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Nitrate sources and lake response in high elevation lakes, Uinta Mountains, Utah

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A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Geography

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NITRATE SOURCES AND LAKE RESPONSE IN HIGH ELEVATION LAKES, UINTA MOUNTAINS, UTAH

(Thesis format: Integrated Article)

by

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Graduate Program in Geography (Environment and Sustainability)

A thesis submitted in partial fulfillment
of the requirements for the degree of
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Abstract

Direct human activities in the Uinta Mountains, Utah, U.S.A., are limited to free-range grazing and recreation, but the larger-scale perturbations of climate warming and atmospheric deposition could also affect these remote sites. As few limnological measurements are available, it is difficult to discern whether changes in the high alpine lake ecosystems are occurring in this area. This study uses a range of paleolimnological and limnological techniques to: (1) identify the timing, nature, and causes of changes in primary production in high elevation Uinta Mountain lakes; (2) pinpoint the relative contributions of different sources of nitrate to these aquatic ecosystems; and (3) use diatom community composition data to determine the nature of lake responses to these large-scale perturbations. The results illustrate that primary production was relatively stable until ~1950 AD when it began to increase. Data from sedimentary δ^{15}N, chlorophyll *a*, and C:N ratios, indicate that the post-1950 AD increase in primary production resulted from increased nitrate deposition from fertilizers and fossil fuel use. However, we suspect phosphate dust from nearby mining and agricultural activities may also be important. The hypothesis of fertilizer-based enrichment is confirmed by a triple-isotope approach (Δ^{17}O, δ^{18}O, and δ^{15}N) to analyzing water and snow nitrates; the results indicate that the dominant source of nitrate inputs to these high elevation sites is atmospheric transport of nitrate- and ammonium-based fertilizers. Atmospherically oxidized nitrate and soil nitrate sources are of secondary importance. Nitrogen deposition is also the primary driver of changes in diatom community composition; these findings are based on synchronous changes in diatom assemblage turnover and δ^{15}N values, and an increase in the nitrophilous diatom species *Asterionella formosa*. Based on analysis of diatom stratigraphies, canonical correspondence analysis and ß-diversity, it is evident that Uinta Mountain lakes differ in their sensitivity to increased nitrogen deposition; this is corroborated by the changes in primary productivity and δ^{15}N. Our findings are significant in not only understanding the implications of urban and agricultural activities to remote Uinta Mountain lakes, but in enhancing our general understanding of alpine nutrient cycling in the Anthropocene.

Keywords

paleolimnology, limnology, stable isotope analysis, nitrates, diatoms, eutrophication, alpine lakes, fertilizer, $\Delta^{17}O$, lake production, sedimentary chlorophyll *a*, species turnover

Co-Authorship Statement

This thesis contains three manuscripts. The first manuscript is entitled "Recent changes in production in oligotrophic Uinta Mountain lakes, Utah, U.S.A., identified using paleolimnology" (Chapter 3), a version of which has been submitted to Limnology and Oceanography. This manuscript is co-authored with Katrina A. Moser (supervisor), Fred J. Longstaffe, Neal Michelutti, and Ryan Hladyniuk. I collected four of the six lake sediment cores, the water samples, and compiled the historical data. I also conducted all of the lab work with the exception the δ^{15}N and δ^{13}C profiles, analyzed the results, and wrote the manuscript. Dr. Katrina Moser provided guidance on the research design, lab methods, field methods, data interpretation and provided funding. Dr. Fred Longstaffe provided stable isotope expertise and funding for the analysis of elemental carbon and nitrogen and sedimentary δ^{15}N and δ^{13}C. Dr. Neal Michelutti provided guidance on the measurement and interpretation of sedimentary chlorophyll *a*. Ryan Hladyniuk supervised the lab work involved in measuring δ^{15}N and δ^{13}C and aided in interpreting the results. All authors were involved in the editing of the manuscript.

A version of Chapter 4 entitled "Nitrate sources in alpine lakes: new insights from Δ^{17}O, δ^{18}O, and δ^{15}N" is in preparation. This manuscript will be co-authored with Sam D. Russell, Fred J. Longstaffe, and Katrina A. Moser. I collected the water and some of the snow samples, others were collected by G. Ingersoll, USGS. I conducted the laboratory analysis at the Laboratory for Stable Isotope Science at the University of Western Ontario with S. D. Russell. I modeled, analyzed, and interpreted the results, and wrote the manuscript. S. D. Russell oversaw the laboratory work, modified and maintained the analytical equipment, and provided guidance on analyzing and interpreting the results. F. J. Longstaffe aided in interpreting results and also funded the analysis of all samples. K. A. Moser was involved in study design, and interpretation. All authors will be involved in the editing of the manuscript.

The third manuscript is entitled "Variable diatom responses to increased nutrients in Uinta Mountain lakes" (Chapter 5). A version of this chapter, co-authored with

Katrina A. Moser, is in preparation. K. Moser provided the calibration set data and provided guidance on study design, analysis and manuscript preparation. I enumerated the diatoms for the six short cores, carried out all analyses, and wrote the manuscript. Both authors will be involved in the editing of the manuscript.

I will be the first author on all three publications.

Dedication

For my parents, Rick and Jane

Acknowledgments

First and foremost, I express my sincere gratitude to Dr. Katrina Moser. You have been a continuously positive, encouraging and supportive mentor throughout this process and for that I am greatly indebted. I am so appreciative of all that you have done, from patient training in the lab and field, to comprehensive exam practice sessions, to encouraging me to seize all opportunities.

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Finally, I am truly thankful for the love and support of my family; it’s amazing to think that we have more than doubled in number since I started grad school. I trace my love of science and nature back to camping and exploring with Mum, Dad, Eric, and Tim, and I cherish those memories. Percy, you make everything fun - my best breaks from writing are playing board games and drawing with you. Seneca, you have done so much. Thank you for your endless encouragement and support, for celebrating each small victory, talking sense, and for making me laugh.

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List of Abbreviations

AON	Atmospherically oxidized nitrate
CCA	Canonical correspondence analysis
Chl *a*	Chlorophyll *a* + derivatives (pheophytin *a* and pheophorbide *a*)
CONISS	Constrained Incremental Sum of Squares cluster analysis
DCCA	Detrended canonical correspondence analysis
DCA	Detrended correspondence analysis
DIC	Dissolved inorganic carbon
DIN	Dissolved inorganic nitrogen
IPCC	Intergovernmental Panel on Climate Change
ka	Thousand years ago
m.a.s.l.	Metres above sea level
N	Nitrogen
N_2	Dinitrogen, Nitrogen gas
NADP/NTN	National Atmospheric Deposition Program/ National Trends Network
NH_4^+	Ammonium
NO_2^-	Nitrite
NO_3^-	Nitrate
NO_x	$NO + NO_2$

P	Phosphorus
PCA	Principal Components Analysis
SCPs	Spheroidal carbonaceous particles
TDN	Total Dissolved Nitrogen
TDP	Total Dissolved Phosphorus
TN	Total Nitrogen
TP	Total Phosphorus
Tg	Teragram (10^{12} grams or 10^{9} kilograms), Equivalent to one megatonne (10^{6} tonnes)

List of Definitions

Ammonia (NH_3)	Reduced nitrogen compound.
Ammonium (NH_4^+)	Oxidized (via nitrification) form of ammonia.
ß-diversity	Also called species turnover. A measure of how different samples are on gradients of species composition.
Calibration set	A standardized set of limnological data collected from a network of sites. In this case, includes surface sediment fossil assemblages and environmental variables for each site.
Colimitation	Ecosystems or organisms that are very near the threshold for both N and P limitation.
Cultural eutrophication	Acceleration of eutrophication by human activities, often via the addition of nutrients.
Denitrification	A microbially facilitated process of converting nitrate (a biologically available form of nitrogen) into $N_{2\ (gas)}$.
Diagenesis	The physical, chemical, and biological change undergone by sediment after it is deposited. In this thesis the term is largely applied to changes in the organic matter component of the sediment.
Dry deposition	The removal of small particles and gases from the atmosphere to Earth's surface without precipitation.
Dust	Small solid particles which may remain suspended in the atmosphere and settle under their own weight.
Eutrophication	Ecosystem response to the addition of nutrients.
Hypolimnion	The dense, bottom layer of water in a thermally stratified lake.
Hypoxia	Low oxygen conditions in which decaying plants and animals remove oxygen to a level below which most aquatic organisms can survive.
Limiting nutrient	The element available in the least amount relative to the needs of the organism.

Limnology	The study of inland waters, including their biological, chemical, physical, and geological attributes.
Nitrification	Aerobic process performed by autotrophic bacteria, involving the oxidation of ammonia into nitrite, then nitrate.
Nitrogen fixation	Process of converting atmospheric N_2 (not biologically available) in to ammonium. Can be a natural process (e.g., by lightning, by nitrogen fixing bacteria) or a synthetic process (e.g., Haber-Bosch Process).
Nitrogen saturation	A condition where previously nitrogen limited ecosystems are no longer nitrogen limited.
Nitrous oxides (NO_x)	Oxidized nitrogen compounds.
Oligotrophic	Low primary production associated with low phosphorus and nitrogen.
Paleolimnology	The science concerned with reconstructing past environments of inland waters based on the physical, chemical, biological and geological properties of lake sediments.
Primary production	Refers to the creation of organic matter from CO_2, and usually occurs using light energy by photosynthesis.
Species evenness	Refers to how close in numbers each species in an ecological community are.
Species richness	The number of different species represented in an ecological community.
Talus	Unconsolidated, poorly sorted deposits of angular boulders that have become detached from bedrock by freeze-thaw cycles, heavy rain, and avalanches.
Wet deposition	The removal of gases and aerosols from the atmosphere and deposited on Earth’s surface by precipitation.

Chapter 1

1 Introduction

High alpine lakes are often considered to be pristine and removed from human disturbance. However, the Anthropocene epoch (Crutzen and Stoermer, 2000) is characterized by global changes that affect even the most remote regions of the world. “Remote” has become an increasingly difficult label to use, as human presence continues to encroach upon natural areas. Remote lakes can be defined as those in which catchment processes and environmental changes are dominated by atmospheric forcing (Catalan et al., 2013). By this definition, alpine areas are among the most remote ecosystems on earth, as they are far removed from most forms of direct human impact relative to adjacent low-lying regions. Even so, alpine environments can be affected by a variety of local, regional and global scale anthropogenic disturbances that are leading to environmental degradation (Beniston, 2003). Potential disturbances to alpine environments include fish stocking, recreation, free-range grazing, metal contamination, nutrient deposition, acidification, and climate change.

High elevation aquatic ecosystems may be particularly sensitive to increased nutrient inputs because they generally have a low nutrient content (i.e., they are ultraoligotrophic to oligotrophic). Several additional factors contribute to their sensitivity, including increased precipitation and atmospheric deposition at high elevations (Lovett, 1994); snowmelt-dominated hydrology and associated spikes in surface water NO_3^- and NH_4^+ concentrations (Campbell et al., 2000); limited uptake of nutrients by the terrestrial system (Campbell et al., 2000); and microbial nitrification within talus slopes (Williams et al., 1997) (see also section 1.5.3).

In this thesis, I investigate trends in primary production and recent eutrophication in high elevation lakes in the Uinta Mountains, U.S.A. Lake eutrophication is defined as enrichment in aquatic primary productivity. Eutrophication can occur naturally, for example when nutrients are released following a forest fire (Hall and Smol, 2001). More commonly, however, ‘cultural eutrophication’ results from anthropogenic increases in nutrient inputs to an aquatic system.

In unpopulated alpine environments, nutrient inputs of anthropogenic origin are more likely to be dominated by atmospheric sources. Direct inputs from sewage, industrial effluent, and agricultural runoff are unlikely to be present. Nitrate and ammonium originating from fossil fuel combustion and agricultural intensification have been commonly identified as major contributors to increased bioavailable nitrogen in alpine environments (e.g., Baron et al., 2000; Wolfe et al., 2001; Saros et al., 2003). However, rather than focusing solely on the potential impacts of atmospheric nitrate and ammonium deposition, this study takes a holistic approach by studying all known factors that could lead to eutrophication in alpine environments (Figure 1.1). These include atmospheric transport of phosphorus from mining and agricultural dust; local grazing activity; and fish stocking. Climate warming, which is occurring more rapidly in the western U.S.A. than in other areas of the contiguous U.S.A. (Saunders et al., 2008), can also increase primary production indirectly by increasing the length of the growing season and stabilizing thermal conditions for phytoplankton growth.

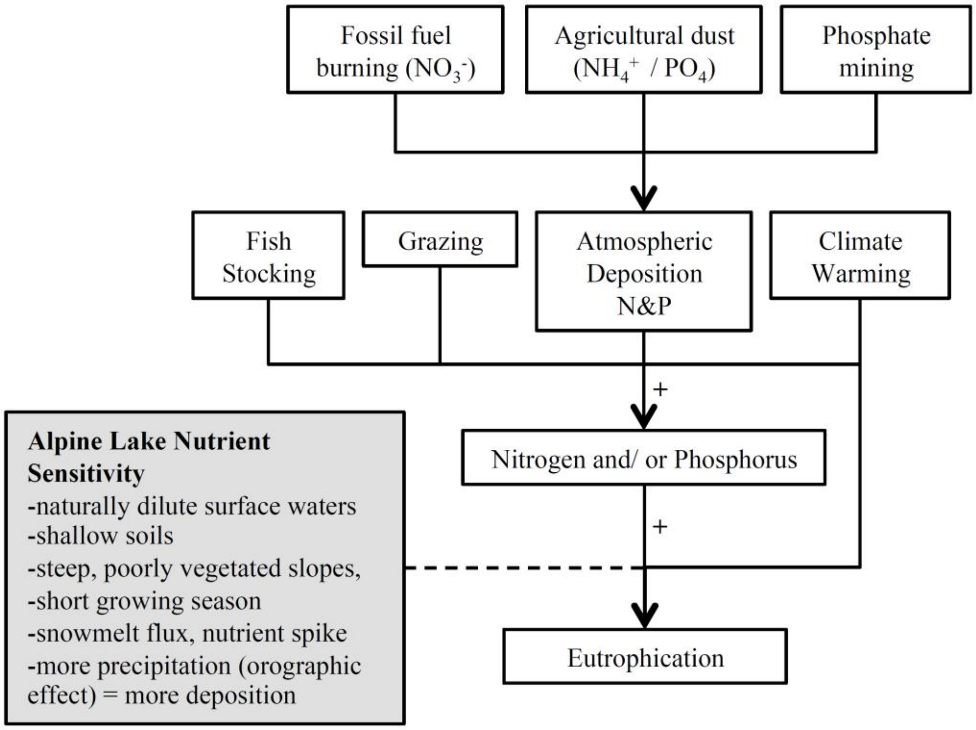

Figure 1.1. Conceptual model of potential causes of eutrophication in high alpine environments. In alpine lake studies, emphasis is often placed on atmospheric deposition of N from fossil fuel burning and agriculture, with little attention given to other potential factors such as fish stocking, grazing, warming, and phosphorus from agricultural dust and mining. Characteristics of alpine lakes that increase sensitivity to eutrophication are listed in the gray box.

1.1 Research Goals

Much of the research on eutrophication has been done in populated, low-elevation regions, where agricultural runoff, urban runoff and industrial effluent are major sources of nutrients. In these regions, eutrophication can result in a number of undesirable traits, including algal blooms, excessive aquatic plant growth, shifts to nuisance and toxic algae, foul odors, oxygen depletion, fish kills, unpalatable drinking water, and loss of biodiversity (Bennett et al., 2001).

There is little evidence of such dramatic consequences of eutrophication in alpine environments. However, alpine lakes are considered to be sensitive to relatively small increases in nutrient inputs (e.g., Burns, 2003) and several studies have demonstrated that atmospheric nitrogen (Baron et al., 2000; Wolfe et al., 2001; Saros, Interlandi et al., 2005) and phosphorus (Psenner, 1999; Sickman et al., 2003) inputs are responsible for recent changes in high elevation lakes. Although no similar investigation has been undertaken in the Uinta Mountains, the mountain range is located downwind of the Wasatch Front, an area of rapidly expanding population and agricultural activity. It is therefore critical to evaluate and improve our understanding of recent changes in primary production in high elevation lakes of the Uinta Mountains. I used algal production measures and sedimentary δ^{15}N and δ^{13}C to address my first research goal:

1. Investigate primary production and potential drivers of any changes in trophic status of the Uinta Mountains over the last two centuries**.**

Several researchers in mountain environments of the Western U.S.A. (Baron et al., 2000; Wolfe et al., 2001; Saros et al., 2003; Holtgrieve et al., 2011) have indicated that recent changes in diatom community composition and decreasing sedimentary δ^{15}N values result from increased nitrogen deposition associated with intensive agricultural activity and fossil fuel combustion. However, many factors can influence δ^{15}N values in lakes and lake sediments (Teranes and Bernasconi, 2000) and so this interpretation remains speculative. I conducted stable isotope analysis of nitrates in modern water, inflow and snow samples to enhance our understanding of alpine nutrient budgets and aid in our interpretation of paleolimnological records in the Uinta Mountains. My second research goal is to:

2. Determine the proportional contributions of nitrates from different sources to the modern aquatic systems of the Uinta Mountain study lakes**.**

How will climate warming and increased atmospheric nutrient inputs affect biota of alpine lakes? Climate warming and nitrogen deposition are not mutually exclusive drivers of ecological change, and the interplay between warming and fertilization by atmospheric deposition is still being widely discussed (e.g., Catalan et al., 2013). By investigating the influence of these factors on diatoms in Uinta Mountain lakes, we can begin to understand the environmental consequences of warming and nutrient deposition on these high elevation lakes. There is also a gap in current understanding of how ecological responses to warming and nutrient deposition vary between lakes in alpine environments. Identifying differences in lake response to warming and nutrient deposition will increase our understanding of the resilience (or lack thereof) of alpine lake ecosystems. I investigated changes in diatom community composition in order to address my third research goal:

3. Determine whether changes in diatom community composition in the Uinta Mountains can be linked to warming and nitrogen deposition, and whether lakes differ in their sensitivity to these environmental changes.

1.2 Thesis organization and research goals

The goals of the thesis and a review of the relevant literature are included in **Chapter 1.** This review includes a background on eutrophication in aquatic systems (section 1.3), rationale for the study of high elevation lakes (1.4) background on eutrophication in mountain environments in the western U.S.A. (1.5); and a brief description of the range of anthropogenic perturbations that potentially affect alpine productivity (1.6). Finally, the rationale for investigating alpine eutrophication in the Uinta Mountains is included in section 1.7.

Chapter 2 provides information on the Uinta Mountain study area based on a review of the literature and field and historical records. It includes a brief description of Uinta Mountain geology and their formation (section 2.1), climate (2.2), biogeography (2.3), information on atmospheric deposition (2.4), and historical land use (2.5). It concludes with descriptions of the six study lakes (2.6).

The three thesis goals listed above are addressed in **Chapters 3, 4,** and **5**, respectively.

Research in **Chapter 3** involved the study of short (~30 to 50 cm) sediment cores from six high elevation lakes that provide records covering the last ~200 years (^{210}Pb dated) of human activity in the region plus several hundred years of natural variability beforehand. We use measures of primary production (percent organics, chlorophyll *a*, chlorophyll *a* flux) and of organic matter properties (C:N ratios) of the lake sediments to track changes in aquatic organic content over this time period. Results of sedimentary stable isotope analyses of $\delta^{15}N$ and $\delta^{13}C$ are used to provide evidence for nutrient sources, the influence of diagenesis, and nutrient cycling. By comparing the timing of these changes to the history of anthropogenic activity in the region, we identify the driving forces behind these changes.

In **Chapter 4**, stable isotopes of nitrogen and oxygen from nitrates ($\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$) were analyzed in water (inflows and lakes) and snow samples from six high elevation lakes and their catchments. This approach allowed for determination of the origin and proportional contribution of atmospheric and terrestrial sources of nitrates to alpine aquatic ecosystems in the Uinta Mountains. Results provide a modern context for paleoenvironmental studies that implicate atmospheric deposition of nutrients in recent ecological changes, such as those identified in Chapter 3. The study also shows the capacity for triple isotope analysis of nitrates to both identify and quantify contributions of different nitrate sources and demonstrates the potential of this technique for addressing a variety of nutrient source questions.

In **Chapter 5**, changes in diatom community composition and species turnover are determined from fossil diatoms preserved in the six study lake sediment cores. These temporal changes are compared to changes in nitrogen deposition (sedimentary $\delta^{15}N$) over time and historical temperature records to determine the relative effects of these two main forcing mechanisms on diatom community structure. Interpretation of the diatom data is improved by using canonical correspondence analysis (CCA) of a 46-lake calibration set to determine the modern relationships between diatom species and environmental variables. Subsequently, the observed changes in the fossil diatom record can be evaluated in the context of this modern environmental variable/ diatom space. Characteristics of lakes and their catchments that lead to differences in lake sensitivity and response to environmental changes are identified. The study demonstrates the range of lake sensitivity to large-scale disturbances, and provides insight into how diatom communities and species turnover have responded to these changes.

The combined significance of the three data chapters of this thesis and future directions for research are discussed in **Chapter 6.**

1.3 Eutrophication and aquatic systems

1.3.1 Ecological effects of eutrophication

Eutrophication can alter the physical, chemical, and biological characteristics of entire aquatic ecosystems, although much of what is known about the impacts of increased nutrient availability comes from studies of low elevation lakes where agricultural and urban runoff are dominant nutrient sources. In these regions, increased algal growth causes decreases in species diversity, often favouring grazing resistant cyanobacteria over small edible algae (Hall and Smol, 2001). Decreased light penetration associated with increased primary productivity can result in decreased macrophyte growth, which in turn alters the habitat and food available for other organisms. With increased algal growth, decomposition and respiration increase, thereby depleting oxygen in the hypolimnion and causing declines in fish habitat and changes in internal cycling and biogeochemical processes (Smol, 2008). Increased algal productivity can enhance biodegradation of pollutants such as pesticides and petrochemicals, but can also increase biological cycling of contaminants like PCBs (Smith and Schindler, 2009). Many of these issues lead to water taste and odor problems and increase water toxicity (Hall and Smol, 2006). The consequences of eutrophication in high elevation lakes may be similar. However, the mechanisms leading to eutrophication are likely to be different in alpine lakes because of differences in limiting nutrients and the sensitivity of alpine lakes and their catchments to increased nutrient inputs (Figure 1.1).

1.3.2 Nutrient limitation in freshwater lakes

Eutrophication is intimately linked to the limiting nutrient of a lake because phytoplankton growth and thus lake primary productivity is dependent upon the availability of the limiting nutrient. Nitrogen and phosphorus are the most common limiting nutrients of freshwater primary productivity, although the prevalence of nitrogen vs. phosphorus-limitation is a source of contention amongst limnologists. Several researchers suggest that alpine lakes are ultimately N-limited (Williams et al., 1996b;

Lafrancois et al., 2003; D. W. Schindler, 2006) or co-limited[1] by nitrogen and phosphorus (Baron et al., 2000). At naturally nitrogen-limited sites, increases in atmospheric nitrogen deposition can induce phosphorus limitation (Bergstrom and Jansson, 2006; Elser et al., 2009; Bergstrom, 2010; Camarero and Catalan, 2012). The phosphorus cycle has also been modified by human activities, and therefore increases in phosphorus must also be considered. For example, in the Pyrenean lake district, Camarero and Catalan (2012) showed that dissolved inorganic nitrogen (DIN) decreased even as atmospheric deposition of nitrogen increased, which is in contrast to the results of the studies by Bergstrom (2010) and Elser et al. (2009). Camarero and Catalan (2012) suggest that increased phosphorus deposition caused the lakes to revert to N-limitation.

The limiting nutrient(s) are important for determining whether increased nitrogen and phosphorus are likely to cause increases in primary productivity. In the next sections, I review the role that humans have played in increasing the availability of nitrogen and phosphorus to ecosystems.

1.3.3 Humans and the nitrogen cycle

Nitrogen is essential for life; it is an important component of many organic molecules including amino acids, nucleic acids, proteins, and in enzymes that mediate important biological reactions like photosynthesis and respiration (Schlesinger, 1991). It is also the most abundant element in Earth's atmosphere (80% by mass) (Galloway and Cowling, 2002). Despite its natural abundance, the majority of atmospheric N is in the form N_2 (dinitrogen gas), which is biologically unavailable to most organisms. A few specialized organisms (e.g., some cyanobacteria species and a group of bacteria called *Rhizobia* that form symbiotic relationships with legumes) are capable of converting N_2 into a useable form (NH_4^+ or NO_3^-) by biological N fixation[2]. Lightning is the only other

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[1] Co-limitation can occur when neither nitrogen nor phosphorus is available in great excess of the metabolic requirements of phytoplankton. Treating these lakes with a single nutrient would only result in brief enrichment until the other nutrient becomes limiting (Elser et al., 1990).

[2] Biological N fixation is the energetically expensive process of breaking triple bonds of N_2 to forms of nitrogen that are usable by organisms (NH_4^+ and NO_3^-)

natural process that creates biologically available nitrogen from atmospheric N_2. Thus, the amount of nitrogen cycling from the atmosphere into the biosphere is naturally limited by the activity of nitrogen-fixing organisms and lightning. As a result, many species are adapted to environments with limited biologically available nitrogen (Vitousek et al., 1997).

Within the last 150+ years, humans have drastically increased the amount of biologically available nitrogen to the extent that all temperate and tropical biomes receive more N deposition today than pre-industrially (Holland et al., 1999). Alterations to the global nitrogen cycle are already dramatic and one of the most serious threats to the global environment (Rockstrom et al., 2009). Increases in biologically available nitrogen are largely due to the Haber-Bosch process, which allowed the production of an unlimited supply of nitrogen fertilizer for growing food (Figure 1.2). Biologically-available nitrogen is also produced as a byproduct of fossil fuel combustion, from intensification of animal husbandry, and increased cultivation of nitrogen-fixing legumes (Vitousek et al., 1997; Holland et al., 1999). The increased in bioavailable nitrogen has several ecologically harmful effects, including eutrophication, acidification, losses in biodiversity, and species invasions by N-loving organisms (Galloway and Cowling, 2002).

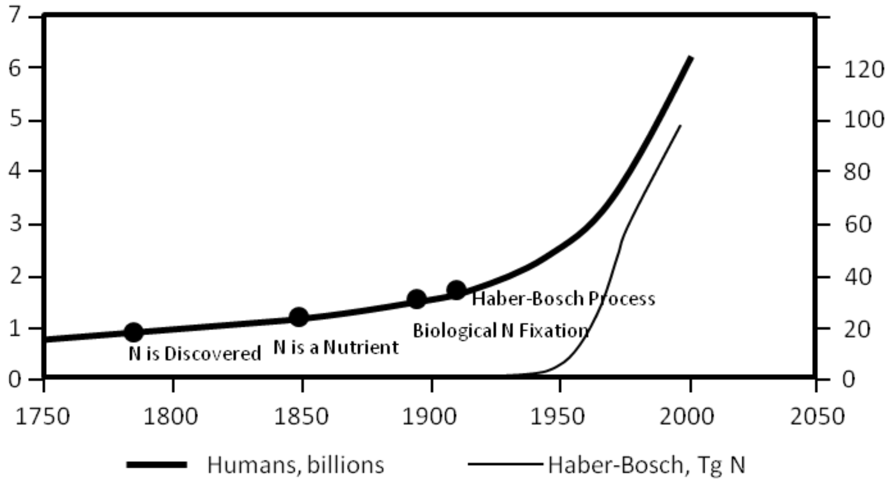

Figure 1.2. Global population trends with key dates for the discovery of N as an element in the periodic table and its role in various biogeochemical processes.

Also shown is an estimate of the annual production of reactive nitrogen by the Haber-Bosch process. Reprinted from *Ambio, 31,* Galloway and Cowling. Reactive nitrogen and the world: 200 years of change, 64-71 © 2002, with permission from The Royal Swedish Academy of Sciences.

Fossil fuel combustion releases NO_x gas into the atmosphere, where it can be converted to NO_3^-. Agricultural production leads to the release of NH_3 gas (which can be converted to NH_4^+ in the atmosphere) and particulate NH_4^+ (transported by wind with dust) (Schlesinger, 1991; Burns, 2003). As production of biologically available nitrogen increases, the atmospheric nitrogen concentration, long-range transport and deposition of nitrogen also increase (Holland et al, 2005). Thus, even though nitrate deposition is highest where the air is most polluted with nitrogen oxides (Porter et al., 2001), remote locations like the Greenland ice sheet (Schlesinger, 1991) and some alpine environments (Baron et al., 2000; Wolfe et al., 2001; Saros et al., 2003) can still be influenced by increased biologically reactive nitrogen, although the spatial pattern is variable (Figure 1.3).

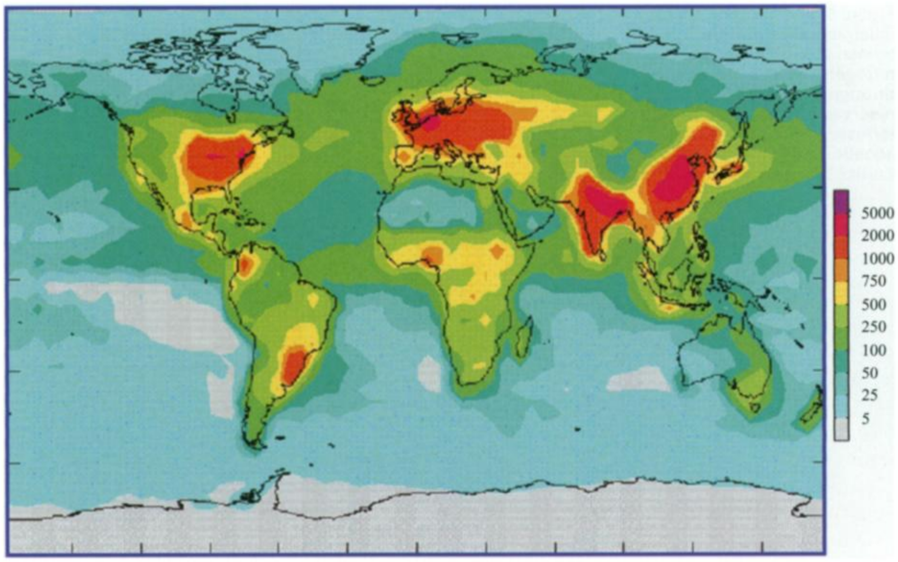

Figure 1.3. Global atmospheric deposition of reactive nitrogen onto the oceans and continents of the Earth in 1993 (mg N m^{-2} yr^{-1}).

Reprinted from *Ambio, 31,* Galloway and Cowling. Reactive nitrogen and the world: 200 years of change, 64-71 © 2002, with permission from The Royal Swedish Academy of Sciences.

1.3.4 Humans and the phosphorus cycle

Phosphorus is scarce in Earth's crust (0.09 weight %) (Filippelli, 2008) and in the biosphere (Smil, 2000). It is an essential nutrient – phosphodiester bonds are components of DNA and RNA; phospholipids form cell membranes; adenosine triphosphate and adenosine diphosphate (ATP and ADP) power photosynthesis and other metabolic pathways; and phosphorus containing hydroxylapatite is a critical component of vertebrate skeletons (Smil, 2000). The phosphorus cycle lacks a stable atmospheric gas phase, so ecosystems rely upon transfer of the nutrient in solution (Filippelli, 2008). Phosphorus is a common growth limiting nutrient in aquatic systems because of its essential role, scarcity, and slow natural cycle.

As with nitrogen, increased food production is the main motivation for increasing the availability of phosphorus. Although the usefulness of mineral fertilizers in crop production was demonstrated in the mid- to late- 19th century, it was not until the mid-

20th century that the use of mineral phosphorus grew exponentially (Ashley et al., 2011) (Figure 1.4). Today, phosphorus in rock is mined, processed into fertilizers, and transported globally to increase crop yields. Much of the phosphorus that is consumed from agricultural products is disposed of (rather than being returned to the agricultural system) and ultimately ends up in aquatic systems. In addition to phosphorus deliberately added to the environment as fertilizer, humans also increase phosphorus inputs via: recycling of crop residues and manure; soil erosion; and discharge of urban and industrial wastes including phosphate detergents. Phosphorus storage in terrestrial and freshwater ecosystems is estimated to be at least 75 % greater than preindustrial levels (Bennett et al., 2001).

