DL66	105.2	667.7	1334.5	15.8
DL34	86.0	507.7	1494.5	17.3	DL67	105.8	672.7	1329.5	16.6
DLPA92A	92.0	507.9	1494.3	15.1	DL68	106.4	677.7	1324.5	14.6
DL35	86.6	512.7	1489.5	15.7	DL69	107.0	682.7	1319.5	14.3
DL36	87.2	517.7	1484.5	15.9	DL70	107.6	687.7	1314.5	9.0
DL37	87.8	522.7	1479.5	15.1	DL71	108.2	692.7	1309.5	10.4
DLPA94A	94.0	523.8	1478.4	16.6	DL72	108.8	697.7	1304.5	9.7
DL38	88.4	527.7	1474.5	16.0	DL73	109.4	702.7	1299.5	13.3
DL39	89.0	532.7	1469.5	19.2	DL74	110.0	707.7	1294.5	17.0
DL40	89.6	537.7	1464.5	18.0	DL75	110.6	712.7	1289.5	16.8
DLPA95A	95.0	539.6	1462.6	15.4	DL76	111.2	717.7	1284.5	18.1
DL41	90.2	542.7	1459.5	16.0	DL77	111.8	722.7	1279.5	15.8
DL42	90.8	547.7	1454.5	15.6	DL78	112.4	727.7	1274.5	15.1
DL43	91.4	552.7	1449.5	17.0	DL79	113.0	732.7	1269.5	17.3
DL44	92.0	557.7	1444.5	17.0	DL80	113.6	737.7	1264.5	16.8
DL45	92.6	562.7	1439.5	17.1	DL81	114.2	742.7	1259.5	17.2
DL46	93.2	567.7	1434.5	17.5	DL82	114.8	747.7	1254.5	18.2
DL47	93.8	572.7	1429.5	16.8	DL83	115.4	752.7	1249.5	20.9
DL48	94.4	577.7	1424.5	16.4	DL84	116.0	757.7	1244.5	19.4
DL49	95.0	582.7	1419.5	15.7	DL85	116.6	762.7	1239.5	17.1
DL50	95.6	587.7	1414.5	16.6	DL86	117.2	767.7	1234.5	14.9
DL51	96.2	592.7	1409.5	12.9	DL87	117.8	772.7	1229.5	12.5
DL52	96.8	597.7	1404.5	11.2	DL88	118.4	777.7	1224.5	15.2
DL53	97.4	602.7	1399.5	11.9	DL89	119.0	782.7	1219.5	16.4
DL54	98.0	607.7	1394.5	14.6	DL90	119.6	787.7	1214.5	17.6
DL55	98.6	612.7	1389.5	15.2	DL95	122.7	812.7	1189.5	15.7
DL56	99.2	617.7	1384.5	15.9	DL98	124.8	827.7	1174.5	16.5
DL57	99.8	622.7	1379.5	16.8	DL99	125.5	832.7	1169.5	15.9
DL58	100.4	627.7	1374.5	16.4	DL100	126.2	837.7	1164.5	12.3
DL59	101.0	632.7	1369.5	16.0	DL101	126.9	842.7	1159.5	11.8
DL60	101.6	637.7	1364.5	13.9	DL104	129.0	857.7	1144.5	13.3
DL61	102.2	642.7	1359.5	14.6	DL106	130.4	867.7	1134.5	17.5

## Appendix C-5: Inferred Salinity Data

Slide	Depth (base)	Age	Date	Inferred Salinity	Slide	Depth (base)	Age	Date	Inferred Salinity
DL107	131.1	872.7	1129.5	16.1	DL143	156.3	1052.7	949.5	0.8
DL108	131.8	877.7	1124.5	15.1	DL144	157.0	1057.7	944.5	1.1
DL109	132.5	882.7	1119.5	15.4	DL145	157.7	1062.7	939.5	5.9
DL110	133.2	887.7	1114.5	14.8	DL146	158.4	1067.7	934.5	5.2
DL111	133.9	892.7	1109.5	15.8	DL147	159.1	1072.7	929.5	9.7
DL112	134.6	897.7	1104.5	14.2	DL148	159.8	1077.7	924.5	9.8
DL113	135.3	902.7	1099.5	13.9	DL149	160.5	1082.7	919.5	9.3
DL114	136.0	907.7	1094.5	15.4	DL150	161.2	1087.7	914.5	9.5
DL115	136.7	912.7	1089.5	14.4	DL151	161.9	1092.7	909.5	11.6
DL116	137.4	917.7	1084.5	15.2	DL152	162.6	1097.7	904.5	9.4
DL117	138.1	922.7	1079.5	14.3	DL153	163.3	1102.7	899.5	10.2
DL118	138.8	927.7	1074.5	10.0	DL154	167.5	1132.7	869.5	6.7
DL119	139.5	932.7	1069.5	4.3	DL155	168.2	1137.7	864.5	10.1
DL120	140.2	937.7	1064.5	1.1	DL156	168.9	1142.7	859.5	9.3
DL121	140.9	942.7	1059.5	0.8	DL157	169.6	1147.7	854.5	11.6
DL122	141.6	947.7	1054.5	0.8	DL158	170.3	1152.7	849.5	12.3
DL123	142.3	952.7	1049.5	0.9	DL159	171.0	1157.7	844.5	15.2
DL124	143.0	957.7	1044.5	0.6	DL160	171.7	1162.7	839.5	14.9
DL125	143.7	962.7	1039.5	0.5	DL161	172.4	1167.7	834.5	17.3
DL126	144.4	967.7	1034.5	0.6	DL162	173.1	1172.7	829.5	15.6
DL127	145.1	972.7	1029.5	0.6	DL163	173.8	1177.7	824.5	16.0
DL128	145.8	977.7	1024.5	0.7	DL164	174.5	1182.7	819.5	15.2
DL129	146.5	982.7	1019.5	0.8	DL165	175.2	1187.7	814.5	14.5
DL130	147.2	987.7	1014.5	0.7	DL166	175.9	1192.7	809.5	14.1
DL131	147.9	992.7	1009.5	0.6	DL167	176.6	1197.7	804.5	12.8
DL132	148.6	997.7	1004.5	0.9	DL168	177.3	1202.7	799.5	11.1
DL133	149.3	1002.7	999.5	0.7	DL169	178.0	1207.7	794.5	10.5
DL134	150.0	1007.7	994.5	0.5	DL170	178.7	1212.7	789.5	14.3
DL135	150.7	1012.7	989.5	0.4	DL171	179.4	1217.7	784.5	9.9
DL136	151.4	1017.7	984.5	0.5	DL172	180.1	1222.7	779.5	9.9
DL137	152.1	1022.7	979.5	0.5	DL173	180.8	1227.7	774.5	6.6
DL138	152.8	1027.7	974.5	0.5	DL174	181.5	1232.7	769.5	12.0
DL139	153.5	1032.7	969.5	0.5	DL175	182.2	1237.7	764.5	8.1
DL140	154.2	1037.7	964.5	0.6	DL176	182.9	1242.7	759.5	2.9
DL141	154.9	1042.7	959.5	0.5	DL177	183.6	1247.7	754.5	1.8
DL142	155.6	1047.7	954.5	0.6	DL178	184.3	1252.7	749.5	1.9

## Appendix C-5: Inferred Salinity Data

Slide	Depth (base)	Age	Date	Inferred Salinity	Slide	Depth (base)	Age	Date	Inferred Salinity
DL179	185.0	1257.7	744.5	2.6	DL216	213.6	1442.7	559.5	15.9
DL180	185.7	1262.7	739.5	2.3	DL217	214.4	1447.7	554.5	16.0
DL181	186.4	1267.7	734.5	2.1	DL218	215.2	1452.7	549.5	14.5
DL182	187.1	1272.7	729.5	1.0	DL219	216.0	1457.7	544.5	15.1
DL183	187.8	1277.7	724.5	1.4	DL220	216.8	1462.7	539.5	14.7
DL184	188.5	1282.7	719.5	2.1	DL221	217.6	1467.7	534.5	13.3
DL185	189.2	1287.7	714.5	0.6	DL222	218.4	1472.7	529.5	13.6
DL186	189.9	1292.7	709.5	0.4	DL223	219.2	1477.7	524.5	11.4
DL187	190.6	1297.7	704.5	1.2	DL224	220.0	1482.7	519.5	5.0
DL188	191.3	1302.7	699.5	0.8	DL225	220.8	1487.7	514.5	3.4
DL189	192.0	1307.7	694.5	1.3	DL226	221.6	1492.7	509.5	2.4
DL190	192.8	1312.7	689.5	0.8	DL227	222.4	1497.7	504.5	2.4
DL191	193.6	1317.7	684.5	1.5	DL228	223.2	1502.7	499.5	7.1
DL192	194.4	1322.7	679.5	3.0	DL229	224.0	1507.7	494.5	7.8
DL193	195.2	1327.7	674.5	3.4	DL230	224.8	1512.7	489.5	6.2
DL194	196.0	1332.7	669.5	4.1	DL231	225.6	1517.7	484.5	12.0
DL195	196.8	1337.7	664.5	5.6	DL232	226.4	1522.7	479.5	12.5
DL196	197.6	1342.7	659.5	3.3	DL233	227.2	1527.7	474.5	13.0
DL197	198.4	1347.7	654.5	3.5	DL234	228.0	1532.7	469.5	14.4
DL198	199.2	1352.7	649.5	5.9	DL235	228.8	1537.7	464.5	14.5
DL199	200.0	1357.7	644.5	10.3	DL236	229.6	1542.7	459.5	14.3
DL200	200.8	1362.7	639.5	15.4	DL237	230.4	1547.7	454.5	15.2
DL201	201.6	1367.7	634.5	15.2	DL238	231.2	1552.7	449.5	15.0
DL202	202.4	1372.7	629.5	16.2	DL239	232.0	1557.7	444.5	15.7
DL203	203.2	1377.7	624.5	11.2	DL240	232.8	1562.7	439.5	14.0
DL204	204.0	1382.7	619.5	12.6	DL241	233.6	1567.7	434.5	15.0
DL205	204.8	1387.7	614.5	15.7	DL242	234.4	1572.7	429.5	15.1
DL207	206.4	1397.7	604.5	16.4	DL243	235.2	1577.7	424.5	16.5
DL208	207.2	1402.7	599.5	17.6	DL244	236.0	1582.7	419.5	16.0
DL209	208.0	1407.7	594.5	17.9	DL245	236.8	1587.7	414.5	16.2
DL210	208.8	1412.7	589.5	16.5	DL246	237.6	1592.7	409.5	16.6
DL211	209.6	1417.7	584.5	15.1	DL247	238.4	1597.7	404.5	13.7
DL212	210.4	1422.7	579.5	13.6	DL248	239.2	1602.7	399.5	15.6
DL213	211.2	1427.7	574.5	13.1	DL249	240.0	1607.7	394.5	14.9
DL214	212.0	1432.7	569.5	14.8	DL250	240.8	1612.7	389.5	13.1
DL215	212.8	1437.7	564.5	14.1	DL251	241.6	1617.7	384.5	12.4

## Appendix C-5: Inferred Salinity Data

Slide	Depth (base)	Age	Date	Inferred Salinity	Slide	Depth (base)	Age	Date	Inferred Salinity
DL252	242.4	1622.7	379.5	13.7	DL288	271.2	1802.7	199.5	2.3
DL253	243.2	1627.7	374.5	12.5	DL289	272.0	1807.7	194.5	2.0
DL254	244.0	1632.7	369.5	13.0	DL290	272.9	1812.7	189.5	2.0
DL255	244.8	1637.7	364.5	12.5	DL291	273.8	1817.7	184.5	1.0
DL256	245.6	1642.7	359.5	12.7	DL292	274.7	1822.7	179.5	1.0
DL257	246.4	1647.7	354.5	13.0	DL293	275.6	1827.7	174.5	0.9
DL258	247.2	1652.7	349.5	14.4	DL294	276.5	1832.7	169.5	1.2
DL259	248.0	1657.7	344.5	12.9	DL295	277.4	1837.7	164.5	0.8
DL260	248.8	1662.7	339.5	14.3	DL296	278.3	1842.7	159.5	1.0
DL261	249.6	1667.7	334.5	14.7	DL297	279.2	1847.7	154.5	1.6
DL262	250.4	1672.7	329.5	13.1	DL298	280.1	1852.7	149.5	1.2
DL263	251.2	1677.7	324.5	14.0	DL299	281.0	1857.7	144.5	0.9
DL264	252.0	1682.7	319.5	15.0	DL300	281.9	1862.7	139.5	1.0
DL265	252.8	1687.7	314.5	9.5	DL301	282.8	1867.7	134.5	3.9
DL266	253.6	1692.7	309.5	12.0	DL302	283.7	1872.7	129.5	1.3
DL267	254.4	1697.7	304.5	5.8	DL303	284.6	1877.7	124.5	2.5
DL268	255.2	1702.7	299.5	6.6	DL304	285.5	1882.7	119.5	3.7
DL269	256.0	1707.7	294.5	6.7	DL305	286.4	1887.7	114.5	4.7
DL270	256.8	1712.7	289.5	3.5	DL306	287.3	1892.7	109.5	5.2
DL271	257.6	1717.7	284.5	5.1	DL307	288.2	1897.7	104.5	3.6
DL272	258.4	1722.7	279.5	3.8	DL308	289.1	1902.7	99.5	6.2
DL273	259.2	1727.7	274.5	3.8	DL309	290.0	1907.7	94.5	7.9
DL274	260.0	1732.7	269.5	3.9	DL310	290.9	1912.7	89.5	2.3
DL275	260.8	1737.7	264.5	4.1	DL311	291.8	1917.7	84.5	9.7
DL276	261.6	1742.7	259.5	3.2	DL312	292.7	1922.7	79.5	13.2
DL277	262.4	1747.7	254.5	2.2	DL313	293.6	1927.7	74.5	10.0
DL278	263.2	1752.7	249.5	1.6	DL314	294.5	1932.7	69.5	15.0
DL279	264.0	1757.7	244.5	1.5	DL315	295.4	1937.7	64.5	14.2
DL280	264.8	1762.7	239.5	1.9	DL316	296.3	1942.7	59.5	16.4
DL281	265.6	1767.7	234.5	1.8	DL317	297.2	1947.7	54.5	15.6
DL282	266.4	1772.7	229.5	1.8	DL318	298.1	1952.7	49.5	15.7
DL283	267.2	1777.7	224.5	2.3	DL319	299.0	1957.7	44.5	14.4
DL284	268.0	1782.7	219.5	1.4	DL320	299.9	1962.7	39.5	14.3
DL285	268.8	1787.7	214.5	1.5	DL321	300.8	1967.7	34.5	16.3
DL286	269.6	1792.7	209.5	1.4	DL322	301.7	1972.7	29.5	14.8
DL287	270.4	1797.7	204.5	1.4	DL323	302.6	1977.7	24.5	14.1

## Appendix C-5: Inferred Salinity Data

Slide	Depth (base)	Age	Date	Inferred Salinity	
DL324	303.5	1982.7	19.5	12.1	
DL325	304.4	1987.7	14.5	11.8	
DL326	305.3	1992.7	9.5	13.1	
DL327	306.2	1997.7	4.5	16.0	
DL328	307.1	2002.7	-0.5	16.7	
DL329	308.0	2007.7	-5.5	15.7	
DL330	308.9	2012.7	-10.5	14.3	

**APPENDIX D**

**DIATOM SEM ANALYSES**

**APPENDIX D-1**

**DIATOM COMPOSITION**

## Diatom composition (Kurt Eylands)

Twelve samples extracted from cores taken from Creel Bay on Devil's Lake were submitted to the NMARL in order to determine if there is any variability in the chemical composition of the diatom frustules.

Diatoms (Phylum Bacillariophyta) are a general name for a group of protists (single celled organisms) than include several types of algae. Diatoms have pigment and chlorophyll for photosynthesis. They have a bivalved siliceous shell whose halves fit together one inside the other like a small box with a lid. Figure 1 shows a diatom collected from the Devils Lake core sample deposited roughly 1000 years ago showing the 2 valves together. Most diatoms are marine and pelagic (swimmers) and have been around since the Cretaceous. Several types have adapted to fresh water since the Miocene and are usually benthic (bottom dwelling). The most common form of the diatom shells are disk-like valves but rod-shaped valves can also be found.