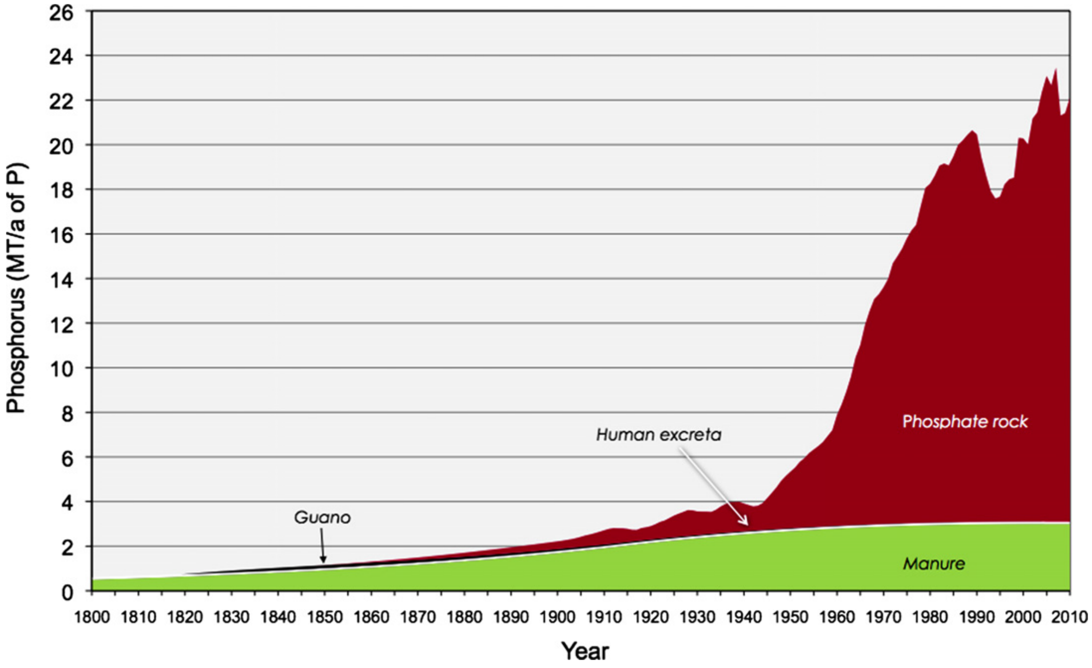

Figure 1.4. Historical sources of phosphorus fertilizers used in agriculture globally (1800-2010). Reprinted from *Chemosphere, 84*, Ashley et al., A brief history of phosphorus: From the philosopher's stone to nutrient recovery and reuse, 737-746, © 2011, with permission from Elsevier.

1.4 Rationale for investigating high elevation sites

Williamson et al. (2008) describe lakes as sentinels of global change, as they respond to the combined effects of local and global environmental changes. Remote lakes in particular provide a unique opportunity to study regional scale perturbations. There are several reasons for investigating high elevation sites:

- The anthropogenic effects on remote lakes are expected to be primarily transmitted atmospherically (Catalan et al., 2013). Therefore, responses to atmospheric stressors can be investigated without the confounding influence of local activities that plague more populated areas, such as sewage input, urban heat island effect, urban run-off, industrial effluent, and agricultural run-off.
- With few local stressors, investigations can focus on whether chronically low additions of nutrients affect lake ecology and function.
- Alpine lakes are particularly sensitive to increases in nitrogen deposition (See section 1.5.3, Figure 1.1).
- Remote areas like alpine ecosystems of the Western U.S.A. can serve as a report card or an early warning indicator of the impacts of nutrient pollution. The sensitivity of alpine sites means they are likely to respond earlier than lowland sites at the same latitude. For example, diatom assemblages showing shifts towards increased *Cyclotella* species with enhanced warming occur first in arctic lakes, then alpine lakes, and lastly in temperate lakes (Rühland et al., 2008).
- If changes in primary productivity can be detected before the consequences of eutrophication are visibly apparent, we may be able to protect these regions.

1.5 Eutrophication in alpine aquatic environments of the Western United States

1.5.1 In terrestrial systems

Increased nitrogen deposition can result in several changes in terrestrial ecosystems, including premature needle drop, reduced amphibian populations, declines in plant, soil bacterial, and fungal communities, and declines in tree health (Baron et al., 2000; Campbell et al., 2000; Burns, 2003). The impact of increased nutrient deposition on terrestrial systems extends to aquatic ecosystems because catchment vegetation and processes are critical mediators between the delivery of nutrients to a catchment and eventual input to a lake. For example, in the Colorado Front Range, gradual increases in wet and dry nitrogen deposition have resulted in many high elevation sites shifting from nitrogen limitation to nitrogen saturation[3] (Williams et al., 1996a). Similarly, Campbell et al. (2000) recorded symptoms of nitrogen excess[4] in the Colorado Front Range with as little nitrogen deposition as 3 kg $ha^{-1}year^{-1}$ although the region may receive greater than 7 kg $ha^{-1}year^{-1}$ at the highest elevations (Burns, 2003)[5]. After being exposed to increased nitrogen deposition over the long-term, terrestrial ecosystems can develop a reduced ability to retain additional nitrogen inputs (Meixner and Bales, 2003) as they shift from efficient nitrogen cycling to excess nitrogen leaching out of the system (Williams et al., 1996a).

1.5.2 In aquatic systems

Several paleolimnological studies indicate that alpine lakes in the western U.S.A. are undergoing recent eutrophication (Baron et al., 2000; Wolfe et al., 2001; Saros et al., 2003). Baron et al (2000) determined that inputs of nitrogen increased after 1950 based on decreasing lake sediment $\delta^{15}N$ values from two lakes (Sky Pond and Lake Louise) in the Colorado Front Range. The increased nitrogen inputs are related to increases in fossil fuel burning, which produces nitrous oxides with $\delta^{15}N$ values ranging from −7 to +12 ‰ (Wolfe, Baron and Cornett, 2001). Diatom community composition at these lakes also shifted ca. 1950 from an oligotrophic diatom assemblage to an increase in species associated with greater inorganic N availability (Wolfe et al., 2001). One major change was a shift in dominance from *Fragilaria* species to *Asterionella formosa* (Wolfe et al., 2001). In alpine environments, *A. formosa* is known to respond to increases in nitrogen

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[3] Under conditions of nitrogen saturation, nitrogen is no longer the limiting factor, and nitrogen is released from the system.

[4] Nitrogen excess refers to the amount of nitrogen that exceeds the ability for organisms to assimilate it.

[5] Background (pre-industrial) inorganic N deposition has been estimated between 0.4 and 0.7 kg $ha^{-1}yr^{-1}$ in the western United States (Holland et al., 1999).

(Saros et al., 2005; Michel et al., 2006). The authors of these studies attribute increased nitrogen inputs to atmospheric deposition from fossil fuel burning and intensive agricultural activity (Baron et al., 2000; Wolfe et al., 2001). The N isotopic ratios and the ecological rates of change since 1950 are also shown to be unprecedented throughout the 14,000 year record (Baron et al., 2000).

1.5.3 Sensitivity of Alpine Lakes to Nutrient Deposition

Alpine lakes have been shown to be particularly sensitive to atmospherically deposited pollutants (Williams et al., 1996a; Campbell et al., 2000; Clow et al., 2002). This sensitivity makes alpine lakes excellent indicator lakes because they should respond rapidly and detectably to small environmental changes. The reasons high elevation lakes are sensitive to environmental change are varied:

- Alpine lake ecosystems tend to be limited by nitrogen (Saros, Michel et al., 2005; McMaster and Schindler, 2005; Lewis and Wurtsbaugh, 2008; Arnett et al., 2012).
- Like arctic lakes, alpine lakes may be particularly sensitive to climate warming, particularly related to ice-duration and lake stratification.
- Alpine environments are subject to greater atmospheric deposition than low-lying areas at similar latitudes because of orographic precipitation, higher wind speeds, and increased cloud presence (Lovett, 1994).
- The hydrology of alpine sites is often snow-melt dominated, which leads to seasonal spikes in surface water nitrate (NO_3^-) and ammonium (NH_4^+) concentrations (Campbell et al., 2000). These spikes come in early spring when the terrestrial vegetation has a limited capacity for taking up nutrients. In the Colorado Front Range, years with greater precipitation tend to have higher nitrate deposition (Williams et al., 1996a).
- Periods of less surface water flow coincide with peak growing season, when the plants have a greater capacity for taking up nutrients (Williams et al., 1996a).
- Short growing seasons and minimal vegetation combined with steep slopes limit N retention in high elevation terrestrial environments (Campbell et al., 2000).

Catchments with greater vegetation cover tend to contribute more phosphorus and organic carbon to the lakes, and less nitrogen (Lafrancois et al., 2003).

- Talus slopes are potential sites of microbial nitrification and can therefore increase the amount of biologically active N that enters water bodies (Williams et al., 1997).

1.6 Other anthropogenic influences on alpine systems

Although the primary focus of this research is increased nutrient deposition in alpine environments, primary production in alpine lakes can also be influenced by climate warming, fish stocking, free-range grazing, and atmospheric pollution of other elements (e.g., metal contamination). An understanding of the range of human influences on alpine lakes is necessary in order to attribute changes in the paleolimnological record to the appropriate stressor(s).

1.6.1 Climate Change

Temperature changes can affect primary productivity and species composition within a lake. Like high latitude lakes, high altitude lakes are expected to be sensitive to the length of the growing season and to the duration of ice-free periods, plus the duration and stability of lake stratification (Smol, 1988; Smol et al., 1991; Catalan et al., 2002; Smol and Douglas, 2007b; Catalan et al., 2013). Changes in duration of ice cover can cause shifts in diatom community composition, such as increased planktonic diatoms (Rühland et al., 2008), or an increase in small-sized diatoms (Catalan et al., 2013). Increased stability of thermal stratification with warming temperatures favours faster growing planktonic algae that can exploit stable epilimnetic conditions (Ruhland et al., 2003). Based on lake sediment diatom stratigraphies from North American and European lakes, (Rühland et al., 2008) found that recent climate warming first affects lake ecology in arctic lakes, then alpine lakes, and lastly, temperate lakes. This implies that alpine lakes respond relatively early (compared to low-lying lakes) to climate warming.

1.6.2 Fish Stocking

Historically, 95% of all western North American mountain lakes were fishless, but many of these lakes (60%) have been stocked for recreational fishing (Bahls, 1992; D. E. Schindler et al., 2001). Commonly the introduction of fish results in changes in herbivory (changes in food web dynamics) and to nutrient regeneration, both of which can cause increases in primary productivity of a lake. For example, benthic fish activity introduces nutrients that would otherwise be unavailable to pelagic photosynthesizers (D. E. Schindler et al., 2001).

1.6.3 Grazing

In alpine lakes with few direct impacts, grazing within catchments could influence nutrient budgets and lake primary productivity. The establishment of high altitude pastures in Europe has lead to shifts in treeline (Lotter and Birks, 2003), changes in fire regimes (Catalan 2013), increased erosion rates (Camarero et al., 1998), and enhanced nutrient loading to lakes resulting in increased anoxia and decreased chironomid abundance (Heiri and Lotter, 2003). Grazing can also alter terrestrial species composition, disrupt nutrient cycling, reduce litter cover, compact soils, reduce infiltration, and increase runoff (Meehan and Platts, 1978; Fleischner, 1994; Belsky and Blumenthal, 1997).

1.6.4 Combined effects

The combined effects of these perturbations are difficult to predict, but as lake sediments incorporate material from the lake, the catchment, and the atmosphere, paleolimnogy is a powerful tool to enhance our understanding of interacting forcings. Catalan et al. (2013) have noted that climate change and atmospheric deposition of biologically available nitrogen are not mutually exclusive drivers of change. For example, Hobbs et al. (2010) analyzed a diatom stratigraphy from Emerald Lake (Wyoming, U.S.A.), which appeared to exhibit an initial species composition shift that is consistent with warming, followed by a later (~1950) shift related to increased nitrogen deposition. Many other “double forcings” have been described from paleolimnological records across Europe, such as the reduction of acidification with increased warming in some areas of the European Alps (Catalan et al., 2013).

1.7 Rationale for studying the Uinta Mountains

The Uinta Mountains are a remote environment in northeastern Utah, U.S.A., in which direct human activities are limited to ranching of free-range grazers (cattle and sheep), fish stocking, and recreational activities like hiking and fishing. A large area (184,882 hectares) of the Uinta Mountains is designated as a wilderness area to protect the natural character of the area (http://www.wilderness.net/NWPS/wildView?WID=246; Figure 2.1B). However, the Uinta Mountains are located 150 km downwind of the Wasatch Front, a region with rapidly expanding urban, agricultural, and industrial activities. Therefore, I expect that the Uinta Mountains may receive elevated nutrient deposition, putting high elevation lakes at risk of eutrophication. Furthermore, the western U.S.A. is also warming rapidly (Saunders et al., 2008), which can also lead to increased primary production in some environments. There is currently little evidence that grazing, fish stocking, warming and nutrient deposition are having any influence on aquatic primary productivity in the Uinta Mountains, although preliminary analysis of diatoms from surface sediments[6] from 57 lakes indicate that nitrophilous[7] diatom species are abundant in some high elevation lakes.

To determine if current activities are negatively impacting this wilderness area, and to protect this ecosystem in the future, it is necessary to investigate if and how primary productivity has changed in the last 200 years. However, the Uinta Mountains lack sufficient monitoring data to determine whether primary productivity or atmospheric nutrient deposition has increased and whether aquatic ecosystems have been altered as a result. Therefore, I use a combination of paleolimnological and limnological records in order to investigate nutrient inputs in this alpine environment.

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[6] Surface sediments (top 1 cm) are taken from the centre of the lake and represent a spatially integrated sample; the sediments and the fossilized organisms within them (in this case diatoms) likely represent the last ~5 years.

[7] Nitrophilous species thrive in a nitrogen rich environment.

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Chapter 2

2 Study Area: The Uinta Mountains

The Uinta Mountains are an east-west trending mountain range stretching nearly 200 km across northeastern Utah (40˚ to 41˚ N, 109˚ to 111˚ W) (Figure 2.1A). The mountain range has summits reaching over 4000 m, contains hundreds of lakes and has experienced little direct human impact. The Wasatch Front, an area characterized by rapid urban and agricultural expansion is located less than 150 km to the west and upwind.

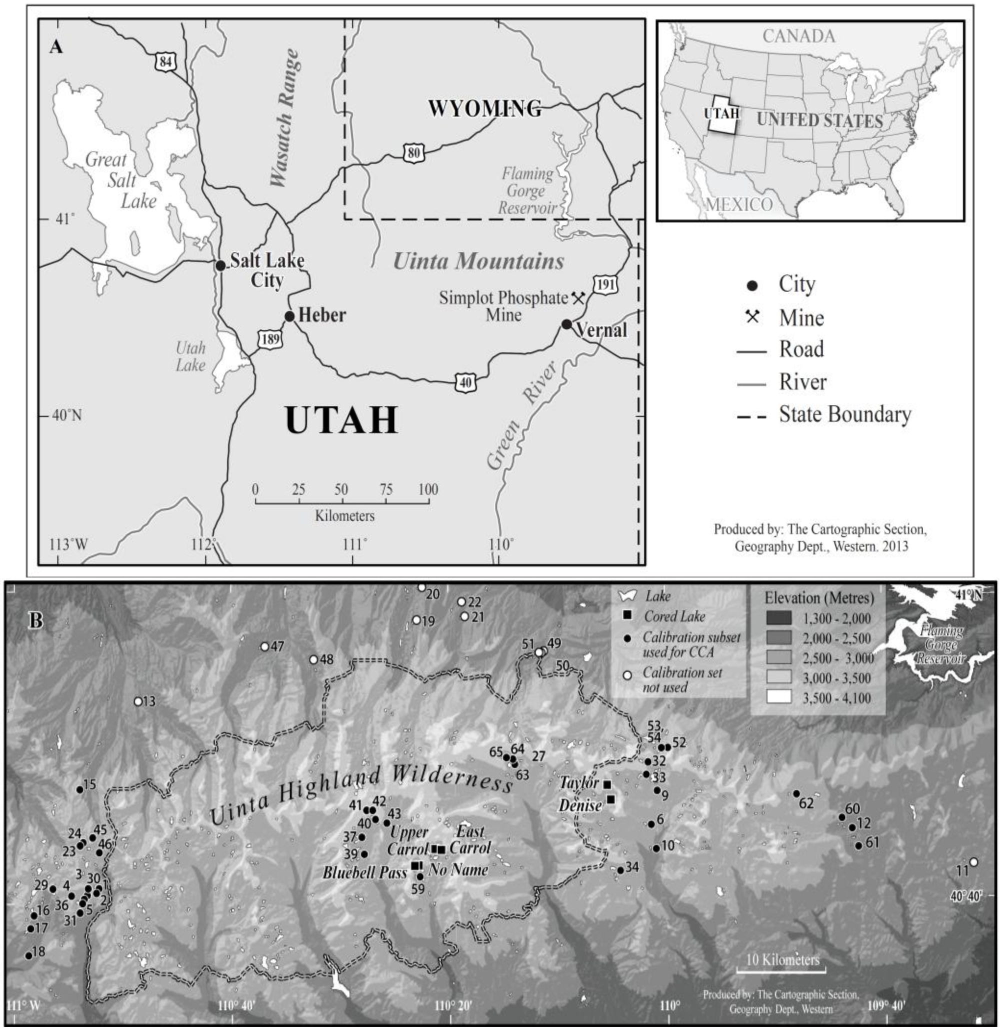

Figure 2.1.(A) The location of the Uinta Mountains in North Eastern Utah, U.S.A, and (B) topographic map of the Uinta Mountains showing the locations of the 57 study lakes.
The High Uinta Wilderness area is outlined with the dotted line.

Six high elevation (> 3000 m.a.s.l.), oligotrophic lakes were selected for intensive study. The reasons for selecting these lakes are discussed in section 2.6. The main study lakes, with the lake codes used in this study in **bold** and with Utah Department of Wildlife Resources codes in parentheses, are: Denise **UN07** (WR-9), Taylor **UN08** (WR-8), Upper Carrol **UN55** (X-18), East Carrol **UN56** (X-21), No Name **UN57** (X-26), and Bluebell Pass **UN58** (X-25). Denise, No Name, and Bluebell Pass are unofficial lake names, but will be used for the remainder of this thesis. These lakes are part of a larger calibration set (consisting of surface sediments and lake water chemistry data) of fifty-seven Uinta Mountain lakes, assembled by K.A. Moser.

2.1 Geology and formation

The Uinta Mountains were produced by a Laramide[8] uplift event of metasedimentary rocks, which consist primarily of quartzite, slate, and shale. There are currently no glaciers in the Uinta Mountains, but the landscape has been modified during numerous glacial periods leading to the formation of cirques, high basins, and u-shaped valleys (Munroe, 2007; Munroe and Laabs, 2009). Uinta Mountain glaciers began to retreat ca. 22-20 ka (in the northern and eastern valleys) and ca. 18-16.5 ka (in the southern and western valleys) (Laabs et al., 2009). The steeper mountain slopes are now characterized by extensive talus[9] slopes and rock glacier deposits with Smith's Fork glacial till on the valley floors (Munroe and Laabs, 2009).

2.2 Climate

Precipitation in the Uinta Mountains increases with elevation due to orographic effects (Nanus et al., 2003; MacDonald and Tingstad, 2007), and high elevation sites are generally snow covered from late October to late May (see USDA National Water and

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[8] The Laramide orogeny was a period of mountain building which occurred from 80 to 35 million years ago.

[9] Talus is unconsolidated, poorly sorted deposits of angular boulders that have become detached from bedrock by freeze thaw cycles, heavy rain, and avalanches (Munroe and Laabs, 2009)

Climate Center, http://www.wcc.nrcs.usda.gov/snotel/Utah/utah.html). The climate of the Uinta Mountains is characterized by two different precipitation regimes. A summer dry/ winter wet regime dominates in the western Uinta Mountains, in which the jet stream moves south in winter bringing Pacific storms eastwards. The summer wet/ winter dry regime dominates the eastern Uinta Mountains, as monsoonal circulation brings moisture from the Gulf of California and the Gulf of Mexico during the summer months (Munroe, 2003). The two regimes are illustrated by the climagraphs of Vernal (eastern Uinta Mountains, higher precipitation during summer) and Heber (western Uinta Mountains, higher precipitation during winter) (Figure 2.2) (MacDonald and Tingstad, 2007). Taylor and Denise lakes are in the summer wet/ winter dry regime, and East Carrol, Upper Carrol, No Name, and Bluebell Pass lakes are on the boundary between the two regimes (i.e., summer and winter precipitation are nearly equal) (Munroe, 2003).

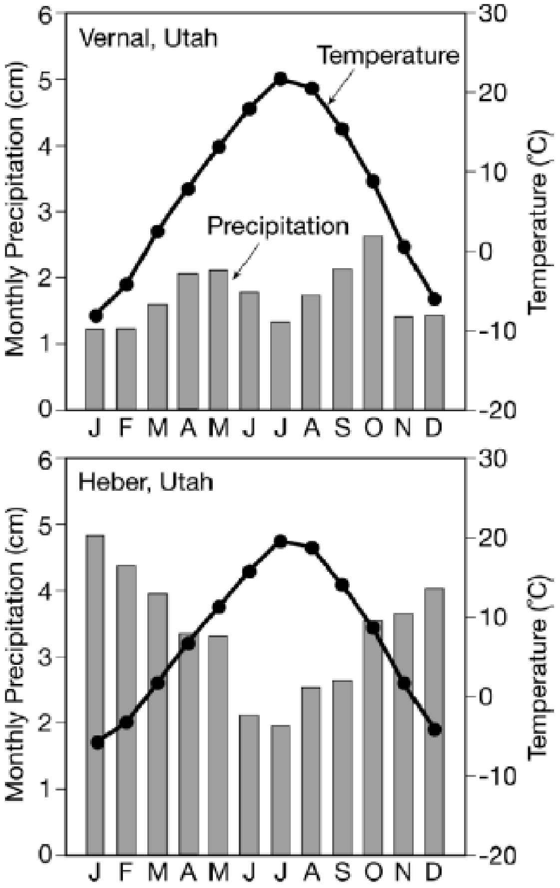


Figure 2.2. Vernal (eastern Uinta Mountains) and Heber (western Uinta Mountains) climagraphs based on the common period for 1928-2005.

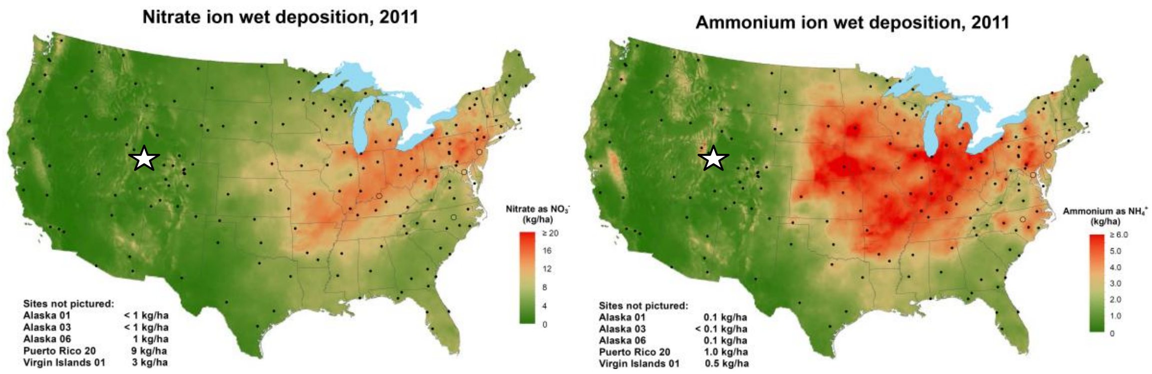
Reprinted from *Arctic Antarctic and Alpine Research, 39*, MacDonald and Tingstad, Recent and multicentennial precipitation variability and drought occurrence in the Uinta Mountains Region, Utah. © 2007, with permission from *Arctic, Antarctic, and Alpine Research*.

2.3 Biogeography

The Uinta Mountains host a range of vegetation as they occupy an ecotone between the Northern and Southern Rocky Mountain vegetation types (Shaw and Long, 2007). From low (~1500-2000 m a.s.l.) to high (3500-4000 m a.s.l.) elevation, the main vegetation zones are sagebrush (*Artemisia)* steppe, Juniper (*Juniperus* spp.) woodland, pinyon-juniper woodland (*Pinus edulis- Juniperus* spp.), ponderosa pine (*Pinus ponderosa*), Douglas fir (*Pseudotsuga menziesii),* aspen (*Populus tremuloides),* lodgepole pine (*Pinus contorta),* spruce fir (*Picea engelmannii- Abies lasiocarpa*), Engelmann spruce (*Picea engelmanii*), and alpine tundra (Shaw and Long, 2007).

2.4 Atmospheric Deposition in the Uinta Mountains

Based on the National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) national scale deposition records, the Uinta Mountains appear to have relatively low atmospheric deposition of nitrate and ammonium (Figure 2.3). However, there are no NADP/NTN monitoring sites in or even near the Uinta Mountains, and relatively few (9 out of 242) high elevation (>3000 m) NADP/NTN monitoring sites in the entire U.S.A. Therefore, trends such as increased deposition related to orographic increases in precipitation cannot be directly determined. In fact, high resolution modeling that combines NADP/NTN records with USGS annual snowpack surveys and precipitation models reveals that remote, high elevation sites have some of the highest levels of atmospheric nitrate deposition in the western U.S.A. (Nanus et al., 2003). According to these models, nitrate deposition in the Uinta Mountains ranges from 1 to 2.5 kg ha^{-1}yr^{-1} (Nanus et al., 2003), which exceeds estimates of preindustrial N (combined NH_4^+ and NO_3^-) deposition in temperate forests in the northern hemisphere (1.02 kg N ha^{-1}) (Holland et al., 1999) but is still dwarfed by the 12 – 20 kg ha^{-1}yr^{-1} of nitrate ion deposition in the Northeast/ Great Lakes regions of the U.S.A. (Figure 2.3a).



(a)

(b)

Figure 2.3. (a) Nitrate and (b) Ammonium ion wet deposition, 2011 (NADP/NTN, http://nadp.sws.uiuc/edu/NTN).

The location of the Uinta Mountains is shown with a star.

Nutrients can also be delivered to high alpine sites via atmospheric transport of dust. Atmospherically transported dust is an important component of lake sediments in Marshall Lake and Hidden Lake, in the Uinta Mountains (Reynolds et al., 2010). In these two lakes, phosphorus is enriched in the post-1950 sediments. Phosphorus in Marshall Lake sediments is elevated relative to Hidden Lake because Marshall Lake is located in the western Uinta Mountains, closer to the Wasatch Front (Reynolds et al., 2010). Dust samples collected in the Uinta Mountains provide further evidence that the likely sources of increased phosphorus in dust are from agricultural fertilizer and phosphate mining (Squire, 2012).

2.5 Historical land use and potential nutrient sources for Uinta Mountains lakes

As illustrated in Figure 1.1, several factors can influence nutrient concentrations in remote lakes. Therefore, it is important to have an understanding of past human activities in the Uinta Mountains and surrounding regions, especially those activities which can influence nutrient sources.

2.5.1 Settling and development of the Wasatch Front

The Wasatch Front is an urban area located east of the Uinta Mountains that stretches from Santaquin in the south to Brigham City in the north, and includes the major cities of Salt Lake City, Provo, and Ogden (Pope et al., 1999). The Wasatch Front is approximately 15-25 km wide and 130 km long, and is now home to approximately 80% of Utah’s residents (Figure 2.4).

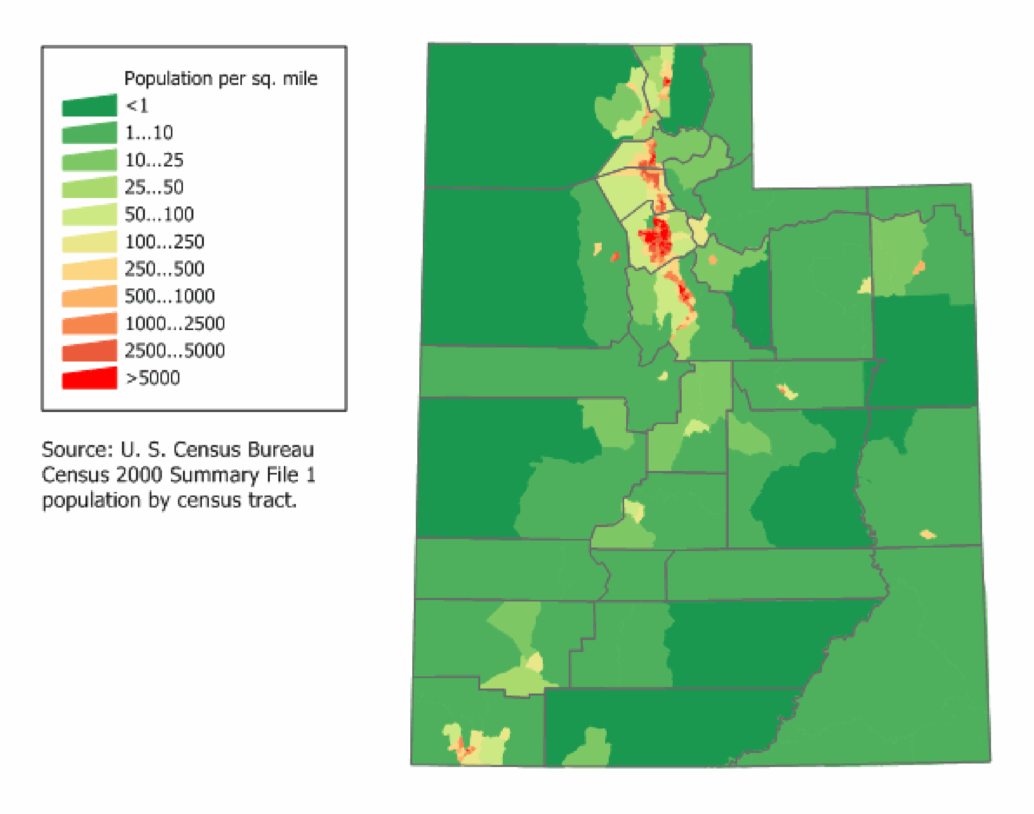


Figure 2.4. Population density in Utah by census tract.
The Wasatch Front is clearly shown as the high density (red and orange) population areas in North-central Utah. Source: U.S. Census Bureau Census 2000 Summary File 1.

The first non-native settlers to the Wasatch Front arrived in 1847[10]. At that time, the Ute Indians were the only inhabitants, and they primarily lived in eastern Utah (May, 1987). Shortly thereafter, agricultural operations were developed (Sillitoe, 1996; Mordecai, 2008). The first mines were developed in the area as early as 1863 (McPhee, 1977) and Kennecott Utah Copper's Bingham Canyon mine opened in 1865. Bingham Canyon Mine continued to expand and grew to produce more copper than any other mine globally since its inception (Kennecott Utah Copper, 2012).

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[10] Other than small numbers of trappers, the first non-native settlers in the Wasatch Front were several thousand followers of the Mormon leader, Joseph Smith.

Agriculture remains an important industry in the Wasatch Front today, although rapid urbanization in the 1940s resulted in the conversion of large areas of farmland into residential and industrial areas (Silletoe, 1996). The population of the Wasatch Front has increased from just over 800,000 in 1970 to 2,200,000 in 2010, an increase of 170 % (US Census Bureau). The population of the Wasatch Front is expected to increase further to 2.7 million residents in 2020 (Envision Utah, 2000), which will be accompanied by increases in automobile use and industrial activity.

2.5.2 Grazing in the Uinta Mountains

Although records are intermittent, sheep grazing was common practice in the Uinta Mountains by 1890. The Uinta Mountains became protected land with the establishment of the Wasatch National Forest in 1906 and the Ashley National Forest in 1908 (USDA Forest Service, http://www.fs.usda.gov/main/ashley/about-forest). Grazing in both the Dry Gulch and Whiterocks River allotments (which together encompass all six study lakes) is likely to have peaked in the 1920s or 1930s (United States Forest Service, 1947). During the post-WWII period, free-range grazing of sheep and cattle became increasingly better managed in the vicinity of the six study lakes, although many areas are still grazed by sheep and cattle. By the early 1990s the Whiterocks and Chepeta grazing allotments (near Denise and Taylor Lake) were closed to livestock grazing (United States Forest Service, 1947).

2.5.3 Fish stocking in the Uinta Mountains

The six Uinta Mountain study lakes have all been stocked with either cutthroat trout (*Oncorhynchus clarkii*) or brook trout (*Salvelinus fontinalis*) multiple times since 1979 (Utah Division of Wildlife Resources, 2012, http://www.utahfishinginfo.com/dwr/) (Figure 2.5). No Name and Bluebell Pass Lakes were stocked as long ago as 1958 (Rabe, 1968), and it is likely that the others were as well. In fact, Taylor Lake was reportedly named after the first person to stock the lake with fish (VanCott, 1990). Before 1956, lakes were stocked by horseback (Hallows, 2009), making it less likely that these remote lakes were stocked (Utah Division of Wildlife Resources, 2012). It is unlikely that the six lakes had natural fish populations (Bahls, 1992), which is corroborated by fish sampling surveys from 1978 at East Carrol, Upper Carrol, No Name, and Bluebell Pass lakes. These reports indicate that there were no natural fish populations and that stocked fish were not reproducing[11] (D.W.R. stocking reports, unpubl.).

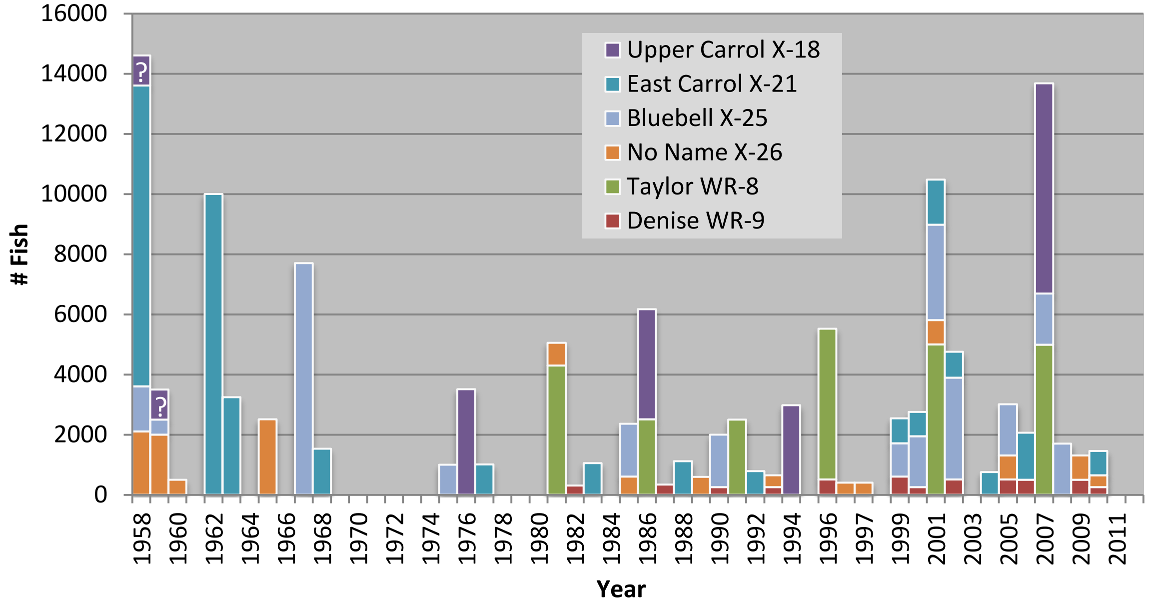

Figure 2.5. Numbers of fish stocked at the six study lakes.

Stocked fish types include brook trout, cutthroat trout and rainbow trout. Bars with question marks indicate that stocking took place at that lake but that the quantity of fish added during that year is unknown. Records are more difficult to obtain before 1980, and so years without data do not necessarily mean that no fish were stocked in the early parts of the record.

2.5.4 Climate Change in the Uinta Mountains

In October 2013, the Intergovernmental Panel on Climate change (IPCC) declared that “Warming of the climate system is unequivocal, and since the 1950s, many of the observed changes are unprecedented over decades to millennia” (IPCC, 2013, p. 2). The increase in radiative forcing is largely caused by increased CO_2 concentrations and “It is extremely likely that human influence has been the dominant cause of the observed warming since the mid-20th century” (IPCC, 2013, p. 13). The western U.S.A.

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[11] All captured fish in these reports had stunted growth and cohorts matched known stocking years.

experienced statistically significant warming during the 20th century (IPCC, 2007), and Utah is warming faster than the national and world average (Saunders et al., 2008).

Climate stations from the Eastern and Western foothills (Vernal and Heber, respectively, Figure 2.1) provide the closest approximation of general climate trends over time in the Uinta Mountains. There are some high elevation climate stations in closer proximity to the study lakes; however these records are at maximum 60 years long and are missing up to 47% of the daily temperature readings, largely due to the difficult of maintaining and reaching sites in the winter. The temperature trends and average temperatures at Heber and Vernal are similar, but the Vernal record has many missing values (Figure 2.6). At the Heber climate station, temperatures fluctuated until around the 1980s when the mean annual temperature begins to increase steadily. This is typical timing for recent climate warming when compared to the regional trend in Utah (Figure 2.7) and the western U.S.A. (Saunders et al., 2008).

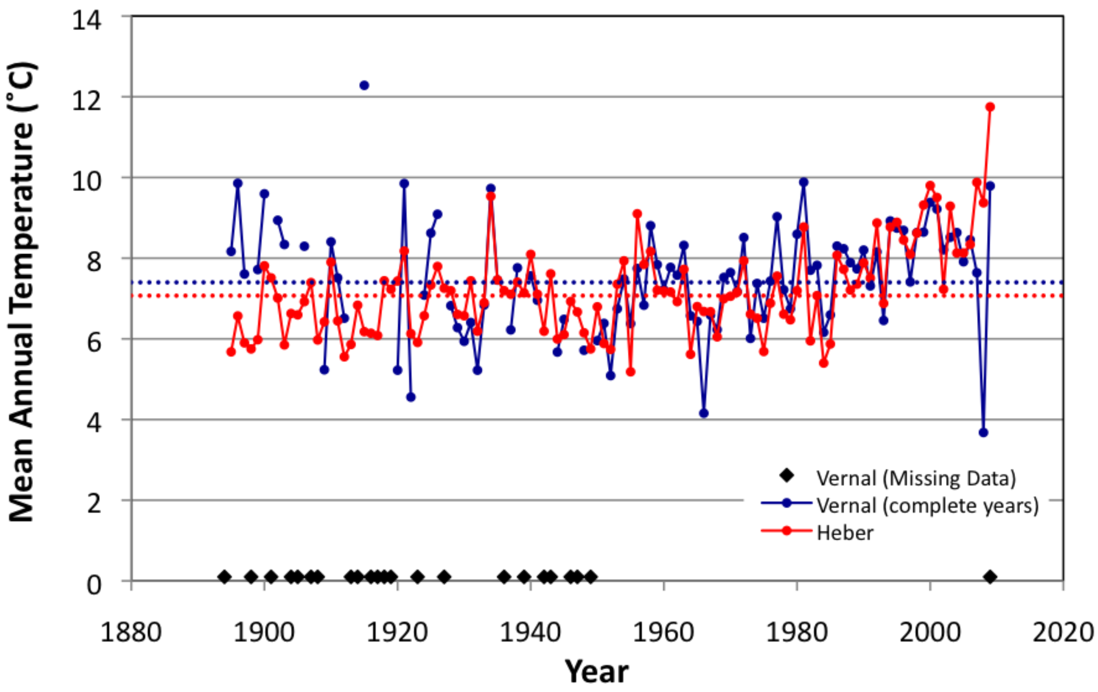

Figure 2.6. Comparison of temperature records from Heber and Vernal, Utah
The dotted red and blue lines mark the 1900-2000 average temperatures for Heber and Vernal, respectively. Years at the Vernal climate station with at least one month missing are shown as black diamonds along the x axis (Western Regional Climate Center, 2009).

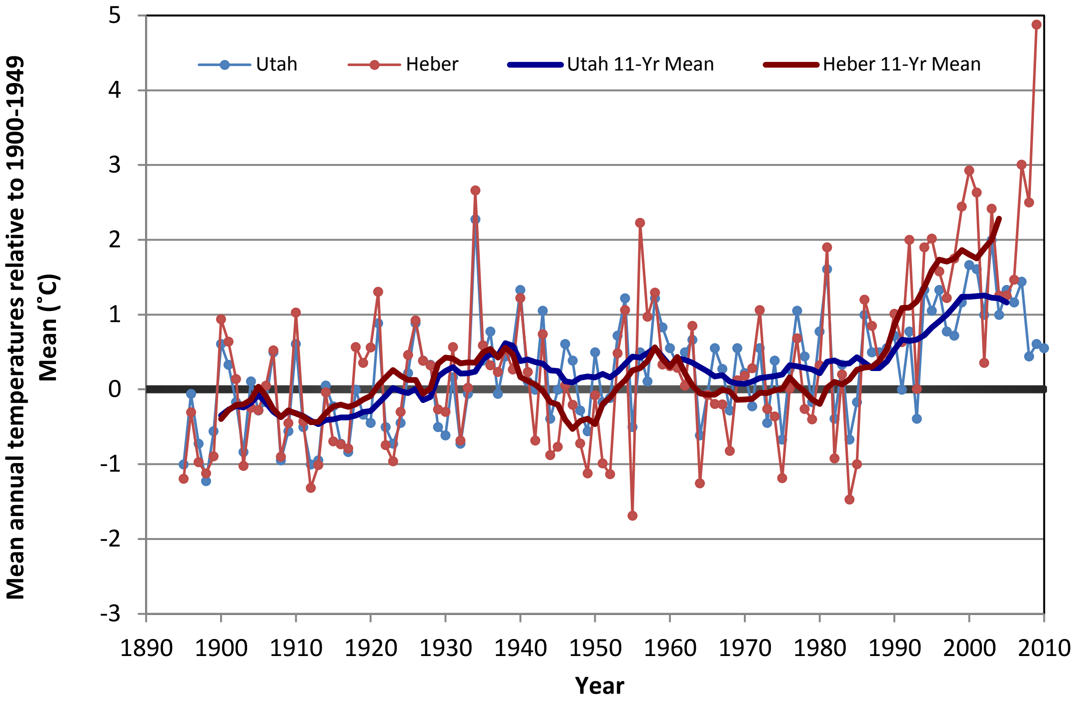

Figure 2.7. Temperature anomalies (relative to 1900 - 1949 mean) for Heber and Utah (Western Regional Climate Center, 2009).

2.6 Site selection and lake characteristics

The six lakes selected for coring (Figure 2.1B, Table 2.1) were chosen from a 57-lake calibration set within the Uinta Mountains (Figure 2.1B). High elevation (>3000 m.a.s.l.) lakes were selected for coring to ensure that climatic differences associated with altitude (e.g., increased precipitation and associated wet deposition) were minimal. Lakes were also selected to capture variation in catchment characteristics (e.g., lake depth, catchment size, percent vegetation cover, through-flow, etc.) to allow for investigation of differences in lake response.

Table 2.1. Summary characteristics of the six Uinta Mountain study lakes.

A_L = lake area, A_C = catchment area.

Lake Name	Site Code	Latitude (°N)	Longitude (°W)	Elevation (m.a.s.l)	Lake Depth (m)	Secchi Depth (m)	A_L (ha)	A_C (ha)	Sediment Core Length (cm)
Denise	UN-07	40.77	110.09	3399	2.4	>2.4	1.1	391.9	52
Taylor	UN-08	40.79	110.09	3414	9.7	5.4	9.0	349.9	32
Upper Carrol	UN-55	40.72	110.35	3395	13.8	3.9	11.6	316.1	31
East Carrol	UN-56	40.72	110.35	3423	5.3	3.5	3.4	35.1	31
No Name	UN-57	40.71	110.38	3355	5.2	>5.2	2.6	83.6	42
Bluebell Pass	UN-58	40.70	110.39	3342	7.7	2.0	3.3	174.5	26

All six lakes are oligotrophic or oligotrophic-mesotrophic (low to medium-low nutrient richness) (Table 2.1) and vary in depth from 2.4 m at Denise Lake to 13.8 m at Upper Carrol Lake. The three deepest lakes (Taylor, Upper Carrol, and Bluebell Pass Lakes) thermally stratify and have reduced oxygen in the hypolimnion (Figure 2.8). The three shallow lakes (Denise Lake, East Carrol Lake, and No Name Lake were not thermally stratified (Figure 2.8).

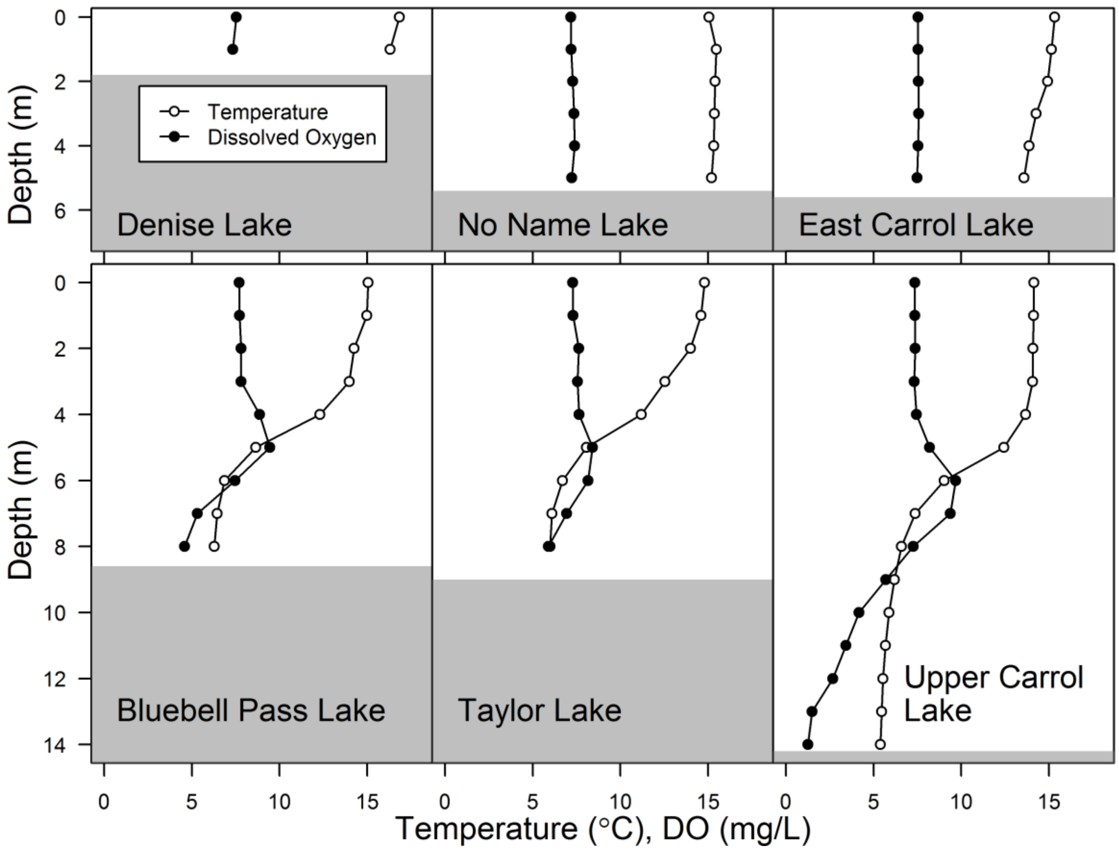

Figure 2.8. Lake water profiles of temperature and dissolved oxygen at the six main study lakes. Profiles were taken at maximum depth (which is reached at the gray box). Measurements obtained in July 2008.

The land surface cover in all six lake catchments are dominated by talus slopes, exposed bedrock and snow (56 to 81 %) (Figure 2.9). Vegetation types within the catchments are varied, but are grouped in two main categories: alpine tundra + meadow, and forest + shrubland (Figure 2.9).

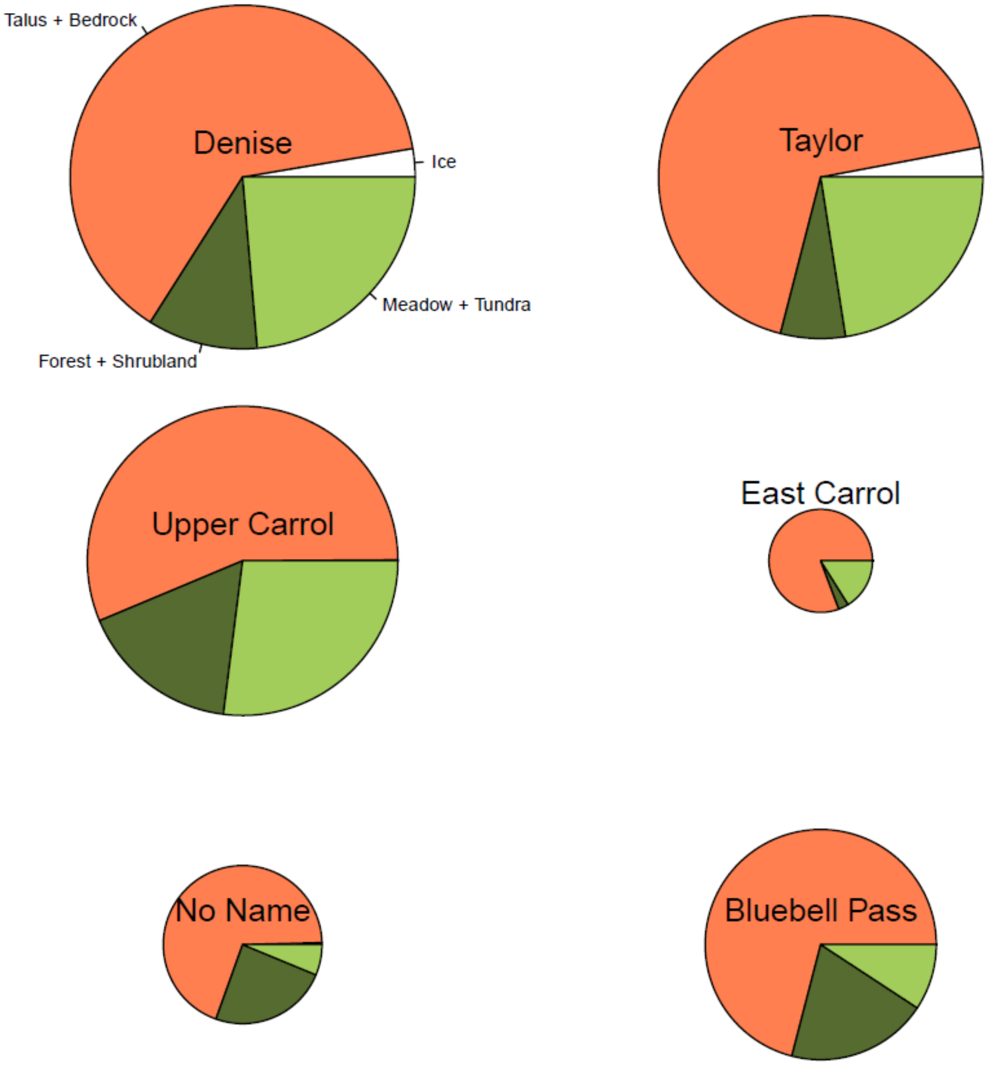

Figure 2.9. Percentage landcover in the six study lakes.

The area of each pie is proportional to the catchment area.

Taylor Lake (Figure 2.10A) and Denise Lake (Figure 2.10C) are located less than 0.5 km apart (Figure 2.10E). Both are headwater lakes in the West Fork of the White Rocks River drainage basin. Several inflows run from snow and through the talus slopes interspersed with meadow and shrub vegetation to Taylor Lake. Denise Lake is slightly lower in elevation than Taylor Lake, and the catchment of Denise Lake includes that of Taylor Lake, which explains the similarity in landcover percentage between the two sites (see Figure 2.9).

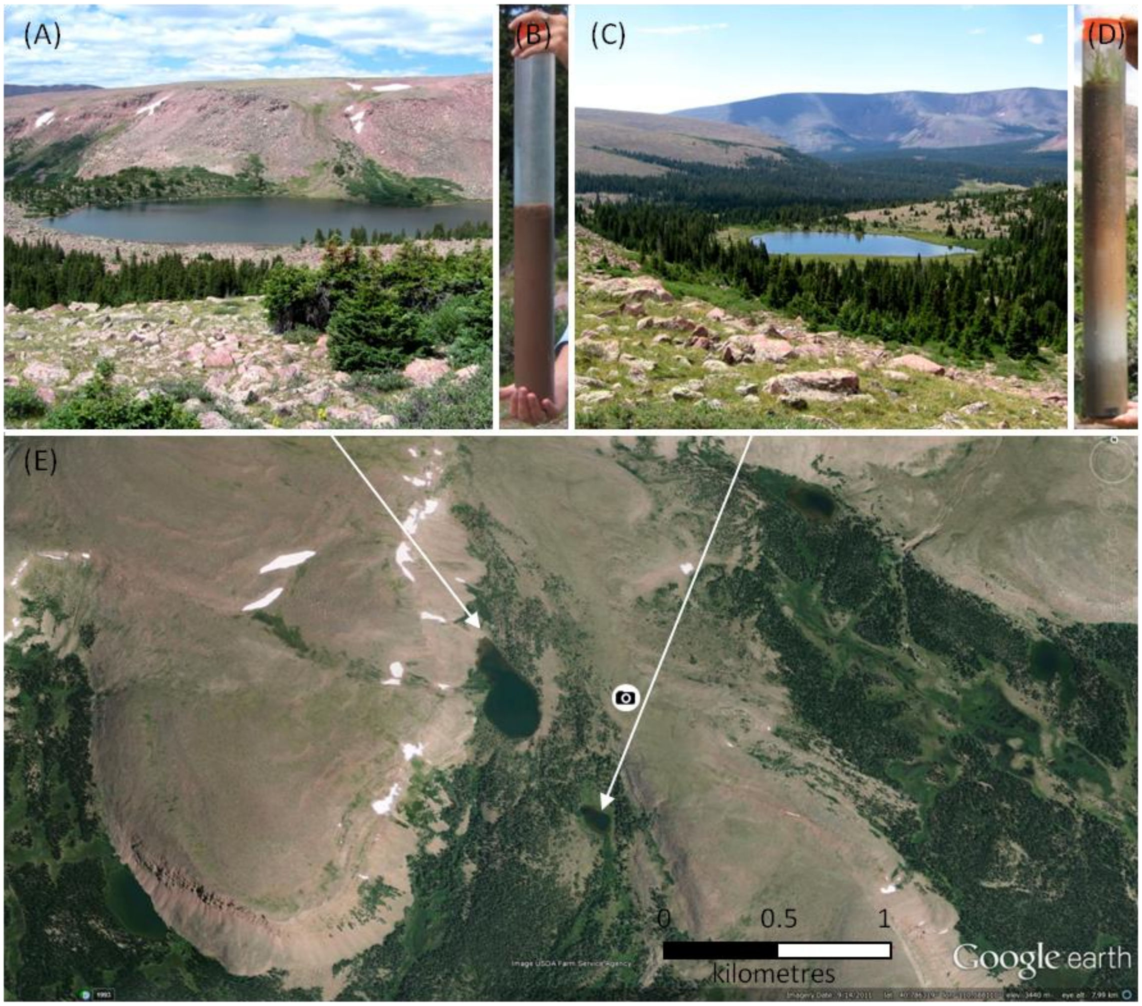

Figure 2.10. Taylor and Denise Lakes. (A) Taylor Lake. (B) The 32 cm sediment core from Taylor Lake. (C) Denise Lake. (D) The 52 cm sediment core from Denise Lake. (E) The locations of Taylor and Denise Lake from Google Earth version 7.1.2.2041.
The camera icon shows the vantage point for photos (A) and (C).

Upper Carrol Lake (Figure 2.11A) and East Carrol Lake (Figure 2.11C) are located roughly 0.5 km apart (Figure 2.11E). Both are headwater lakes of the Swift Creek drainage basin (above the Timothy Lakes). Upper Carrol Lake is the largest of the six study lakes in terms of both area and depth and has permanent inflows through meadow and shrub-like vegetation. East Carrol Lake has a small, talus-dominated catchment (Figure 2.9) with an intermittent inflow and an outflow.

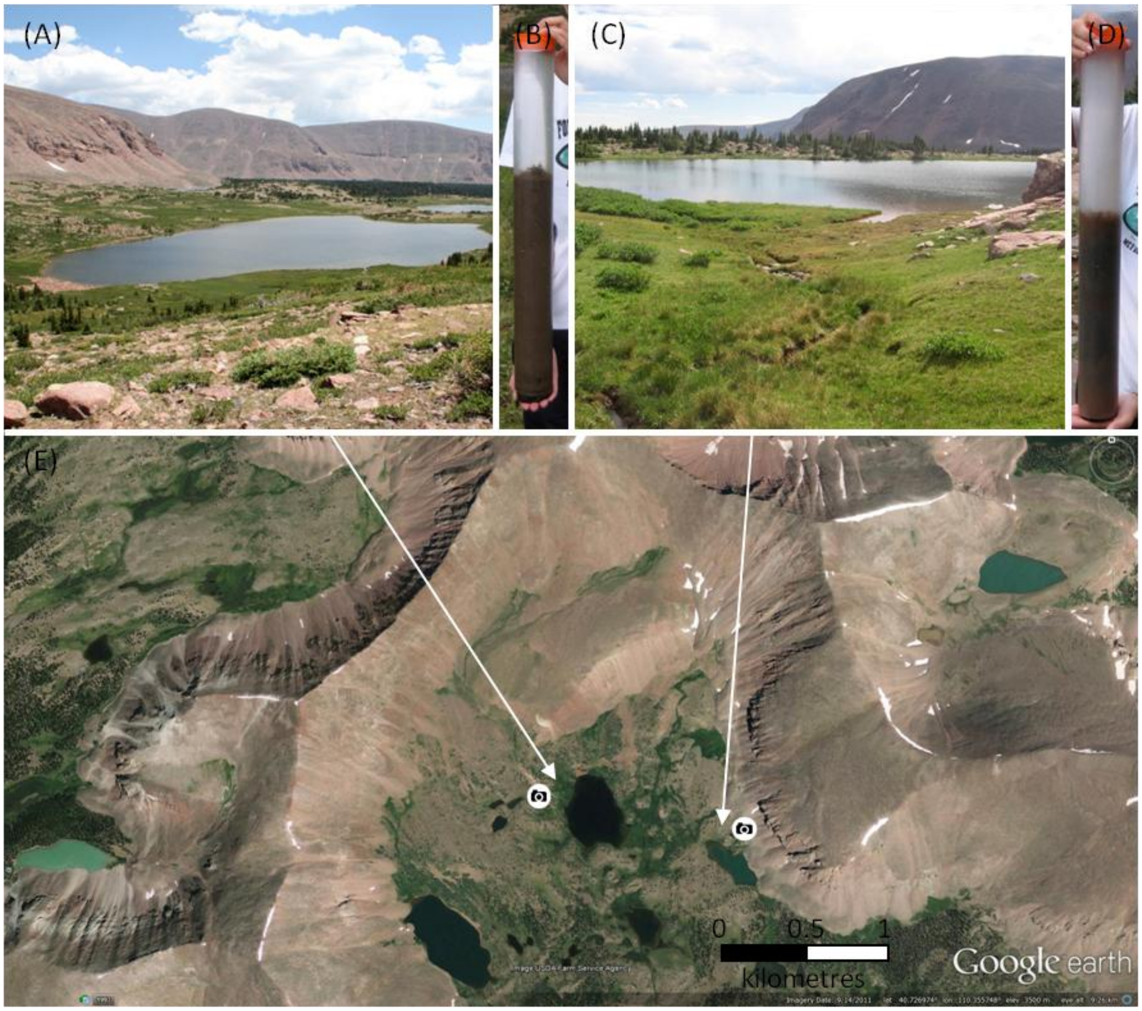

Figure 2.11. Upper Carrol and East Carrol Lakes. (A) Upper Carrol Lake. (B) The 31 cm lake sediment core from Upper Carrol Lake. (C) East Carrol Lake. (D) The 31 cm sediment core from East Carrol Lake. (E) The locations of Upper Carrol and East Carrol Lake from Google Earth version 7.1.2.2041.

The camera icons show the vantage points for photos (A) and (C).

Bluebell Pass Lake (Figure 2.12A) and No Name Lakes (Figure 2.12C) are located less than 0.5 km apart (Figure 2.12E). Both are headwaters in the west branch of the Swift Creek drainage basin (above Farmer’s Lake). Bluebell Pass Lake is fed from steep talus slopes on its west and north sides and surrounded by forest and shrub vegetation on its south, east, and northeast sides. No Name Lake is a small, closed basin lake. A lighter band at ca. 5 cm in the No Name lake sediment core (visible in Figure 2.12D) is thought to correspond with a landslide event.

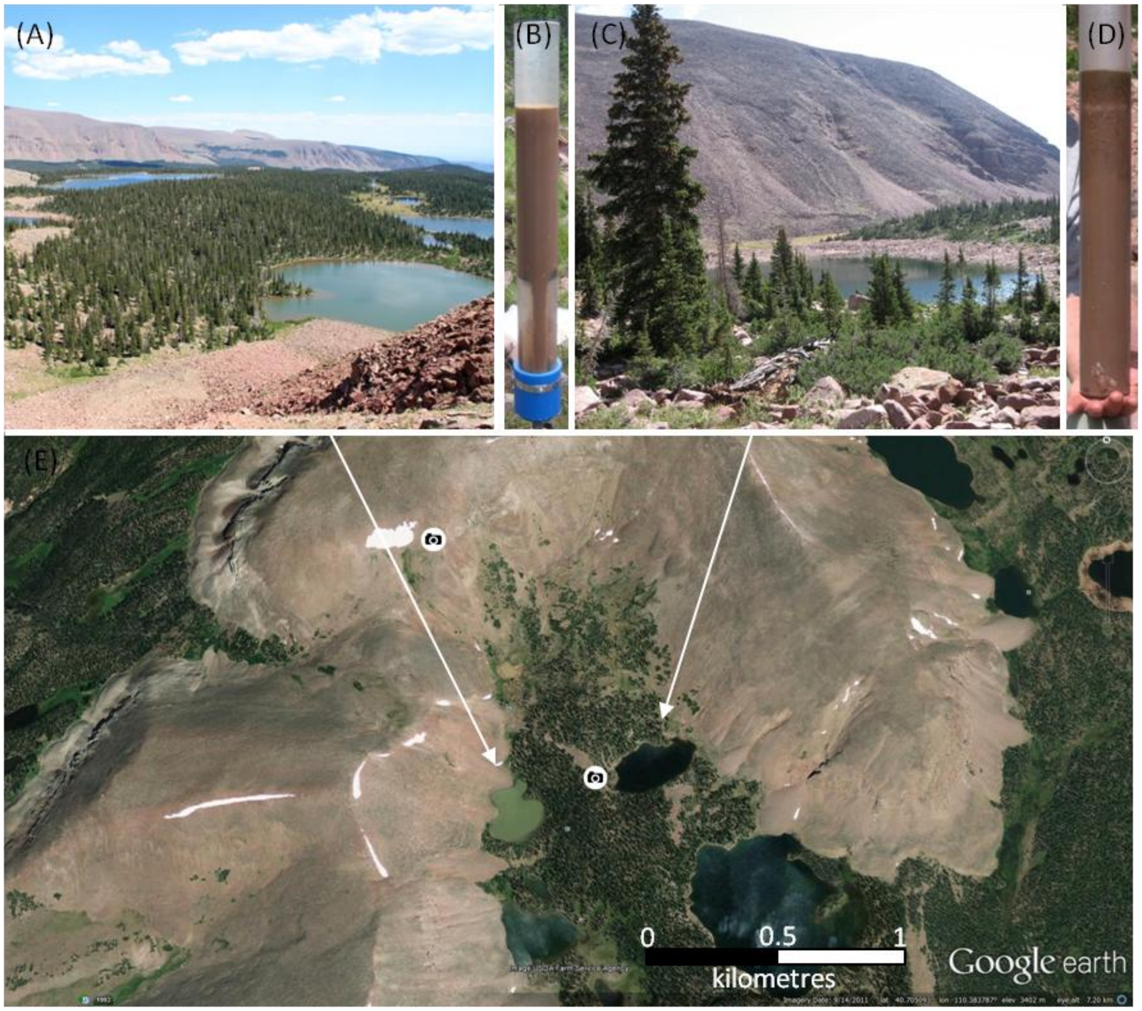

Figure 2.12. Bluebell Pass and No Name Lakes. (A) Bluebell Pass Lake (lower right). (B) The 26 cm lake sediment core from Bluebell Pass Lake. (C) No Name Lake. (D) The 42 cm sediment core from No Name Lake. Note the light band at ~ 5 cm, most likely from a rock slide event. (E) The locations of Bluebell Pass Lake and No Name Lake from Google Earth version 7.1.2.2041.
The camera icons show the vantage points for photos (A) and (C).

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Chapter 3

3 Recent changes in primary production in oligotrophic Uinta Mountain lakes, Utah, U.S.A., identified using paleolimnology

3.1 Introduction

In this study, we investigate the potential drivers of changing primary production since the 19th century in alpine lakes in the Uinta Mountains, Utah, U.S.A. (Figure 3.1). Because phosphorus (P) and nitrogen (N) are the elements that most often limit freshwater production, changes in inputs of N or P can alter ecosystem processes, reduce biodiversity, and lead to surface water eutrophication (Vitousek et al., 1997; Schindler, 2006). Although few symptoms of eutrophication have been reported for Uinta Mountain lakes, the rapid industrial, agricultural and urban expansion occurring upwind of the Uinta Mountains along the Wasatch Front may place Uinta Mountain lakes at risk of enhanced deposition of fixed nitrogen species (NO_3^- and NH_4^+) and phosphorus.