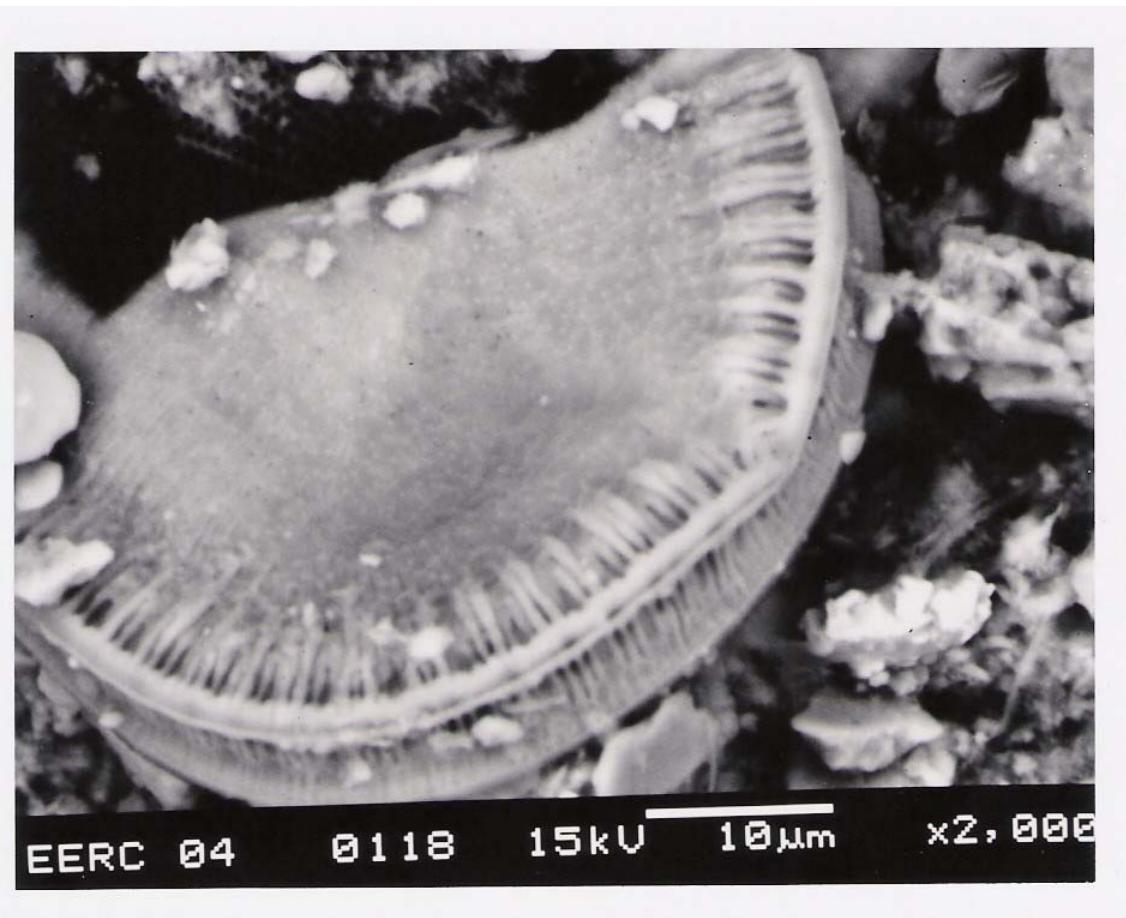


Figure 1. A diatom *Surirella peisonis* from Devils Lake deposited roughly 1000 years ago with both valves intact. From core Arch DLB -1 estimated date of 994 A.D.

A relationship between salinity and diatom species has been determined and salinity reconstructions have been made based on species and relative abundance of diatoms recovered from the cores. The purpose of this part of the study was to determine if the chemical composition of the diatom valves themselves vary when water stands are high (fresh water) or low (more saline).

A plot of inferred salinity from Devils Lake over the last 2000 years was made with resolution of 10 years per data point. From this, six of the twelve samples were selected to represent early freshwater and saline events, middle aged fresh and saline events, and more recent fresh and saline events.

Table 1  
Core Data

Core Samples from Creel Bay, Devils Lake

Core	Depth	Estimated Date	Fresh/Saline	Inferred Salinity
DLPA	1321-1323	1997	Fresh	2.4
DLPA	1403-1405	1525	Saline	18
Arch DLB-1	1466-1467	994	Fresh	2.5
Arch DLB-2	1490-1491	819	Saline	14.6
Arch DLA-2	1556-1557	394	Saline	17.2
Arch DLA-2	1588-1589	194	Fresh	8.8

Table 1 shows the core, the depth at which it was taken, the estimated date at which the sediments were deposited, and the salinity. The early fresh water event was not as fresh as the more recent events.

Because of the significant amount of organic material associated with each of the samples, a procedure using hydrogen peroxide ( $H_2O_2$ ) to oxidize any organic matter and small amounts of hydrochloric acid (HCl) to neutralize the  $H_2O_2$  and dissolve any carbonates that may be present was used. The treated samples were then mounted on a rectangular piece of vitreous carbon. Several species of diatoms were found and analyzed. The images of the various types of diatoms can be found in Appendix 1. A decision was made to focus on a single type of diatom that was found in both fresh and saline events. *Cyclotella quillensis* was found in both fresh and saline waters and was found to be common in the samples looked at. Many of the frustules were fragments but *Cyclotella* could be identified fairly easily. There were a few species of *Cyclotella* reported and several were found in this study as well. The object of this work was not to identify the species, but take a chemical analysis of the frustules found. It is very likely that many of the analyses are not of *Cyclotella quillensis* but are a species of *Cyclotella*. Figure 2 shows the morphology of the diatom identified as *Cyclotella* for this study. There were other similar diatoms that were thought to be of the same genus but likely a different species based on their smaller size and longer radiating spines around the edges. Examples of these diatoms can be found in Appendix 2.

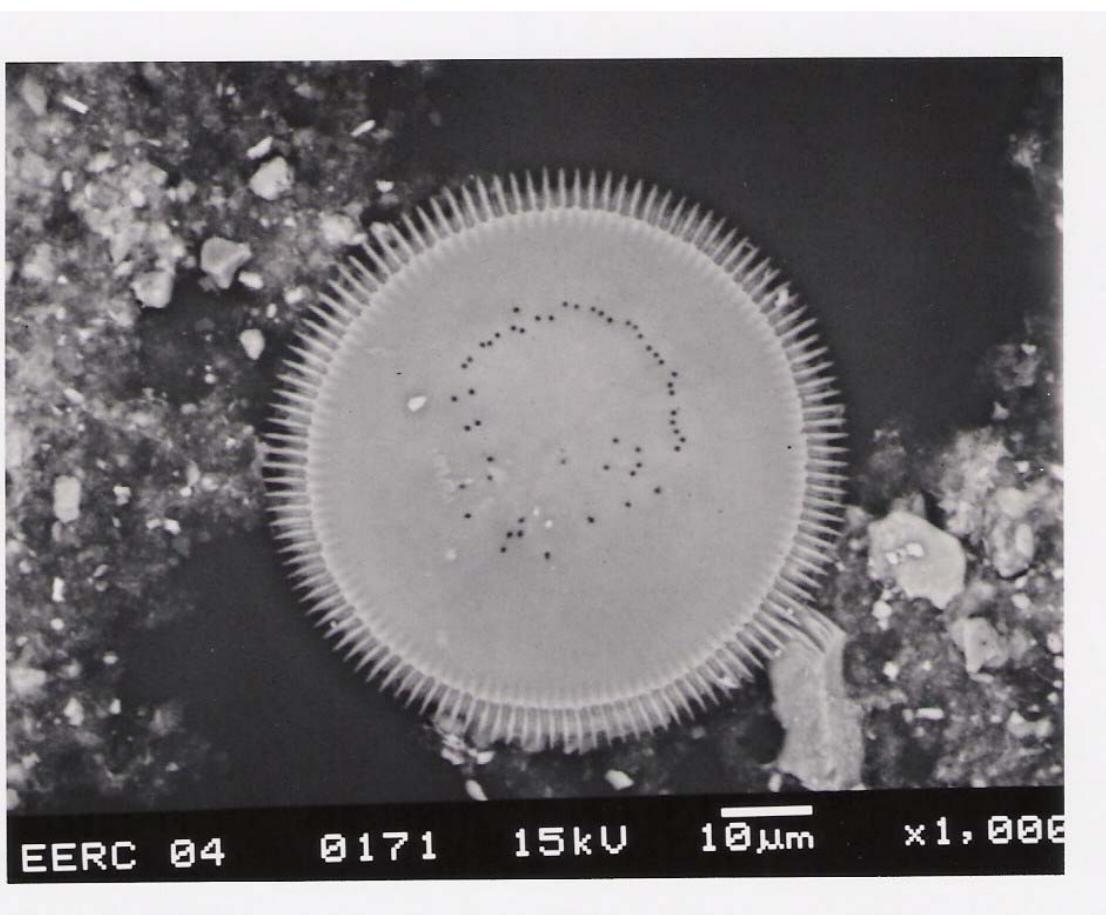


Figure 2. A diatom identified as *Cyclotella quillensis* from Devils Lake core Arch DLA-2 deposited at an estimated date of 394 A.D. when lake conditions were saline.

Chemical analyses of individual diatoms show a stable chemical composition from both high water (low salinity) and low water (high salinity) events. Table 1 shows the average of the chemical analyses for each element, the minimum and maximum values for each element, and the standard deviation for the high water or low salinity samples.

Table 1  
Elemental Data by Core for the Low Saline Samples

Core DLPA	Depth 1321-1323	Corrected Depth 6 cm	Estimated Date 1997	Fresh/Saline Fresh
Inferred Salinity = 2.4				
	Average	Minimum	Maximum	std dev
Na	0.49	0.00	1.80	0.52
Mg	0.87	0.00	2.45	0.74

Al	3.71	0.00	10.86	2.97
Si	88.02	68.40	98.77	8.61
P	0.34	0.00	1.94	0.50
S	0.12	0.00	1.47	0.29
Cl	0.15	0.00	1.52	0.30
K	1.63	0.00	5.66	1.46
Ca	0.46	0.00	1.63	0.47
Ti	0.27	0.00	1.98	0.46
Cr	0.40	0.00	4.13	0.85
Fe	2.95	0.00	6.88	2.19
Ba	0.59	0.00	5.97	1.23

Core	Depth	Corrected Depth	Estimated Date	Fresh/Saline
Arch DLB-1	1466-1467	150 cm	994	Fresh

Inferred Salinity = 2.5

	Average	Min	Max	Std Dev
Na	0.51	0.00	3.49	0.68
Mg	0.71	0.00	1.53	0.50
Al	1.95	0.00	6.23	1.93
Si	90.51	78.78	98.03	5.96
P	0.80	0.00	6.51	1.34
S	0.41	0.00	2.61	0.57
Cl	0.14	0.00	1.43	0.33
K	0.90	0.00	3.76	1.06
Ca	0.55	0.00	2.54	0.71
Ti	0.43	0.00	2.06	0.68
Cr	0.61	0.00	7.21	1.43
Fe	1.87	0.00	5.44	1.87
Ba	0.62	0.00	4.31	1.14

Core	Depth	Corrected Depth	Estimated Date	Fresh/Saline
Arch DLA-2	1588-1589	272 cm	194	Fresh

Inferred Salinity = 8.8

	Average	Min	Max	Std Dev
Na	0.69	0.00	4.32	0.91
Mg	0.83	0.00	2.53	0.77
Al	3.74	0.00	11.00	3.76
Si	87.20	67.83	97.77	9.42
P	0.51	0.00	3.05	0.79
S	0.18	0.00	0.67	0.22
Cl	0.22	0.00	1.57	0.37
K	1.43	0.00	7.03	1.72

Ca	0.76	0.00	4.91	1.14
Ti	0.17	0.00	1.45	0.32
Cr	0.32	0.00	2.51	0.58
Fe	3.39	0.00	9.19	2.84
Ba	0.57	0.00	2.30	0.73

The variability of the chemical analyses can be at least partially attributed to submicron particles attached to the surface of the diatom. The greatest variability is with Si which is the main element along with oxygen composing the frustules. Table 2 shows the same data for the high-salinity samples. As in Table 1, the greatest variability was in Si.

Table 2  
Elemental Data by Core for the High Salinity Samples

Core DLPA	Depth 1403-1405	Corrected Depth 88 cm	Estimated Date 1525	Fresh/Saline Saline
--------------	--------------------	--------------------------	------------------------	------------------------

Inferred Salinity = 18				
	Average	Minimum	Maximum	std dev
Na	0.94	0.00	2.99	0.70
Mg	2.49	0.03	8.87	1.95
Al	3.51	0.00	8.14	2.32
Si	76.57	25.00	98.43	15.70
P	0.26	0.00	1.20	0.39
S	2.38	0.00	37.21	6.64
Cl	0.39	0.00	2.32	0.54
K	1.69	0.00	4.30	1.19
Ca	7.29	0.00	31.61	6.92
Ti	0.19	0.00	1.57	0.42
Cr	0.37	0.00	2.33	0.62
Fe	3.30	0.00	12.48	3.17
Ba	0.62	0.00	3.22	0.82

Core Arch DLB-2	Depth 1490-1491	Corrected Depth 174 cm	Estimated Date 819	Fresh/Saline Saline
--------------------	--------------------	---------------------------	-----------------------	------------------------

Inferred Salinity = 14.6				
	Average	Min	Max	Std Dev
Na	0.47	0.00	1.78	0.54
Mg	1.02	0.00	4.53	1.41
Al	2.14	0.00	13.83	3.69
Si	88.72	64.29	98.09	9.53
P	0.35	0.00	1.59	0.42
S	0.27	0.00	1.50	0.45
Cl	0.49	0.00	1.93	0.60
K	0.71	0.00	4.80	1.17

Ca	0.65	0.00	5.42	1.15
Ti	0.76	0.00	2.95	0.93
Cr	0.90	0.00	4.20	1.30
Fe	2.80	0.00	13.52	4.14
Ba	0.73	0.00	2.93	0.98

Core Arch DLA-2	Depth 1556-1557	Corrected Depth 240 cm	Estimated Date 394	Fresh/Saline Saline
Inferred Salinity = 17.2				
	Average	Min	Max	Std Dev
Na	0.62	0.00	2.83	0.57
Mg	1.29	0.00	3.73	1.04
Al	3.10	0.00	7.26	2.50
Si	88.77	75.36	97.04	6.68
P	0.29	0.00	1.15	0.32
S	0.11	0.00	0.45	0.16
Cl	0.22	0.00	0.77	0.25
K	1.17	0.00	2.33	0.79
Ca	0.75	0.00	3.96	0.88
Ti	0.11	0.00	0.52	0.17
Cr	0.24	0.00	1.31	0.35
Fe	2.99	0.00	7.14	2.23
Ba	0.35	0.00	1.70	0.49

While the standard deviations show variability, they were not consistently variable between the fresh water events and the saline water events. The possible exception to this is with Mg, which is consistently higher in the saline samples. There were not enough data points to do the statistical analyses required and obtaining hundreds or data points was cost prohibitive.

The diatoms were abundant and relatively easy to identify from the cores provided. But no automated method of finding and analyzing the frustules was found to be effective. Some effort was made to do this so that many more diatoms could be analyzed, but the results were not reliable in that all particles of a certain size (10 $\mu$ m to 50 $\mu$ m) were analyzed whether they were of diatomaceous origin or not. This often included particle agglomerations that may or may not include diatom fragments.

Since this work was to focus mostly on *Cyclotella quillensis* because of its abundance and ability to tolerate a wide variety of salinities, there was a need to manually operate the SEM to find and analyze each individual. An image of each individual was collected and the spot where the chemical analysis was taken was marked on each photograph. Other particles often adhere to the diatom frustules and sometimes are reflected in the chemical analysis. The electron beam used for the chemical determination has a depth of penetration of several micrometers ( $\mu\text{m}$ ). Some of the frustules are thin enough that x-rays are generated from particles not seen under the diatom or else part of the mounting media. The mounting media is usually not a problem because the samples were mounted on a carbon substrate to conduct the electrons away from the sample acting as a grounding circuit. Carbon x-ray peaks do not interfere with any of the elements of interest used for the analysis. The elements that were looked for were; sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), chromium (Cr), iron (Fe), barium (Ba), and oxygen (O). The results were also normalized to an oxygen free basis. The oxides of each element can then be calculated using gravimetric conversions. The normalized elemental weight per cent values for each of the chemical analyses can be found in Appendix 1.

While the chemical analyses of the individual diatom frustules did not show significant variation between the fresh and saline deposits, it is possible that other organisms may. Diatom frustules are composed primarily of  $\text{SiO}_2$  with no recognizable structure.  $\text{SiO}_2$  can be cryptocrystalline, meaning that the  $\text{SiO}_2$  tetrahedral structure is smaller than can be detected by x-rays making the structure appear amorphous. Because the component parts ( $\text{SiO}_2$  tetrahedra) of the diatoms are so small, there is very little or no room for other elements to be incorporated into frustules. It is possible that organisms with  $\text{CaCO}_3$  shells such as ostracods may show more chemical variability just by simply having room in the lattice of the shell forming compounds to incorporate other elements.