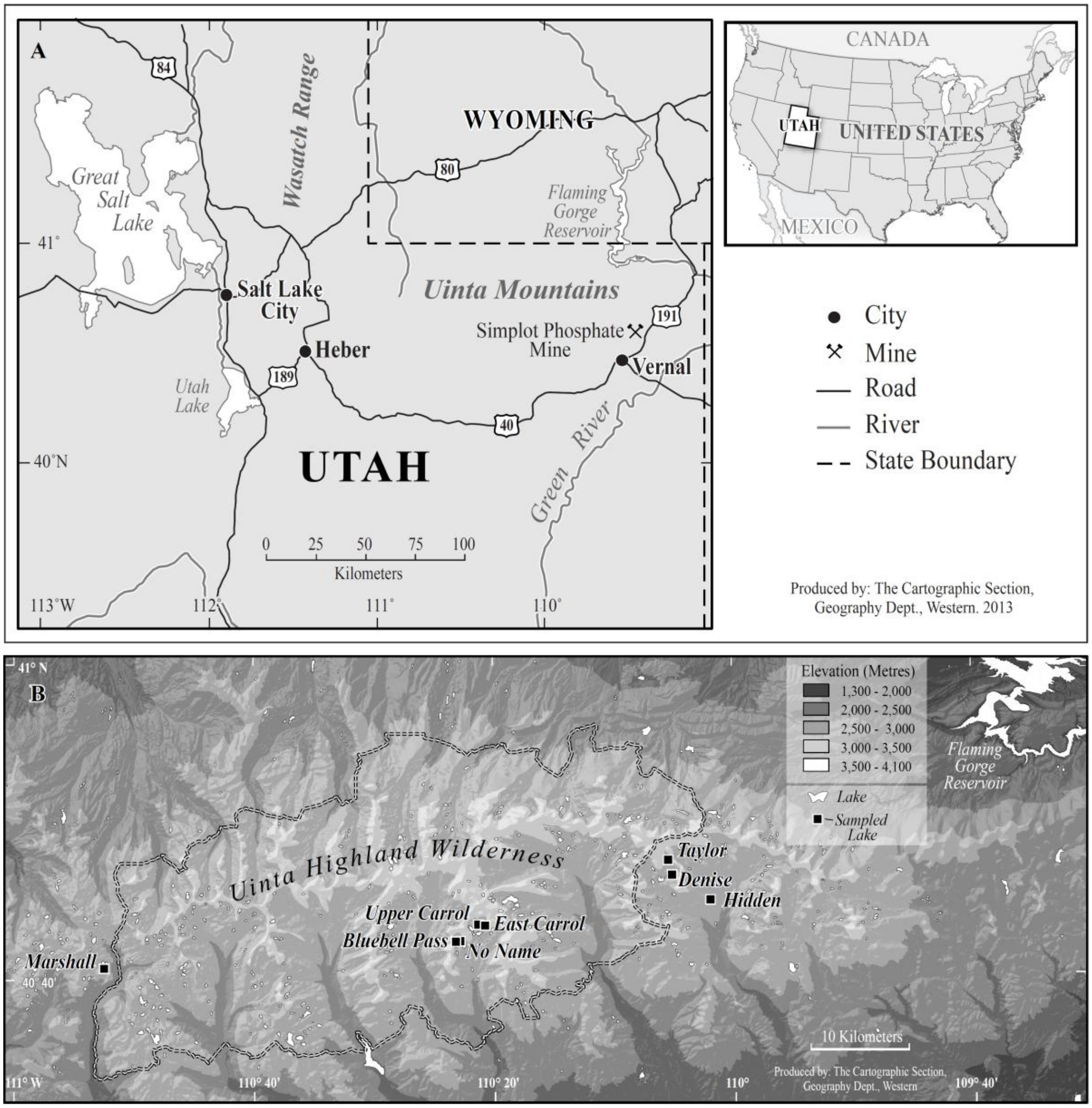

Figure 3.1. Map of Northeastern Utah showing (A) the location of the Uinta Mountains in Utah and U.S.A., and (B) the topography of the Uinta Mountains with the locations of the six study lakes, and Hidden and Marshall Lakes.

In the last century, humans have drastically increased the amount of biologically available N (NO_3^- and NH_4^+) on a global scale, largely via synthetic fertilizer use, fossil fuel burning, intensive animal husbandry, and the cultivation of leguminous crops (Vitousek et al., 1997). Records maintained by the National Atmospheric Deposition Program National Trends Network (NADP/NTN) (http://nadp.sws.uiuc.edu/ntn/) for the U.S.A. show that on a national scale, areas with the greatest wet deposition of NO_3^- and

NH_4^+ generally coincide with areas of high population density and intensive agriculture. In these areas, runoff from fields and urban areas, sewage, and industrial effluent tend to be much greater sources of N to aquatic systems than atmospheric deposition. In contrast, at remote alpine sites, atmospherically derived N makes up a larger proportion of anthropogenic N inputs, as many of the other sources are absent (Lepori and Keck, 2012). High resolution modeling of N deposition that combines NADP/NTN records with USGS annual snowpack surveys and precipitation models reveals that remote, high elevation sites have some of the highest levels of atmospheric nitrate deposition in the Western U.S.A. (Nanus et al., 2003). Elevated atmospheric nitrogen deposition resulting from N volatilized from farmers' fields and feedlots, or from fossil fuel combustion has been linked to subtle ecological changes in alpine lakes in the Colorado Front Range (Baron et al., 2000; Wolfe et al., 2001) and in the Beartooth Range of Wyoming (Saros et al., 2003). On a wider scale, Holtgrieve et al. (2011) suggest that low δ^{15}N values in lake sediments from many remote alpine, arctic, boreal, and temperate sites in the Northern Hemisphere indicate elevated N-deposition resulting from anthropogenic activities.

Although it is evident that δ^{15}N values of lake sediments are decreasing in a variety of remote aquatic systems (Holtgrieve et al., 2011), there are still uncertainties regarding the influence of factors other than enhanced atmospheric N deposition on primary production in dilute alpine systems (Figure 1.1). For example, P has been given relatively little attention in these environments, even though atmospheric deposition can contribute substantial amounts to an alpine lake (Psenner, 1999). Recent increases in P loading to Emerald Lake, Sierra Nevada Mountains, California, have been attributed to organophosphate pesticide deposition or aeolian transport of dust from the San Joaquin Valley (Sickman et al., 2003). Climate warming, local grazing, and fish stocking, can influence primary production and result in changes in δ^{15}N; diagenesis of organic matter can also mimic some of the geochemical changes expected with increasing primary production.

Alpine environments have several characteristics that make them sensitive to changes in nutrient inputs (Figure 1.1). First, some alpine environments are subject to greater atmospheric deposition than low lying areas at similar latitudes because of orographic precipitation, higher wind speeds, and increased cloud presence (Lovett, 1994). Second, snowmelt-dominated hydrology, combined with low biological N demand in spring, leads to seasonal spikes in surface water NO_3^- and NH_4^+ concentrations (Campbell et al., 2000). Third, short growing seasons, minimal vegetation, and steep slopes limit N retention in the terrestrial environment (Campbell et al., 2000). Finally, talus slopes are potential sites of microbial nitrification and can therefore increase the amount of biologically active N that enters water bodies (Williams et al., 1997).

The Uinta Mountains have no NADP/NTN sites, limited lake water monitoring records, and only short-term snow water chemistry records (< 5 years). Therefore, we collected and analyzed lake sediment cores from six high elevation Uinta lakes. These cores contain several proxies that were used to explore and evaluate potential causes of recent primary production changes in these alpine environments. The percentage of organic matter (determined by loss-on-ignition) along with chlorophyll *a*, a photosynthetic pigment produced by all plants and algae, can be useful indicators of primary production. Stable isotopic ratios of organic matter nitrogen ($^{15}N/^{14}N$) provide evidence for changing N sources and cycling, and are useful for comparison with previous research. Stable isotopic ratios of organic matter carbon ($^{13}C/^{12}C$) can contribute to our understanding of changes in primary production. Carbon: nitrogen ratios (C:N) are used to evaluate the relative proportions of algal versus terrestrial organic matter contributions to the lake (Meyers and Ishiwatari, 1993). Diatoms are expected to be among the first organisms to respond to greater N availability due to their sensitivity to changing nutrients (Wolfe et al., 2001). *Asterionella formosa* in particular responds to enhanced N in alpine environments (Saros et al., 2005).

This research will show that Uinta Mountain lakes have experienced recent increases in aquatic primary production, as indicated by increases in the percentage of organic matter and chlorophyll *a* concentrations, combined with decreasing C:N ratios. The timing of these changes coincides with agricultural intensification and industrial expansion in the region of the Wasatch Front around 1950 A.D.

3.2 Study Area

The Uinta Mountains are an east-west trending mountain range that reaches elevations over 4000 m, and stretches 200 km across the northeastern part of Utah (40˚ to 41˚ N, 109˚ to 111˚ W) in to northwestern Colorado (Figure 3.1). The mountain range contains hundreds of lakes and has experienced little direct human impact, making it ideal for investigating nutrient inputs and lake response. The geology is primarily quartzite, sandstone, and shale. Model results combining NADP/NTN and snow chemistry data indicate that the highest elevations of the Uinta Mountains received 2-3 kg ha^{-1} inorganic N annually, and exceed critical loads of N deposition by 1-3 kg N ha^{-1} annually (Nanus et al., 2012). Inorganic N deposition in the Uinta Mountains is higher than most low-lying areas of the western U.S.A., but similar to other high elevation regions such as the Colorado Front Range, which receives 2-4 kg ha^{-1} inorganic N annually (Nanus et al., 2012).

Six high elevation (> 3000 m.a.s.l.) lakes were selected for this study in order to detect variability in lake responses and control for altitudinal-related variables such as differences in temperature and precipitation. The lakes, with Utah Department of Wildlife Resources codes in parentheses, are: Denise (WR-9), Taylor (WR-8), Upper Carrol (X-18), East Carrol (X-21), No Name (X-26), and Bluebell Pass (X-25) (Table 3.1).

Table 3.1. Summary characteristics of the six study lakes.

Secchi depths are averages of single measurements taken in 2007 and 2008. Trophic status was determined by comparison of Secchi depth, TP, TN, and chlorophyll *a* concentrations to those listed in Table 13-18 of Wetzel (2001).

Lake Name	Latitude (˚N)	Longitude (˚W)	Elevation (m.a.s.l)	Lake Depth (m)	Stratifies	Secchi Depth (m)	Trophic Status
Denise	40.77	110.09	3399	2.4	No	>2.4	Oligo
Taylor	40.79	110.09	3414	9.7	Yes	3.4	Oligo/ meso
Upper Carrol	40.72	110.35	3395	13.8	Yes	4.7	Oligo/ meso
East Carrol	40.72	110.35	3423	5.5	No	3.3	Oligo/ meso
No Name	40.71	110.38	3355	5.4	No	>5.4	Oligo
Bluebell Pass	40.70	110.39	3342	7.7	Yes	2.1	Oligo/ meso

3.3 Methods

3.3.1 Water Chemistry

Water samples were obtained from each lake in late July and early August of 2007 – 2010. Water samples were collected in pre-cleaned polyethylene Nalgene® bottles from the deepest part of the lake, 0.5 m below the surface and were kept cool in the field (~1-3 days) until they were returned to the Forest Service in Vernal, Utah. The water samples were used for chemical analysis (nitrite + nitrate, nitrites, ammonium, phosphate, total phosphorus, and total nitrogen) and filtered for chlorophyll *a*. The samples were frozen immediately after filtering and sent to Chesapeake Biological Laboratory in Maryland, U.S.A. for analyses. The Chesapeake Biological Laboratory protocols are available from http://nasl.cbl.umces.edu/.

3.3.2 Temperature record selection

There are high elevation climate stations in close proximity to the study lakes. However, these records are at maximum 60 years long and are missing up to 47% of the daily temperature readings, largely because of the difficulty of reaching the sites in winter. Vernal, Utah, is the closest record (up to 74 km from the six lakes) of at least a century in duration, but is missing 20% of the daily data. Heber, Utah (Figure 3.1) is located up to 117 km from the six lakes, has a near complete (99.5%) 117-year record, has similar trends to Vernal (Western Regional Climate Center, http://www.wrcc.dri.edu/), and thus was selected for comparison to the lake sediment profiles.

3.3.3 Sediment Coring

Lake sediment cores between 25 and 50 cm in length with an undisturbed sediment-water interface were obtained from the deepest part of each lake during the summers of 2006 (Taylor and Denise lakes) and 2007 (East Carrol, Upper Carrol, No Name, and Bluebell Pass lakes). The cores were obtained from an inflatable boat using a Kajak-Brinkman gravity corer fitted with a plastic coring tube of 6.5 cm diameter. Lake sediments were extruded on site using a specially designed extruder (Glew et al., 2001) and were sub-sampled at 0.5 cm contiguous intervals, except at greater than 20 cm depth in Taylor and Denise lakes, which were sub-sampled at one cm intervals. The sub-samples were stored in Whirlpak bags in dark conditions at 4˚C at the Lakes and Reservoir Systems Research Facility at the University of Western Ontario, London, Ontario, Canada.

3.3.4 Chronology

Lake sediments were dated using ^{210}Pb (half-life = 22.26 years) techniques (Appleby, 2001) on 15 dried and ground samples per lake from between 0 and 22 cm core depth. Samples were initially analyzed using α-spectrometric measurements of ^{210}Po, a decay product of ^{210}Pb, at MyCore Scientific Inc. in Deep River, Canada (Cornett et al., 1984). The ^{210}Pb ages were calculated using the constant rate of supply (CRS) model, in which lake sediments are assumed to be receiving a constant input of unsupported ^{210}Pb from the atmosphere (Appleby, 2001). The background (supported ^{210}Pb) was determined as the average of the constant ^{210}Pb concentrations in the three to five deepest sections of the core. The errors on the dates in the oldest sediments were large (27 to 418 years; Figure 3.2), so to verify these dates, γ-spectrometry was used for two lakes (Taylor and East Carrol). This method allows for a more accurate determination of background ^{210}Pb in this type of lake (Appleby, 2001), and for simultaneous analysis of ^{137}Cs, an artificial radioisotope produced by nuclear weapons testing, which peaked in 1963. The γ-spectrometry measurements were made at the Paleoecological Environmental Assessment and Research Laboratory (PEARL) at Queen's University, Canada. Dates were calculated following procedures described in Binford (1990) using the "Binford" package (Jeziorski and Thienpont, 2010) for the R software environment (R Development Core Team, 2011).

3.3.5 Production Measures

Loss-on-ignition (LOI) was performed on each of the six lake sediment cores following the methods in Dean (1974). Briefly, 1 cm^3 of sample was dried, weighed, and then heated in a Lindberg/ Blue M Box Furnace for one hour at 550˚C to combust organic matter. For each sample, the difference in dry weight before and after combustion was used to calculate the percentage of organic matter.

Sedimentary chlorophyll *a* concentrations were inferred using visible reflectance spectroscopy (VRS) at PEARL. This technique takes advantage of the spectral signal of preserved chlorophyll *a* and its diagenetic products in lake sediments as detailed in Michelutti et al. (2005) and Wolfe et al. (2006). Briefly, sediments were freeze-dried and sieved to only retain material <125 µm, thus preventing water content and grain size from affecting the spectral signal. Sediment reflectance spectra were measured between 400 and 1100 nm at 2 nm intervals using a Model 6500 series Rapid Content Analyzer (FOSS NIRSystems Inc.), which provides the output of percent absorbance as an average of 32 scans. Chlorophyll *a* has a distinct absorption peak between 650 and 700 nm wavelength. The area under this curve is strongly linearly correlated with the concentration of chlorophyll *a* plus its isomers and its major derivatives, pheophytin *a* and pheophorbide *a* (Michelutti et al., 2005). Hereafter, chlorophyll *a* refers to this group of pigments plus its derivatives. Chlorophyll *a* flux rates were calculated on the dated portions of the cores to take into account the influence of sedimentation rate on chlorophyll *a* concentrations.

3.3.6 Sediment geochemistry

Prior to isotopic analysis, powder X-ray Diffraction (pXRD) was used to test for the presence of carbonate in the samples. No carbonates were present in the sediment samples, thus ensuring that only organic carbon contributed to the measured $^{13}C/^{12}C$ ratio. Stable isotope results are reported using δ notation,

$$\delta_P = \frac{(R_P - R_{std})}{R_{std}}$$

where R is the $^{15}N/^{14}N$ or $^{13}C/^{12}C$ ratio of the sample (*P*) and standard (*std*), respectively, for $\delta^{15}N$ and $\delta^{13}C$. Measured $\delta^{13}C$ values dated from 1700 AD and after were corrected for the Suess effect[12], following the polynomial correction factor described by Verburg (2007). Samples were freeze-dried and homogenized with a mortar and pestle to a consistent (<125 µm) grain size. The stable isotopic compositions of nitrogen and carbon were analyzed using a Costech Elemental Combustion System connected to a Thermo Finnigan Delta^{PLUS} XL mass spectrometer. Sample δ^{13}C and δ^{15}N values were calibrated to VPDB and AIR, respectively, using USGS40 (accepted values: δ^{13}C = –26.39 ‰, δ^{15}N = –4.52 ‰) and USGS41 (accepted values: δ^{13}C = +37.63 ‰, δ^{15}N = +47.6 ‰). In addition, internal (keratin) and international (IAEA-N-2) standard reference materials were analyzed to monitor analytical precision and accuracy. A δ^{13}C value of –23.99 ± 0.08 ‰ was obtained for 10 analyses of the internal keratin standard, which compares well with its average value of –24.04 ‰. Sample reproducibility was ± 0.09 ‰ for δ^{13}C (SD, n=5). A δ^{15}N value of 6.29 ± 0.13 ‰ (SD, n=11) was obtained for an internal keratin standard, which compares well with its average value of +6.36 ‰. A δ^{15}N value of +20.44 ± 0.01 ‰ (n=2) was obtained IAEA-N-2, which compared well with its accepted value of +20.3 ‰. Sample reproducibility was ± 0.04 ‰ for δ^{15}N (SD, n=5).

Organic carbon and total nitrogen contents were determined using a Fisons 1108 elemental analyzer. These results were used to calculate atomic C:N ratios. Sample reproducibility was ± 0.33 for % C (SD, n=9) and ± 0.02 for % N (SD, n=9). The pXRD, δ^{13}C, δ^{15}N, % C, and % N analyses were carried out at the Laboratory for Stable Isotope Science at The University of Western Ontario, Canada.

3.3.7 Diatoms

Samples were prepared for diatom analysis using the method described by Battarbee et al. (2001). Approximately one cm^3 subsamples were treated with 10 % hydrochloric acid to eliminate any calcium carbonate, followed by a 50:50 molar weight solution of nitric and sulfuric acid to digest organic matter. After 24 hours the samples were heated to 80˚C for two hours. Treated subsamples were rinsed a minimum of 10 times (at least

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[12] The Suess effect is the decrease in atmospheric δ^{13}C resulting from the release of CO_2 with low ^{13}C content by fossil fuel burning and deforestation (Keeling, 1979).

24 hours between washes) with distilled water until neutrality was reached, and then mounted onto slides using Naphrax® or Z-rax®. For each sample a minimum of 500 diatom valves were identified and counted using a Leica E-600 light microscope outfitted with differential interference contrast optics and 100× magnification. A Retiga® 2000 Fast 1394 digital camera was used to facilitate identification.

3.4 Results

3.4.1 Water chemistry

The six study lakes are oligotrophic or on the cusp between oligotrophic and mesotrophic (Table 3.1), as determined by TP, TN, chlorophyll *a*, and Secchi depth values. The limiting nutrient for each lake is difficult to discern regardless of method used (Table 3.2). Downing and McCauley (1992) suggest that N-limitation is more common in lakes with TN:TP <14 (mass ratio), whereas lakes with TN:TP >17 (mass ratio) tend to be P-limited (Sakamoto, 1966). Using water chemistry data from lakes and oceans, Guildford and Hecky (2000) found that N-deficiency is likely at TN:TP < 20 (molar) and P-deficiency at TN:TP > 50 (molar). Because TN can contain a large proportion of biologically unavailable N (e.g., 34-97% at the six study lakes), Bergstrom (2010) suggests that the TN:TP ratio may not be a realistic indicator of limiting nutrients, and that the DIN:TP ratio is a better predictor of limiting nutrient conditions in oligotrophic lakes. DIN:TP < 1.5 is likely to be N-limited whereas and DIN:TP > 3.4 is likely to be P-limited (Bergstrom, 2010). Based on our data, some lakes are N-limited and some are P-limited; others lie between the thresholds for N- and P-limitation (Table 3.2). These results also show that there is likely temporal variation in nutrient limitation. For example, the DIN:TP ratio indicates that Taylor Lake is P-limited in summer 2011, uncertain or shifting between N- and P-limitation in fall 2011, and N-limited in spring 2012 (Table 3.2).

Table 3.2. Summary of nutrient measurements of study lake water samples and N:P relationships. The shading represents three separate characterizations of limiting nutrients. Black shading represents N limitation, dark gray shading represents shifting or uncertain limitation, and light gray represents phosphorus limitation. Limitation thresholds are taken from *Bergstrom (Bergstrom, 2010), and **Downing and McCauley (1992) and Sakamoto (1966), and ***Guildford and Hecky (2000).

Lake	Month/ year	DIN (µg/L)	TN (µg/L)	TP (µg/L)	DIN/TP mass ratio*	TN/TP mass ratio**	TN/TP atomic ratio***	Chl *a*
Denise	07/11	-	230	9.5	-	24.2	53.5	-
	06/12	10.8	150	13.2	0.8	11.4	25.1	4.4
	09/12	12.7	470	29.3	0.4	16	35.5	3.8
Taylor	07/11	139.0	240	15.4	9.0	15.6	34.5	1.0
	09/11	28.0	210	11.0	2.5	19.1	42.2	3.1
	06/12	17.0	190	18.5	0.9	10.3	22.7	7.0
	09/12	9.7	220	10.8	0.9	20.4	45.0	1.5
Upper Carrol	05/12	28.3	270	16.4	1.7	16.5	36.4	3.8
East Carrol	05/12	28.0	130	6.7	4.2	19.4	42.9	1.1
No Name	05/12	18.3	180	9.1	2.0	19.8	43.7	2.4
Bluebell Pass	05/12	12.0	180	8.0	1.5	22.5	49.8	2.9

3.4.2 Chronology

The total ^{210}Pb activity of the six lakes decreases predictably with depth, allowing for the development of robust CRS chronologies (Figure 3.2). Background ^{210}Pb was reached within 9-12 cm in each of the six lakes, indicating average sedimentation rates of 0.5 to 1 mm yr^{-1}. The dating models developed using α and γ spectrometry for East Carrol Lake are strikingly similar (Figure 3.2). Cesium-137 peaks at 1961 ± 1.3 years, which coincides with the peak of nuclear bomb testing in 1963. The peak ^{137}Cs in Taylor Lake occurs at 1976 ± 3.25 years. However, samples were measured for ^{137}Cs only at every other half-centimeter in this section of the Taylor Lake core. At this resolution, peak ^{137}Cs could be off by a decade in either direction. Despite the larger errors for dates determined from deeper intervals using α-spectrometry, there is no statistical difference between dates attained by α and λ spectrometry, given the measurement errors. For consistency among lakes, all dates presented hereafter are based on the CRS depth-age curves using the dates obtained by α-spectrometry. In the absence of terrestrial organic material suitable for ^{14}C dating, the ^{210}Pb dating models were extended using linear regression ($R^2 > 0.95$ for all six lakes), and give basal dates ranging from AD 1187 at No Name Lake (at 42.5 cm depth) to AD 1671 at Bluebell Pass Lake (at 25.75 cm depth). These extrapolations provide historical context for the observed post ~1850 trends, although the pre-1850 dates are considered with caution, as basal ^{210}Pb sedimentation rates tend to be systematically overestimated compared to models that include ^{14}C dates (Cooke et al., 2010).

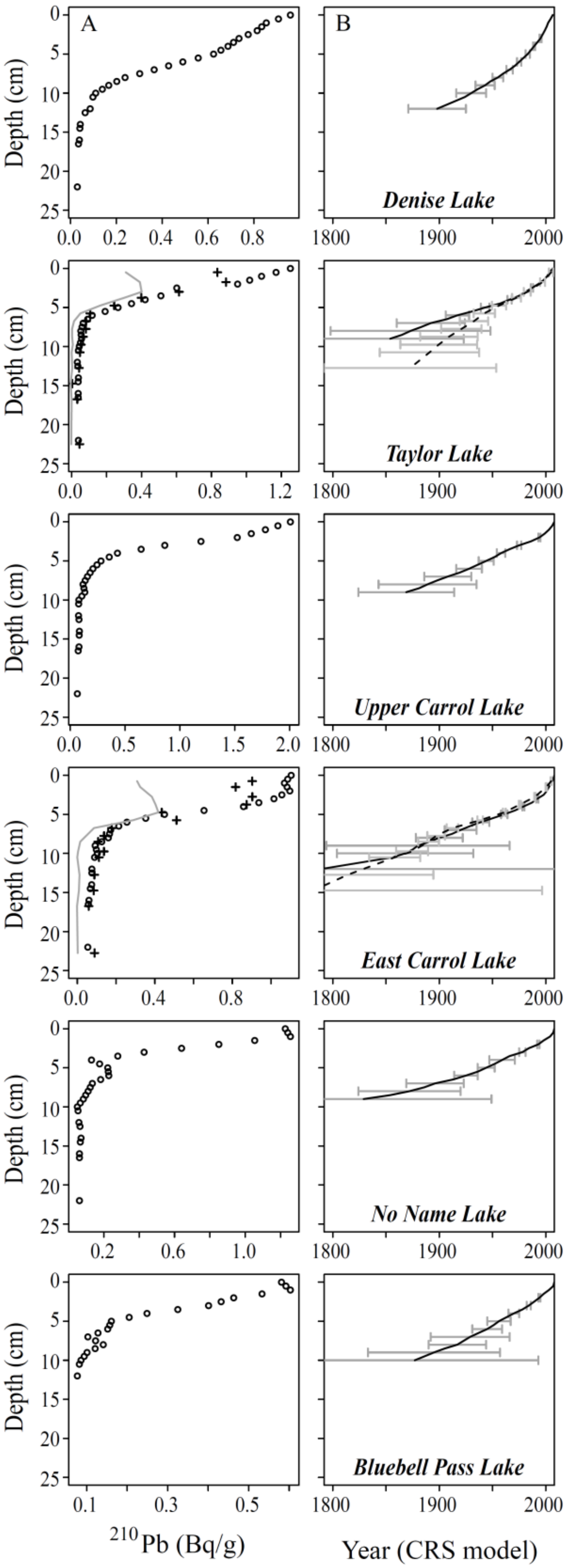

Figure 3.2. ^{210}Pb activities and core chronologies for the six study lakes.

(A) ^{210}Pb activities from the six study lakes using α-spectrometry performed at MyCore Scientific Inc. (open circles) and γ-spectrometry performed at PEARL (crosses). Cesium-137, measured (*note continues*)

Figure 3.2 (Continued). using γ-spectrometry at PEARL, is represented by the gray line. (B) Core chronology based on the constant rate-of-supply model from α-spectrometry at MyCore (black line) and γ-spectrometry performed at PEARL (dashed line). Error bars represent one standard deviation above and below the date.

3.4.3 Lake Production Indicators

In three of the six lakes (East Carrol, No Name, and Taylor Lakes) the chlorophyll *a* and percentage of organic matter are relatively constant from the beginning of the record until 1940-1960 when production increases, reaching magnitudes that exceed levels at any other time in the record (Figure 3.3). The highest values also occur in the top sediments at Denise and Upper Carrol Lakes, but unlike the other sites, Denise Lake exhibits a peak in chlorophyll *a* and percentage organic matter centered at ~AD 1580. By comparison, Upper Carrol Lake exhibits a gradual upward increase in chlorophyll *a* and percentage organic matter throughout the record. Primary production measures from Bluebell Pass Lake are relatively stable throughout the record with only a minor increase in chlorophyll *a* near the top of the core. The chlorophyll *a* flux (calculated as a rate) illustrates the primary production trend without the influence of sediment accumulation rate on concentration, and reveals that all but Upper Carrol Lake experienced increased production in the surface sediments (Figure 3.3).

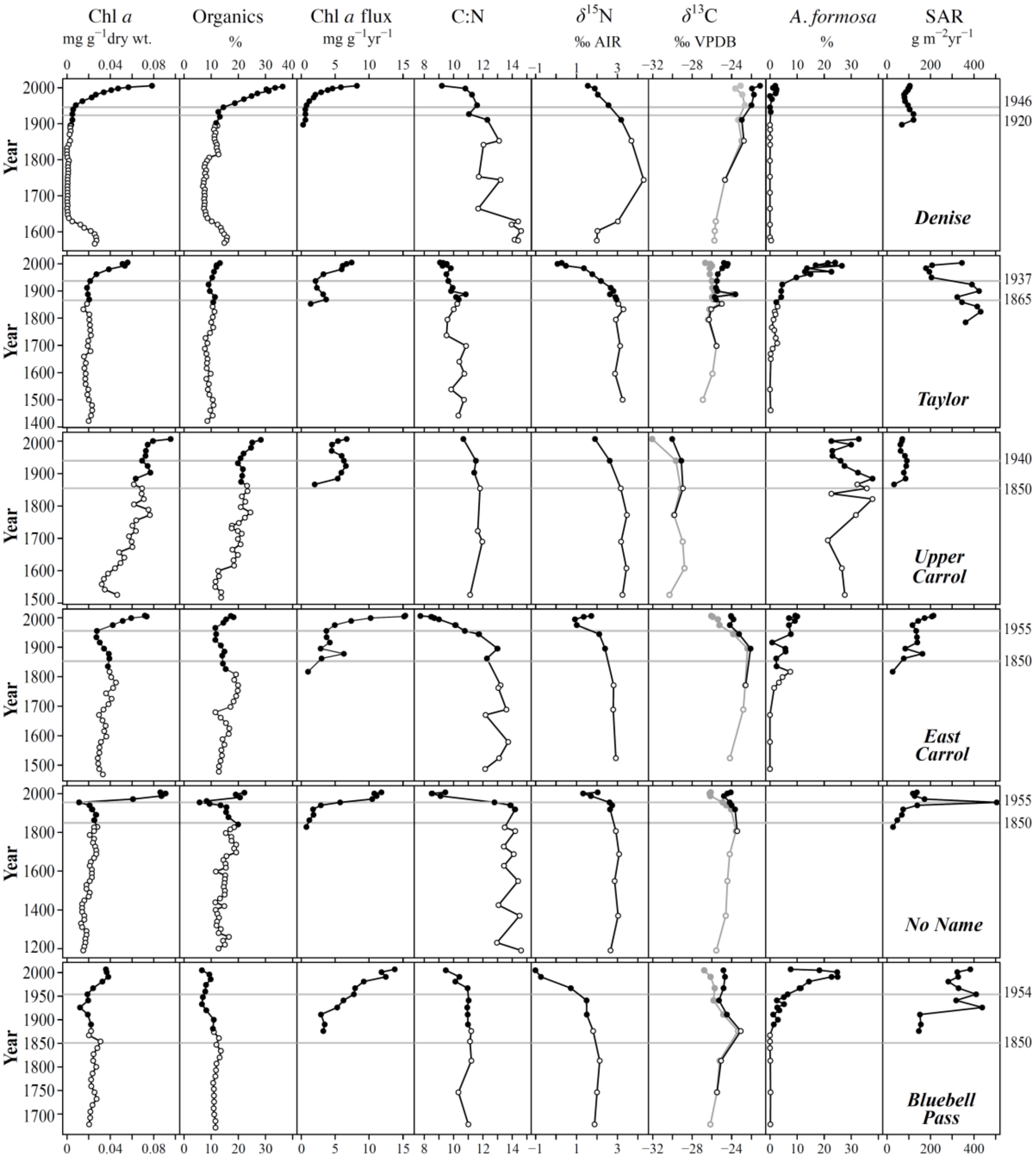

Figure 3.3. Key biological and biogeochemical data for Denise, Taylor, Upper Carrol, East Carrol, No Name, and Bluebell Pass Lake sediment cores.

Filled circles represent data constrained by the ^{210}Pb dated section of the cores, whereas open circles represent data for which the chronology was established by fitting a linear regression to the dates and extending below the ^{210}Pb dated section. Chlorophyll *a* flux and sediment accumulation rate (SAR) are both calculated as rates, and are limited to the ^{210}Pb-dated section of each core. Measured δ^{13}C values are shown in grey, whereas Suess-corrected δ^{13}C values (applied only to years after 1700) are shown in black. On each plot, the upper horizontal grey line indicates the main change in chlorophyll *a* (determined by visual inspection), which occurred ~1950, and the lower horizontal grey line indicates when δ^{15}N became significantly different than mean pre-settlement (pre-1850) values.

The C:N ratios at Denise Lake decrease over the duration of the record from ~14 to ~9. In the other lakes, C:N ratios are relatively constant at ~10 to 14 (depending on the lake) until ~1950, at which time they decrease to <10, except at Upper Carrol Lake in which C:N remains at pre-1955 values.

3.4.4 Nitrogen and carbon isotope compositions of organic matter

The nitrogen isotopic compositions in all but Denise Lake remain constant in the earlier parts of the records. Beginning around the mid 1850s, δ^{15}N begins to decrease in all of the lakes except No Name. A sharper decrease follows in the last ~60-70 years (decreases of up to 3 ‰), including at No Name, which did not exhibit an earlier decrease (Figure 3.3). Upper Carrol Lake is the exception to this trend, as the decrease in δ^{15}N values remains relatively gradual after 1940 for a total shift of only ~1 ‰. Organic matter from Denise Lake also exhibits decreasing δ^{15}N toward the top of the core, but this record is unique among these lakes because similarly low δ^{15}N values are also present at the bottom of the core.

The Suess-corrected δ^{13}C values range between –31 and –21 ‰, which is within the typical range for lake sediment containing organic matter dominated by aquatic primary producers (Finlay and Kendall, 2007). The δ^{13}C values recorded for Upper Carrol Lake (–31 ‰) are low compared to the other sites (–26 to –21 ‰). In Denise, Taylor, and No Name lakes, δ^{13}C gradually increases by 1 or 2 ‰ over the entire record, whereas for Upper Carrol, East Carrol, and Bluebell Lake, the δ^{13}C values are fairly constant throughout the cores.