## **APPENDIX D-2**

## **SEM ANALYTICAL RESULTS**

Core DLPA	Depth 1321-1323 6 cm	Corrected Depth 6 cm	Estimated Date 1997	Fresh/Saline Fresh	Inferred Salinity 2.4	Sample Number 03-1071
--------------	-------------------------	-------------------------	------------------------	-----------------------	--------------------------	--------------------------

Sample # 03-1071 - DL Diatom chemical analysis

Hi water stand - low salinity

*Cyclotella quillensis*

	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Fe	Ba
#1	0.00	0.17	2.99	86.40	1.94	1.47	0.00	0.98	1.63	0.00	0.00	3.17	1.25
#2	0.06	0.00	0.00	98.29	0.70	0.00	0.39	0.00	0.00	0.00	0.00	0.56	0.00
#3	0.59	1.38	4.10	85.41	0.19	0.00	0.00	1.84	0.19	0.38	0.33	5.58	0.00
#4	0.00	0.00	0.00	95.55	0.00	0.00	0.00	0.59	0.00	0.00	0.00	2.81	1.05
#5	0.25	0.42	2.12	94.75	0.00	0.00	0.00	0.63	0.05	0.22	0.29	1.28	0.00
#6	0.00	0.34	0.08	97.59	0.13	0.24	0.00	0.27	0.24	0.75	0.00	0.35	0.00
#7	0.00	0.10	0.11	96.80	0.62	0.36	0.00	0.10	0.55	0.00	1.38	0.00	0.00
#8	0.00	0.21	3.33	90.46	0.01	0.00	0.00	4.13	0.25	0.00	0.00	1.27	0.33
#9	1.63	2.23	10.86	70.57	0.21	0.28	0.00	5.66	1.09	0.00	0.44	6.84	0.17
#10	0.49	0.65	2.50	94.18	0.03	0.05	0.42	0.00	0.07	0.15	1.05	0.41	0.00
#11	0.63	0.88	4.39	89.04	0.38	0.00	0.10	1.08	0.69	0.00	0.00	2.01	0.80
#12	0.45	0.86	4.41	87.80	0.00	0.01	0.00	1.56	0.46	0.84	0.13	3.49	0.00
#13	1.80	2.35	9.19	74.09	0.19	0.04	0.25	2.80	1.17	1.98	0.00	6.15	0.00
#14	1.37	1.84	5.89	80.60	0.00	0.00	0.00	2.83	1.09	0.00	0.95	5.41	0.00
#15	0.48	0.73	2.26	91.61	0.75	0.00	0.18	0.95	0.32	0.03	0.00	1.52	1.17
#16	1.29	1.46	8.34	74.45	0.51	0.01	0.28	2.99	1.32	0.74	0.48	6.88	1.25
#17	0.51	2.10	7.64	79.28	0.00	0.19	0.00	2.45	1.06	0.00	1.16	5.09	0.52
#18	1.13	1.08	6.32	82.54	0.00	0.00	0.03	1.87	0.40	0.00	0.00	4.09	2.55
#19	0.06	0.55	2.37	92.52	0.06	0.00	0.19	0.89	0.67	0.20	0.00	2.48	0.00
#20	0.19	0.51	2.10	92.48	0.65	0.00	0.00	0.84	0.00	1.03	0.00	1.91	0.30
#21	0.59	0.51	4.36	89.70	0.31	0.31	0.08	2.01	0.34	0.00	0.22	1.33	0.25
#22	0.00	2.45	6.64	68.40	1.72	0.00	1.52	4.38	0.00	0.00	4.13	4.79	5.97
#23	0.41	0.58	1.53	93.01	0.50	0.27	0.18	1.42	0.15	0.00	0.03	1.61	0.32
#24	0.16	0.10	0.10	98.77	0.00	0.00	0.22	0.00	0.13	0.16	0.27	0.10	0.00
#25	0.35	0.75	4.42	86.01	0.00	0.00	0.00	2.13	0.39	0.25	0.00	5.70	0.00
#26	0.41	0.58	1.21	95.92	0.34	0.00	0.21	0.00	0.25	0.00	0.00	1.07	0.00
#27	0.28	0.70	2.93	90.19	0.00	0.00	0.00	1.64	0.01	0.51	0.00	3.73	0.00

Core DLPA	Depth 1403-1405	Corrected Depth 88 cm	Estimated Date 1525	Fresh/Saline Saline	18	Inferred Salinity 03-1072	Sample Number						
Sample # 03-1072 - DL Diatom chemical analysis													
Cyclotella quillensis													
Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Fe	Ba	
#1	0.03	0.03	0.82	98.43	0.00	0.00	0.00	0.00	0.00	0.00	0.69	0.00	
#1B	1.66	2.20	4.49	78.59	1.07	0.00	0.62	4.22	1.47	1.57	0.00	2.74	1.37
#2B	0.27	2.93	7.09	66.89	0.53	2.25	0.00	1.68	9.55	0.00	0.00	7.10	1.71
#3B	0.18	0.84	1.47	87.85	1.20	1.00	0.63	0.84	2.66	0.00	0.00	1.65	1.69
#4B	0.00	0.58	0.13	97.59	0.00	0.51	0.42	0.45	0.32	0.00	0.00	0.00	0.00
#5B	1.28	4.20	8.14	62.44	0.37	1.90	0.00	3.45	7.84	1.46	0.99	7.94	0.00
#6B	0.88	2.85	5.06	77.68	0.00	2.45	0.00	0.95	2.98	0.00	0.00	6.36	0.80
#7B	0.62	0.34	0.67	94.01	0.00	0.00	0.48	0.00	2.51	0.00	1.38	0.00	0.00
#8B	1.46	2.58	3.38	72.31	1.18	2.02	0.00	2.20	12.23	0.50	0.00	2.14	0.00
#9B	0.85	5.95	6.73	62.43	0.00	1.12	0.00	2.45	10.87	0.93	1.22	6.61	0.84
#10B	0.87	2.82	4.51	59.56	0.25	1.92	0.37	2.30	14.44	0.00	1.59	8.15	3.22
#11B	1.89	1.42	4.71	85.27	0.00	0.00	0.00	1.77	3.50	0.00	0.00	1.44	0.00
#12B	0.00	3.31	4.81	65.93	0.00	3.66	0.89	2.97	12.04	0.00	0.33	6.06	0.00
#13B	0.34	2.11	6.12	79.12	0.26	1.85	0.06	1.28	5.64	0.00	0.99	1.33	0.89
#14B	2.99	8.87	4.94	25.00	0.14	37.21	2.32	0.98	14.65	0.00	0.00	2.90	0.00
#15B	1.62	4.36	4.77	70.44	0.00	1.72	0.00	1.62	9.10	0.00	0.00	6.38	0.00
#16B	0.49	1.87	3.03	59.15	0.00	0.92	0.57	1.34	31.61	0.00	0.00	0.00	1.02
#17B	0.38	0.80	1.73	87.96	0.24	0.63	0.26	0.96	5.90	0.00	0.00	0.31	0.83
#18B	1.04	0.41	0.00	97.04	0.00	1.16	0.00	0.34	0.00	0.00	0.00	0.00	0.00
#19B	1.74	1.54	0.00	86.62	0.31	0.08	1.58	1.26	1.54	0.00	0.91	2.37	2.07
#20B	1.18	4.39	4.86	61.54	0.87	1.74	0.49	2.77	16.06	0.00	0.00	5.92	0.18
#21B	0.94	3.37	4.78	76.62	0.00	1.40	0.00	4.30	3.25	0.15	0.00	3.88	1.31
#22B	1.67	1.78	1.95	83.49	0.00	1.45	1.33	2.05	3.94	0.00	2.33	0.00	0.00
#23B	1.06	4.47	4.53	70.54	0.00	0.94	0.66	2.07	3.24	0.00	0.00	12.48	0.00
#24B	0.03	0.03	0.82	98.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.69	0.00
#1A	1.09	4.09	6.36	65.91	0.06	2.75	0.10	3.73	11.13	0.26	0.00	3.60	0.92
#2A	1.31	2.88	4.34	75.50	0.00	0.73	0.00	1.49	9.18	0.00	0.36	4.19	0.00
#3A	0.32	0.59	1.14	90.24	0.54	0.58	0.36	0.87	2.14	0.45	1.00	1.78	0.00
#4A	1.46	2.01	2.29	84.03	0.86	0.72	0.20	1.62	4.14	0.00	0.03	1.24	1.40
#5A	0.59	1.10	1.54	76.60	0.03	0.67	0.26	0.65	16.83	0.35	0.00	0.97	0.41

Core Arch DLB-1	Depth 1466-1467 150 cm	Corrected Depth 994	Estimated Date	Fresh/Saline Fresh	Inferred Salinity 2.5	Sample Number 04-0118
--------------------	---------------------------	------------------------	----------------	-----------------------	--------------------------	--------------------------

Sample #04-0118 - DL Diatom Chemical analysis

High water stand - low salinity

*Cyclotella quillensis*

	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Fe	Ba
#1	0.72	0.44	0.86	90.40	0.00	0.42	0.00	1.81	0.00	0.82	0.98	1.77	1.78
#2	0.38	0.13	1.46	97.20	0.24	0.00	0.39	0.00	0.20	0.00	0.00	0.00	0.00
#3	0.77	1.47	3.57	84.65	0.37	0.37	0.00	0.77	0.06	0.00	0.76	5.09	2.11
#4	0.00	0.83	2.53	93.49	0.81	0.78	0.00	1.31	0.25	0.00	0.00	0.00	0.00
#5	0.50	1.18	1.08	93.51	0.00	0.00	0.00	0.00	2.22	0.00	0.62	0.89	0.00
#6	0.35	1.40	6.23	84.99	0.00	0.00	0.16	2.72	0.72	0.19	0.00	3.24	0.00
#7	0.23	1.29	4.29	85.87	0.41	0.00	0.14	1.01	0.97	0.80	0.16	4.01	0.83
#8	0.86	1.38	3.21	78.78	2.15	0.59	0.00	3.76	0.31	1.82	0.00	3.73	3.41
#9	0.00	0.91	2.16	84.74	0.83	2.61	0.00	0.00	2.54	2.06	0.61	3.54	0.00
#10	0.34	1.53	5.11	83.99	0.00	0.39	0.00	1.72	1.72	0.00	0.64	3.61	0.93
#11	0.44	0.79	1.52	88.63	0.00	0.29	1.43	0.00	1.13	0.00	1.46	0.00	4.31
#12	0.00	0.00	0.95	92.31	1.82	0.85	0.87	0.24	0.00	2.00	0.00	0.96	0.00
#13	0.62	1.08	0.00	87.16	1.65	0.83	0.25	2.37	0.00	1.17	0.00	4.86	0.00
#14	3.49	0.00	0.00	82.80	6.51	0.00	0.00	0.00	0.00	0.00	7.21	0.00	0.00
#15	0.65	0.68	0.65	95.64	0.97	0.16	0.00	0.37	0.02	0.00	0.03	0.84	0.00
#16	0.00	0.36	0.00	97.86	0.54	0.00	0.00	0.81	0.43	0.00	0.00	0.00	0.00
#17	0.70	0.63	0.68	95.87	0.00	0.05	0.00	0.36	0.00	0.00	0.00	0.82	0.89
#18	0.54	0.61	3.74	90.79	0.06	0.49	0.00	1.87	0.87	0.00	0.17	0.86	0.00
#19	0.00	0.27	0.86	97.51	0.80	0.00	0.00	0.00	0.00	0.08	0.49	0.00	0.00
#20	0.61	0.73	2.81	87.86	0.37	0.45	0.19	0.81	0.58	0.92	0.28	3.91	0.48
#21	0.38	0.35	0.10	97.63	0.00	0.00	0.18	0.00	0.40	0.00	0.91	0.05	0.00
#22	0.00	0.00	0.26	94.32	1.45	1.27	0.00	0.00	0.23	0.00	0.74	1.73	0.00
#23	0.59	0.00	0.00	98.03	0.27	0.20	0.00	0.08	0.00	0.00	0.00	0.83	0.00
#24	0.48	1.11	5.94	81.47	0.58	0.11	0.00	2.28	0.83	0.86	0.07	5.44	0.81
#25	0.05	0.54	0.63	97.20	0.09	0.40	0.00	0.25	0.27	0.11	0.00	0.46	0.00

Core	Depth	Corrected Depth		Estimated Date	Fresh/Saline		Inferred Salinity	Sample Number					
Arch DLB-2	1490-1491	174 cm	819	Saline	14.6	14.6	04-0119						
Sample #04-0119 - DL Diatom Chemical Analysis													
Cyclotella quillensis													
Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Fe	Ba	
#1	0.00	2.79	9.49	73.33	0.00	0.00	0.00	2.90	0.88	2.12	1.27	7.22	0.00
#2	0.12	4.53	7.79	77.27	0.91	0.00	0.51	1.53	0.00	0.00	2.30	5.04	0.00
#3	0.00	0.00	0.00	94.24	0.49	0.00	0.00	0.00	0.52	0.00	3.27	1.47	0.00
#4	0.00	3.99	8.72	68.33	0.00	0.63	0.17	2.04	0.31	0.00	0.00	13.52	2.27
#5	0.84	2.08	1.51	88.80	0.09	0.00	1.77	0.00	0.37	1.96	0.96	0.00	1.60
#6	0.99	1.20	2.80	76.31	0.11	1.32	0.00	4.80	5.42	0.00	0.00	6.73	0.32
#7	0.09	0.81	0.57	95.81	0.00	0.23	0.83	0.27	0.12	0.00	0.77	0.00	0.50
#8	0.40	0.00	2.67	90.42	0.49	1.50	0.99	0.00	0.00	1.71	0.00	0.00	1.83
#9	0.64	0.00	1.16	82.53	0.00	0.09	1.21	0.72	1.88	0.95	0.00	10.82	0.00
#10	0.44	0.40	0.00	95.71	1.59	0.30	0.00	0.00	0.91	0.00	0.00	0.00	0.65
#11	0.00	4.09	13.83	64.29	0.22	0.00	0.00	0.72	1.65	2.95	0.00	12.25	0.00
#12	0.68	0.05	0.56	96.01	0.46	0.46	0.00	0.37	0.00	0.62	0.08	0.71	0.00
#13	0.00	0.00	0.00	98.09	0.44	0.00	0.00	0.00	0.28	0.00	0.27	0.60	0.32
#14	1.37	0.71	0.78	95.71	0.00	0.00	0.00	0.75	0.00	0.00	0.00	0.68	0.00
#15	0.79	1.12	0.00	94.56	0.88	0.00	0.99	0.00	0.00	0.84	0.64	0.00	0.18
#16	0.00	0.00	0.67	96.92	0.00	0.00	0.00	0.00	0.00	0.00	2.40	0.00	0.00
#17	0.43	0.00	1.13	87.00	0.70	0.00	0.00	0.00	1.75	2.15	3.92	0.00	2.93
#18	0.00	0.30	0.51	90.34	0.38	0.00	0.85	0.00	0.33	0.73	4.20	2.36	0.00
#19	1.78	1.81	0.00	92.93	0.00	1.22	1.12	0.00	0.00	0.00	1.13	0.00	0.00
#20	1.68	0.69	0.00	90.66	0.00	0.35	0.96	0.42	0.35	2.17	0.00	0.00	2.73
#21	0.00	0.00	0.00	90.14	0.26	0.61	0.00	2.04	0.00	0.68	1.12	3.89	1.26
#22	0.10	0.00	0.00	96.28	0.00	0.00	0.48	0.00	0.83	0.10	0.13	0.00	2.09
#23	0.00	0.61	1.34	93.86	0.00	0.00	0.53	0.00	0.63	0.45	0.00	2.58	0.00
#24	0.81	0.33	0.00	96.28	0.48	0.00	0.00	0.00	0.00	0.00	0.00	2.10	0.00
#25	0.60	0.00	0.00	92.07	1.14	0.00	1.93	1.16	0.00	1.66	0.00	0.00	1.45