3.4.5 Diatoms

In Taylor, East Carrol, and Bluebell Pass Lakes, *A. formosa* begins to increase in the early to mid-1800s, prior to the increase in chlorophyll *a.* In Taylor and Bluebell Pass Lakes, *A. formosa* increases more rapidly after ~1950, mirroring the pattern observed in δ^{15}N. In Denise Lake, *A. formosa* is only found in low abundances and increases only after ~1950. Although the increase in *A. formosa* at Denise Lake appears small, the increase is ecologically important because *A. formosa* would not typically prefer a lake as shallow as Denise (2.4 m) and because it was near-absent prior to ~1950. In Upper

Carrol Lake, *A. formosa* is a dominant species throughout, whereas in No Name Lake it is absent.

3.5 Discussion

We show that high alpine Uinta Mountain lakes experienced a recent increase in production in five of the six study lakes as documented by the increases in chlorophyll *a* and percentage of organic matter beginning between 1940 and 1960. Low C:N ratios indicate that the increase in organic matter is likely algal, as C:N ratios <10 are observed post-1950 in five of six lakes. C:N ratios from 10 to 20 (as is seen before 1950 at these sites) indicate either a mixed source of algae, aquatic macrophytes, and terrestrial material (Meyers and Ishiwatari, 1993) or algal growth under N-limiting conditions (Hecky et al., 1993). The increasing chlorophyll *a* flux in all but Upper Carrol Lake demonstrates that the rise in primary production is independent of sedimentation rate. Although the most prominent decreases in δ^{15}N recorded in four of the six lakes coincide with these changes in primary production, initial decreases in δ^{15}N began in the mid-1800s in three of these lakes. An increase in primary production generally results in progressively higher δ^{13}C values, given that algae preferentially utilize ^{12}C and subsequently draw the lighter isotope out of the photic zone (Hollander and Mckenzie, 1991). Trends in the Suess-corrected δ^{13}C values vary between lakes from slightly decreasing to slightly increasing, and therefore do not suggest a strong influence of productivity on carbon isotope composition. The changes in δ^{13}C values at these sites are more subtle than would be expected given an increase in productivity, but it is possible the effects of increasing primary production on δ^{13}C values are being offset by other ecological changes. For example, Wang et al. (2013) suggested that decreasing δ^{13}C values despite increasing production at a maar lake in China were linked to shifts from benthic to planktonic diatoms.

The changes in percentage of organics, chlorophyll *a* concentration, and C:N ratios all point to increasing primary productivity. Although diagenesis of organic matter can also produce such patterns, this explanation is unlikely. First, while C:N ratios would be expected to increase down core during diagenesis due to selective degradation of N-rich organic compounds, the opposite diagenetic effect has also been demonstrated for oligotrophic lakes (Meyers and Lallier-Verges, 1999). Second, diagenesis is expected to result in downcore decreases in chlorophyll *a* and percentage organics (Meyers and Lallier-Verges, 1999). However, the sedimentary chlorophyll *a* measurements used in this research include the spectral signal for chlorophyll *a* and its diagenetic products, pheophytin *a* and pheophorbide *a* (Michelutti et al., 2005), and therefore track both primary and degraded chlorophyll *a* products. Third, the Uinta Mountain lake sediment cores exhibit decreasing δ^{15}N values toward the core tops (Figure 3.3), which are opposite to the downward depletion of ^{15}N expected within a typical diagenetic profile (Galman et al., 2009). Fourth, diagenetic effects are expected to result in increased δ^{13}C values downcore in the most recent 5-10 years of sediment (Galman et al., 2009), whereas the trends in the Uinta sediment δ^{13}C values are inconsistently expressed in the upper portion of the cores. Therefore, we conclude that the interpreted increase in primary production is real.

What is causing this change in the primary productivity of these remote lakes? Recent climate warming has been linked to enhanced primary production in arctic environments (Michelutti et al., 2005) and to altered community compositions of diatoms in alpine, arctic and temperate sites in North America (Rühland et al., 2008). The mechanisms by which warming could result in enhanced production in oligotrophic ecosystems include lengthening the ice-free season, increasing nutrients in the catchment, and increasing residence time (Rühland et al., 2008). Alpine habitats are more sensitive to warming relative to low-elevation regions at similar latitudes (Beniston, 2003), and the western U.S.A. is warming at a faster rate than the world average (Saunders et al., 2008). Mean annual temperature at Heber, Utah, steadily increases beginning in the mid-1980s, which is typical timing when compared to the regional trend for the mid-western U.S.A. (Saunders et al., 2008). However, this warming trend post-dates the changes observed in chlorophyll *a* (Figure 3.4), indicating that warming was not the trigger for enhanced lacustrine primary production at these sites. Our findings do not rule out climate as a contributing factor, particularly since the 1980s and even more importantly in the future when further warming is anticipated (Solomon et al., 2007).

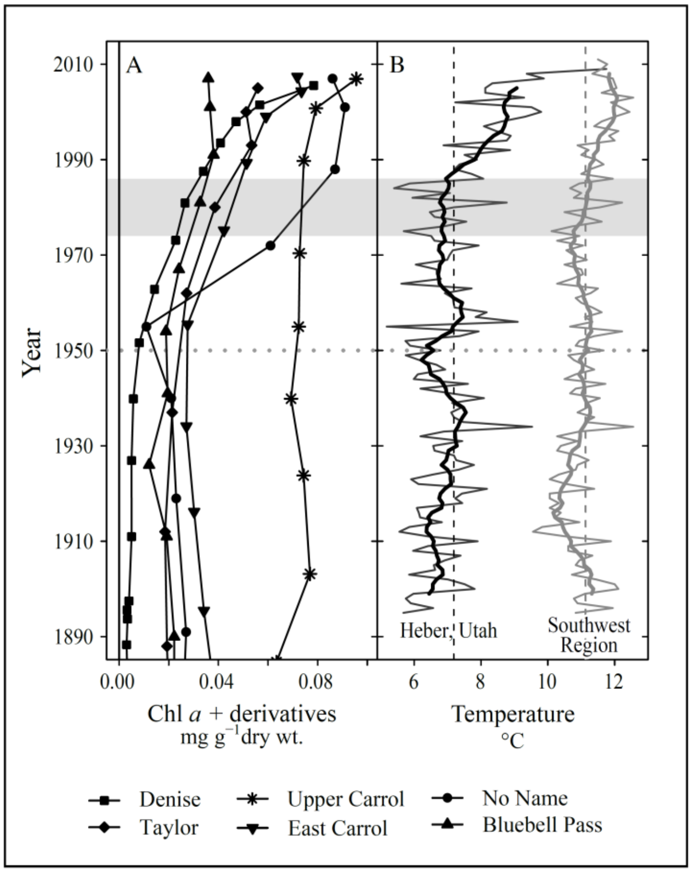

Figure 3.4. Comparison of Chlorophyll a + derivatives for Uinta Mountain study lakes (A) and mean annual temperature for Heber, Utah, and for the Southwest Region of the U.S.A. (B). The thick lines are 9-year running means and the dashed lines are mean temperatures for the entire record. The beginning of increased primary production is marked by the gray dotted line, and the beginning of modern climate warming in the southwestern U.S.A. and at Heber is marked by the gray band. Temperature data have been obtained from the Western Regional Climate Centre, http://www.wrcc.dri.edu/ (Heber) and National Climatic Data Center, National Oceanic and Atmospheric Administration http://www.ncdc.noaa.gov/cag/time-series/us (Southwest Region of the U.S.A.).

Increased lake production can be caused by human disturbance within the catchment, which results in increased transfer of nutrients from the catchment to the aquatic system (Hall and Smol, 2001). In the Uinta Mountains, humans have had relatively little effect on the landscape, with the exception of changes resulting from grazing. Grazing can alter species composition, disrupt nutrient cycling, reduce litter cover, compact soils, reduce infiltration, increase runoff, and increase soil erosion (Fleischner, 1994), and through these mechanisms increase production in aquatic systems. Although records are intermittent, sheep grazing was common practice in the Uinta Mountains by 1890, and many areas are still grazed by sheep and cattle. Grazing in both the Dry Gulch and Whiterocks River allotments (which together encompass all six study lakes) is likely to have peaked in the 1920s or 1930s (United States Forest Service, 1947). Trampling and grazing-related vegetation changes can reduce soil stability and enhance soil erosion (Fleischner, 1994). This should result in increased inorganic sedimentation rates coincident with the 1920-1930s peak in grazing, which then subside as grazing became less intense and the catchments recovered. However, the inorganic flux does not exhibit any trends consistent with such a history (Figure 3.3). If grazing resulted in increased transport of nutrients to the lake from manure, production should have been greatest in the 1930s and δ^{15}N values should have increased moderately, as livestock manure typically has δ^{15}N of ~ +9 ‰ (Szpak et al., 2012). In contrast, the δ^{15}N values decrease and primary production is low during peak grazing, indicating that local free-range grazing is not directly responsible for changes in primary production at these lakes.

Fish stocking is another anthropogenic perturbation that could lead to increased lake production. This can result in increased primary production by changing patterns of herbivory and by re-introduction of benthic nutrient sources to pelagic communities (D. E. Schindler et al., 2001). The six Uinta Mountain study sites have all been stocked with either cutthroat trout (*Oncorhynchus clarkii*) or brook trout (*Salvelinus fontinalis*) multiple times since 1979 (Utah Division of Wildlife Resources, 2012, http://www.utahfishinginfo.com/dwr/). No Name, Bluebell Pass, East Carrol, and Upper Carrol Lakes were stocked as early as 1958 (Rabe, 1968), and it is likely that Denise and Taylor Lakes were stocked as well (Figure 2.5). Before 1956, however, lakes were stocked from horseback (Hallows, 2009), making it unlikely for remote lakes like those studied here to have been stocked. Fish sampling surveys from 1978 at East Carrol, Upper Carrol, No Name, and Bluebell Pass lakes indicate no natural fish populations, and that stocked fish were not reproducing (D.W.R. stocking reports, unpubl.). The timing of fish stocking at these sites is similar or slightly lagging the changes in chlorophyll *a* and percentage organics, making it a possible explanation for the increased primary production.

Based on the δ^{15}N record, however, fish stocking is unlikely to be the main cause of increased lake production. Organic matter δ^{15}N typically increases by ~3-4 ‰ with each trophic level (Minagawa and Eitaro, 1984; Adams and Sterner, 2000), so the repeated introduction of fish to these lakes over the last 50 years should result in ^{15}N-enrichment of the lakes. Fish undernourishment, as has been observed in Bluebell Pass Lake (Rabe, 1968), No Name Lake and East Carrol Lakes (D.W.R. stocking reports, unpubl.), can result in further increases in δ^{15}N values (Adams and Sterner, 2000). However, δ^{15}N values decrease towards present, making fish stocking an unlikely dominant factor causing increased production at these sites.

Many researchers have commented that alpine lakes are ultimately N-limited (Vitousek et al., 1997; D. W. Schindler, 2006) or co-limited by nitrogen and phosphorus (Baron et al., 2000). However, recent research indicates that enhanced anthropogenic N deposition can result in a shift to P limitation (Arnett et al., 2012) and higher N:P ratios (Elser et al., 2009). Shifting N:P ratios and corresponding changes in the limiting nutrient imply that P (via eolian transport of dust from intensive livestock grazing and fertilizer use (Neff et al., 2008; Reynolds et al., 2010), or mining) could contribute to enhanced primary production at times. Focusing only on N inputs may be an oversimplification in this environment.

The timing of the production changes illustrated by chlorophyll *a* and organic matter contents at five of the six Uinta study lakes coincides with the rise of intensive agriculture and rapid population growth upwind at the Wasatch Front, both of which are associated with the increase in fossil fuel combustion and the use of synthetic N fertilizers produced via the Haber-Bosch process (Figure 3.5). These activities increase the availability of fixed N, and result in enhanced atmospheric N deposition. The recent increase in the percentage of *A. formosa* in the Denise, Taylor, East Carrol, and Bluebell Pass Lake sediment cores is also consistent with increased fixed N availability, particularly in alpine environments (Saros et al., 2005). The decrease in δ^{15}N values observed for the lakes examined here is consistent with a change in the source of fixed N. Bateman and Kelly (2007) report a mean δ^{15}N of +0.2 ± 1.9 ‰ for synthetic nitrogen fertilizer, which is sufficiently low that transport of agricultural dust could produce the observed decrease in N isotopic compositions. Enhanced fossil fuel combustion related to population growth and industrial expansion could also have contributed to the observed pattern in N isotopic compositions, given that nitrates derived from fossil fuel combustion typically have low δ^{15}N values (–10 to +5 ‰) (Finlay and Kendall, 2007).

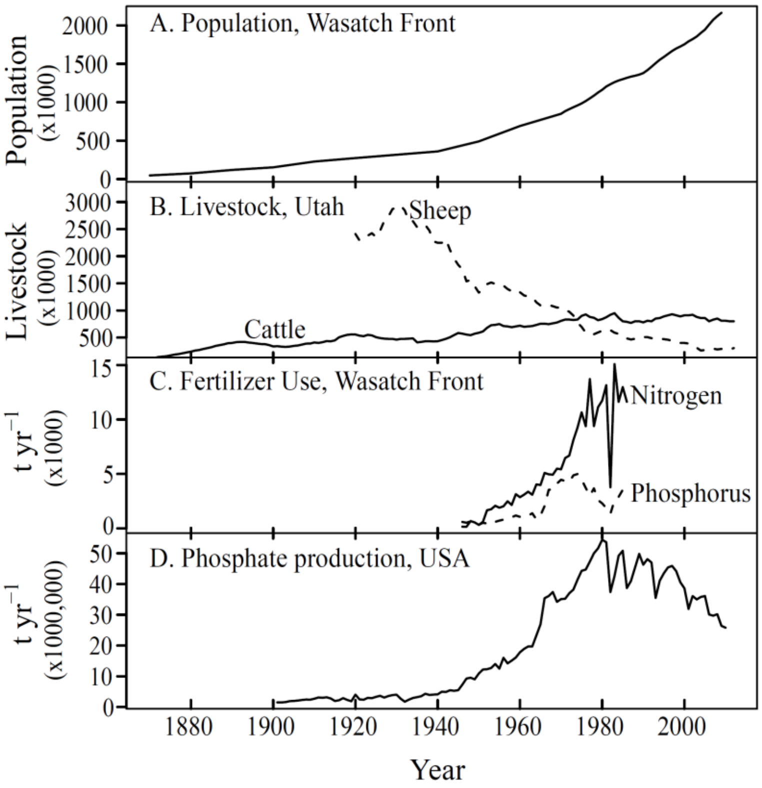

Figure 3.5. Trends in potential supply of nitrogen and phosphorus to the Uinta Mountains.

Data have been obtained from the following sources: (A) Population in the Wasatch Front (Davis, Salt Lake, Weber, Box Elder and Utah Counties) (United States Census Bureau, http://www.census.gov/popest/data/historical/index.html; University of Virginia, Geospatial and Statistical Data Center. 2004, http://mapserver.lib.virginia.edu/collections/). (B) Livestock in Utah State (United States Department of Agriculture, National Agricultural Statistics Service, http://quickstats.nass.usda.gov/). (C) Nitrogen and phosphorus fertilizer use in the Wasatch Front (Davis, Salt Lake, Weber, Box Elder, and Utah Counties) in thousands of metric tonnes per year (Alexander and Smith, 1990). (D) Production of phosphate rock in the U.S.A. in millions of metric tonnes per year (Kelly et al., 2011).

Although the natural phosphorus cycle does not have a significant atmospheric component, the recent increase in phosphate mining and phosphate fertilizer use (Figure 3.5) has resulted in greater atmospheric transport of P. A study of the sediments from

Marshall Lake and Hidden Lake, Uinta Mountains, shows that P levels have become increasingly elevated since 1950, which is attributed to atmospheric dust fallout from intensive agricultural activity (Reynolds et al., 2010). This timing coincides with the increase in primary productivity at the Uinta Mountain study sites (Figure 3.6) and with the rise in phosphate use in the Wasatch Front and overall phosphate production in the U.S.A. (Figure 3.5). Phosphate in Uinta Mountain dust samples is elevated relative to the underlying bedrock; the higher P contents have been attributed to either nearby phosphate mining based on the presence of apatite in dust, or agricultural intensification based on elevated soil and fertilizer minerals like calcium, sodium, and cadmium (Squire, 2012).

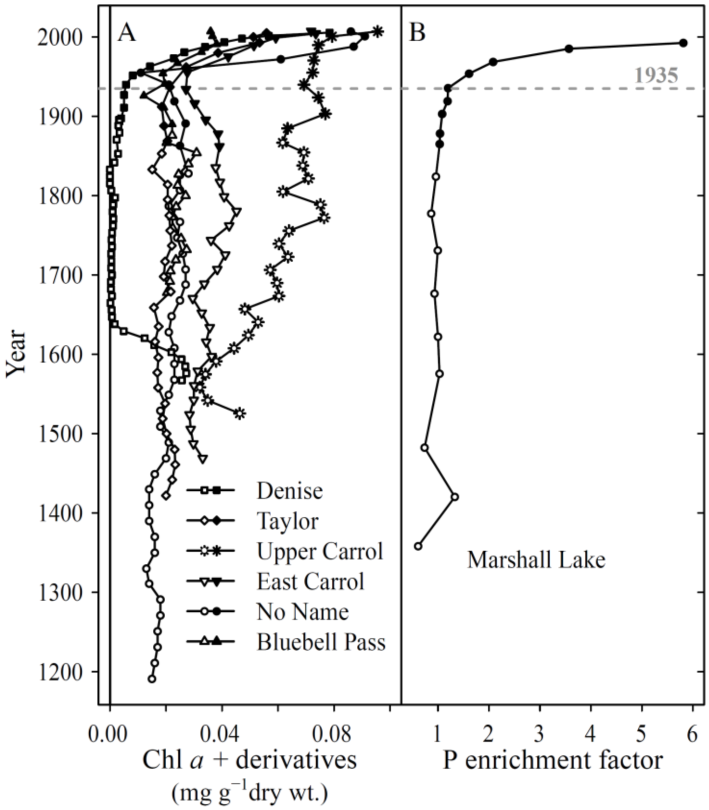

Figure 3.6. (A) Chlorophyll a + derivatives for each of the six study lakes compared to (B) the phosphorous (P) enrichment factor for Marshall Lake, Uinta Mountains (Reynolds et al. 2010). Data with solid symbols are constrained by ^{210}Pb dates, whereas open symbols are extended below the ^{210}Pb-dated section by fitting a linear regression to the dates. The gray dotted line at 1935 represents the point in time after which phosphorus became elevated above background levels.

Although the recent (~1950) increase in lake primary production is the most prominent change observed in these sediment records, several of the lakes (Taylor, East Carrol, and Bluebell Pass) indicate an earlier, more subtle shift. From approximately 1850, *A. formosa* increases and δ^{15}N values decrease suggesting an increase in nutrient delivery. This change predates local grazing activity and fish stocking, and shows no relation to temperature. We suspect these changes may result from an initial increase in land clearance in the southwest and mining activities after the settlement of the Wasatch Front in 1847 (Reynolds et al., 2010). Grazing along the Wasatch Front could have produced a supply of excess nutrients to these high alpine sites, similar to the changes observed in the San Juan Mountains in the late 19th Century (Neff et al., 2008). NO_x from smelting associated with local mining at this time could also have contributed to the small changes in δ^{15}N and the slight increase in the abundance of the mesotrophic diatom, *A. formosa*.

3.6 Conclusions

Uinta Mountain lake sites are critical bellwethers for environmental change, as they record an increase in production in the last 60 years. This adds to evidence that long-distance transport of nutrients is causing detectable changes in lake ecosystems. Although evidence of more serious effects of eutrophication (e.g., algal blooms), has only rarely been reported in the Uinta Mountains (K. Moser, unpubl.), we can already detect subtle shifts in ecosystem function. By studying several lake sites, we have shown that not all high elevation lakes are responding equally to increased nutrient deposition. The present study indicates that enhanced N and P deposition may both be important factors in increasing primary production in Uinta Mountain lakes. This result comes at a critical time as populations, fossil fuel combustion, and agricultural activities are on the rise, and two phosphate mines are planned to join the current large phosphate mining operation near Vernal, Utah (Figure 3.1) (Squire, 2012). Changing primary production may be further compounded by future increases in temperature in western North America, which are anticipated to increase by ~2.1 to 5.7 ˚C by the end of the 21st century (Solomon et al., 2007). In the arctic, where warming began in the mid to late 1800s, ecosystem functioning and structure are strongly correlated with temperatures (Smol et al., 2005).

Such changes may be delayed in the Uinta Mountains because temperatures in the western U.S.A have only recently begun to rise (Saunders et al., 2008). Previous nutrient inputs may only serve to compound the impacts of future warming (D. W. Schindler, 2006). In other words, the full impact of warming in alpine regions that might be anticipated based on research on arctic lakes, where nutrient delivery has been less (Galloway et al., 2008) may not yet be realized.

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Chapter 4

4 Nitrate sources in alpine lakes: new insights from Δ^{17}O, δ^{18}O and δ^{15}N

4.1 Introduction

Reactive nitrogen (NO_x and NH_4^+) is added to the environment from natural sources including lightning, biogenic sources, biomass conversion, and wildfires, which globally account for about 90 to 140 Tg Nitrogen (N) deposition per year (Vitousek et al., 1997; Alexander et al., 2009)[13]. However, the nitrogen cycle is now dominated by anthropogenic sources of reactive nitrogen, which, as of 2005, contributed 187 Tg N per year to the global nitrogen cycle (Vitousek et al., 1997; Galloway et al., 2008). The anthropogenic sources of reactive nitrogen include synthetic fertilizers, by-products of fossil fuel combustion ($NO_x = NO + NO_2$), cultivation of nitrogen-fixing legumes, and mobilization of previously unavailable nitrogen sources (Vitousek et al., 1997).

Reactive nitrogen inputs are greatest in urban and agricultural areas, but locations with little human activity may also receive increased nitrogen inputs due to the mobile nature of NO_x emissions and dust. For example, in alpine regions of the Midwestern U.S.A., nitrate (NO_3^-) deposition models indicate that inputs of NO_3^- are locally higher than the monitoring records from the National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) would suggest (Nanus et al., 2008). The modeled rates of nitrate deposition are lower than those observed in the eastern U.S.A., but alpine ecosystems are relatively sensitive to increased nutrient availability (Williams et al., 1996a). Therefore, even modest increases in nitrogen deposition could result in changes such as forest decline (Tsunogai et al., 2010), eutrophication, acidification, and changes in biodiversity (Nanus et al., 2008) in these environments.

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[13] Tg = teragram = 1,000,000,000 kilograms

Paleoenvironmental research on alpine ecosystems of the western U.S.A. suggests that nitrogen deposition associated with agricultural intensification and fossil fuel combustion is a factor leading to recent ecological changes. For example, several researchers have suggested that decreasing sedimentary δ^{15}N values and coincident ecological changes are at least in part a result of increased nitrogen inputs from agricultural[14] and fixed and mobile fossil fuel combustion sources[15] in the Colorado Front Range (Baron et al., 2000; Wolfe et al., 2001; Saros et al., 2003), the Uinta Mountains (Chapter 3, Hundey et al., (submitted)), and other arctic and alpine regions (Holtgrieve et al., 2011). Decreasing δ^{15}N has also been observed in places as remote as Greenland, where Sowers et al. (2002) report that the δ^{15}N value of N_2O in ice core air bubbles has dropped by 1.7 ‰ during the 20th century. They attribute this change to increased agricultural activities whereas Hastings et al. (2009) suggest that decreasing δ^{15}N-NO_3 in a Greenland ice core is due to increased fossil fuel combustion in the last 150 years.

Past studies have documented decreasing δ^{15}N, however the postulation that this change is due to increasing anthropogenic nitrate inputs remains speculative. In the arctic, for example, nutrient deposition is generally very low (Smol and Douglas, 2007b), and a number of lakes show the opposite (increasing) trend in δ^{15}N values (Catalan et al., 2013). McLaughlan et al. (2013) analyzed a global sample of 58 paleolimnological records covering the last 500 years and report that 10 sites showed significant increases in δ^{15}N, 18 sites showed significant decreases, and the remainder were unchanged. The interpretation of δ^{15}N values within lake sediments is also complicated by overlapping source δ^{15}N values (Figure 4.1), internal lake N cycling, kinetic isotope fractionation effects, and coincident timing of other perturbations (e.g., rising temperatures). Thus, a gap remains in our understanding of the cause(s) of documented changes in δ^{15}N in remote alpine ecosystems.

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[14] Synthetic fertilizer δ^{15}N: 0 ± 3 ‰ (Kendall and McDonnell, 1998)

[15] Fossil fuel NO_x δ^{15}N: -7 to +12‰ (Heaton, 1990)

In this study, the stable isotopes of nitrates (δ^{15}N, δ^{18}O and Δ^{17}O)[16] in modern water (inflows and lakes) and snow samples from the Uinta Mountains, Utah, U.S.A., were analyzed to determine the proportional contribution of various sources of nitrates to these alpine aquatic ecosystems. Successful identification of the sources of nitrogen in these lakes may reduce speculation about the relative contributions of different anthropogenic inputs to the nitrogen cycle of these alpine systems. This knowledge should enhance our understanding of alpine nutrient budgets and provide a modern context (i.e., current nutrient sources) to aid our interpretation of paleolimnological records in the region.

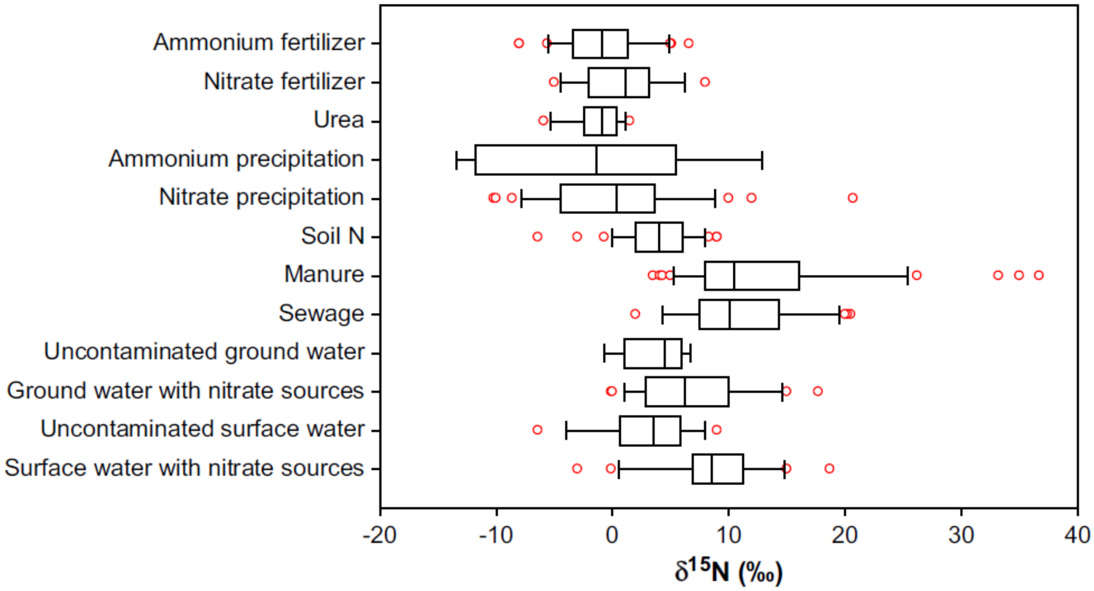

Figure 4.1. Box plots of δ^{15}N values of NO_3^- from various sources and sinks.

Box plots illustrate the 25th, 50th and 75th percentiles; the whiskers indicate the 10th and 90th percentiles, and the circles represent outliers. Reprinted from *Water Research, 43*, 5, Xue et al., Present limitations and future prospects of stable isotope methods for nitrate source identification in surface and groundwater, 1159-1170, © 2009, with permission from Elsevier.

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[16] There are three stable isotopes of oxygen. The most plentiful is ^{16}O (99.759%), followed by ^{18}O (0.204 %), and ^{17}O (0.037 %) (Junc and Svec, 1958). Nitrogen has two stable isotopes, in the forms ^{14}N (99.6447 %), and ^{15}N (0.3663 %) (Cook and Lauer, 1968).

A dual isotope approach ($\delta^{15}N$ and $\delta^{18}O$ of nitrates) can be used to make inferences about nitrate sources, but there is ambiguity associated with only analyzing these isotopes. Nitrate-$\delta^{18}O$ has been used to trace atmospheric nitrate because it has distinctly higher $\delta^{18}O$ values than nitrate originating from microbial processes (i.e., nitrification) (Durka et al., 1994). However, if the contribution of atmospheric nitrate is small, it can be difficult to quantify because of overlap with the $\delta^{18}O\text{-}NO_3^-$ from other sources (Michalski et al., 2002). Values of $\delta^{15}N$ can also be used to differentiate NO_3^- , but interpretation can be complicated by mixing of different sources (Xue et al., 2009). Further problems arise with both $\delta^{15}N$ and $\delta^{18}O$ when nitrate species undergo biological transformations (e.g., assimilation, nitrification, and denitrification), because these processes result in mass-dependent fractionation (Kendall and McDonnell, 1998).

The 'triple isotope' approach to the analysis of nitrates allows us to take advantage of the anomalous enrichment of $^{17}O\text{-}NO_3^-$ that results from transfers of ^{17}O in ozone during photochemical conversion of NO_x to NO_3 in the atmosphere (Michalski et al., 2002). This mass-dependent fractionation, quantified by the term $\Delta^{17}O$, differs from the mass-dependent relationship between $\delta^{17}O$ and $\delta^{18}O$ during terrestrial processes, which is described by the Terrestrial Fractionation Line (TFL). Using $\Delta^{17}O\text{-}NO_3^-$, therefore, allows for clear differentiation between nitrate of atmospheric and terrestrial origin. Like other isotopes, over time, and through multiple mixing events, $\Delta^{17}O$ can be diluted. However unlike $\delta^{18}O$, the ^{17}O anomaly is maintained and still measurable after wet or dry deposition of atmospherically oxidized (and ^{17}O enriched) NO_3^- at the earth's surface, and through subsequent biological transformations (Tsunogai et al., 2010). Values for $\Delta^{17}O$ provide us with a clear atmospheric/ terrestrial distinction, and analysis of $\delta^{15}N$ and $\delta^{18}O$ provides further insight into the particular sources of atmospheric and terrestrially derived nitrates.

In this paper, we further quantify the contributions of particular nitrate sources identified using the triple isotopes of nitrate by using these data as inputs to a stable isotope mixing model in the software package SIAR (stable isotope analysis in R) (Parnell et al., 2010). SIAR was designed to estimate dietary proportions from stable isotope data, but can also be used to determine source proportional contributions of nitrate sources. The SIAR method uses a Bayesian framework to determine the probability distribution of proportional contribution of different sources to a mixture, fit via a Markov chain Monte Carlo permutation.

4.2 Study Area

The Uinta Mountains are an east-west trending mountain range that reaches elevations over 4000 m, and stretches 200 km across the northeastern part of Utah (40˚ to 41˚ N, 109˚ to 111˚ W) into northwestern Colorado (Figure 4.2). The mountain range contains hundreds of lakes and has experienced little direct human impact, making it ideal for investigating the influence of atmospheric nitrate. Model results combining NADP/NTN and snow chemistry data indicate that the highest elevations of the Uinta Mountains receive 2-3 kg ha^{-1} inorganic N annually, exceeding critical loads of N deposition by 1-3 kg N ha^{-1} (Nanus et al., 2012). Inorganic N deposition in the Uinta Mountains is greater than most low-lying areas of the western U.S.A., but similar to other high elevation regions such as the Colorado Front Range, which receives 2-4 kg ha^{-1} inorganic N annually (Nanus et al., 2012).

Six high elevation (> 3000 m.a.s.l.), oligotrophic lakes were selected for this study. It complements a paleolimnological study that reports recent changes in primary production in the same lakes (Chapter 3). The main study lakes, with Utah Department of Wildlife Resources codes in parentheses, are: (1) Denise (WR-9), (2) Taylor (WR-8), (3) Upper Carrol (X-18), (4) East Carrol (X-21), (5) No Name (X-26), and (6) Bluebell Pass (X-25) (Figure 4.2). Lake water and inflow samples were collected from each site, and snow pack samples were collected both in summer and at peak snow accumulation (March- April). An additional water sample from Walk-Up Lake (WR-55) (also > 3000 m.a.s.l) was also collected. A water sample was also obtained from Great Salt Lake in order to compare nitrates originating from this highly polluted lake to the compositions of nitrates in the Uinta Mountains.

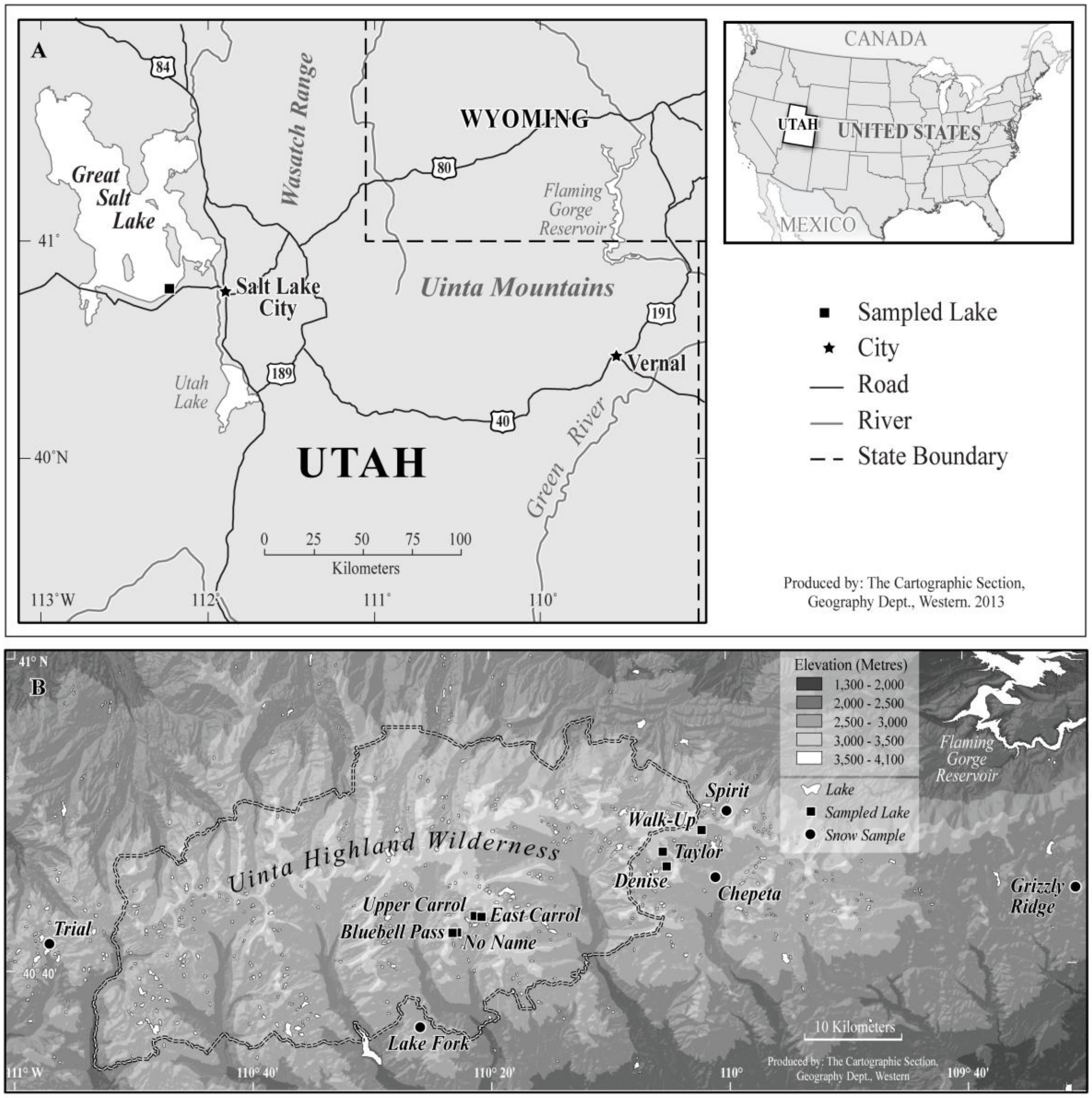

Figure 4.2. Map of (A) the location of the Uinta Mountains in northeastern Utah and U.S.A., including the water sampling point in Great Salt Lake, and (B) the topography of the Uinta Mountains with the locations of study lakes and snow sampling sites.

4.3 Methods

4.3.1 Water and snow sampling

The six study lakes and their inflows and snowpack were sampled for isotope analyses in late July/ early August of 2008 and 2009, with some additional sampling in 2011 and 2012. For the lake water samples, the bottles were filled ~ 0.5 m below the water surface at the deepest portion of the lake, determined based on several point measurements of depth. Samples were collected for stable isotope analysis in 250 mL amber Nalgene® bottles, kept cool in the field, and frozen as soon as we returned from the field (1-3 days). Summer snowpack samples were taken in zip lock bags after scraping off ~2 cm of surface snow. The snow samples were transferred to tightly sealed sample bottles in the field after melting. Samples for stable isotope measurements were shipped to the Lakes and Reservoirs Systems (LARS) Research Facility at the University of Western Ontario and stored frozen until transferred to the Laboratory for Stable Isotope Science (LSIS), also at the University of Western Ontario.

In addition to samples taken from summer snowpack, snow samples were collected around the time of maximum snow accumulation but before spring snowmelt (March 2009 and April 2011), at snow sampling locations shown in Figure 4.2. These samples ensure that the isotopic signature of winter snow deposition is captured, as there is little snow pack left during the July-August sampling period. Furthermore, it is possible that the isotopic composition of the snow and residual snow pack could change between winter and summer because solutes, such as nitrate and ammonium, are eluted from snowpack early in the melt period (Williams and Melack, 1991). The March 2009 snow samples (Lake Fork, Spirit Lake, Chepeta Lake, and Trial Lake sites) were collected by the U.S. Forest Service with a standard federal snow sampler using standard snow sampling techniques (United States Department of Agriculture Soil Conservation Service., 1984). The April 2011 samples (Grizzly Ridge and Lake Fork sites) were collected by G. Ingersoll from snow pits as detailed in Ingersoll et al., (2002). The samples were shipped frozen in clean, 19 L paint buckets to LARS Research Facility, where they were melted and aliquots provided to other laboratories for stable isotopic (LSIS) and chemical analyses, as described below.

Samples for water chemistry analysis (NO_2, NH_4, PO_4, $NO_2 + NO_3$, TDP, TDN, Si, DOC, DIC) and chlorophyll *a* were taken concurrently with the isotope samples. A portion of the sample was filtered using a 0.7 μm Whatman GF/F filter. All water samples were frozen before sending for analysis. The filtered samples and the filters were analyzed for water chemistry and chlorophyll *a*, respectively, at the Chesapeake

Biological Laboratory in Maryland, USA. A list of the samples analyzed for both nutrients and stable isotopic compositions of nitrates is provided in Appendix A.

4.3.2 Nitrate Triple-isotope analysis

Stable isotope analyses are expressed as ratios of the heavier to the lighter isotopes, relative to an international standard, using the δ notation,

$$\delta\ {}^{i}E = \frac{R({}^{i}E/{}^{j}E)_{P} - R({}^{i}E/{}^{j}E)_{std}}{R({}^{i}E/{}^{j}E)_{std}} \qquad 1$$

where R is the isotope ratio of the heavier (${}^{i}E$) to the lighter (${}^{j}E$) isotope (e.g., ${}^{15}N/{}^{14}N$, ${}^{18}O/{}^{16}O$, and ${}^{17}O/{}^{16}O$) for the sample (P) and the standard (std). The $\delta^{18}O\text{-}NO_3^-$ values are reported relative to Vienna Standard Mean Oceanic Water (VSMOW) and $\delta^{15}N\text{-}NO_3^-$ values are reported relative to standard atmospheric air (AIR).

Values of $\delta^{17}O$ are linearly related to $\delta^{18}O$ at the Earth's surface in a relationship defined as the Terrestrial Fractionation Line (Figure 4.3) (Thiemens, 2006),

$$\delta^{17}O = 0.52 \text{ x } \delta^{18}O \qquad \mathbf{2}$$

Atmospheric ozone provides an exception to this relationship. This ozone undergoes mass independent fractionation such that it is enriched in ${}^{17}O$ relative to the expected relationship shown in equation 2 (see $\Delta^{17}O$ in Figure 4.3). This anomaly is transferred to NO and NO_2 during oxidation in the atmosphere (Alexander et al., 2009). The mass-independent isotopic variation, that is, the deviation of the isotopic composition of a sample from the terrestrial fractionation line relationship (equation 2), is reported as

$$\Delta^{17}O = \delta^{17}O - 0.52 \text{ x } \delta^{18}O \qquad \mathbf{3}$$

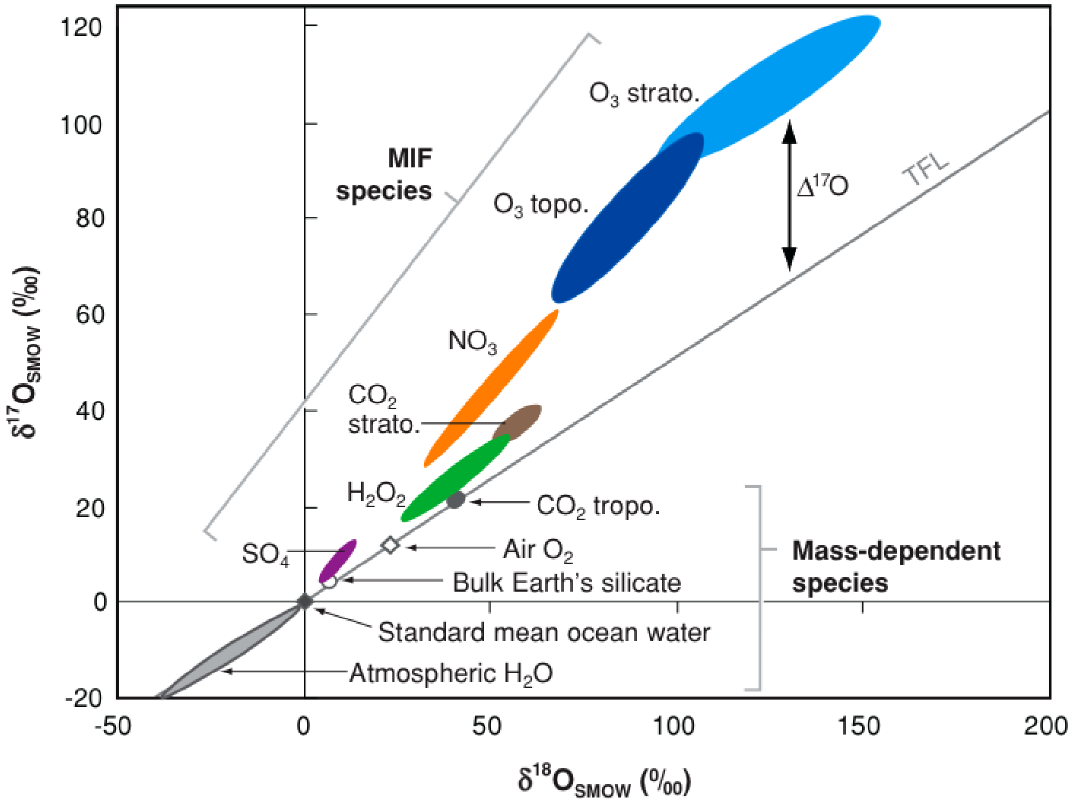

Figure 4.3. Mass-independent (MIF) and mass-dependent oxygen containing species relative to the Terrestrial Fractionation Line (TFL).

The TFL describes the mass dependent fractionation of ^{18}O and ^{17}O in terrestrial processes, (Equation 2). The exception to this relationship occurs in the atmosphere, where nitrate experiences mass independent isotopic fractionation. Values of $\Delta^{17}O$, therefore, measure the difference between measured $\delta^{17}O$ and the expected relationship dictated by the Terrestrial Fractionation Line (Equation 2), such that $\Delta^{17}O > 0$ if mass independent fractionation has occurred. Mean $\Delta^{17}O$ of tropospheric ozone ranges from +25 to +35 ‰ (Costa et al., 2011). The $\delta^{17}O$ isotope anomaly is transferred to NO and NO_2 during oxidation in the atmosphere (B. Alexander et al., 2009) resulting in a $\Delta^{17}O$ of atmospheric nitrate of +20 to +32 ‰ (Costa et al, 2011). Therefore, atmospherically derived nitrates will have $\Delta^{17}O$ values that are greater than 0. Republished with permission of *Annual Review of Earth and Planetary Sciences* from History and Applications of Mass-Independent Isotope Effects, *34*, Thiemens, © 2006; permission conveyed through Copyright Clearance Center, Inc.

We used the coupled cadmium-azide reduction method described by McIlvin and Altabet (2005) with modifications described by S. Russell and Longstaffe (in prep) to prepare nitrate for analysis of δ^{18}O, Δ^{17}O and δ^{15}N. The methods are briefly summarized below and described in greater detail in Appendix B (S. Russell and Longstaffe, in prep). The chemical procedure involves two main steps. The first is conversion of nitrate to nitrite using activated cadmium, and the second is the conversion of nitrite to N_2O using a 1:1 molar solution of sodium azide and acetic acid (S. Russell and Longstaffe, in prep). The isotope ratios of the resulting N_2O are measured using a Thermo Finnigan Delta^{plus} XL Isotope Ratio Mass Spectrometer (IRMS) accessorized with a Gas Bench II and CTC CombiPal autosampler. Nitrous oxide isotope ratios are collected by monitoring the masses 44, 45, and 46 ($^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$ + $^{14}N^{14}N^{17}O$, and $^{14}N^{14}N^{18}O$, respectively).

A number of corrections (detailed in Appendix C) are made to the raw δ-values to account for overlapping masses and memory effects. Briefly, for δ^{15}N, two corrections are made to account for the mass overlap between $^{15}N^{14}N^{16}O$ and $^{14}N^{14}N^{17}O$. The first is a "Craig Correction", which is applied by the IRMS operating system (ISODAT), and accounts for the mass-dependent overlap of these isotopologues[17]. The second is applied to account for the mass independent (i.e., $\Delta^{17}O>0$) overlap between these same isotopologues. Corrections are also made to δ^{18}O in each analytical run to account for exchange between sample water and laboratory water. This is necessary because a fraction (~13%, (S. Russell and Longstaffe, in prep.)) of oxygen that ends up in the measured nitrous oxide product is derived from exchange with water oxygen, rather than from the original nitrate oxygen.

Calibration of the raw isotopic ratios to AIR (nitrogen) and VSMOW (oxygen) is achieved using international standards USGS-32, USGS-34, USGS-35 (Table 4.1), and an internal standard, GSI-NO-3 (δ^{15}N = +1.3 ‰, δ^{18}O = +14.13 ‰, courtesy of the Geological Survey of Israel). Accuracy of isotope values was determined by comparing to the standard IAEA-NO-3 value. The mean δ^{18}O, Δ^{17}O and δ^{15}N values obtained on repeat measurements (n = 10) of IAEA-NO3 are summarized and compared to accepted values (from Bohlke et al., 2003) in Table 4.1. Precision was calculated on duplicates

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[17] Isotopologues are molecules that differ only in their isotopic composition

from each analytical session, and excellent reproducibility was achieved (± 0.04 ‰, ± 0.23 ‰, and ± 0.5 ‰ for Δ^{17}O, δ^{18}O, and δ^{15}N, respectively). Internal data from LSIS (N=48) has shown long-term precision as determined from sample duplicates as well (± 0.50 ‰, ± 1.00 ‰, and ± 0.7 ‰ for Δ^{17}O, δ^{18}O, and δ^{15}N, respectively).

Table 4.1. Standard values used for calibration (±1 standard deviation) and comparison to IAEA-NO-3 used to assess measurement accuracy.

δ^{15}N and δ^{18}O values are obtained from www.nucleus.iaea.org. Δ^{17}O values are obtained from (Bohlke et al., 2003).

		δ^{15}N (‰$_{AIRN2}$)	δ^{18}O (‰$_{VSMOW}$)	Δ^{17}O (‰$_{VSMOW}$)
International Standards	USGS-32	+180 ± 1	+ 25.7 ± 0.4	Unknown
	USGS-34	–1.8 ± 0.2	–27.90 ± 0.6	–0.3
	USGS-35	+2.7 ± 0.2	+57.50 ± 0.6	21.60
Precision	IAEA-NO-3 Accepted value	+4.7 ± 0.2	+25.60 ± 0.4	–0.10
	IAEA-NO-3 Check	+4.8 ± 0.1 (n=10)	+25.49 ± 0.11 (n=10)	–0.48 ± 0.21 (n=10)

Statistical analyses were made to determine differences between sample groups (lakes, inflows, and snow) with respect to nitrate isotope ratios. The sample groups violate assumptions of the parametric ANOVA tests, namely that sample groups should be normally distributed (rejected via Shapiro-Wilks tests), and equal variance between sample groups (rejected via Fligner-Killeen tests). Therefore, the non-parametric Kruskal-Wallace test was used to test for a significant difference between δ^{15}N, δ^{18}O and Δ^{17}O values among different sample types (snow, lake, and inflows). *Post-hoc* Kruskal-Wallace multiple comparison tests were used to identify the differences between pairs of sample groups.

4.3.3 SIAR mixing model

Proportional contributions of nitrate sources to Uinta Mountain lakes and streams were estimated using the stable isotope mixing model Stable Isotope Analysis in R (SIAR). SIAR uses a Bayesian framework to determine the probability distribution of the proportional contribution of each source to a mixture, as outlined in Parnell et al. (2010).

The model is fit via Markov chain Monte Carlo, which produces simulations of plausible source proportions for each sample group (Parnell et al., 2010), and models were run for 500,000 iterations. The strengths of the model that are particularly relevant to nitrate source allocation are (i) uncertainty in the system can be accounted for by factoring in variability in source values; (ii) solutions can be found for systems with more potential sources than previous approaches, and (iii) probability distributions are generated for each of the sources (Parnell et al., 2010).

Source parameters (mean and standard deviation) for soil nitrate, NO_3^--based fertilizer, NH_4^+-based fertilizer + rain NH_4^+, and septic + manure sources for input into the SIAR model were drawn from Xue et al. (2009) (Table 4.2). Although the review by Xue et al. (2009) also contains source isotopic compositions for atmospheric nitrate, we instead used the mean and standard deviation of the Uinta Mountain snow samples. Using snow samples should better represent the regional atmospherically oxidized nitrate source. Still, we acknowledge that only winter precipitation is represented in our sample set, and that atmospheric $\Delta^{17}O$ can vary seasonally (Alexander et al., 2009). The atmospherically oxidized nitrogen source does not include reactive nitrogen present in forms that are delivered but not oxidized atmospherically (e.g., particulate nitrate and ammonium from fertilizers, etc.), as they lack the $\Delta^{17}O$ enrichment acquired during atmospheric oxidation.

Table 4.2. SIAR input values for nitrate sources.

Source values for fertilizer and rain NH_4^+, soil, septic waste + manure were estimated from the ranges provided in Xue et al. (2009).

Source	**$\delta^{15}N$ ‰**		**$\Delta^{17}O$ ‰**	
	Mean	**SD**	**Mean**	**SD**
Atmospherically oxidized NO_3^-	+0.94	1.57	+23.66	5.58
Fertilizer NO_3^-, Fertilizer NH_4^+ & Rain NH_4^+	–1.4	5.1	0	1
Soil	+4.15	3.4	0	1
Septic waste & manure	+16.05	12.75	0	1

After initial model runs, which contained five possible nitrate sources and all of $\delta^{15}N$-, $\delta^{18}O$-, and $\Delta^{17}O$-NO_3^-, we simplified the model in two ways: (1) NO_3^- fertilizer and NH_4^+ fertilizer + rain NH_4^+ were aggregated into a single source; and (2) the model inputs were reduced from three isotopes of nitrate to only include $\Delta^{17}O$ and $\delta^{15}N$. The rationale for these modifications is given below:

> (1) We combined the NO_3^- fertilizer and NH_4^+ fertilizer + rain NH_4^+ source values into a single source because they have similar stable isotopic signatures. Furthermore, both NO_3^- -based and NH_4^+-based fertilizers are associated with intensive agricultural activity. NH_4^+ in rain is also largely derived from fertilizer, although soil and manure can also contribute (Russell et al., 1998; Li et al., 2007; Zhang et al., 2008). Isotopically, NO_3^- fertilizer and NH_4^+ fertilizer + rain NH_4^+ isotope ratios are similar, and are primarily differentiated based on $\delta^{18}O$ (mean $\delta^{18}O$ of NO_3^- fertilizer is ~+21 ‰, mean $\delta^{18}O$ of NH_4^+ fertilizer + NH_4^+ in rain is ~+7 ‰ (Xue et al., 2009)). However, higher $\delta^{18}O$ values can also be indicative of a larger proportional contribution of atmospherically oxidized nitrate, which complicates interpretation of the two fertilizer types when interpreted as separate end-members.

(2) The parameter δ^{18}O-NO_3^- was removed from the models because it is redundant given its high correlation with Δ^{17}O ($R^2 = 0.94$). In other words, at this site, both Δ^{17}O and δ^{18}O are tracking atmospherically oxidized nitrate.

4.4 Results

4.4.1 Nitrogen concentrations and sample selection for isotopic analysis

Nitrate concentrations for all (70) Uinta Mountain samples range from below the detection limit (< 0.016 μM) to 56 μM, with a median value of 1.8 μM (Appendix D, Table D.2). Inflows have the highest mean nitrate concentrations (25.5 μM-NO_3^-), followed by snow (4.9 μM-NO_3^-), and lakes (0.7 μM-NO_3^-). Ammonium concentrations range from 0.5 to 8.1 μM, with a median value of 0.9 μM. Snow has the highest mean concentration of ammonium (4.5 μM-NH_4^+), with lower mean concentrations in lakes (0.9 μM-NH_4^+) and inflows (1.0 μM-NH_4^+).

We limited our nitrate isotope analysis to inflows, lakes, and snow, disregarding eight outflow samples because the outflows had low nitrate concentrations and we expected similar results in the outflows as in the lakes. Of the remaining samples, 34 had sufficiently high nitrate concentrations (> 1.6 μM) for analysis of δ^{15}N-, δ^{18}O-, and Δ^{17}O-NO_3^-. Because only two lake samples (one each from Walk-Up and Taylor Lake) met this nitrate concentration threshold, we analyzed 10 additional lake samples with <1.6 μM-NO_3^-. Of these, we were able to obtain δ^{15}N and δ^{18}O for seven samples, three of which yielded Δ^{17}O data. In addition to the 41 Uinta Mountain samples for which we obtained results, results were also obtained for one sample from Great Salt Lake. Two snowmelt samples (see Figure 4.4) are not included in the SIAR model. These two samples are located directly below snowpack, and with such a location they are not clearly categorized into either the snowpack or inflow sample group. However, these data still provide information on transitional waters between snow and stream. The four lake samples for which we were unable to measure Δ^{17}O-NO_3^- (unfilled diamonds in Figure 4.4) were also not included in the SIAR model.

The stable isotope compositions of the samples, illustrated in Figure 4.4, reveal several patterns. The snow samples group together with high δ^{18}O- and Δ^{17}O-NO_3^- values. Lakes and inflows have lower δ^{18}O- and Δ^{17}O-NO_3^- than snow, but still have Δ^{17}O-NO_3^- values that plot above the TFL. Great Salt Lake has a similar isotope composition to inflows and lakes with respect to Δ^{17}O- and δ^{18}O-NO_3^- but has significantly elevated δ^{15}N-NO_3^-.

The δ^{15}N-NO_3^- values range from –3.7 to +6.9 ‰, not including Great Salt Lake, which has a δ^{15}N-NO_3^- value of +10.4 ‰ (Figure 4.5). Mean lake (+1.6 ‰) and snow (+0.9 ‰) δ^{15}N-NO_3^- values are higher than mean inflow (–1.5 ‰) δ^{15}N-NO_3^- values. The δ^{18}O values range from –4.7 to +75.1 ‰. All but one sample (an inflow of Denise Lake sampled in 2008, darkest blue lake in Figure 4.4) are significantly elevated above the Terrestrial Fractionation Line (along which $\Delta^{17}O = 0$ ‰). The snow samples are particularly elevated, with a mean Δ^{17}O-NO_3^- of +23.7 ‰ (see Appendix E).

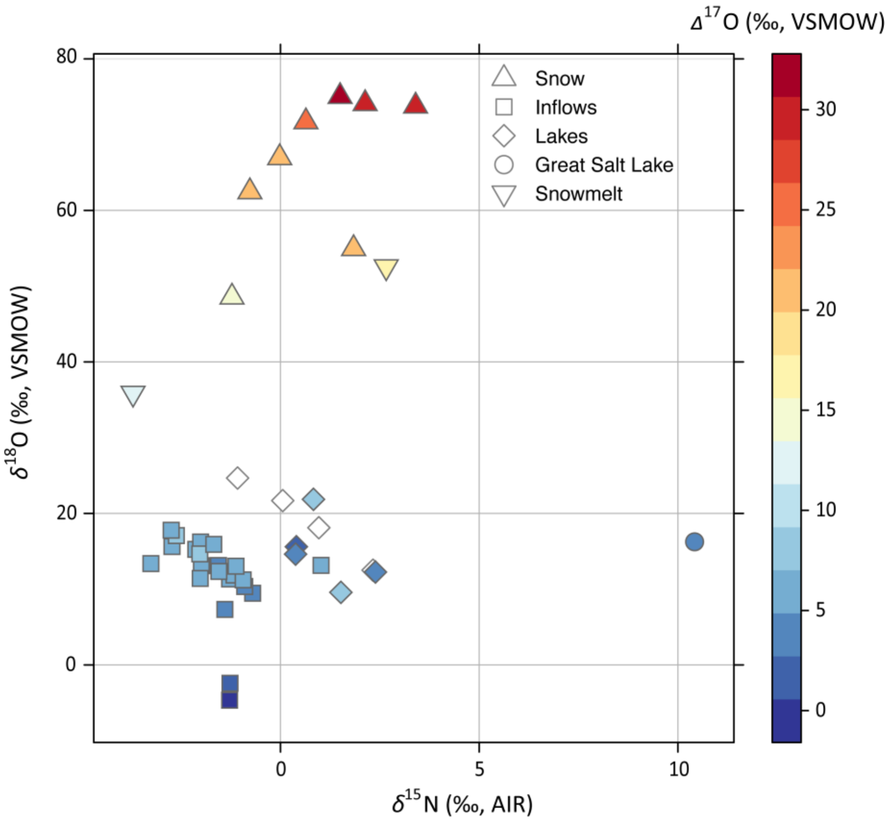

Figure 4.4. A triplot ($\delta^{15}N$-, $\delta^{18}O$-, and $\Delta^{17}O-NO_3^-$ values) of snow, lake, inflow, snowmelt, and Great Salt Lake samples.

$\Delta^{17}O$ is represented by colour, with blue representing lower values and red representing higher values. It was not possible to accurately measure $\Delta^{17}O$ on the points with no fill colour due to low nitrate concentrations. This figure was created using the "Lattice" package (Sarkar, 2008) for the R software environment (R Development Core Team, 2011)

A Kruskal-Wallis analysis of variance test revealed significant differences ($p < 0.05$) between at least two sample groups for each of $\delta^{15}N$-, $\delta^{18}O$- and $\Delta^{17}O-NO_3^-$. According to *post-hoc* Kruskal-Wallis multiple comparisons tests[18], $\delta^{15}N-NO_3$ in inflows are significantly different than lakes and snow, whereas lake and snow values cannot be differentiated ($p < 0.05$). For both $\delta^{18}O-NO_3^-$ and $\Delta^{17}O-NO_3^-$ values, snow samples are

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[18] The Kruskal-Wallis analysis of variance test is a separate test from the Kruskal-Wallis multiple comparisons test, and the use of the latter to determine which groups are different is carried out after significant differences have been demonstrated using the former.

significantly different from both inflow and lake samples, whereas the inflow and lake sample values cannot be differentiated ($p > 0.05$). Thus, using a combination of δ^{18}O-, Δ^{17}O- and δ^{15}N-NO_3^- we can differentiate among three sample types (Figure 4.5, Appendix D).

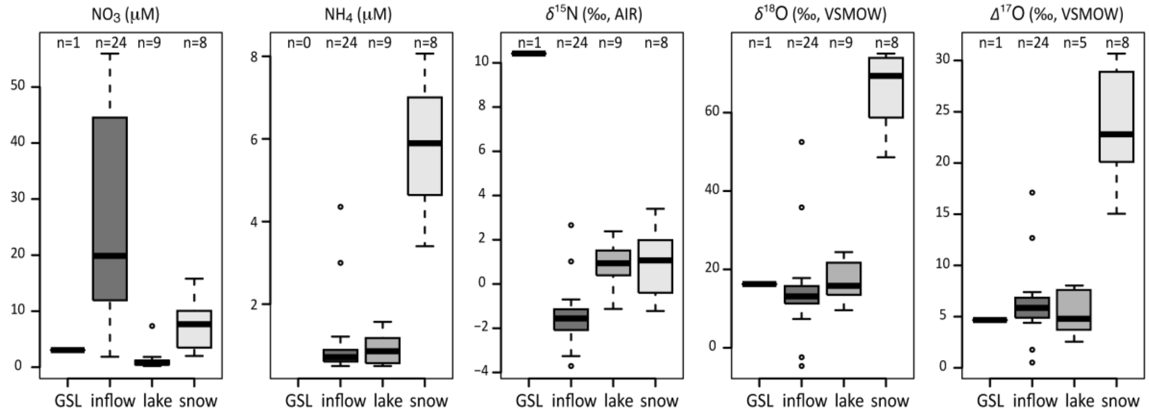

Figure 4.5. Summary boxplots for (A) NO_3^- (μM), (B) NH_4^+ (μM), (C) δ^{15}N-NO_3^-, (D) δ^{18}O-NO_3^-, and (E) Δ^{17}O-NO_3^-.

The median is represented by the horizontal black bar, the lower and upper boundaries of the box represent the lower (25%) and upper (75%) quartiles of the data, and the whiskers represent the minimum and maximum values, excluding outliers. Outliers are represented as points outside the whiskers. The NO_3^- concentrations of the samples are elevated above the true average for these Uinta Mountain sites, because sample selection for isotopic analysis was limited by nitrate concentration**.**

4.4.2 Source contribution model

The δ15N and Δ17O values of lake inflow, GSL and snow samples are depicted relative to the SIAR model source parameters in Figure 4.6. In Figure 4.7, the proportional contribution of these sources to inflows and lakes are graphically summarized by SIAR using 95 %, 75 %, and 50 % Bayesian credible intervals for each source of nitrates at lakes and inflows.

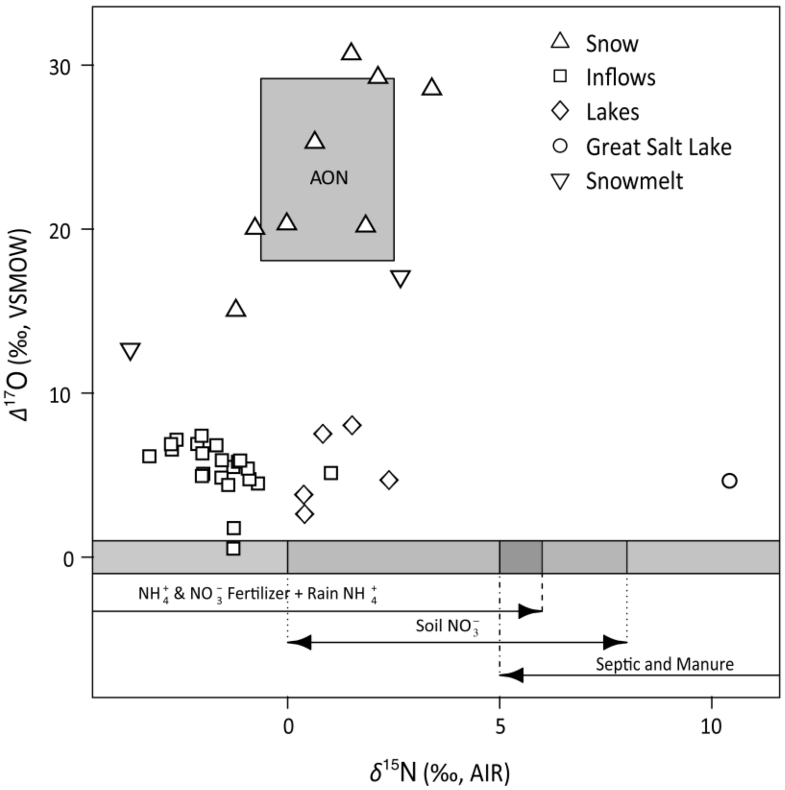

Figure 4.6. Snow, lake, and inflows from the Uinta Mountains, and a sample from Great Salt Lake (GSL) are shown relative to source values (± 1 standard deviation) for δ^{15}N and δ^{18}O. AON = Atmospherically oxidized nitrate. The source parameters are listed in Table 4.2, and are derived from a review by Xue et al. (2009).

For inflows, NO_3^- and NH_4^+ fertilizer + rain NH_4^+ are the largest contributor of nitrate with 62 % modal probability estimate (MPE)[19]. Atmospherically oxidized nitrate contributes 23 % MPE to the total nitrates in inflows, soil contributes 13 % MPE, and manure contributes 0 % MPE (all p values > 0.01) (Figure 4.7).

NH_4^+ and NO_3^- based fertilizers + rain NH_4^+ are also the top contributor to lake nitrate (35 % MPE), although a much greater proportional contribution comes from soil nitrates (34 % MPE) than inflows. Atmospherically oxidized nitrate contributes 24 %

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[19] The modal probability estimate, or MPE, is the solution (proportion contributed by that source) with the highest probability.