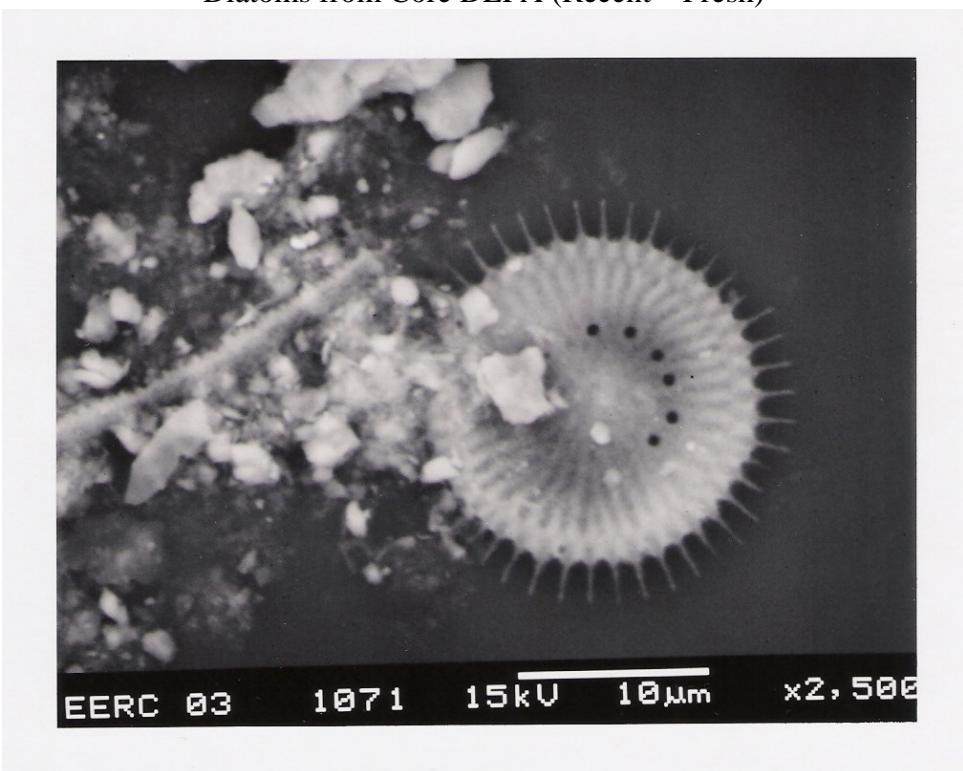
Core Arch DLA-2	Depth		Corrected Depth		Estimated Date		Fresh/Saline		Inferred Salinity		Sample Number		
	1556-1557	240 cm	394		Saline		17.2		04-0171				
Cyclotella quillensis	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Fe	Ba
#1	0.00	0.00	0.72	95.42	0.44	0.00	0.77	0.26	0.34	0.00	0.67	0.00	1.38
#2	0.51	1.82	3.31	87.50	0.00	0.00	0.00	1.68	0.58	0.00	0.00	3.33	1.28
#3	0.70	0.22	0.33	95.65	0.25	0.33	0.16	0.28	0.53	0.42	0.64	0.50	0.00
#4	1.01	2.23	4.99	80.26	0.10	0.40	0.69	1.90	1.09	0.23	0.74	5.75	0.59
#5	0.00	1.61	2.16	89.52	0.74	0.26	0.60	1.64	0.00	0.00	0.00	3.47	0.00
#6	0.83	0.44	0.56	93.31	0.00	0.00	0.00	0.12	0.00	0.00	1.31	3.43	0.00
#7	0.84	2.03	7.26	79.07	0.58	0.41	0.22	1.97	1.33	0.00	0.00	6.08	0.23
#8	0.07	0.22	0.65	95.16	0.00	0.00	0.04	0.27	0.30	0.30	0.42	1.97	0.60
#9	0.67	0.58	2.01	93.57	0.28	0.00	0.00	1.73	0.22	0.00	0.00	0.95	0.00
#10	2.83	0.43	7.23	87.03	0.10	0.36	0.01	1.08	0.43	0.32	0.17	0.00	0.00
#11	0.64	1.68	2.58	88.79	0.00	0.00	0.45	0.79	0.73	0.00	0.12	3.48	0.73
#12	0.32	2.38	5.64	81.66	0.13	0.00	0.25	1.23	0.57	0.38	0.28	7.14	0.00
#13	0.00	0.16	0.82	92.78	1.15	0.00	0.10	1.15	0.05	0.52	0.54	2.25	0.48
#14	0.22	0.72	1.43	95.00	0.00	0.08	0.45	0.43	0.00	0.00	0.00	1.67	0.00
#15	0.32	0.19	0.00	97.04	0.08	0.00	0.00	0.46	0.56	0.00	0.00	1.34	0.00
#16	0.96	2.43	4.07	83.09	0.31	0.00	0.05	2.09	2.06	0.00	0.17	3.07	1.70
#17	1.11	3.73	5.99	75.36	0.91	0.15	0.42	2.33	3.96	0.00	0.00	6.05	0.00
#18	0.72	1.50	6.23	84.86	0.17	0.11	0.20	1.17	1.93	0.00	0.00	2.79	0.31
#19	0.77	0.12	0.22	95.15	0.83	0.00	0.66	0.37	0.85	0.00	0.00	0.51	0.52
#20	0.18	1.28	4.10	89.76	0.16	0.45	0.06	2.04	0.25	0.00	0.00	1.72	0.00
#21	0.37	2.11	5.07	83.87	0.00	0.04	0.28	2.02	1.13	0.37	0.00	4.76	0.00
#22	0.62	0.37	0.24	96.83	0.33	0.00	0.13	0.00	0.00	0.00	0.06	1.42	0.00
#23	0.73	0.85	0.58	96.77	0.33	0.00	0.00	0.11	0.00	0.00	0.00	0.64	0.00
#24	0.73	2.30	5.00	82.12	0.06	0.07	0.00	2.20	0.66	0.00	0.76	5.60	0.48
#25	0.30	2.87	6.23	79.60	0.24	0.09	0.00	1.91	1.18	0.13	0.16	6.83	0.47

Core	Depth		Corrected Depth		Estimated Date		Fresh/Saline		Inferred Salinity		Sample Number		
Arch DLA-2	1588-1589 272 cm		194		Fresh		8.8		04-0172				
Cyclotella quillensis	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Fe	Ba
#1	2.16	0.30	3.17	87.01	0.20	0.00	0.00	0.00	0.00	0.00	0.00	7.16	0.00
#2	0.38	0.20	0.00	96.79	1.47	0.55	0.61	0.00	0.00	0.00	0.00	0.00	0.00
#3	0.00	0.00	0.42	96.02	0.26	0.17	0.20	0.48	0.15	0.00	0.00	0.00	2.30
#4	0.92	1.40	4.90	85.74	0.00	0.00	0.00	2.03	0.27	0.26	0.00	2.27	2.21
#5	1.41	0.82	0.00	97.77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
#6	0.44	0.10	0.18	95.05	0.03	0.00	0.00	0.59	0.82	0.00	0.64	1.18	0.98
#7	0.14	0.42	2.07	91.77	0.49	0.12	0.00	0.35	0.94	0.00	0.00	3.17	0.52
#8	0.00	1.30	2.24	88.13	0.00	0.34	0.00	1.54	0.00	0.36	1.22	3.55	1.33
#9	0.54	1.82	6.20	80.34	0.44	0.32	0.25	1.64	1.70	0.00	0.41	6.35	0.00
#10	0.34	2.53	8.84	75.96	0.37	0.00	0.85	2.81	1.19	0.00	0.00	5.40	1.71
#11	0.30	0.00	0.36	96.72	0.00	0.00	0.00	0.49	0.00	0.00	0.21	1.08	0.84
#12	0.23	1.20	6.53	82.90	0.20	0.00	0.00	1.78	1.73	0.49	0.00	4.94	0.00
#13	0.00	0.00	0.25	95.83	0.49	0.65	0.51	0.29	0.00	0.14	0.86	0.71	0.28
#14	0.44	0.00	0.00	97.73	0.08	0.03	0.38	0.00	0.05	0.15	0.10	1.05	0.00
#15	0.72	2.14	10.56	72.75	0.08	0.41	0.31	2.51	2.37	0.27	0.05	7.82	0.00
#16	0.80	0.48	2.38	83.91	3.05	0.67	1.57	0.27	0.55	0.65	2.51	2.53	0.65
#17	0.00	0.38	0.54	92.36	1.09	0.00	0.51	0.44	0.65	0.00	0.00	4.04	0.00
#18	4.32	0.48	11.00	78.02	0.74	0.00	0.01	1.26	0.32	0.22	0.00	2.27	1.36
#19	0.32	2.08	7.61	68.13	2.67	0.30	0.00	4.76	4.91	0.00	1.09	7.85	0.28
#20	0.93	1.82	10.24	67.83	0.47	0.07	0.00	7.03	2.38	0.04	0.00	9.19	0.00
#21	0.31	1.11	6.71	79.92	0.06	0.00	0.11	3.76	0.46	0.00	0.11	6.91	0.53
#22	0.51	0.37	0.68	95.85	0.00	0.10	0.00	0.11	0.14	0.00	0.00	1.03	1.21
#23	1.21	0.06	0.00	96.39	0.37	0.51	0.00	0.00	0.00	1.45	0.00	0.00	0.00
#24	0.62	0.94	5.44	86.62	0.00	0.14	0.05	2.01	0.43	0.12	0.33	3.30	0.00
#25	0.14	0.78	3.15	90.41	0.27	0.10	0.10	1.70	0.00	0.06	0.40	2.88	0.00

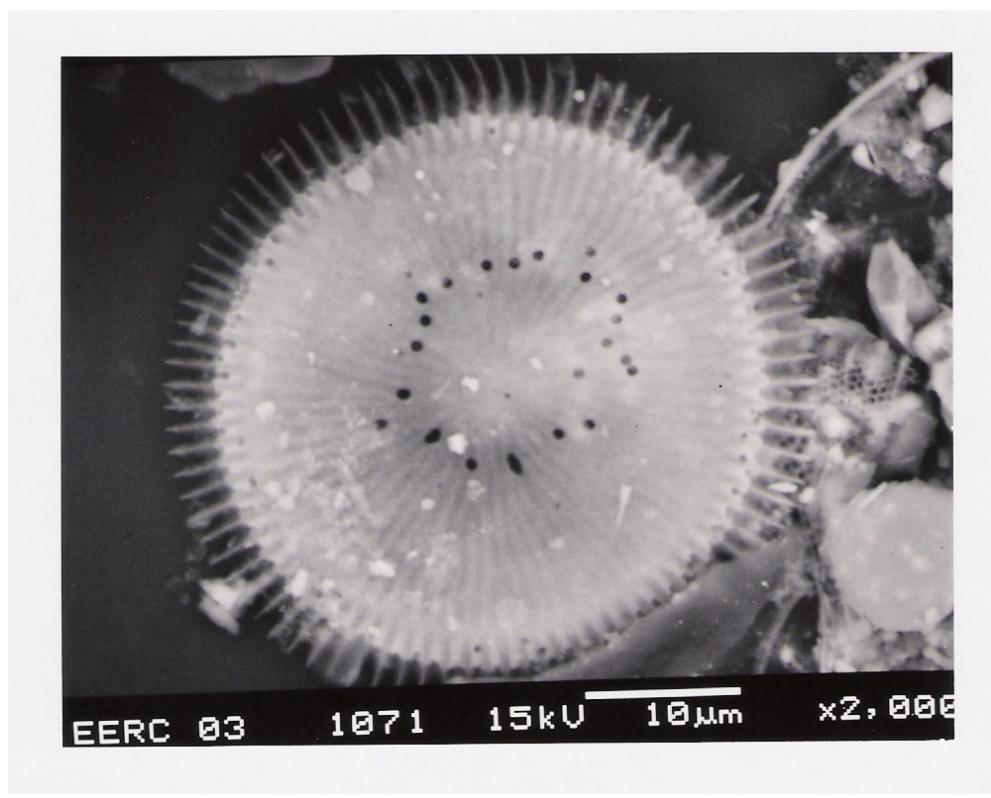
## **APPENDIX D-3**

### **DIATOM MORPHOLOGY FOR SELECTED SAMPLES**

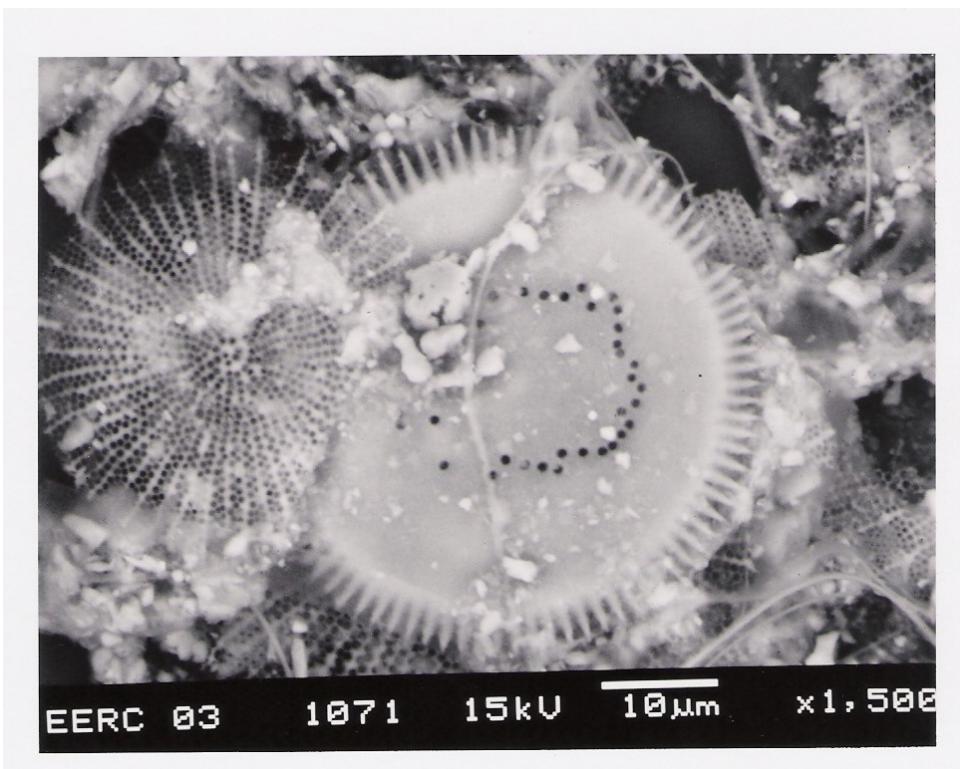
Diatoms from Core DLPA (Recent – Fresh)



*Cyclotella* cf. *meneghiniana*

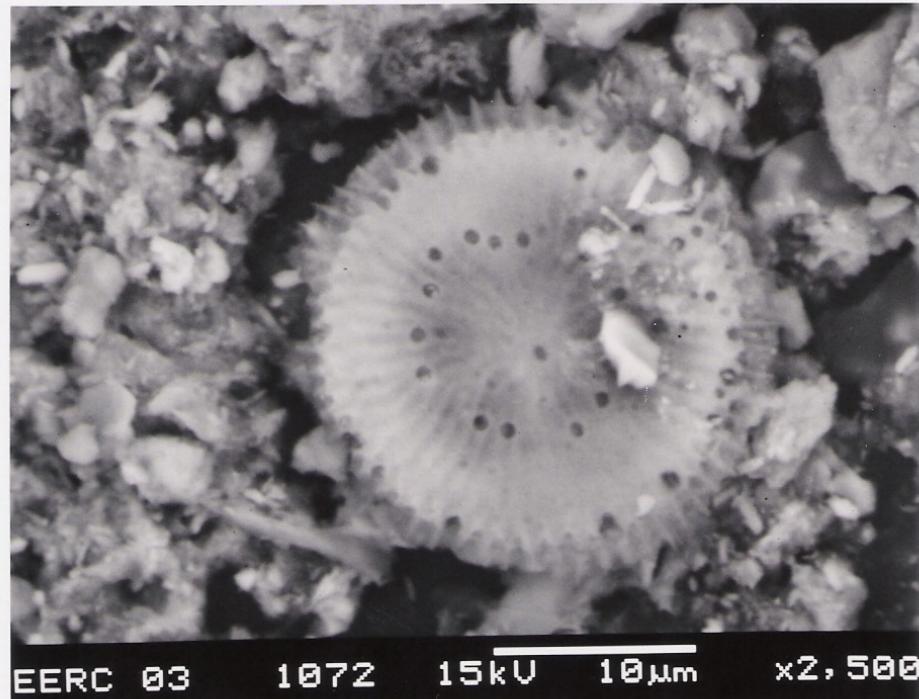


*Cyclotella quillensis*



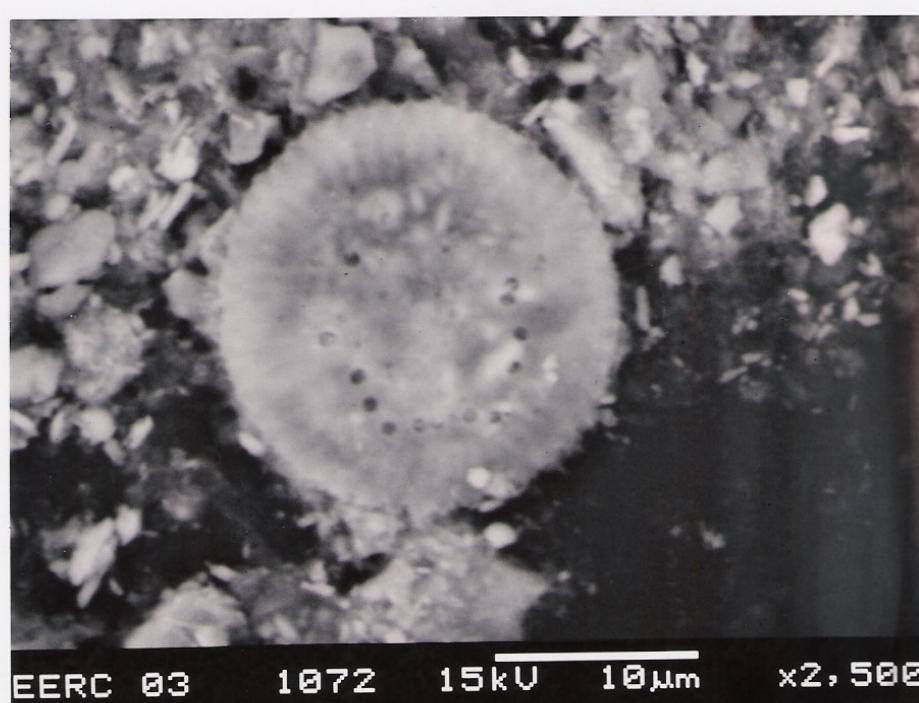
*Cyclotella quillensis* (center), *Stephanodiscus niagarae* (left)

Diatoms from Core DLPA (Recent – Saline)



EERC 03 1072 15kV 10 $\mu$ m x2,500

*Cyclotella quillensis*



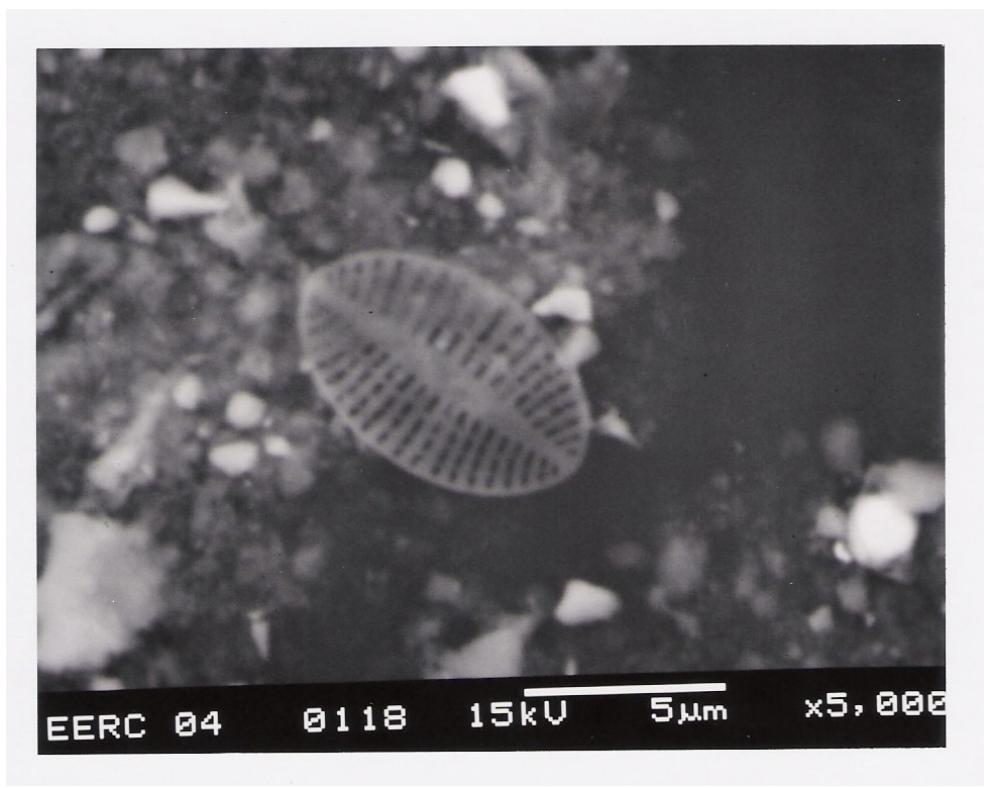
EERC 03 1072 15kV 10 $\mu$ m x2,500

*Cyclotella quillensis*

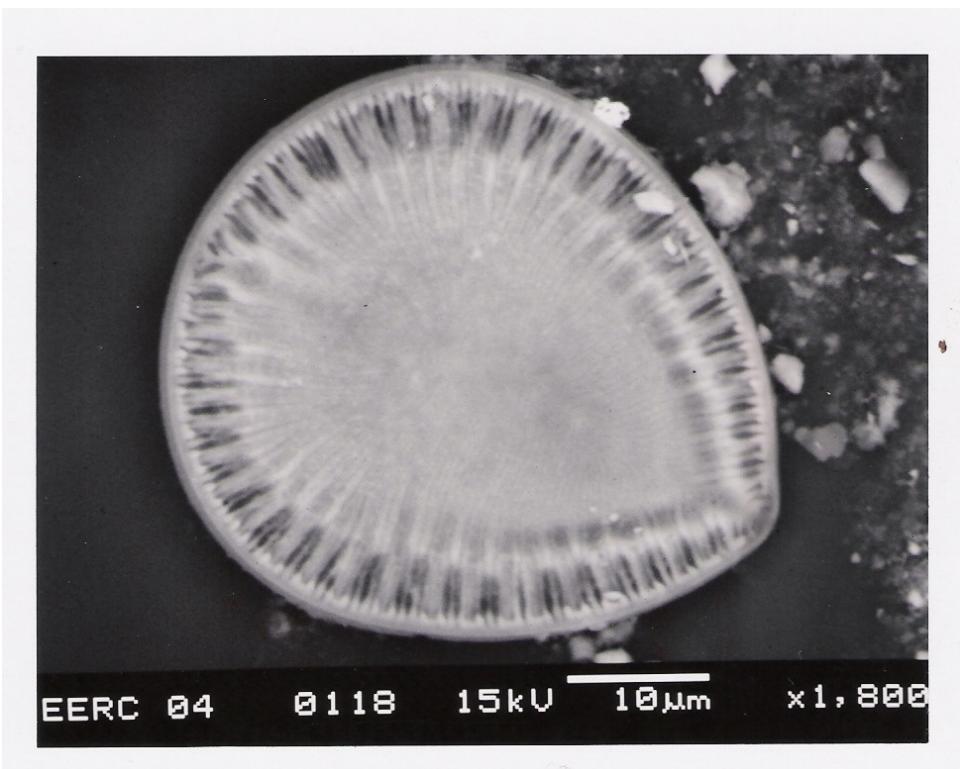
Diatoms from Core Arch DLA – 1 (Middle – Fresh)



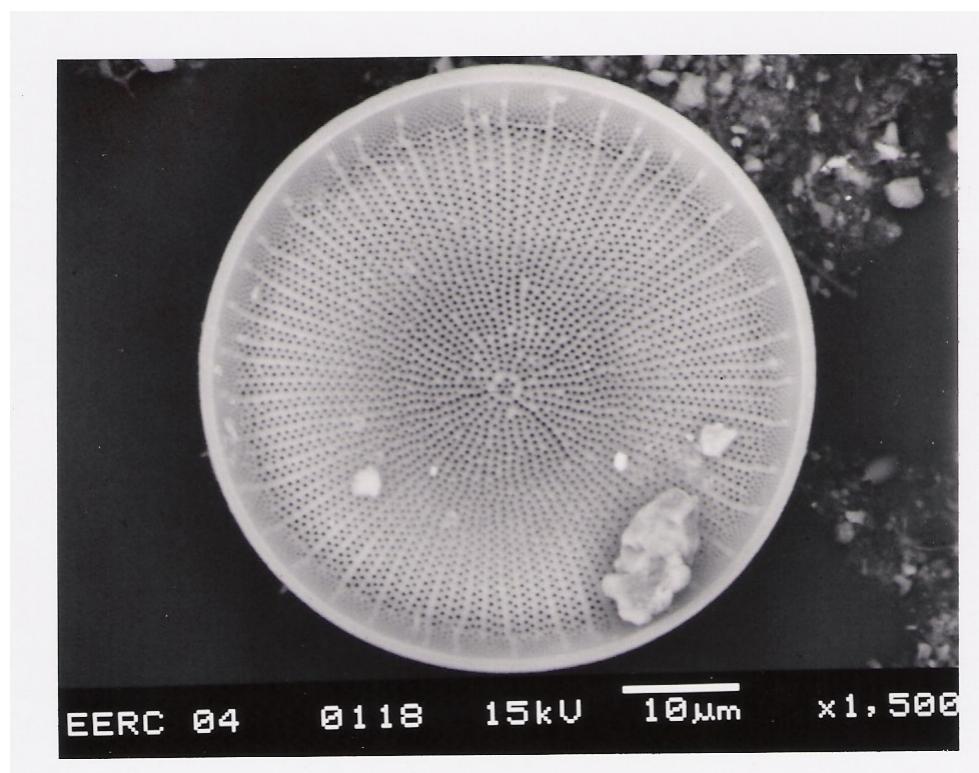
*Surirella ovalis*



*Cocconeis placentula* var. *euglypta*



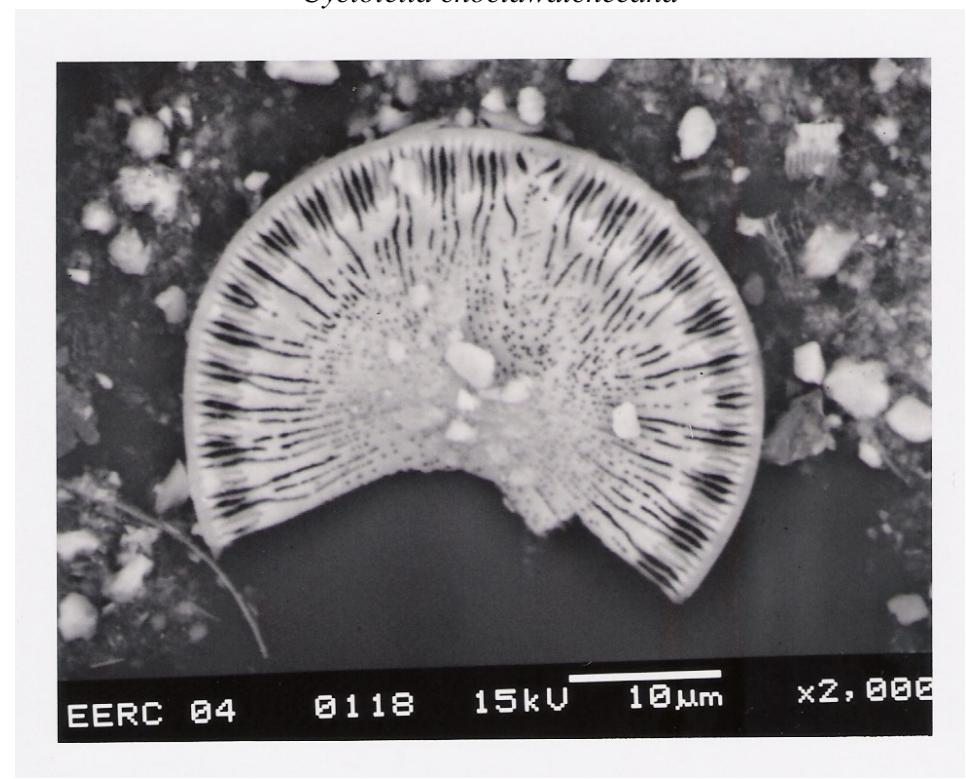
*Surirella peisonis*



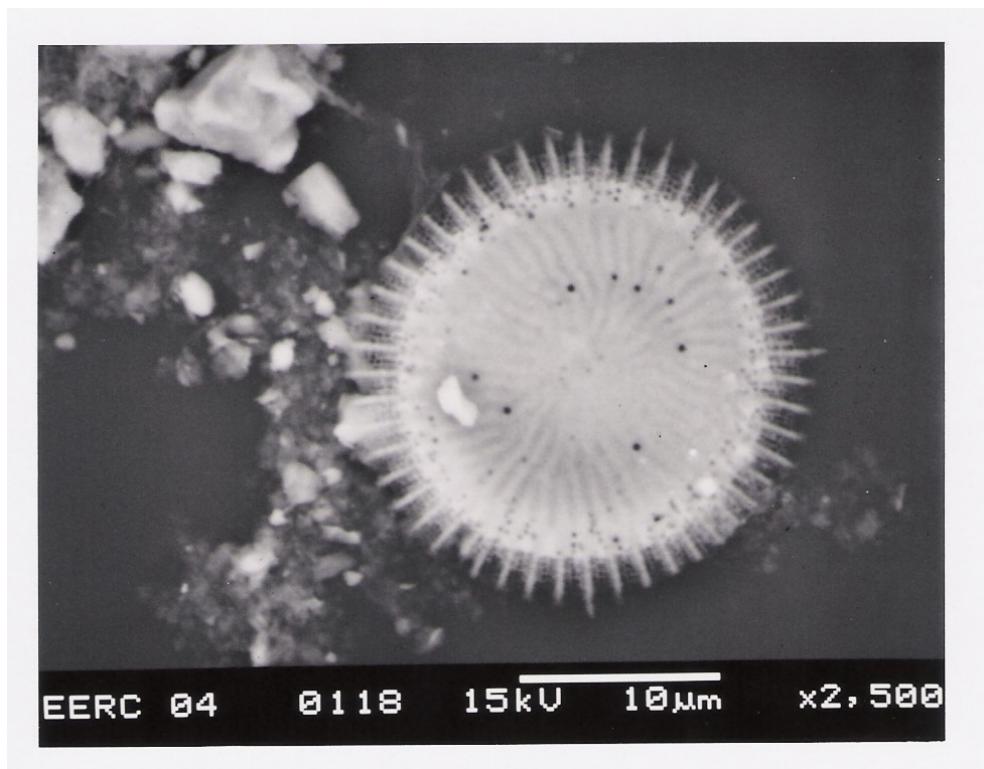
*Stephanodiscus niagarae*



*Cyclotella choctawatcheeana*

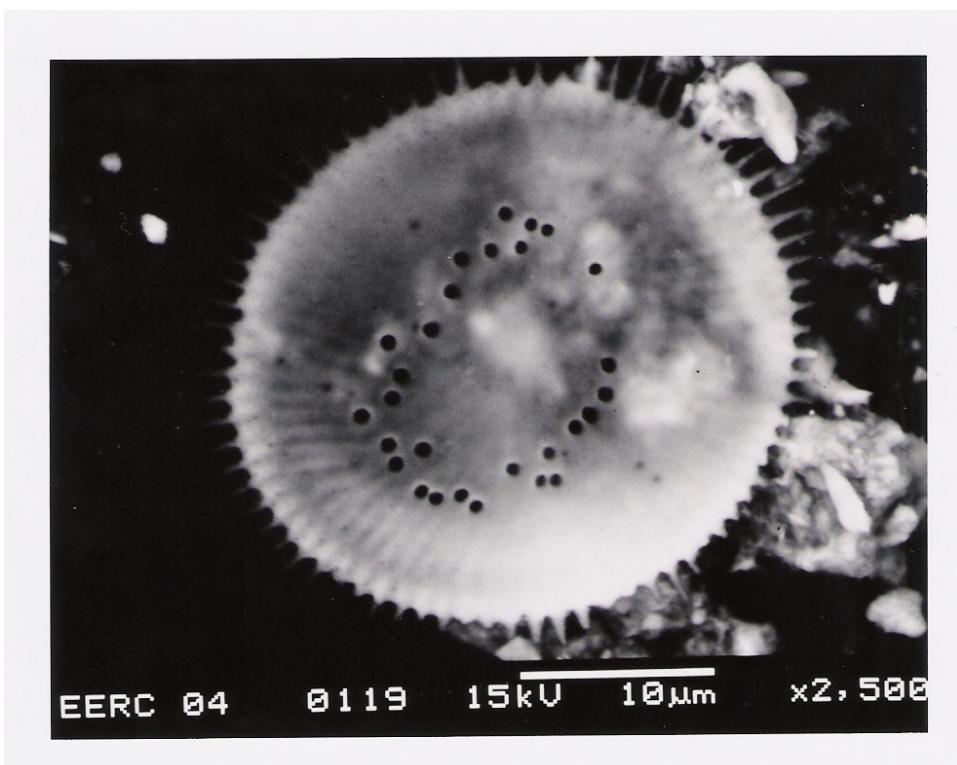


*Surirella peisonis*



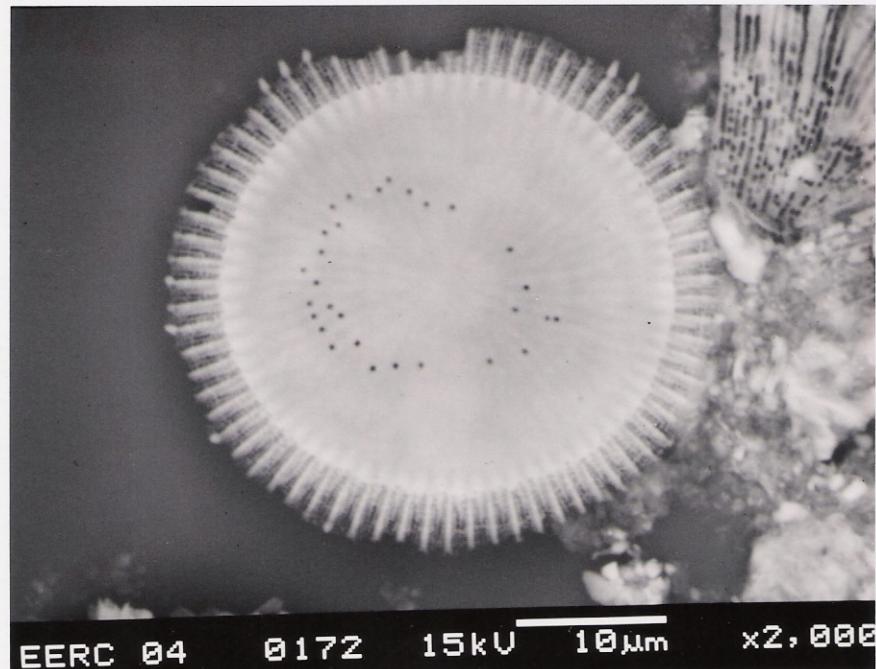
*Cyclotella quillensis*

Diatom from Core Arch DLB – 2 (Middle – Saline)