MPE to lakes, only slightly higher than inflows, and manure contributes 2 % MPE (Figure 4.7).

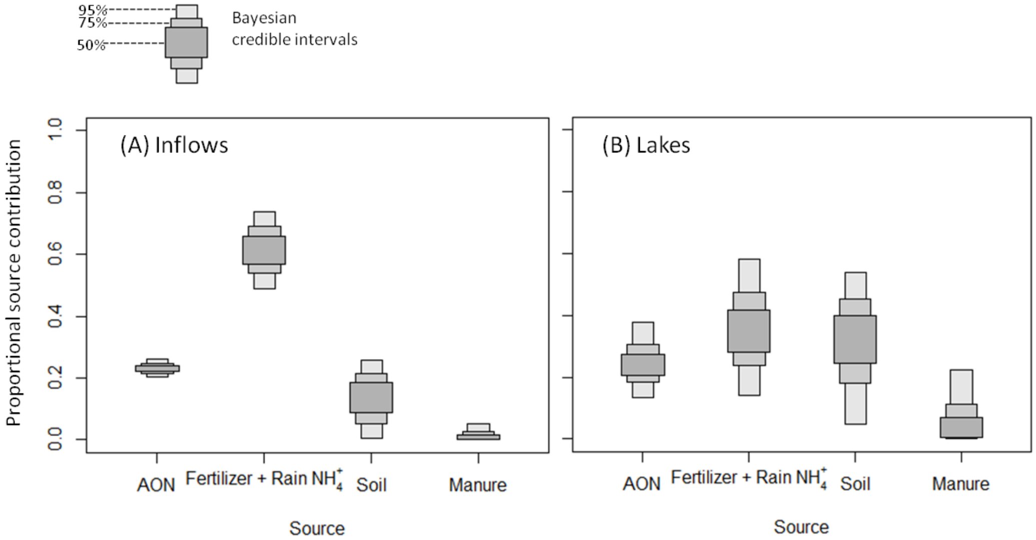

Figure 4.7. Mixing model estimated contributions of nitrate sources to (A) inflows and (B) lakes based on δ^{15}N, and Δ^{17}O of samples.

Bayesian credible intervals show estimated contributions of each source to inflows and lakes, as determined using the stable isotope mixing model SIAR. The source types are atmospherically oxidized nitrate (AON), NH_4^+ fertilizer (upon nitrification) + NO_3^- fertilizer + rain NH_4^+, soil nitrate, and manure.

4.5 Discussion

4.5.1 Isotopic composition of snow

We compared the δ^{18}O-NO_3^- from Uinta Mountain snow to other atmospheric nitrate and precipitation records to establish whether our Uinta Mountain snow nitrate results are reasonably representative of atmospheric nitrate composition. The average snow Δ^{17}O-NO_3^- from the Uinta Mountains (+23.7 ± 5.6 ‰) is within the documented atmospheric range of +20 to +35 ‰ according to Morin (2009), and comparable to the average Δ^{17}O-NO_3^- values obtained from snow pits in the Colorado Front Range (+28.6 ± 0.2 ‰) by Darrouzet-Nardi et al. (2012). There is also considerable overlap between Uinta Mountain snow nitrates (δ^{18}O-NO_3^- range: +48.6 to +75.1, median: +69.4 ‰) and precipitation nitrate from NADP/NTN sites in several national parks in the Rocky Mountains (δ^{18}O-NO_3^- range: +71 to +78 ‰, median: +74.5 ‰) (Nanus et al., 2008).

4.5.2 Source contributions to inflows and lakes

4.5.2.1 NO_3^- and NH_4^+-based fertilizer + rain NH_4^+

Inflows have low δ^{15}N-NO_3^- values indicating a high proportion of fertilizer-derived nitrates, whereas lake samples have slightly higher δ^{15}N-NO_3^- values than inflows, indicating a contribution from soil or manure in addition to fertilizer inputs. The SIAR model results confirm the important role of fertilizer in the inflows and lakes at the Uinta Mountain sites (Figure 4.7). Since neither NH_4^+- nor NO_3^--based fertilizers are used directly in the catchments, this contribution is attributed to atmospherically-delivered fertilizers from lowland agricultural areas.

The range in isotopic variation of inflow nitrates is quite small (Figure 4.6) considering the large range in nitrate concentrations (Figure 4.5A), site locations, and inflow types (e.g., through wetland, talus slopes, etc.), which suggests a widespread and homogenous source. The consistency in isotopic composition among different inflow samples is best explained by the dominance of atmospheric fertilizer deposition at these sites.

Snow samples have higher and more variable δ^{15}N-NO_3^- values, and therefore appear to be less influenced by the atmospherically transported fertilizers (particles and dust) than do inflow samples. However, it is more likely that some fertilizer-derived N is still in the form NH_4^+ in the snowpack, where nitrification does not occur (Williams et al., 1996b). This explains the high concentrations of NH_4^+ in snow samples (Figure 4.5B) relative to the inflows and lakes. Upon release from the snow into soil, snowmelt, or inflows, the NH_4^+ can be nitrified to NO_3^-, resulting in the high NO_3^- concentrations of inflows (Figure 4.5A). If we therefore assume that the inflow δ^{15}N reflects the combined isotopic composition of snow ammonium and nitrate, we approximate the δ^{15}N of snow ammonium by solving for $\delta^{15}N_{NH4snow}$ in equation 4.

$$\delta^{15}N_{inflow} = \delta^{15}N_{NH4snow} \times \frac{[NH4_{snow}]}{[total_{snow}]} + \delta^{15}N_{NO3snow} \times \frac{[NO3_{snow}]}{[total_{snow}]} \qquad \mathbf{4}$$

where $\delta 15N_{inflow}$ and $\delta^{15}N_{snow}$ are average values (from Appendix D, Table D.2); concentrations are reported in units NH_4 as N and NO_3 as N; $[total_{snow}]$ is the sum of $[NH4_{snow}]$ and $[NO3_{snow}]$; and $\delta^{15}N_{NO3snow}$ is assumed to be equal to $\delta^{15}N_{snow}$. This also assumes that there is little fractionation during conversion from ammonium to nitrate.

From this, we approximate that the snow ammonium $\delta^{15}N$ is -4.5‰, which falls in the range of fertilizer isotope composition (Figure 4.6).

4.5.2.2 Atmospherically oxidized nitrate

A comparison of the $\delta^{15}N\text{-}NO_3^-$ and $\Delta^{17}O\text{-}NO_3^-$ of the samples and sources (Figure 4.6) suggests that both lakes and inflows are influenced by atmospherically oxidized nitrate ($\Delta^{17}O > 0$). The SIAR model results indicate a contribution of atmospherically oxidized nitrate to lakes and inflows of 23 and 24 % MPE, respectively (Figure 4.7). Some sources of atmospherically oxidized nitrate are natural (lightning, soil emissions, and wildfire), and some are anthropogenic (fossil fuel combustion and biomass burning). It is beneficial to estimate the proportion of atmospherically oxidized nitrate originating from each of these sources. In practice, this task is difficult because the source of atmospherically oxidized nitrate varies depending on the region, and the contribution of nitrate from sources like lightning is difficult to estimate. Nevertheless, we apply global estimates (Table 4.3; Price et al. (1997)) of atmospherically oxidized nitrates of the overall contribution of atmospherically oxidized nitrates in the Uinta Mountains (which accounts for ~ 24% MPE for lakes and inflows based on the SIAR model, Figure 4.7). From this, we estimate that ~10 % of total nitrate inputs to Uinta Mountain lakes are originally derived from fossil fuel combustion.

Table 4.3. Sources of tropospheric NO_x and their estimated contribution to Uinta Mountain lake nitrates.

The estimated contribution of each tropospheric NO_x source to Uinta Mountain lakes is calculated based on the global percentage contribution to the troposphere and an overall contribution of atmospherically oxidized nitrate to Uinta Mountain lakes of 24 % MPE, based on the proportional contribution of atmospherically oxidized nitrate to lakes and inflows determined using the SIAR model (Figure 4.7). The sources of tropospheric NOx and their contributions to the global N cycle are taken from Price et al (1997) and sources within.

Source of tropospheric NO_x	**Contribution ($Tg\ N\ yr^{-1}$) to tropospheric NO_x**	**Contribution (%) to tropospheric NO_x**	**Estimated contribution to Uinta Mountain lakes (%)**
Fossil fuels	24	40	10
Lightning	12	20	5
Soil emissions	12	20	5
Biomass burning	8	13	3
NH_3^+ oxidation	3	5	1
Transport from stratosphere	0.4	0.7	0.2
Aircraft	0.4	0.7	0.2
Total	**60**	**100**	**24**

4.5.2.3 Soil nitrate

The soil NO_3^- contribution to Uinta Mountain lakes and inflows is 34 and 13 % MPE, respectively. The lower impact of soil NO_3^- is not surprising, given that alpine environments are typically low nutrient, tightly cycled systems.

4.5.2.4 Septic effluent and manure

Our results suggest that septic effluent and manure have little to no influence on the nitrate concentrations in the Uinta Mountains (0 % and 2 % MPE for lakes and inflows, respectively), despite that free-range grazing is commonplace in Uinta Mountain catchments. Septic and manure inputs to Great Salt Lake are likely responsible for the high δ^{15}N present in the Great Salt Lake water sample (Baskin et al., 2002) (Figure 4.6).

4.5.2.5 Biological fractionation processes

Denitrification involves conversion of NO_3^- to N_2O and N_2 under oxygen-limiting conditions and when organic carbon is available (Mayer et al., 2002). During microbial denitrification, ^{14}N and ^{16}O are preferentially utilized, leaving the remaining NO_3^- relatively enriched in ^{15}N and ^{18}O (Roadcap, 2001). Therefore, during denitrification, as concentrations of NO_3^- decrease (as NO_3- is converted to N_2), δ^{15}N- and δ^{18}O-NO_3^- increase (Mayer et al., 2002). Values of Δ^{17}O, on the other hand, do not undergo fractionation during denitrification so any changes in Δ^{17}O result from dilution. A longer-term sampling plan would be required to determine the extent of denitrification at these sites. However, we speculate that denitrification may explain the higher δ^{15}N and, to a lesser extent, δ^{18}O-NO_3^- values in lakes relative to inflows (Figure 4.5C, Figure 4.5D), and the relatively stable values for Δ^{17}O-NO_3^- (Figure 4.4 and Figure 4.5E). Inflow nitrate is less likely to undergo denitrification than lake nitrates, given the high oxygen availability in running water (dissolved oxygen concentrations of > 5 mg L^{-1} are not suitable for denitrification) (Xue et al., 2012)). In contrast, three of the six study lakes (Taylor, Bluebell, and Upper Carroll), are known to stratify, and can reach dissolved oxygen concentrations below 5 mg L^{-1} (Figure 2.8).

4.5.3 Comparison to other high elevation sites

A comparison of the Uinta Mountain lake δ^{15}N- and δ^{18}O-NO_3^- data with that from five National Parks in the U.S.A. Rocky Mountains (Nanus et al., 2008) shows considerable overlap in isotopic composition of nitrates. The high δ^{18}O-NO_3^- values, particularly in Glacier, Grand Teton, and Rocky Mountain National Parks indicate that these lakes are, as Nanus et al. (2008) suggest, influenced by wet deposition of dissolved inorganic nitrogen (DIN = NO_3^- + NH_4^+), while the low δ^{15}N values (all < 5 ‰) present in the National Park lakes are indicative of fertilizer sources of DIN. Future measurements of Δ^{17}O-NO_3^- and application of a mixing model would have great potential for determining the source contributions of DIN from fertilizer and atmospherically oxidized nitrate at these sites.

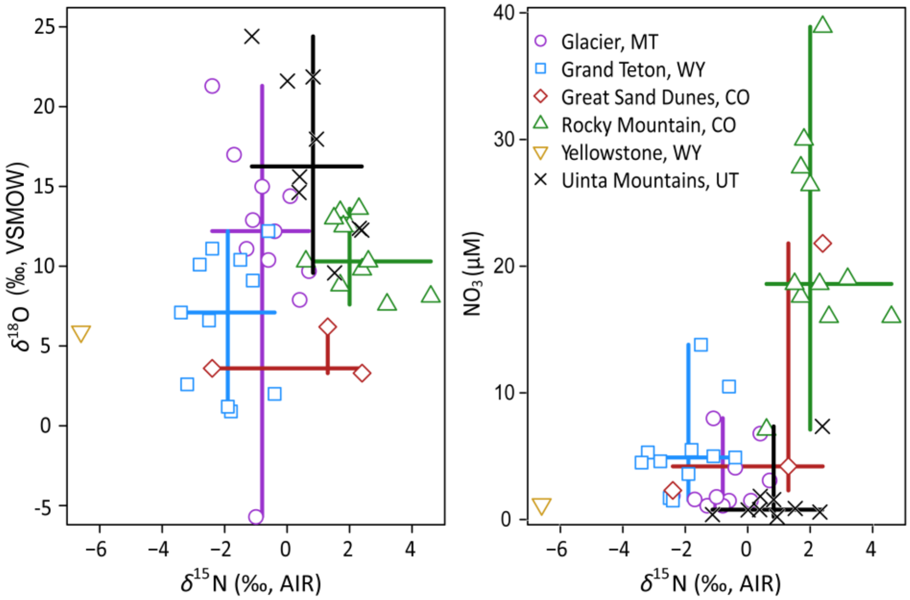

Figure 4.8. Range of (A) $\delta^{18}O$ versus $\delta^{15}N$, and (B) NO_3^- concentration versus $\delta^{15}N$ for the Uinta Mountain lakes compared to lakes from five National Parks in the U.S. Rocky Mountains (Nanus et al., 2008).

The extent of each cross spans the range of the data from each set of lakes, and centre of the cross is the median value. Yellowstone is represented by one measurement.

A study of $\Delta^{17}O$-NO_3- along a stream in the Colorado Front Range indicated that during early snowmelt, stream nitrates range from 95 % atmospherically produced NO_3- at the headwater wetland to 65 % in the lower reach of the stream (Darrouzet-Nardi et al., 2012). At later sampling dates, which are more comparable to our sampling period of late July, the percent of atmospherically derived NO_3^- is less variable between sample locations, and very similar (~20 - 25 %) to the percentage of atmospherically oxidized nitrate in the Uinta Mountain inflows (24 % MPE). Darrouzet-Nardi et al. (2012) recognized the presence of two end-members, atmospherically derived nitrate and microbially derived nitrate. Measurement of $\Delta^{17}O$ values will allow for a close estimate of atmospherically derived nitrate. The microbially derived nitrate source is, more accurately, a simplification of all non-atmospherically oxidized sources. For example, at the Uinta Mountain study sites, 77 % of inflow nitrates are not derived from atmospherically oxidized nitrate, and of this fraction, only 13 % is actually soil nitrate (microbially-derived). An investigation of the influence of other important sources, such as NH_4^+- and NO_3^--based fertilizers, at the Colorado stream study site would allow us to compare the contribution of fertilizer nitrate in the Uinta Mountains to the Colorado sites.

4.6 Conclusion

This research demonstrates that agricultural activities are currently the most important influence on the nitrate concentrations in small, high elevation sites in the Uinta Mountains, with atmospherically delivered fertilizers contributing 62 % MPE of nitrates to inflows and 35 % MPE of nitrates to lake waters. About 10 % MPE of total lake and inflow nitrates (or 40 % MPE of atmospherically oxidized nitrates) originate from byproducts of fossil fuel combustion. Combined, anthropogenic sources (primarily atmospherically delivered fertilizers and fossil fuel combustion) comprise 72 % MPE of inflow nitrates and 45 % MPE of lake nitrates at the Uinta Mountain sites.

The triple-isotope approach for analyzing nitrates combined with SIAR mixing models has the potential to improve our understanding of nitrogen sources and cycling in high alpine environments. Similarities in nitrate isotope composition ($\delta^{15}N$ and $\delta^{18}O$) between our results and National Parks in other areas of the U.S.A. Rocky Mountains (Nanus et al., 2008) suggest that these findings may be applicable to other mountain regions in Western North America. Increasing nutrient delivery has been shown to have profound effects on lake primary production for more than fifty years in the Colorado Front Range (Baron et al., 2000; Wolfe et al., 2001; Saros et al., 2003), and the Uinta Mountains (Chapter 3). This history of primary aquatic production combined with our results that identify fertilizers as the largest modern source of nitrates to the Uinta Mountains underline the importance of careful management of fertilizer application in surrounding lowlands.

4.7 References

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Chapter 5

5 Variable diatom responses to increased nutrients in Uinta Mountain lakes

5.1 Introduction

Unprecedented changes in the nitrogen cycle are occurring on a global scale. Anthropogenic reactive nitrogen emissions have increased nine-fold in the last century, to the point that humans now fix more N_2 than all natural processes combined (Galloway and Cowling, 2002). Evidence from alpine environments indicates that lakes in the U.S.A. Rocky Mountains are susceptible to enhanced nitrogen deposition (Williams et al., 1996a; e.g., Nanus et al., 2003; Saros et al., 2003; Wolfe et al., 2003). Mountain lakes may also be susceptible to the effects of warming temperatures, which can affect the length of the growing season and ice-free period, plus the duration and stability of lake stratification (Smol, 1988; Smol et al., 1991). These changes, in turn, can affect lake water properties, water chemistry, light availability, nutrient cycling, habitat availability, and ultimately, biological communities within a lake (Rühland et al., 2003; Rühland et al., 2008). Researchers have recognized that climate warming and nitrogen deposition are not mutually exclusive drivers of ecological change, and the interplay between warming and fertilization by atmospheric deposition is not well understood (Catalan et al., 2013). Climate warming and nitrogen deposition may influence different limnological variables to varying degrees in different environments. For example, it has been suggested that climate has the strongest influence on diatom ß-diversity (species turnover) in arctic environments where 20th century warming has been rapid but atmospheric nitrogen deposition is still relatively low (< 50 mg N m^{-2} yr^{-1}) (Galloway and Cowling, 2002; Hobbs et al., 2010). Conversely, reactive nitrogen deposition has a stronger influence on diatom ß-diversity in mid-latitude alpine environments where nitrogen deposition is greater (100-500 mg N m^{-2} yr^{-1}) (Hobbs et al., 2010).

The main goal of this study is to determine whether past changes in diatom community composition recorded in lake sediments from remote, high elevation sites in the Uinta Mountains, U.S.A. can be linked to warming and/or nitrogen deposition. The

Uinta Mountains provide an ideal setting for this investigation because direct human impacts are restricted to free-range grazing and moderate recreational use. However, the Uinta Mountains are exposed to atmospheric nitrogen deposition as they are located east and downwind of the Wasatch Front, a densely populated region that has seen a rapid increase in population, industry, and agricultural activity since initial settlement in 1847. The Uinta Mountains have also experienced recent, rapid warming. Temperature data from nearby meteorological stations (Heber and Vernal, Utah) show a fluctuating pattern until the mid-1980s when mean annual temperatures increase[20] (Chapter 1), which is comparable to the regional trend in the mid-western U.S.A. The western U.S.A. is predicted to undergo further warming in the coming decades (McAfee and Russell, 2008).

A second goal is to determine the range of potential responses by selecting lakes of varying characteristics and catchments. This will provide a deeper understanding of how lake ecosystem sensitivity varies with these forcings. Lake response to climate warming or nitrogen deposition may be affected by several factors including water depth, vegetation cover, talus slopes and through-flow. Water depth is linked closely to the thermal inertia of arctic lakes and therefore the susceptibility of the lake to temperature changes (Smol and Douglas, 2007a); closed basin lakes are more likely to retain nutrients than lakes with high throughflow; well-vegetated catchments may have a greater ability to take up nutrients; and talus slopes are potential sites of microbial nitrification (Williams et al., 1997).

In order to investigate the influence of both warming and nitrogen deposition on Uinta Mountain lake ecosystems, fossil diatom (Class Bacillariophyceae) assemblages from six Uinta Mountain lakes were examined in relation to a calibration set (modern limnological data + surface sediment diatom assemblages) of 57 Uinta Mountain lakes. The six study lakes are all at high elevations and share a similar geology, but differ in lake depth, catchment landcover, catchment area, and through-flow. By selecting lakes

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[20] The trends in mean summer (NDJFM) and mean winter (MJJAS) temperature are similar to mean annual temperature trends and magnitude of change in Heber.

with different characteristics we will gain an understanding of which lakes most vulnerable to these regional-scale stressors.

Diatoms are useful biological indicators of ecosystem response because the numerous species have specific ecological preferences and respond rapidly to environmental changes, including lake water nutrient concentrations (Hall and Smol, 2001) and indirectly to changes in temperature (Lotter et al., 2001). We establish the relationship between diatoms and their contemporary aquatic environment using the calibration set. Diatom stratigraphies from lake sediment cores can be superimposed upon this modern diatom-environment relationship to aid our understanding of past environmental conditions and changes in diatom community composition. The findings will improve our understanding of ecosystem response and biological sensitivity to climate warming and nutrient deposition, which has been identified as a remaining challenge in paleolimnology of remote lakes (Catalan et al., 2013).

5.1.1 Anticipated ecological changes resulting from climate warming and nitrogen deposition

Although some expected changes in diatom community composition in response to warming climates and nitrogen deposition are similar, there are also some differences that help distinguish between the ecological effects of these two forcings. Warming temperatures can affect the length of the growing season, the length of the ice-free period and the duration and stability of stratification (Smol, 1988; Smol et al., 1991). These changes can affect lake water chemistry, light availability, nutrient cycling, habitat availability, and aquatic biology. Several paleolimnological studies in arctic regions and in European alpine lakes have shown striking changes in diatom assemblages due to recent warming (Lotter and Bigler, 2000; Catalan et al., 2002; Koinig et al., 2002; Rühland et al., 2003; Smol et al., 2005). Fewer studies illustrate the response of aquatic biota to warming in alpine regions of North America (e.g. a chironomid-based temperature inference model by Porinchu et al., 2007). Because arctic ecosystems are often grouped with high alpine ecosystems based on similarities in climate, vegetation, and diatom species composition (Lotter et al., 2001), we can use the results from both arctic and alpine studies to hypothesize the expected changes with warming of Uinta Mountain lakes.

Increases in nitrogen deposition can affect freshwater lakes by causing acidification and eutrophication. Lake acidification is rare in U.S.A. alpine systems, including the Colorado Front Range (Williams et al., 1996a; Wolfe et al., 2001) and the Uinta Mountains, where it is speculated that $CaCO_3$ supplied from dust may neutralize the effects of acid deposition (Squire, 2012). However, changes in primary production associated with increased nitrogen deposition have been recorded in several alpine ecosystems, including in the Colorado Front Range (Wolfe et al., 2001), and in the Uinta Mountains (Chapter 3, Hundey et al., (submitted)). Changes in primary production, in turn, can influence biodiversity, water quality, and oxygen levels in the hypolimnion. Diatoms are sensitive to these changes because individual species have specific water chemistry and habitat requirements, and are sensitive to changes in nutrient concentrations (Hall and Smol, 2001).

Based on findings from arctic and alpine lakes, warmer temperatures should result in an increased abundance of planktonic species (Lotter and Bigler, 2000; Koinig et al., 2002; Catalan et al., 2002; Rühland, Smol et al., 2003; Smol et al., 2005). This shift results from a longer ice-free season and associated increase in habitat availability, plus stronger, longer periods of stratification, which favour fast growing planktonic species that can exploit the stable conditions of the epilimnion (Rühland et al., 2003). Although diatom assemblages are complex, planktonic *Cyclotella* species have been consistently linked to warming trends in many circumpolar, alpine and temperate northern hemisphere lakes (Sorvari and Korhola, 1998; Rühland et al., 2003; Rühland et al., 2008). *Cyclotella* species do well in warmer lakes with increased thermal stratification (Rühland et al., 2008; Hobbs et al., 2010) and a longer ice-free season (Rühland et al., 2003; Smol et al., 2005). Conversely, during colder conditions with longer ice-covered seasons, benthic species like *Fragilaria* are abundant and competitive whereas planktonics under ice cover quickly sink to the bottom (Lotter and Bigler, 2000). An increase in planktonic diatoms is also associated with increased nutrient inputs (Wolin and Duthie, 2001). However, unlike with warming, the increase in planktonic diatoms is not expected to feature substantial increases in *Cyclotella* species, as lower abundances of *Cyclotella* have been associated with higher nutrient concentrations (Rühland et al., 2003). With increased biologically available nitrogen, we would instead expect an increased abundance of species such as *Asterionella formosa* (Saros et al., 2005; Michel et al., 2006). In temperate systems, *A. formosa* has been associated with human settlement, the introduction of agriculture, and P enrichment (Baron et al., 2000; Hall and Smol, 2001), but in alpine systems, *A. formosa* populations are stimulated by N additions and not P (Interlandi and Kilham, 1998). The maximum abundance of *A. formosa* in Sky Pond, Colorado Front Range, coincides with elevated NO_3^- concentrations (Wolfe et al., 2003), and increased prevalence of the species has been linked to increased reactive nitrogen availability (Wolfe et al., 2001; Saros et al., 2005).

It is expected that species assemblage turnover (ß-diversity) will increase with climate warming. With enhanced lake stratification and decreased ice cover, algae are able to exploit newly available habitats and as a result, ß-diversity increases (Smol et al., 2005). Smol et al. (2005) studied 42 diatom records from circumpolar sites and all experienced increasing ß-diversity over the last 150 years, with the largest changes occurring in the high arctic where the temperature change is greatest. It is also expected that ß-diversity would increase with increased nitrogen deposition and higher primary productivity as occurred in alpine lakes that were influenced by nitrogen deposition in North American mountain lakes (Hobbs et al., 2010). Few studies have evaluated the relationship between ß-diversity and algal productivity, however the most common response to increased productivity is a unimodal response among phytoplankton (Declerck et al., 2007; Leps, 2013; Skácelová and Leps, 2014). However, experiments have illustrated that phytoplankton species richness declines with increasing plankton productivity (Jeppesen et al., 2000; Declerck et al., 2007). Still other experiments reveal that community evenness is negatively correlated with nutrient enrichment, meaning that a few species become abundant at the expense of others when nutrient inputs increase (Larson and Belovsky, 2013). These shifts in diversity that coincide with increased productivity are likely to be accompanied by shifts in species composition, in which case ß-diversity should increase.

Changes in ß-diversity and the timing of major shifts in species assemblages (determined by CONISS zones) are expected to be linked to known changes in temperature and/ or nitrogen deposition. If changes in ß-diversity and species assemblages are being driven by warming temperatures, the variables should track temperature change. For example, in the Hudson Bay Lowlands, changes in diversity and percent planktonics coincide with climate trends, including with recent warming since 1990 (Rühland et al., 2013). If, on the other hand, the changes in diatom community composition are being driven by nitrogen deposition, they should track δ^{15}N (often linked to changing N sources) in the sediments. For example, in the Colorado Rocky Mountains, a change in the diatom assemblage and declining sedimentary δ^{15}N beginning around 1950 coincides with increasing nitrogen fixation via fossil fuel combustion and fertilizer production (Wolfe et al., 2001). Similarly, recent (since ~1950 AD) decreases in sedimentary δ^{15}N values in Uinta Mountain lakes have been attributed to increased contributions of N from fertilizer and fossil fuel combustion (Chapter 3, Hundey et al., (submitted)).

5.2 Study Area

The Uinta Mountains are an east-west trending mountain range that reaches elevations over 4000 m, and stretches 200 km across the northeastern part of Utah (40˚ to 41˚ N, 109˚ to 111˚ W) (Figure 5.1). The bedrock geology is comprised of the Uinta Mountain Group, which includes quartz, arenite, silitite, arkose, and shale (Condie et al., 2001). Cirques, U-shaped valleys, and many glacial lakes have been formed during multiple glacial events (Munroe et al., 2007).

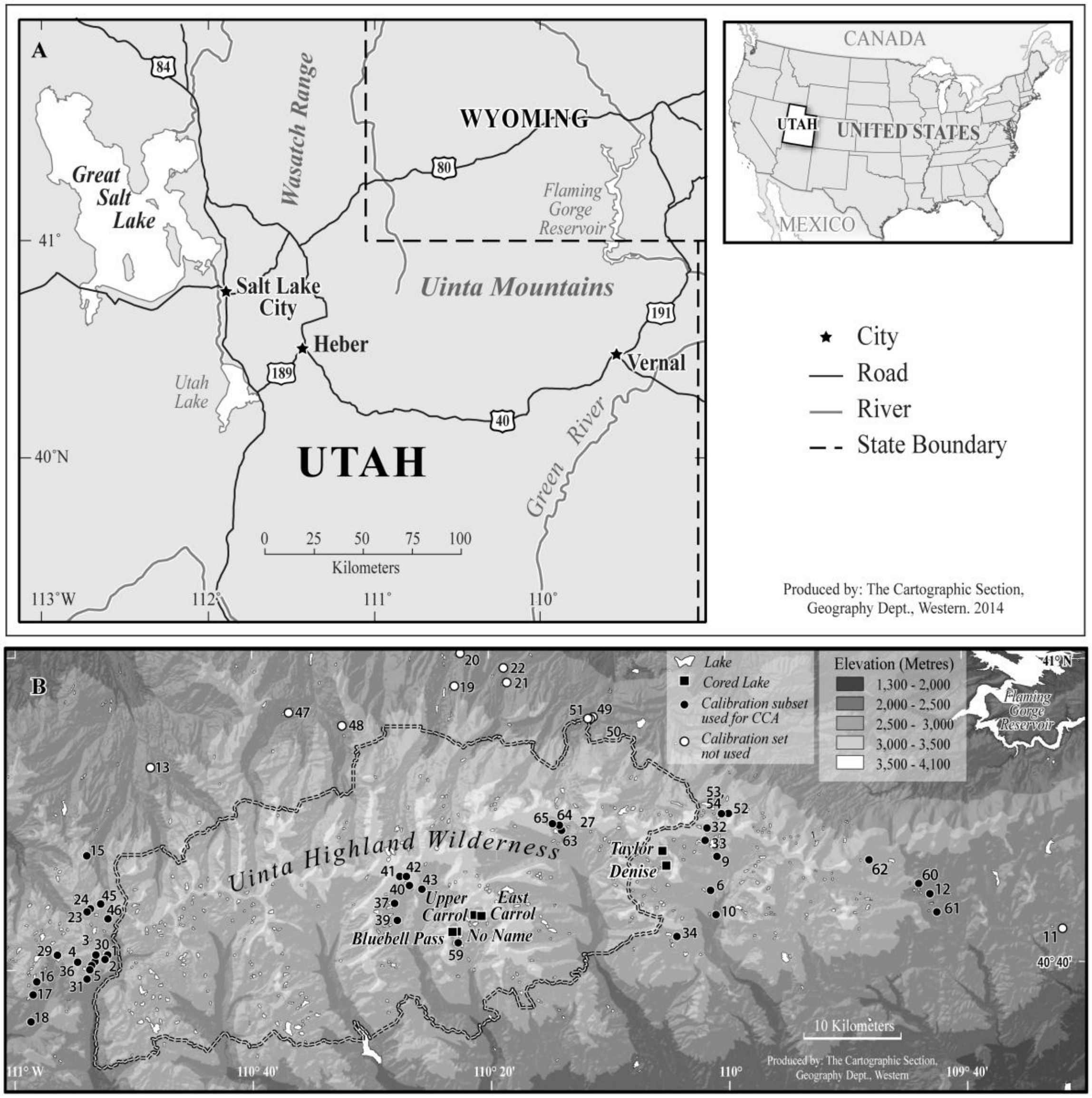

Figure 5.1. Location of study sites. (A) The position of the Uinta Mountains in northeastern Utah and U.S.A., and (B) the topography of the Uinta Mountains with the locations of the 6 study lakes, the 57-lake calibration set, including the 46-lake subset that was used for statistical analyses.

The steep elevation gradients and the location of the Uinta Mountains in an ecotone between the northern and southern U.S.A. Rocky Mountain vegetation zones result in a range of vegetation types in the Uinta Mountains (Shaw and Long, 2007). At tree line, catchments are covered by a mix of alpine tundra and forest-tundra vegetation, including subalpine fir (*Abies lasiocarpa*) and Engelmann spruce (*Picea engelmanii*), either as erect trees or krummholz (Shaw and Long 2007).

The Uinta Mountains have an alpine climate with short but warm summers. They are snow covered from mid-October to mid-May at higher elevations (e.g., Chepeta Snotel site, 3228 m.a.s.l.), and all but the highest peaks are snow free in summer. Precipitation varies substantially with elevation and longitude; higher elevation sites receive more precipitation than lower elevation sites, and the western slopes receive nearly twice the average annual precipitation as the eastern slopes (MacDonald and Tingstad, 2007).

A 57-lake calibration set (Figure 5.1B) has been assembled consisting of surface sediment diatom assemblages and water chemistry (Tingstad, 2010). The lakes were selected to maximize the elevation range and climatic variability. These lakes vary in elevation from 2652 to 3650 m.a.s.l., and alkalinity from 1 to 16.7 mg L^{-1} $CaCO_3^-$ (see Appendix 1, summary).