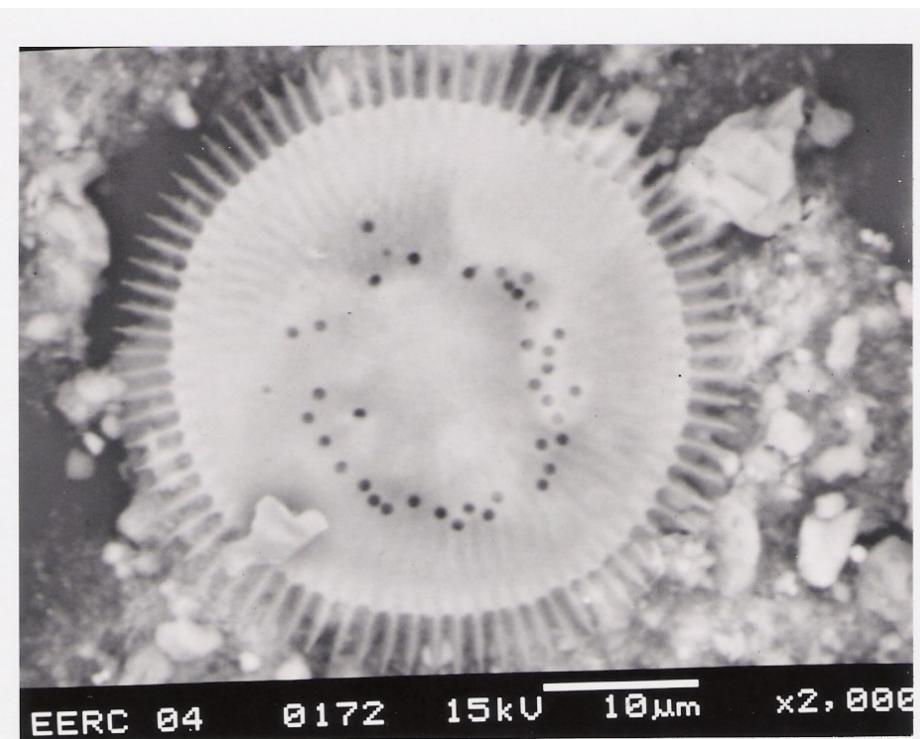


*Cyclotella quillensis*

Diatoms from Core Arch DLA – 2 (Early – Fresh)

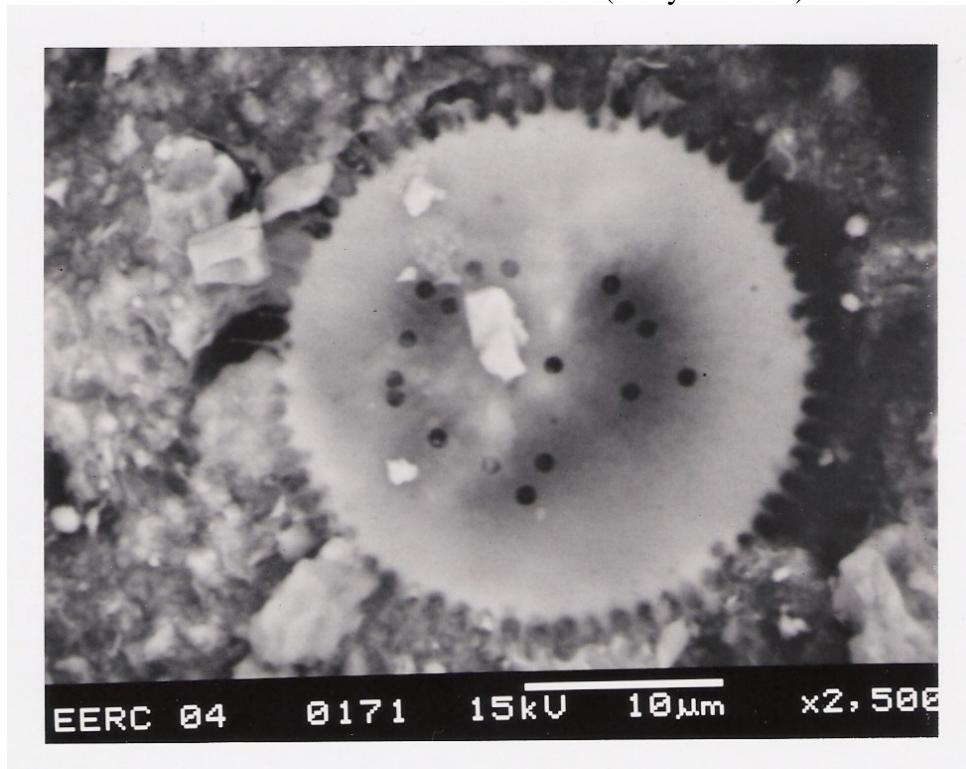


*Cyclotella quillensis*

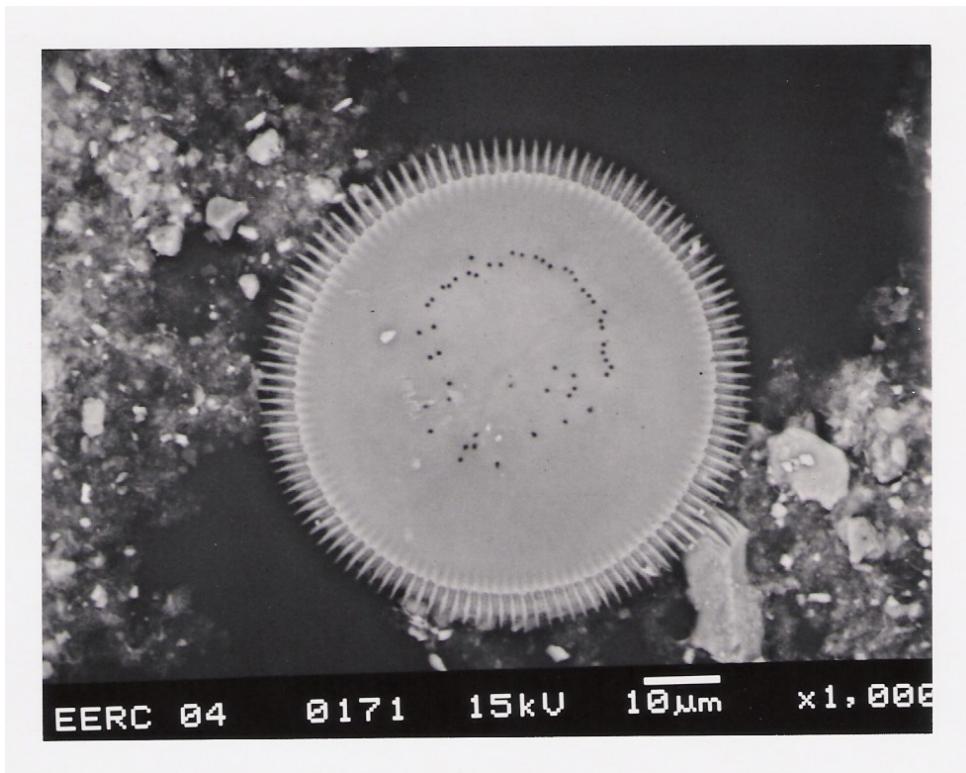


*Cyclotella quillensis*

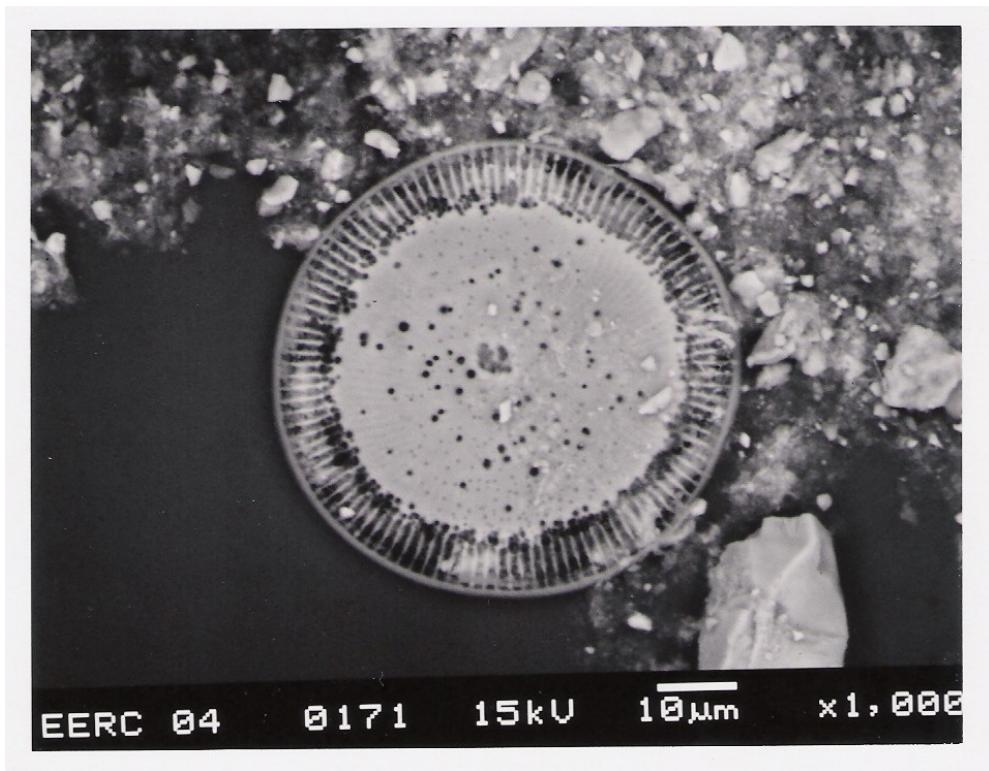
Diatoms from Core Arch DLA-2 (Early – Saline)



*Cyclotella* sp.



*Cyclotella quillensis*



*Cyclotella quillensis*

# **SUBTASK 7.2 – GLOBAL WARMING AND GREENHOUSE GASES**

Final Report For Task 7.2, Activity 2

*(for the period April 1, 2001, to June 30, 2002)*

*Prepared for:*

AAD Document Control  
U.S. Department of Energy  
National Energy Technology Laboratory  
PO Box 10940, MS 921-0940  
Pittsburgh, PA 15236-0940

Cooperative Agreement No.: DE-FC26-98FT40320  
Performance Monitor: Dr. Robert Patton  
UND Fund Nos. 4348, 4389, 4350, and 4245

*Prepared by:*

Ronald C. Timpe  
Ted R. Aulich

Energy & Environmental Research Center  
University of North Dakota  
Box 9018  
Grand Forks, ND 58202-9018

January 2005

## **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

## **ACKNOWLEDGMENT**

This report was prepared with the support of the U.S. Department of Energy (DOE) National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-98FT40320. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors(s) and do not necessarily reflect the views of DOE.

## **EERC DISCLAIMER**

**LEGAL NOTICE** This research report was prepared by the Energy & Environmental Research Center (EERC), an agency of the University of North Dakota, as an account of work sponsored by the U.S. Department of Energy. Because of the research nature of the work performed, neither the EERC nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement or recommendation by the EERC.

## **SUBTASK 7.2-ACTIVITY 2 – GLOBAL WARMING AND GREENHOUSE GASES**

### **ABSTRACT**

Of the anthropogenic contributions to atmospheric gases, H<sub>2</sub>O and CO<sub>2</sub> are contributed in the largest quantities. Owing to the potential for evaporation from the water covering 70% of the earth's surface in response to shifts in equilibrium moisture, it is doubtful that attempting to control anthropogenic H<sub>2</sub>O contributions would have any appreciable effect on atmospheric content. On the other hand, CO<sub>2</sub> concentrations in the atmosphere are increasing with continued use of fossil fuel combustion to provide energy. Unlike H<sub>2</sub>O, anthropogenic CO<sub>2</sub> emissions are the result of point source production, making collection and control for disposal in repositories other than the atmosphere a distinct possibility. Technology for sequestration of CO<sub>2</sub> emissions from power plants and industry and even commercial and domestic sources is one current focus of environmental research. Since most power plants and much industry are inland, interest in disposing of CO<sub>2</sub> underground using saline aquifers, salt deposits, oil fields and coal-methane fields are commonly discussed and evaluated as repositories. The economic impact of CO<sub>2</sub> sequestration is improved since most point sources of the gas are sited over one or more of these potential repositories. This brief study supposed that CO<sub>2</sub> from power plants would be collected and pumped into nearby depleted oil fields for sequestration and secondary oil recovery similar to the demonstration currently underway in the oil fields near Weyburn, Saskatchewan, Canada. The experimental portion of this study involved measuring the CO<sub>2</sub> uptake and retention at pressure and temperature.

## TABLE OF CONTENTS

LIST OF TABLES.....	ii
EXECUTIVE SUMMARY .....	iii
INTRODUCTION .....	1
EXPERIMENTAL .....	2
RESULTS AND DISCUSSION.....	3
Sequestration of CO <sub>2</sub> .....	3
CO <sub>2</sub> Sequestration in Inland U.S. ....	6
Site Selection in the Midcontinent .....	6
Test Results.....	8
CONCLUSION .....	9
REFERENCES .....	9

## LIST OF TABLES

1	CO <sub>2</sub> Absorption and Retention by Core Samples from depth of ~3000 meter .....	3
2	Relative GWP of Major GHG, Excluding Water and Ozone .....	3
3	U.S. CO <sub>2</sub> Production Partition as C - 2000*.....	4
4	Global Annual CO <sub>2</sub> Production as C*.....	4
5	Chemical and Physical Properties of the Two Formations for CO <sub>2</sub> Sequestration*.....	8

## **SUBTASK 7.2-ACTIVITY 2 – GLOBAL WARMING AND GREENHOUSE GASES**

### **EXECUTIVE SUMMARY**

Processes used to maintain and advance human civilization (anthropogenic advances) nearly always involve an energy component. This energy usually involves combustion of fossil fuel which results in production of large quantities of H<sub>2</sub>O and CO<sub>2</sub> along with lesser amounts of gases such as CO, NO<sub>x</sub>, and SO<sub>2</sub> and fugitive gaseous fuel that enter the atmosphere, altering its composition and causing it to absorb and emit increasing amounts of infrared radiation. This change results in “global warming”.

Owing to the potential for evaporation from the water covering 70% of the earth’s surface in response to shifts in equilibrium moisture, it is doubtful that attempting to control anthropogenic H<sub>2</sub>O contributions would have any appreciable effect on atmospheric content. On the other hand, CO<sub>2</sub> concentrations in the atmosphere are increasing with continued use of fossil fuel combustion to provide energy. Unlike H<sub>2</sub>O, anthropogenic CO<sub>2</sub> emissions are the result of point source production, making collection and control for disposal in repositories other than the atmosphere a distinct possibility. Technology for sequestration of CO<sub>2</sub> emissions from power plants and industry and even commercial and domestic sources is one current focus of environmental research. Since most power plants and much industry are inland, interest in disposing of CO<sub>2</sub> underground using saline aquifers, salt deposits, oil fields and coal-methane fields are commonly discussed and evaluated as repositories. The economic impact of CO<sub>2</sub> sequestration is improved since most point sources of the gas are sited over one or more of these potential repositories. This brief study supposed that CO<sub>2</sub> from power plants would be collected and pumped into nearby depleted oil fields for sequestration and secondary oil recovery similar to the demonstration currently underway in the oil fields near Weyburn, Saskatchewan, Canada.

The experimental portion of this study involved measuring the CO<sub>2</sub> uptake and retention under increased pressure and temperature in core samples taken from oil fields at a depth (approximately 9000 feet) of oil deposits. Two sets of core samples were used. The first was a dense carbonate (evaporite) and the second set was a feldspathic quartz (sandstone). Sandstone cores of two different porosities were tested. Selection of the core sets was based on the vast difference in the properties of the two. Porosity and chemistry differed widely in the two sets of cores. Test conditions in all tests exceeded the critical conditions for CO<sub>2</sub> (31°C and 72.9 atm.) giving the CO<sub>2</sub>-supercritical fluid characteristics. The carbonate core sample absorbed 15 parts per thousand by weight of CO<sub>2</sub> under pressure and retained 1 parts per million by weight on depressurization. The sandstone cores gave two sets of results. The more porous (S2) absorbed 353 parts per thousand while the less porous (S1) absorbed 250 parts per thousand CO<sub>2</sub>. S2 retained 1.2 parts per thousand while S1 retained no measurable quantity of CO<sub>2</sub>. These tests indicated that, with knowledge of geologic formations, success of CO<sub>2</sub> sequestration can be predicted. Oil companies, seismograph companies and government geological organizations have a wealth of data and expertise regarding formations from the core sampling inherent with their business. Collection of CO<sub>2</sub> from combustion systems is an immature science with several methods being tested. Most of the methods currently holding promise have efficiencies in the 30% range. Early estimates suggest that the cost of power will vary widely depending on which capturing method is used. Using a base of 49 mills/kWh without capture, power costs can range from 74 mills to 179 mill per kWh when adding CO<sub>2</sub> capture while decreasing the CO<sub>2</sub> emissions by 60 to 93%.

## SUBTASK 7.2-ACTIVITY 2 – GLOBAL WARMING AND GREENHOUSE GASES

### INTRODUCTION

Depleting fuel supplies, pollution associated with fuel usage and global warming are current topics of worldwide concern. While on one hand, there is urgency in continuing to maintain and even increase fuel supplies, there is, on the other hand, renewed concern over the effects of combustion emissions on the environment. Carbon dioxide (CO<sub>2</sub>) emissions had dropped worldwide by 6% during the 1990's, somewhat easing concerns over environmental effects of combustion, but then rose again in 2000 and 2001 due to increased coal usage during colder winters (1). Meanwhile, the worldwide demand for energy is expected to increase by as much as 60 percent over the next two decades and the increased energy consumption, supplied largely by oil, will increase carbon dioxide emissions by as much as 3.8 billion metric tons per year in 2020.(2) With each additional MWh(e) of electricity generated 800 kg of CO<sub>2</sub> is produced.(3) The depletion of easily obtained fossil fuel supplies has resulted in increased interest in renewable fuels, e.g., biodiesel, ethanol, hybrid forest, and renewable energy supplies, e.g., wind, hydro, waves and tides, to help with the predicted increase in demand, but during the development phase of renewable technologies, the world continues to depend on fossil fuels. Concern over pollution resulting from energy production and utilization of fossil fuels, although not shared by all (4). has stimulated development in pollution controls, e.g., scrubbing systems and particulate traps for electrical generation, and catalytic conversion units for automobiles, to reduce impact on the environment. More recently emphasis has been placed on decreasing emissions that absorb energy and reemit thermal energy to the atmosphere resulting in a global increase in temperature, so-called "global warming". A recent high resolution transient climate change experiment predicts this "global warming" when calculated for the time when the concentration of greenhouse gases are will be doubled, i.e., at sometime between 2030 and 2040 a..d. (5) The six gases below are listed in the Kyoto Protocol as the "greenhouse" gases (GHG) and are the focus of atmospheric reduction in the effort to decrease global warming potential of the earth as stated in the Kyoto document:(6)

- Carbon dioxide (CO<sub>2</sub>)
- Methane (CH<sub>4</sub>)
- Hydrofluorocarbons (HFCs)
- Nitrous oxide (N<sub>2</sub>O)
- Perfluorocarbons (PFCs)
- Sulfur Hexafluoride (SF<sub>6</sub>)

Other than water, carbon dioxide is by far the most plentiful gaseous emission in the atmosphere, originating from natural sources, e.g., geologic sources, forest fires, animal and plant respiration as well as anthropogenic sources such as power plants, man-made fires, vehicular, domestic and commercial fuel combustion. Most fluorinated compounds in the atmosphere are from anthropogenic contributions and these volatile fluorine compounds in common use, e.g., as propellants or air conditioning coolants, are best controlled by being replaced with substitutes which have less global warming potential (GWP). Occasionally emissions are treated such that the emissions have reduced GWP. For example, natural gas producers occasionally flare gas to convert it to CO<sub>2</sub> rather than release the hydrocarbon, which has 20x the GWP.,to the atmosphere. (7) Fluoride compounds from automobiles are limited to leaks from air conditioning systems but several other vehicle emissions contribute to potential for global warming. The GWP of the automobile emissions are based on molecular comparison with CO<sub>2</sub> and are shown in Table 2. Automobile exhaust is a large contributer to GHG.

Carbon dioxide emissions greatly exceed those of the other pollutants since it is the ultimate product of combustion of carbonaceous fuel and is therefore produced in any process where heat from carbonaceous fuel, whether fossil or renewable, is used. The annual anthropogenic production of CO<sub>2</sub> by the USA was estimated to be 1535.6 million metric tons (C equivalent) (1) and that of the world was estimated at 6270 million metric tons (C equivalent) in 1999. (8) Table 3 gives the breakdown of 2000 US contributions to CO<sub>2</sub> in the atmosphere. Table 4 shows similar data for the world in the early 1990's. That produced by renewable carbonaceous fuels, e.g., hybrid wood, grasses, is considered to be CO<sub>2</sub>-neutral since CO<sub>2</sub> is required to replace the plant material used for fuel. Because of this, the anthropogenic contribution to CO<sub>2</sub> is considered to be the result of burning fossil fuels. Reducing the anthropogenic contribution to CO<sub>2</sub> emissions is seen as one means of controlling global warming.

## EXPERIMENTAL

In the interest of supplying preliminary "hands-on" laboratory testing data, a few tests were designed to determine the efficacy of such studies for measuring CO<sub>2</sub> uptake by subterranean geologic formations, particularly those containing oil and saline water and for which core samples could be obtained. The tests were carried out on dry, oil-free cores using pressurized CO<sub>2</sub> and temperatures slightly higher than ambient. Each test continued until equilibrium pressure was reached. Pressure drop was used to determine CO<sub>2</sub> uptake and pre- and post-test weights were used as an indicator of sequestration. A sandstone core was impregnated with NaOH to neutralize acid sites to encourage deposits of CO<sub>2</sub>.

A heated 1-Gallon pressure vessel (autoclave) mounted in a test stand and outfitted with thermocouples and pressure transducer was used to carry out CO<sub>2</sub> absorption tests on geologic core samples at varying conditions of temperature (T) and pressure (P).

Core samples of oil bearing dolomite or sandstone were obtained from remnants of oil exploration in two different formations. The specific depth and location of the cores are not available for publication.

The dolomitic core designated "Core I" was a single cylinder of mass 1881.59 g as shown in Table 1. The sandstone core consisted of 6 uniform cylinders with total mass shown in Table 1. Two of the sandstone core samples were treated with sodium hydroxide neutralize to acid sites in the cores and to simulate deposits from a saline aquifer. Following alkali treatment the cores were dried and subjected to sorption testing.

The first core was approximately 3.47 inches in diameter and 5.11 inches in length (A = 74.61 in<sup>2</sup>, V = 48.32 in<sup>3</sup>). The core had been in storage under dry conditions for several years. Prior to testing it was dried for 17 hours at 124 degrees centigrade. After allowing the core to cool to ambient temperature the test was begun. The core was weighed, placed in the vessel and pressurized at a temperature where it remained for the duration of the test. Operating conditions and data for this test are shown in Table 1. When the pressure became constant, the vessel was vented slowly and the heater turned off. On reaching ambient conditions the core was removed and weighed. A very small quantity of oil residue was recovered from the autoclave with solvent and weighed. The test data is recorded in Table 1.

The second test was carried out on six sandstone core samples. The test conditions and core measurements are included under "Core II" in the Table 1. This sample consisted of six smaller cylindrical cores 1.50 inches in diameter x 3.09 inches high. (A = 97.98 in<sup>2</sup>, V = 32.76 in<sup>3</sup>)

**Table 1. CO<sub>2</sub> Absorption and Retention by Core Samples from depth of ~3000 meter**

Core Sample	Core I	Core II	Core III
Test Temperature, °C	36	38	36
Beginning Pressure, psig	1200	3167	4250
Final Pressure, psig	1050	2552	4002
CO <sub>2</sub> absorbed under pressure, g	28	328	142
Initial Weight, g	1881.59	1171.05	402.17
Final Weight, g	1881.88	1170.9	402.66
Weight of oil recovered, g	0.13	NA	NA
Weight gain, g (CO <sub>2</sub> )	0.29	-0.15	0.49
CO <sub>2</sub> Sequestered, ambient conditions, Ton/Ton	0	0	0.0012
Test Duration, hrs	160	96	72

The test data contained in Table 1 under “Core III” was obtained by using the two sandstone cores which had been treated with sodium hydroxide. (A = 32.66, V = 10.92 in<sup>3</sup>).

## RESULTS AND DISCUSSION

### Sequestration of CO<sub>2</sub>

Reductions in CO<sub>2</sub> emissions could be accomplished by less fuel combustion or by disallowing escape of CO<sub>2</sub> into the atmosphere. Efforts in lowering consumption of fossil fuels for combustion processes is being addressed by such measures as increasing efficiency of heating units and engines, improving insulation, recycling commodities, switching to renewable fuels, among others. Additional control of CO<sub>2</sub> emissions can be accomplished by long-term sequestration. Eight of the world’s leading companies, including BP, Chevron-Texaco, Eni, Norsk Hydro, PanCanadian, Royal Dutch/Shell Group of Companies, Statoil, and Suncor Energy are leading the sequestration efforts through the CO<sub>2</sub> Capture Project (CCP) in finding successful methods. (9)

**Table 2. Relative GWP of Major GHG, Excluding Water and Ozone**

GHG	Molecular Formula	GWP
Carbon Dioxide	CO <sub>2</sub>	1
Carbon Monoxide	CO	3
Nitrogen Dioxide	NO <sub>2</sub>	7
Nonmethane Hydrocarbons	NMHC	11
Methane	CH <sub>4</sub>	21
Nitrous Oxide	N <sub>2</sub> O	310

**Table 3. U.S. CO<sub>2</sub> Production Partition as C - 2000\***

Sector	Quantity MM tonnes C	1-year Increase
Electrical Production **	641.6	4.7%
Residential & Commercial	581.2	
Residential	313.4	4.9%
Commercial	267.8	5.8%
Industrial	465.7	0.0%
Transportation	514.8	3.1%
Other***	21.6	16.8%
<b>Total</b>	<b>1583.3</b>	<b>3.1%</b>

\* Energy Information Administration, USDOE,

\*\* C production dispersed where used, i.e., among the following categories

\*\*\* Gas flaring, waste combustion, limestone calcination, etc.

**Table 4. Global Annual CO<sub>2</sub> Production as C\***

Origin	Quantity Billion Tonnes °C
Ocean	90
Vegetative decay	30
Respiration, fauna & flora	30
Anthropogenic	7
 Total Production	 157
 Nature Uptake of C as CO <sub>2</sub>	 153.5
 Net annual increase in C as CO <sub>2</sub>	 3.5

\* Energy Information Administration, U.S. DOE - Early 1990's

Sequestration of CO<sub>2</sub> is preceded by capture, storage and transport of the gas. Capture represents as much as three-fourths of the cost of containing combustion CO<sub>2</sub> since it involves high tech processes such as:

- Absorption (chemical and physical)
- Adsorption (physical and chemical)
- Low-temperature distillation
- Gas separation with membranes
- Mineralization and biomimetic mineralization

Sequestration of CO<sub>2</sub> from processing natural gas or from a gasification plant would be significantly more economical than from a combustion process since the infrastructure for these industries are built to capture the gases. (10) Although capture of CO<sub>2</sub> is a technology that has been around for 60 years it was applied to captive streams. Application to capture from coal fired plants presents new capital cost as well as a significant "energy penalty." (11) The cost of collecting CO<sub>2</sub> for sequestration is substantial. Industry has not yet settled on a best method of capturing the gas although owing to poor economics, cryogenics is already out of the running. Methods using membranes with and without methylethylamine (MEA), pressure and temperature swing adsorption (PSA and TSA), and absorption (MEA) are being evaluated. Most of the methods mentioned have

efficiencies in the 30% range. Early estimates suggest that the cost of power will vary widely depending on which capturing method is used. Using a base of 49 mills/kWh without capture, power costs can range from 74 mills to 179 mill per kWh when adding CO<sub>2</sub> capture while decreasing the CO<sub>2</sub> emissions by 60 to 93%. (12). In addition, collecting the exhaust emissions from vehicles on the move would present a nearly impossible task without new technology.

Once capture has occurred, sequestration can be accomplished by transporting the CO<sub>2</sub> to an appropriate repository. The following have been suggested for containing the CO<sub>2</sub>:

- Ocean sequestration
- Geologic sequestration
- Terrestrial sequestration
- Advanced concepts (chemical and/or biological conversion)

The most appealing method of sequestration would be one that had the best economics. One such method is currently being demonstrated on a commercial scale in the Weyburn Oil Field, Saskatchewan, Canada, by the PanCanadian Petroleum Company at a cost of Canadian \$1.1 billion. In this application, 5000 tons CO<sub>2</sub>/day from the Dakota Gasification Company Synfuels Plant in North Dakota is transported through a 325 km pipeline to the Weyburn Field where it is injected into existing wells to recover additional oil. An additional 120 million barrels of oil will be recovered while sequestering 14 million (net) metric tons (tonnes) of CO<sub>2</sub>. (13)

During the early development stages of the sequestration technology, projects are designed around point sources of CO<sub>2</sub> and nearby repositories which have massive volume and provide an environment conducive to retaining the gas. The ocean is an obvious choice for a repository because of its depth, volume and proximity to most of the populous areas of a country. The largest CO<sub>2</sub> sequestration project in the world currently is the Norwegian Statoil project which is stripping CO<sub>2</sub> from natural gas in the North Sea and reinjecting it - 700,000 tons of CO<sub>2</sub> in 1997. (14) Large populations use large amounts of energy provided by power plants, and require jobs provided by factories and service industries, transportation, and personal needs, all of which contribute to the CO<sub>2</sub> build-up in the atmosphere. Some countries, however, have little or no seacoast from which to deposit CO<sub>2</sub> generated within their country. Other countries, e.g., the U.S., Russia, China, India, etc. are very large and have point sources of CO<sub>2</sub> inland substantial distances from the coast. Sequestration of CO<sub>2</sub> is more reasonable if the gas can be pumped into the ground, absorbed by mineral matter or used by flora over a vast area. (14) A variety of approaches to CO<sub>2</sub> collection and sequestration currently involve 40 different projects in 19 countries. Examples of some major projects (in addition to the PanCanadian project in Canada) taking place in other countries that illustrate various approaches to controlling CO<sub>2</sub> emissions are:

- CESSA Cement Energy Efficiency Project - El Salvador  
Construction of dry type (more efficient) cement kiln requiring less fuel saving 909,000 metric tons CO<sub>2</sub> over 12 years accompanied by a major reforestation project sequestering 14,600 metric tons of CO<sub>2</sub>.
- The Rio Hondo II Project - Guatemala  
Construction of a hydroelectric plant to replace fossil fuel plants saving 135,000 metric tons of CO<sub>2</sub>/year.
- The Central Selva Climate Action Project - Peru  
Forest protection and reforestation sequestering 13.9 million metric tons of CO<sub>2</sub> over 30 years.

- Energy Efficient Street Lighting Project - the Philippines  
Convert 4604 mercury vapor lamps to high pressure sodium lamps to reduce electricity usage by 45% per lamp saving 35000 metric tons CO<sub>2</sub> over 25 years.
- Japan is developing and testing an inverted J method of delivering CO<sub>2</sub> from a power plant to the ocean depths

The concept of CO<sub>2</sub> sequestration will be a successful technology when the economics become realistic. Many sites in the US may be technically suitable for CO<sub>2</sub> sequestration in underground saline aquifers, oil fields and coal methane beds. In addition the oceans, one of the largest natural sinks for CO<sub>2</sub> is a probable repository for CO<sub>2</sub> but the economics must be acceptable. The atmosphere deposits an estimated 90 Gtonnes/yr of CO<sub>2</sub> in to the oceans with a net 2 Gtonnes/yr from surface water to the deep water. (15) DOE has targeted a significant fraction of 1 billion tons of CO<sub>2</sub> as carbon by the year 2025 and a significant fraction of 4 billion tons by 2050. Currently the cost of carbon capture and storage is \$100-300/ton C. The target price is \$10/ton by 2015. (14) Sequestration cannot be for the short term. Carbon held for a hundred or better a thousand years is the goal of some researchers. Japan, US, Norway, Canada, Australia and a private company in Switzerland work independently and cooperatively in field experiments in the Pacific, e.g., off Hawaii and Japan where CO<sub>2</sub> is deposited at depths of 1000 to 3000 feet. Japan is developing and inverted J method of delivering CO<sub>2</sub> from a power plant to the ocean depths.

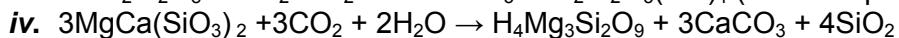
### **CO<sub>2</sub> Sequestration in Inland U.S.**

This project was designed to provide technical information regarding potential suitable sites for sequestering CO<sub>2</sub> in land-locked regions of the U.S. near point-sources of large quantities of CO<sub>2</sub> gas emissions. A large majority of natural gas treatment plants, fossil fuel power plants and commercial gasifiers, all of which produce large amounts of CO<sub>2</sub>, are located inland. They are scattered throughout the internal US, making it necessary to find suitable CO<sub>2</sub> repositories within reasonable distances from the plants as shown in a map by Preuss. (16) The technologies associated with collecting the CO<sub>2</sub> from gas streams currently vented to the air are still in the development stages and no attempt is made to evaluate the merits of them in this study except to assume that a feasible technology for collecting CO<sub>2</sub> from combustion gas will become available by 2010. Gas streams from commercial gasifiers are contained and separated such that the CO<sub>2</sub> stream is available for pipelining with minimal additional treatment. The focus of the project was on sites near point sources of CO<sub>2</sub> which has porous formations and/or subterranean water in the form of saline aquifers below the useable water supplies and in geologic formations suitable to accept and store the gas.

### **Site Selection in the Midcontinent**

Incorporating CO<sub>2</sub> into structures, i.e., flora, concrete, lime, on the surface of the earth is already occurring with the result being the net annual production of CO<sub>2</sub>. Thus, sequestration of CO<sub>2</sub> in regions of the continental U.S. away from the coasts necessarily requires injection into the earth. The CO<sub>2</sub> must be entrapped by some chemical or mechanical mechanism to prevent it from escaping to the surface and into the atmosphere. This is best accomplished by dissolving it underground in a porous medium preferably containing alkaline, saline water. Examples of classic chemical reactions that can occur to trap the CO<sub>2</sub> are: (2, 17)

- i.*  $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{+2} + 2 \text{HCO}_3^{-1}$  (Limestone and dolomite trap)
- ii.*  $\text{KAlSi}_3\text{O}_8 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{K}^+ + \text{HCO}_3^{-1} + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4 \text{SiO}_2$  (K-Feldspar trap)



The combination of  $CO_2 + H_2O$  in *ii.* and *iii.* forms carbonic acid which will dissolve the feldspars to initiate the reaction. Formation of the carbonates results in a specie that has a vapor pressure that is negligible and therefore return to the atmosphere is prevented.

In a less chemically suitable repository but one that has substantial void volume,  $CO_2$  can be injected into porous formations and sealed under pressure to keep it in condensed form. One such porous repository is the coal bed source of methane. Currently, studies are being conducted in the San Juan Basin in southern Colorado and northern New Mexico under the U.S. Coal~Seq Project. This, the most prolific methane producing basin in the world, has studies being conducted at the Allison Unit operated by Burlington Resources and at the Tiffany Unit operated by BP(America).<sup>(9)</sup> Internationally, similar secondary studies are being conducted at Fenn/Big Valley, Alberta, Canada by the Alberta Research Council and in Poland under the RECOPEL Project funded by the European Union. <sup>(9)</sup> The idea is to inject the  $CO_2$  concurrent with the collection of the gas. Another US Basin, the Powder River Basin (northern Wyoming and southern Montana) is projected to have as many as 70,000 coalbed methane wells brought in during the next 30 to 35 years with ultimate gas production from the basin predicted to be as high as 25 trillion scf (505 million tonnes). In addition, an estimated 7.27 billion tonnes of water will be produced. <sup>(18)</sup> This water would be enough to dissolve 14.5 million tonnes of  $CO_2$  if it were reinjected with the gas. <sup>(19)</sup> This leaves a huge void as a potential repository for  $CO_2$ . The coal bed methane resource is not a small player in the energy field as indicated by the fact that by 1996, production of the total US gas supply had risen to 6%. <sup>(20)</sup> This resource, much of it untapped and unmineable, is scattered across the inland areas of the US.

Injection of  $CO_2$  into underground formations is not a trivial task. It requires drilling a system of holes to depths below the useable water table and in an environment that will retain the  $CO_2$ . Regions where oil or natural gas production are nearing the end of their productive life become attractive as repositories because some of the drilling has been completed and will reduce the cost of preparing the site for the intended use. <sup>(21)</sup> In addition, the voids left in geologic formations by the extraction of oil or gas provides the voids needed to deposit the  $CO_2$  targeted for sequestration. Wells are normally sealed before abandonment reducing the expense of using them as holding tanks for the gas. In some cases, the economics of sequestration can be improved by using  $CO_2$  for profitable ventures, e.g., recovering oil or gas, that may otherwise be left in the ground. In such a case, the produced water, if saline, when reinjected into the well, will sequester  $CO_2$ .

North Dakota has eight power plants and one lignite gasification plant located in the west-central region situated over the eastern edge of the Williston Oil Basin. Sequestration of  $CO_2$  from these plants could be an asset to secondary oil recovery in the Basin, a technique which has already been demonstrated in the Basin. In 1980-81 enhanced oil recovery with  $CO_2$  was tested in the Little Knife Field, Billings County, North Dakota. Wells were drilled to a depth of 3000 meters into the Madison Formation in an inverted four-spot configuration on a five-acre plot. The injection well was near the center and the others were observation wells. The oil-bearing reservoir was dolomitized carbonate. Water-alternating-gas (WAG) injection sequence was used injecting 1150 barrels/day water followed by 40 tons/day  $CO_2$  at a pressure in excess of 3400 psig. At the time no direct measurements were made to determine trapped  $CO_2$  and may have gone unrecognized, as indicated by a report of 52% sweep efficiency in the test. One potential cause for reduction in sweep efficiency may have been sequestered  $CO_2$ . <sup>(22)</sup>

The Madison Formation is of current interest because it may be the best formation in the stratigraphic column of the Williston basin for depositing CO<sub>2</sub>. A description of the Formation is shown in Table 5 . (23)

Similarly a second potential site for sequestering CO<sub>2</sub> is Michigan Basin and Ohio Area. The point sources of the gas are there and the environment for sequestration is favorable. The properties of the basin are found in Table 5.

### Test Results

Absorption of CO<sub>2</sub> by core samples was measured by observing change in pressure in the vessel at a predetermined temperature. The fine pore structure of Core I resulted in extended absorption time for the CO<sub>2</sub> into the core. On reaching equilibrium pressure, the core contained 0.015 ton CO<sub>2</sub> /ton of core material at approximately the critical conditions of CO<sub>2</sub>. On return to ambient pressure, 99% of the CO<sub>2</sub> was released by the core. A second test on the core material (a previously untested sample) was unsuccessful when the vessel seal began to leak.

**Table 5. Chemical and Physical Properties of the Two Formations for CO<sub>2</sub> Sequestration\***

Properties	Madison Formation - Williston Basin	Mt. Simon Formation - Michigan Basin and Ohio Area
Mineralogy	Carbonate - Evaporite group	Feldspathic Quartz Sandstone
Depth, meters	2400-3200	1600-5000
Formation Thickness, meters	1000-2000	50-800
Temperature, °C	100-150	20-150
Normal Pressure, undrilled, psi	4400	1000-5000
Normal Pressure, drilled, psi	3350	NA
Salinity, TDS, ppm	10,000-300,000	NA
Transmissivity, ft <sup>2</sup> /sec	0.013	Porosity/permeability r <sup>2</sup> = 0.86
Brine Composition, mg (Ca)/L	500	NA

\* UTex

Following repair of the seal on the vessel, Core II was tested at the conditions shown in Table 1. On reaching the equilibrium pressure, the core contained 0.280 ton CO<sub>2</sub> /ton of core material On pressure release and return to ambient temperature, the CO<sub>2</sub> quantitatively effused from the core. This was expected since the acid gas has little affinity for the acidic sand. To be sequestered in formations of this type, the injection hole would require sealing against pressure.

Core III was impregnated with NaOH (lye). On reaching the equilibrium pressure in the vessel, the core absorbed 0.353 ton CO<sub>2</sub> /ton of core material. On return to ambient conditions the core continued to adsorb 0.0012 tons CO<sub>2</sub> /ton of core material. The CO<sub>2</sub> was probably retained as carbonate as a result of neutralization reaction of acid sites with NaOH in fractures and on the surface and in the macro- and some meso-pores of the sandstone. It is doubtful that the NaOH penetrated the micropores or most of the internal mesopores, which probably make up most of the surface area and void volume of the core.

Injection of CO<sub>2</sub> into the geologic formation under pressure at conditions in excess of critical (P<sub>c</sub> = 72.9 atm, T<sub>c</sub> = 88°F ) will reduce the fluid tendency to return to the gas phase and readily escape the formation. In situ formations, preferably salt-water aquifers below the useable water table or porous media such as methane-containing coalbeds or unexploitable subterranean caverns, chosen on the basis of porosity, permeability, salinity, and pH would appear to be the best repositories for the sequestered gas. Laboratory testing of cores from prospective sequestration sites provide data for determining the properties mentioned above as well as for providing informed data on which to predict injection parameters, formation capacities, and subterranean environmental impact.

A practicable sequestration program of the magnitude required to reduce CO<sub>2</sub> emissions to the extent described in the introductory part of this report requires a huge information and data base. Some of this data is already on record. However, data such as that obtained in this brief study could provide information that would significantly reduce the cost of selecting and preparing a site. Cooperation from oil and gas companies which have a wealth of knowledge and core samples from previous and current underground surveys as well as cooperation from state and federal geological survey organizations are essential in developing a siting program for sequestration of CO<sub>2</sub>

## CONCLUSION

CO<sub>2</sub> is quantitatively the second-most prominent anthropologic contribution to the atmosphere (H<sub>2</sub>O is first). In the early 1990's the net contribution was estimated at approximately 3.5 billion tonnes per year on a C basis. Consumption of fossil fuel has increased since that time, suggesting that the net contribution of CO<sub>2</sub> has also increased. In 2000 EIA reported that 2776 electric utility power plants were providing electric power to the U.S. and 68% of that power was provided through combustion of fossil fuels. (24) To return to steady state concentration of CO<sub>2</sub> in the atmosphere feasible methods of collection and storage of the excess must be developed and implemented. Major anthropologic contributors are power generating plants, industrial and domestic energy needs, and motor vehicle operation. Collection methods for CO<sub>2</sub> from point sources has been demonstrated on a commercial scale. Collection from motor vehicles has not been seriously addressed. Storage in landlocked regions is currently being demonstrated commercially in a cooperative effort between Dakota Gasification and Pan Canadian. Researchers in Norway and Japan are leaders in experimental efforts on disposal of CO<sub>2</sub> in ocean bottoms. A wealth of data concerning subterranean environments is held by oil and gas companies, geological survey offices and universities.

Most US power plants have subterranean repositories suitable for CO<sub>2</sub> disposal easily within 200 miles (the approximate length of the Dakota Gasification Plant-PanCanadian pipeline) of their site. Many inland power plants in the western U.S. are sited on, or within just a few miles of a suitable repository and those in the east are easily within the distance that the DGC-PanCanadian venture is demonstrating is workable.

The test results indicated that absorption and retention of CO<sub>2</sub> is highly dependent on the chemistry and physical structure of the formation into which it will be injected. Although porosity may allow the formation to absorb CO<sub>2</sub>, and retain it subject to pressure, when the pressure is released the gas will effuse unless chemisorption occurs. A study of core samples with more complete histories would clearly define properties of formations best suited for CO<sub>2</sub> sequestration.

## REFERENCES

1. <http://www.eia.doe.gov/oiaf/1605/ggrpt/carbon.html>.
2. "Carbon Dioxide Disposal from Power Stations", IEA Greenhouse Gas R & D Programme, ISBN 1898373 07 8.
3. Mangin, A., Gueval, P., Murray, C.N., "Renewable Energy Sources and Requirements Needed to Substitute One Million Tons of CO<sub>2</sub> Atmospheric Emissions in Europe", IEA Greenhouse Gas Conference "Technologies for Activities Implemented Jointly", Vancouver, Canada, May 26-29, 1997. Pergamon Press.
4. Michaels, Patrick J., "Carbon Dioxide: A Satanic Gas?", Testimony to Subcommittee on National Economic Growth, Natural Resources, and Regulatory Affairs, U.S. House of Representatives, October 6, 1999. <http://www.cato.org/testimony/ct-pm100699.html>.
5. Crawford, E., "A Numerical Simulation of Anthropogenic Climate Change", *Ambio*, Vol. 26, No. 1, Feb. 1997, Royal Swedish Academy of Science.
6. Kyoto Protocol, found at [www.unfccc.de/index.html](http://www.unfccc.de/index.html).
7. Bruno, EyeForEnergy.com, April 4, 2002. <http://www.eyeforenergy.com/print.asp?news>.
8. Birol, Farib, and Keppler, J.H., "World Energy Outlook", (1999) International Energy Agency, IEA Publications, Paris, France.
9. Wright, Ian W., "Update on the CO<sub>2</sub> Capture Project", IEA Greenhouse Gas R & D Programme, Number 59, March 2002, ISSN 0967 2710.
10. Socolow, R., ed. "Fuels Decarbonization and Carbon Sequestration: Report of a Workshop", Publication, PU/CEES 302, Princeton University, Princeton, NJ; [www.princeton.edu/~ceesdoe/](http://www.princeton.edu/~ceesdoe/) (1997).
11. Kane, R.L., "Carbon Sequestration: An Option for Mitigating Global Climate Change", CEP, June 2001, pp 44-52. [www.aiche.org/cep/](http://www.aiche.org/cep/).
12. "Carbon Dioxide Capture from Power Stations", IEA Greenhouse Gas R & D Programme ISBN 1898373 15 9, <http://www.ieagreen.org.uk/capt8.htm>.
13. Canada NewsWire,; <http://www.newswire.ca/releases/October2000/19/c4778.html>.
14. Rawls, R.E., "Sequestering CO<sub>2</sub>", *Chem. & Eng.News*, 78, (38). (2000), pp 66-69.
15. <http://www.eia.doe.gov/oiaf/ieo/index.html>.
16. Preuss, P., scienceBEAT, [enews.lbl.gov](http://www.energyscience.org).
17. "Matisoff, G, Saylor, B.Z., Morrison, P., "Carbon Dioxide Sequestration in the Rose Run Formation of Eastern Ohio", Proposal Summary, OCRCIII - Year 2, (2001-2002)
18. [http://www.westernresearch.org/content/technology\\_areas/coal/cbm.shtml](http://www.westernresearch.org/content/technology_areas/coal/cbm.shtml).
19. <http://scifun.chem.wisc.edu/chemweek/CO2/CO2.html>.

20. Byrer, C.W., Guthrie, H.D., "Carbon Dioxide Sequestration Potential in Coalbed Deposits", USDOE, FETC, Morgantown, WV.
21. Dreher, George R; [http://members.aol.com/drehergeo/3D\\_Economics/index.htm](http://members.aol.com/drehergeo/3D_Economics/index.htm).
22. Desch, J.B., Larsen, W.K., Lindsay, R.F., Nettle, R.L., "Enhanced Oil Recovery by CO2 Miscible Displacement in the Little Knife Field, Billings County, North Dakota", Journal of Petroleum Technology, Society of Petroleum Engineers of AIME, Sept. 1984, pp 1592-1602.
23. Utex Bureau of Economic Geology, University of Texas at Austin, <http://www.beg.utexas.edu/environqlty/co2seq/0madison.htm>.
24. Electric Power Annual, Volume II, Energy Information Administration, USDOE, October 2000. <http://www.eia.doe.gov/cneaf/electricity/ipp/ipp00.pdf>.