Six high elevation (> 3000 m.a.s.l.) oligotrophic lakes from this calibration set were cored and analyzed to provide an historical record of change in diatom community composition. The lakes were selected to maximize the range of lake and catchment characteristics to evaluate the full range of potential responses in diatom community composition. The six study lakes are Denise (WR-9)[21], Taylor (WR-8), Upper Carrol (X-18), East Carrol (X-21), No Name (X-26), and Bluebell Pass (X-25) (Figure 5.1). The catchment surfaces are characterized by a thin glacial till cover over bedrock (Munroe and Laabs, 2009). Two lakes (Bluebell Pass and Upper Carrol Lakes) have rock glaciers within their catchments (Munroe and Laabs, 2009). The lakes range from closed-basin (No Name Lake) to one with high inflow (Upper Carrol Lake); from shallow (Denise Lake, 2.4 m maximum depth) to deep (Upper Carrol Lake, 13.8 m); from large catchment (Denise Lake, 391.9 ha) to small (East Carrol Lake 35.1 ha), and with a range of catchment landcover.

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[21] Utah Department of Wildlife Resources codes in parentheses. Denise, No Name, and Bluebell Pass are unofficial lake names.

5.3 Methods

5.3.1 Catchment landcover

Variables describing the characteristics of the lakes and their catchments were determined using GIS analysis. Watershed boundaries were determined using a digital elevation model (10 m resolution) (U.S. Geological Survey, 2006). The extent of each landcover type within each catchment were determined by overlaying the watershed boundaries with landcover data from the USGS National Gap Analysis Program (2004) (30 m resolution) using the Terrain Analysis System (Lindsay, 2005). Several land use categories from the USGS National Gap Analysis Program were merged for comparison between sites, as follows: **talus + bedrock** combines bedrock and scree and alpine fell field; **forest + shrubland** includes subalpine dry-mesic spruce-fir forest and woodland, subalpine mesic spruce-fir forest and woodland, alpine dwarf shrubland, subalpine-montane riparian shrubland; and **meadow + tundra** combines dry tundra, subalpine mesic meadow, southern montane subalpine grassland, and alpine-montane wet meadow[22].

5.3.2 Sediment cores

5.3.2.1 Field methods

Lake sediment cores between 25 and 50 cm in length with an undisturbed sediment-water interface were obtained from the deepest part of each of six lakes during the summers of 2006 (Taylor and Denise lakes) and 2007 (East Carrol, Upper Carrol, No Name, and Bluebell Pass lakes) using a Kajak-Brinkman gravity corer fitted with a 6.5 cm diameter plastic tube (Glew et al., 2001). Lake sediments were extruded on site using a specially designed extruder (Glew et al., 2001) and were subsampled at 0.5 cm contiguous intervals, except at greater than 20 cm depth in Taylor and Denise lakes, which were sub-sampled at 1 cm intervals (daylight was limited and weather was threatening). The sub-samples were stored in Whirlpak bags in dark conditions at 4 ˚C at

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[22] Detailed landcover descriptions are provided by the Southwest Regional Gap Analysis Project (Utah State University) at http://earth.gis.usu.edu/swgap/data/landcover/descriptions/landc_database_report.pdf

the Lakes and Reservoir Systems Research Facility at the University of Western Ontario, London, Canada.

5.3.2.2 Chronology

Lake sediments were dated using ^{210}Pb (half-life = 22.26 years) techniques (Appleby, 2001) on 15 dried and ground samples per lake between 0 and 22 cm core depth. Samples were analyzed using α-spectrometric measurements of ^{210}Po, a decay product of ^{210}Pb, at MyCore Scientific Inc. in Deep River, Canada (Cornett et al., 1984). The ^{210}Pb ages were calculated using the constant rate of supply (CRS) model, in which lake sediments are assumed to be receiving a constant input of unsupported ^{210}Pb from the atmosphere (Appleby, 2001). Due to the absence of suitable organic material for ^{14}C dating, the ^{210}Pb dating models were extended using linear regression ($R^2 = 0.95$ for all six lakes) below the dateable sections. The ^{210}Pb chronology is discussed in further detail in Chapter 3.

5.3.2.3 Diatoms

Samples were prepared for diatom analysis using the method described by Battarbee et al. (2001). Approximately one cm^3 subsamples were treated with 10% hydrochloric acid to eliminate excess calcium carbonates, followed by a 50:50 molar weight solution of nitric and sulfuric acid to digest organic matter. After 24 hours the samples were heated to 80 ˚C for two hours. Treated subsamples were rinsed a minimum of 10 times (at least 24 hours between washes) with distilled water until neutrality was reached, and then mounted to slides using Naphrax® or Z-rax®. For each sample, a minimum of 600 diatom valves were identified and counted, except in select cases in which half of a cover slip was counted before 600 diatoms were reached. In these cases, counting was stopped at half of a cover slip as long as 500 diatoms were identified and counted. Counts were done using a Leica E-600 light microscope outfitted with differential interference contrast optics and 100x magnification and a Retiga ® 2000 Fast 1394 digital camera. The main reference for taxonomy used was Krammer and Lange-Bertalot (1986-1991). Diatom assemblages are presented as relative frequencies of taxa (in some cases groups of taxa) relative to the total number of valves counted. Groups of similar species were created to overcome discrepancies between the downcore and calibration set counts. Two of the major groups were the small *Fragilaria* species (*F. construens* var. *venter, F. pinnata* varieties and *F. brevistriata*) and three of the *Cyclotella* species (*C. stelligera, C. pseudostelligera,* and *C. atomus*).

5.3.3 Calibration set

The calibration set used for this study consists of 57 lakes in the Uinta Mountains sampled in July and August from 2000 to 2004 by Moser (Figure 5.1). These data will be presented elsewhere in more detail (Tingstad et al., in prep), but briefly, at each lake both water samples and surface sediments were collected for analysis. Lake environmental variables were recorded over the deepest part of the lake, which was approximated based on several depth measurements near the centre of the lake. At this location, surface water temperature and specific conductivity were measured using a YSi-M85 meter, and pH was measured using a minimum of three Hanna PH meters. Alkalinity was determined using a Hach kit. At the same location, 0.5 m below the water surface, samples were collected for analysis of water chemistry. The samples were filtered in the field using a 0.45 μm filter and collected in 30 ml pre-cleaned Nalgene bottles. Samples were analyzed for several ions and elements, including fluorine, chlorine, nitrate, sulfate, sodium, magnesium, aluminum, silica, potassium, calcium, manganese, strontium, barium, lithium, boron, chromium, cobalt, nickel, copper, zinc, arsenic, rubidium, lead, uranium, iron, dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC). Water samples were kept cool in the field until they were shipped to Rick Knurr at the Aqueous Geochemistry Lab at the University of Minnesota. Dissolved organic carbon and dissolved inorganic carbon were analyzed by David Lean at the University of Ottawa.

The surface sediments (top 0-1 cm), which represent a spatially (from all parts of the lake) and temporally (the last ~5 years) integrated sample of diatoms, were collected with a Glew Mini Corer (Glew, 1991) and stored in WhirlPak ® bags and kept cool until shipped. Diatom slides were prepared in the same fashion as described in section 5.3.2.3.

5.3.3.1 Zonation

Zonation in the diatom assemblages was determined by Constrained Incremental Sums of Squares cluster analysis (CONISS) (Grimm, 1987). CONISS was performed using the “rioja” package (Juggins, 2013) for the R software environment (R Development Core Team, 2011). The dispersion of the hierarchical zones was compared to that of a broken stick model (Bennett, 1996) in order to determine the number of significant splits (zones = splits + 1). The precise placement of the splits between zones is determined by visual inspection and by the CONISS hierarchy. The dendrograms returned from CONISS and the broken stick models for each lake are displayed in Appendix H.

5.3.4 Ordination

Diatom taxa that occurred in the calibration set with a relative abundance of at least 1 % in one lake and present in at least three lakes formed the diatom species dataset used for statistical analysis of the calibration set. Prior to analysis the percentage data were square root transformed with the intention of stabilizing the variance in each dataset. All ordinations were determined using the computer program CANOCO V. 4.55. Ordination plots were drawn by CANODRAW 3.0. A detrended canonical correspondence analysis (DCCA), detrended by segments with Hill’s scaling, was used to determine whether diatom species in the calibration set primarily follow a unimodal (DCCA gradient length > 4) or linear distribution (DCCA gradient length < 3) by assessing the dominant gradient lengths (ter Braak & Prentice, 1988; Leps and Smilauer, 2009). DCCA axis 1 had a gradient length of 3.083, so either linear or unimodal methods are appropriate. We quantified the diatom compositional responses to the explanatory environmental variables by using canonical correspondence analyses (CCA), which assumes unimodal species distributions.

Diatom species from the six study lake sediment cores were included if they were also in the calibration set described above (relative abundance of at least 1 % in one calibration set lake and present in at least three calibration set lakes). The lake sediment core diatom data was plotted as supplementary data only (thus not influencing the ordination axes). A CCA on the 57-lake calibration set with the downcore data from the six study lakes plotted as supplementary revealed that multiple outlying sites in the modern calibration set reduced the visibility of any variability in the downcore data. The outlying sites shared several characteristics that differentiated them from the study lakes; they were low elevation, situated in limestone, and had high alkalinity. Therefore, the calibration set was reduced, eliminating sites with alkalinity > 10 mg L^{-1} $CaCO_3$. All of the following statistical analyses were performed on the remaining 46-lake calibration set. A CCA performed on these lakes revealed that the first two axes collectively explained 30.5 % of the variance in diatom species data ($\lambda_1 = 0.307$ [18.9 %]; $\lambda_2 = 0.190$ [11.6 %]) and 37.5 % of the variation in the species environment relationship.

A series of CCAs were performed on the calibration subset in order to exclude environmental variables with high colinearity and those with variance inflation factors (VIFs) above 20. During this step we removed the following variables, one at a time: lead, chlorine, sodium, zinc, and specific conductivity. Barium, boron, rubidium, uranium, and fluorine were also removed as there are no known influences of these elements on diatom species abundances, leaving 24 remaining environmental variables (Appendix F). The first two axes collectively explained 23.1 % of the variance in diatom species data ($\lambda_1 = 0.237$ [14.5 %]; $\lambda_2 = 0.140$ [8.6 %]) and 37.4 % of the variation in the species environment relationship.

A forward selected CCA was performed with the following manually selected variables: nitrate, temperature, depth, Secchi depth, and magnesium. Each of these variables explains more than would be expected of a random contribution ($p < 0.05$), which was determined by performing separate CCAs with one variable as the sole explanatory variable, and the previously selected variable(s) as covariables. This is problematic only for the first selected variable, which is likely to be judged as significant even if the species are unrelated to the variable (Leps and Smilauer, 2003). The eigenvalues of the first two CCA axes were $\lambda_{1 =}$ 0.184 and $\lambda_2 = 0.093$, and the variables accounted for 39 % of the variance explained by all variables. The first two axes explain 17 % of the species variance and 70.8 % of the species environment relationship. Monte

Carlo permutation tests indicate that the canonical axes of the reduced environmental dataset are significant ($p < 0.01$).

Using this subset of environmental variables, a CCA biplot was made which included the sediment core samples from the six lakes; these samples were made supplementary. This biplot allowed us to assess historical lake response in the context of modern lake properties and diatom assemblages.

5.3.4.1 Turnover of diatom assemblages

The diatom assemblages of each of the six study lakes were ordinated individually using detrended correspondence analysis (DCA). Similar to ordination of the calibration data, the diatom percentage data was square root transformed. The data were detrended by segments and rare taxa were downweighted. The first axis of a DCA is a representation of turnover units of ß-diversity in standard deviation units, so the difference between samples estimates species turnover (Birks, 1998; Smol et al., 2005). That means that the difference between two sample scores approximates the variation in species composition among samples, in this case, along a temporal gradient. This technique allows for the analysis and comparisons of the magnitude and timing of compositional changes between samples (Birks, 1998). The statistical significance of the first four axes were determined by comparing the variance explained by each additional axis to that of a random model with the same total variance and number of axes using the broken stick model (Bennett, 1996).

5.4 Results

5.4.1 Lakes and catchment landscapes

The six study lakes vary in depth from 2.4 m (Denise) to 13.8 m (Upper Carrol). Four of the lakes are under 3.4 ha in area (Denise, East Carrol, No Name, and Bluebell Pass) whereas Taylor Lake and Upper Carrol Lake are 9 and 11.6 ha respectively (Table 5.1). The lakes are all low nutrient systems, but due to their naturally dilute nature are likely susceptible to small changes in nutrients. The lake catchments are dominated (56 to 81 %) by talus and bedrock cover (Table 5.2), with the remainder covered by vegetation types ranging from alpine tundra to alpine dwarf shrubland and subalpine mesic spruce-fir.

Table 5.1. Summary characteristics of the six study lakes, including lake area (A_L), depth, pH, and trophic status.

Trophic status was determined by comparison of Secchi depth, TP, TN, and chlorophyll *a* values (Tables 3.1 and 3.2) to those listed in Table 13-18 of Wetzel (2001).

Lake	Depth (m)	Stratifies	A_L (ha)	pH	Trophic status
Bluebell Pass	7.7	Yes	3.3	8.03	Oligo/ meso
Taylor	9.7	Yes	9	7.5	Oligo/ meso
Denise	2.4	No	1.1	7.7	Oligo
East Carrol	5.3	No	3.4	7.5	Oligo/ meso
No Name	5.2	No	2.6	7.53	Oligo
Upper Carrol	13.8	Yes	11.6	7.73	Oligo/ meso

Table 5.2. Summary catchment characteristics, including catchment area (A_C), catchment area: lake area ratio (A_C:A_L), throughflow, and land cover.

Land cover absolute area and percentage area have been combined into three major categories.

Catchment	A_C (ha)	A_C:A_L	Throughflow	Talus, bedrock & ice %	Talus, bedrock & ice (ha)	Subalpine spruce-fir & shrubland %	Subalpine spruce-fir & shrubland (ha)	Meadow & tundra %	Meadow & tundra (ha)
Bluebell Pass	174.5	52.9	Low	69.7	121.7	19.4	33.9	10.8	18.9
Taylor	349.9	38.9	medium	71.0	242.7	6.5	22.2	22.5	76.8
Denise	391.9	359.5	Low	66.1	252.5	10.3	39.4	23.6	90.3
East Carrol	35.1	10.3	Low	80.7	25.7	3.2	1.0	16.0	5.1
No Name	83.6	35.2	closed-basin	69.6	56.6	24.2	19.7	6.2	5.1
Upper Carrol	316.1	27.25	High	56.3	172.8	16.7	51.2	27.0	82.9

5.4.2 Chronology

The ^{210}Pb activity of each lake decreases predictably with depth, and background ^{210}Pb was reached within 9-12 cm in each of the six lakes (Hundey et al., (submitted)). This allowed us to develop robust CRS chronologies for all six lakes (Figure 5.2). These extrapolations provide a historical context, but we interpret pre-1850 trends with caution, as basal ^{210}Pb sedimentation rates tend to be systematically overestimated compared to models that include ^{14}C dates (Cooke et al., 2010), and the errors associated with early ^{210}Pb dates are large.

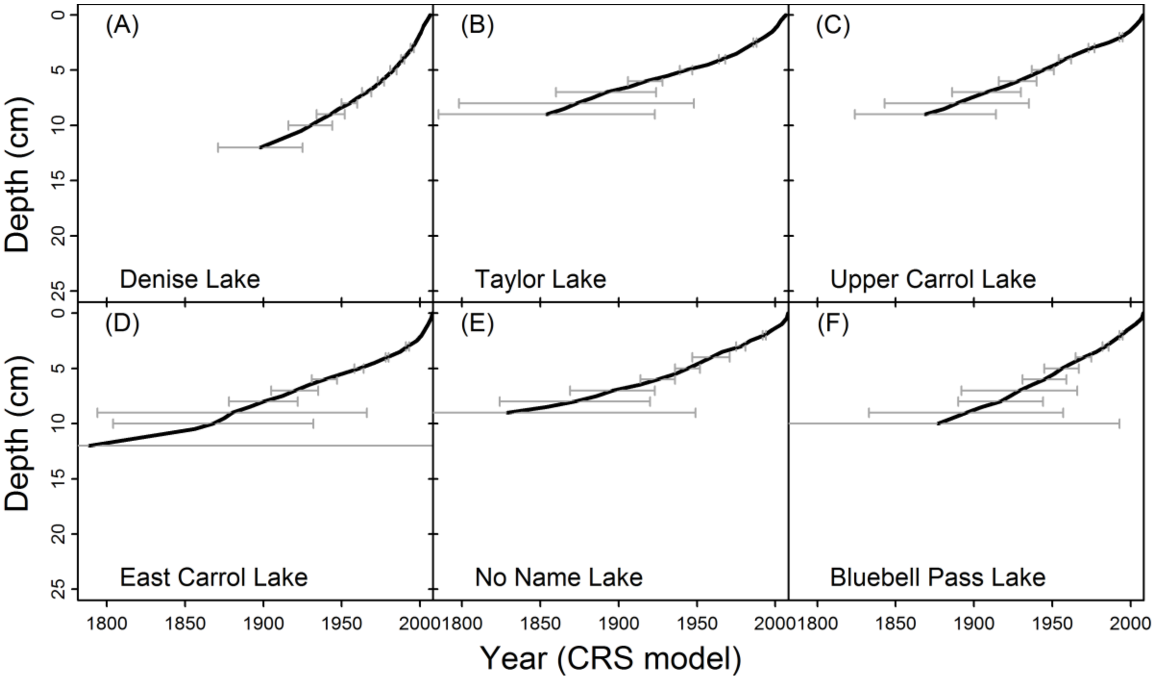

Figure 5.2. (A-F) Core chronologies for each study lake based on the constant rate-of-supply model from alpha-spectrometry.

Error bars represent one standard deviation above and below the date.

5.4.3 Calibration set

5.4.3.1 Diatom flora characteristics

In total, 220 diatom taxa representing 31 different genera were identified to the species level from the surface sediment collections. When this data was reduced to include only those diatoms present in at least three lakes, with at least one percent abundance in one lake, the dataset included 93 taxa from 19 different genera, and represented, on average, 95% of total diatoms enumerated. Diatom species codes, names, and species authorities are listed in Appendix G. The diatom taxa (or groups of taxa) found in the greatest abundance in the calibration set surface sediments, with species code in square brackets, were small benthic *Fragilaria* species (*F. brevistriata, F. construens* var. *venter*, *F. construens* var. *construens*, and *F. pinnata* varieties)

[*Fra.pin.con.bre*] (mean abundance: 36%). Several other abundant taxa with mean relative abundance between 8 and 2 % (in order of decreasing abundance) were *F. virescens* [*Fra.vir*]; *Cyclotella species* (*C. stelligera, C. pseudostelligera, C. atomus*) [*Cyc.ste.pse.ato*]; *Asterionella formosa* [*As.for*]; *F. tenera* [*Fra.ten*]; *Achnanthes minutissima*; *Tabellaria flocculosa* [*Ta.flo*]; and *Pinnularia mesolepta* [*P.mes*]. On average, 85 % of diatoms from the six study lake sediment core (unscreened) were represented in the calibration set. Those species from the sediment cores that were not in the calibration set represented at most 1.5 % mean abundance in the core.

5.4.3.2 Relationships between environmental variables

Summary statistics of the manually selected environmental variables included in the CCA are shown in Table 5.3. The t-values of regression coefficients indicate that depth and temperature are important for defining CCA axis 1, and Secchi depth, depth, and temperature are important in defining axis 2. NO_3 and Mg are not important for either of the first two axes, although Mg is an important variable in explaining axis 3 and NO_3 is an important variable in explaining axis 4.

Table 5.3. Summary statistics for forward selected calibration set variables (Secchi depth, depth, temperature, nitrate, and magnesium), plus elevation, which is included as a supplementary variable.

	Elevation (m)	Secchi depth (m)	Depth (m)	Temp (°C)	NO_3 (ppm)	^{26}Mg (ppm)
Min	2850	0.88	1.12	4.60	0.00	0.13
Max	3560	7.00	22.33	21.00	0.502	0.82
Median	3199	2.66	5.55	14.4	0.001	0.38
Mean ± 1 SD	3210±192	2.95±1.41	6.65±4.86	14.5±3.0	0.033±0.092	0.42±0.18

The relationships between environmental variables are illustrated in Figure 5.3. As is expected, temperature is significantly negatively correlated to elevation (Pearson = -0.644, $p < 0.001$). Nitrate appears positively correlated with elevation although the correlation is not significant (Pearson Correlation = +0.122), and nitrate values are generally low (Table 5.3). Greater nitrate concentrations are expected at higher relative to low elevations because increased orographic precipitation in high elevations has been linked to greater wet deposition of nitrate at other Rocky Mountain sites (e.g., Nanus et al., 2003). The group of lakes that plot positively on axis 1 (e.g., 32, 33, 34, 52, 53, 54 and 55) are therefore generally high elevation lakes that are colder and have greater nitrate concentrations (Figure 5.4). Lakes that plot positively on axis 2 are characterized by greater Secchi depth (3.6 to 7 m) (e.g., 36, 57, 59, 63 and 65), and because of their medium depth (5 to 7 m) often are visible to the bottom. Magnesium values are generally low (Table 5.3), but are significantly correlated with specific conductivity (Pearson = 0.694, $p < 0.001$), and significantly correlated to temperature (Pearson = 0.400, $p<0.01$). Higher temperatures result in more evaporation and increased ionic concentrations, including Mg. Therefore the lakes that plot negatively on axis 1 (e.g., 10, 12, 15) are warmer, low elevation lakes with greater salinity.

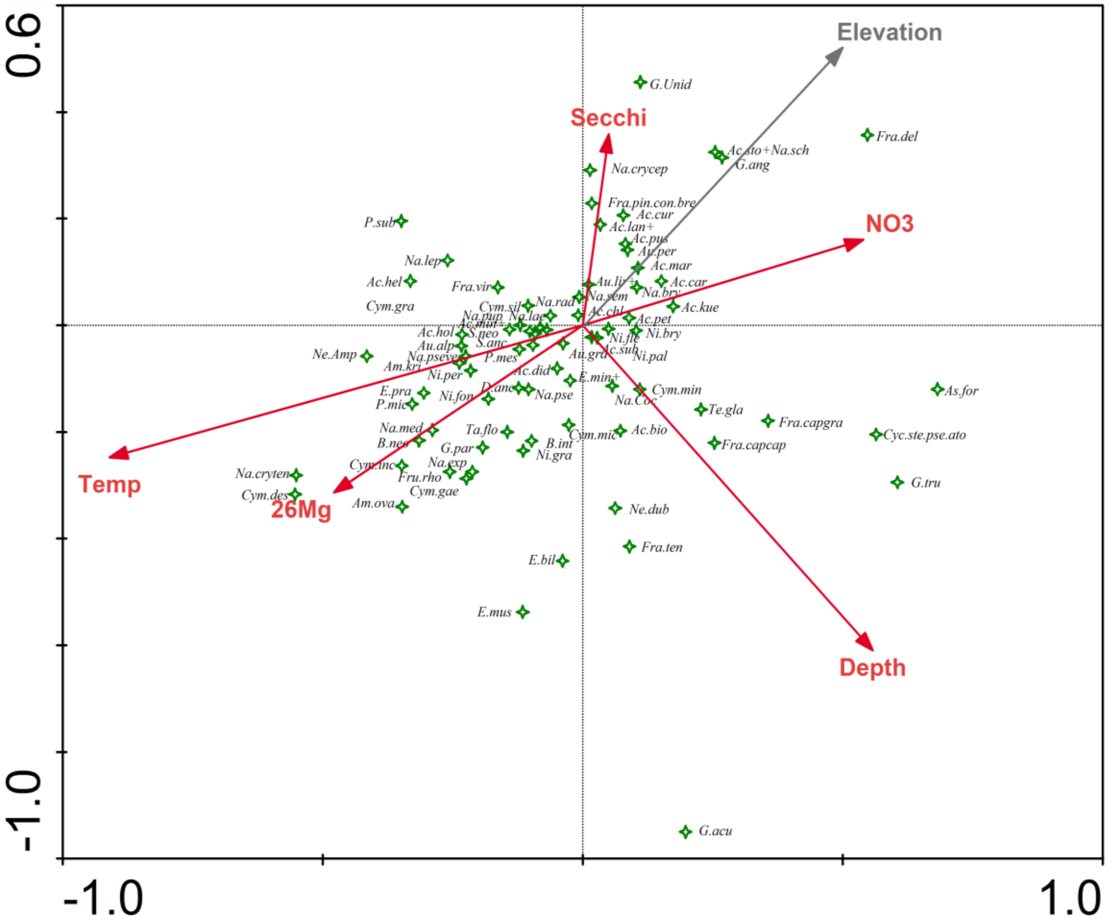

Figure 5.3. Results of the CCA ordination displayed as a biplot of diatom species (green diamonds) and environmental variables (red arrows) for the 46 lake subset of Uinta Mountain lakes.

Although elevation is not expected to directly influence diatom growth, it is a possible control on other variables that do (e.g., temperature, nitrate), and thus was plotted as a supplementary environmental variable (gray arrow). The length of each red arrow relates to its relative importance in affecting each axis. The angle of the arrow relative to an axis indicates the environmental variable's correlation to that axis. The relative weighted-average optimum of a diatom species can be estimated based on the diatom species-position. For example, species with a preference for higher temperatures and lower nitrate are found on the negative side of axis 1 (horizontal axis), whereas those with a preference for lower temperatures and higher nitrate are found on the positive side of axis 1. Species found in the middle of the graph are cosmopolitan species. Species codes and authorities are listed in Appendix G.

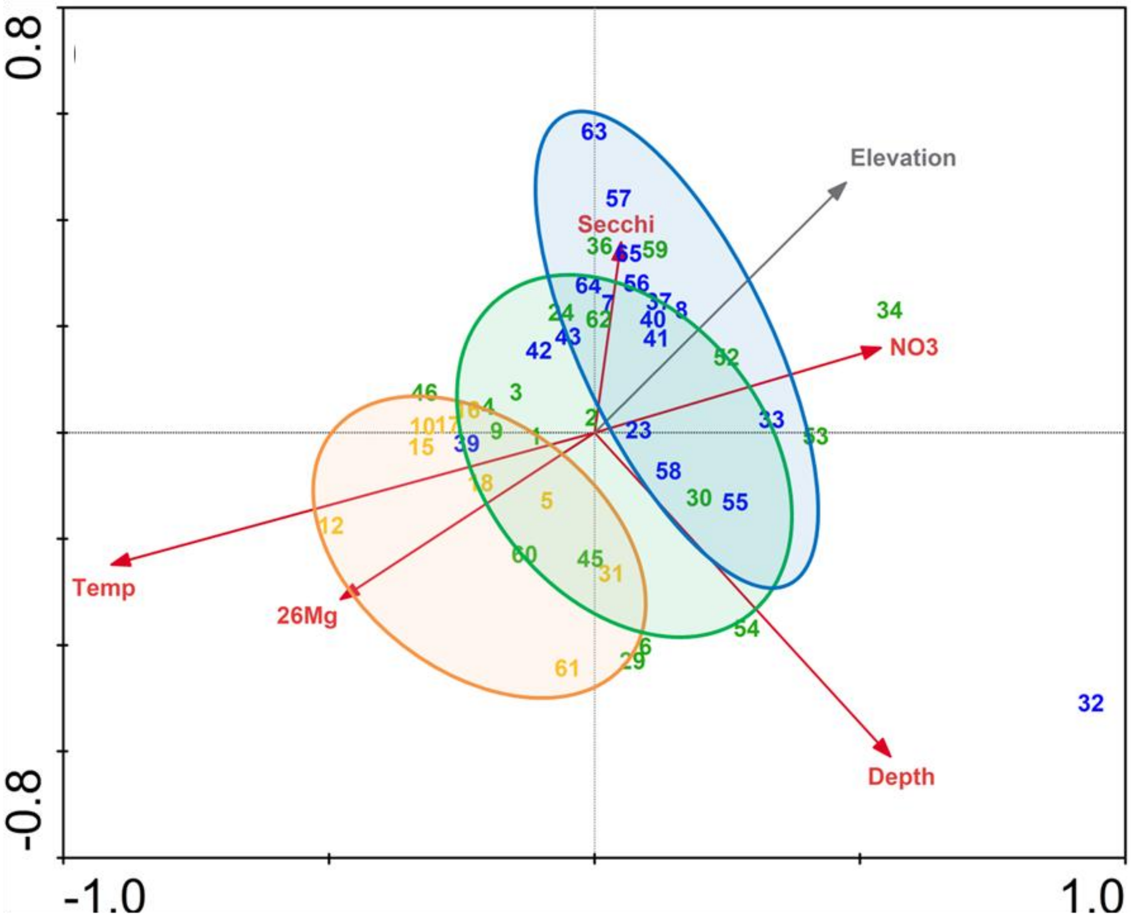

Figure 5.4. Results of the CCA ordination displayed as a biplot of environmental variables and sites.

The modern lakes (numbered) are colour-coded by elevation. Orange sites are situated at 2600-3000 m.a.s.l., green are 3000-3300 m.a.s.l., and blue sites are located above 3300 m.a.s.l. The circles outline the three elevation groupings.

5.4.3.3 Species-Environment Relationships

The results of the CCA plotted in Figure 5.3 display the weighted average optimum of diatom species in relation to the environmental variables. Several dominant planktonic species, including *Asterionella formosa* [*As.for*] (species score[23] = 1.3) and small *Cyclotella* species (*C. stelligera, C. pseudostelligera,* and *C. atomus*) [*Cyc.ste.pse.ato*] (species score = 1.1) are positively correlated with axis 1, and are therefore typical of

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[23] The species score for a given latent variable (i.e. the axis in consideration) is the estimate of the species optimum on that axis.

high elevation lakes with elevated nitrate concentrations, and also deep water lakes. Other species correlated with the first axis, and therefore also typical of high elevation lakes with elevated nitrate concentrations are *Fragilaria delicatissima* [*Fra.del*] (species score = 1.0), *Fragilaria capucina* var. *gracilis* [*Fra.capgra*] (species score = 0.7), *Fragilaria capucina* var. *capucina* [*Fra.capcap*] (species score = 0.5), and *Tetracyclus glans* [*Te.gla*] (species score = 0.4).

Diatoms with large negative scores on the first axis include larger pennate diatoms and *Navicula cryptonella* [*Na.cryten*] (species score = −1.06), several *Cymbella* species, and *Pinnularia microcephela* [*P.mic*] (species score = −0.28). This diverse community of pennates is associated with warmer temperatures and higher salinity.

Diatoms with positive scores on axis two include several species that are typical of undisturbed oligotrophic lakes (Lotter et al., 1997; Koinig et al., 1998), and are associated with higher Secchi depth (clearer waters), such as small *Achnanthes (*e.g., *A. curtissima* [*Ac.cur*], *A. stolida* [*Ac.sto*] and *A. lanceolata* [*Ac.lan*]), and small benthic *Fragilaria (F. brevistriata, F. pinnata,* and *F. construens* varieties) [*Fra.pinconbre*] (species score = 0.44).

5.4.4 Downcore diatom assemblages and ordination

5.4.4.1 Diatom flora characteristics: Six lake sediment cores

A large number of taxa were identified in the lake sediments of the six study lake sediment cores (on average 200 per lake). However, many were rare and were eliminated when the data was screened for taxa whose relative abundances were present in three samples and at an abundance of 1 % in at least one. After screening, 60 (Denise Lake), 44 (Taylor Lake), 53 (Upper Carrol), 37 (East Carrol), 57 (No Name Lake), and 58 (Bluebell Pass Lake) species remained, which represented an average of 94% of total diatom valves counted per interval. The diatom stratigraphies, including dominant taxa and notable changes in diatom species abundance are included in Figure 5.5 through 5.10. The most consistent change in diatom species composition is an increase in *A. formosa* in four (Denise, Taylor, East Carrol, and Bluebell Pass lakes) of the six lakes around ~1950 AD. In Denise, Taylor, and Bluebell Pass lakes, planktonics like *Cyclotella* species and

Fragilaria tenera and tychoplanktonic *F. capucina* var. *gracilis* also increase, while small benthic *Fragilaria* (*F. construens* var. *venter, F. pinnata* and *F. brevistriata*) and *Achnanthes* species decrease. This shift in the diatom community composition is marked by a CONISS zone in Taylor (1956 AD), Denise (1973 AD), and Bluebell Pass (1961 AD) lakes. A coinciding shift and CONISS zone occurs in No Name Lake (1960 AD) as well, but this rapid shift in species composition consists of a decrease in *C. stelligera*, *C. pseudostelligera*, *C. atomus* and *Aulacoseira* species and an increase in small benthic *Fragilaria* species. In East Carrol Lake, there is a shift within the planktonic diatom community from mainly *Aulacoseira* and *Cyclotella* species to *A. formosa, F. capucina* var. *gracilis* and *F. tenera,* although this change is more gradual and is marked by an earlier (1869 AD) CONISS zone. In Upper Carrol Lake, there is almost no change in the diatom community composition and *A. formosa* is a dominant species throughout.

East Carrol, Taylor, and Bluebell Pass lakes each also have an earlier CONISS zone. Few similarities can be drawn between these shifts, aside from a gradual increase in *A. formosa*. In East Carrol Lake, the shift at 1807 AD is marked by increasing *A. formosa*, and *Aulacoseira* species and decreasing benthic *Fragilaria* species. In Taylor Lake, the shift at 1800 AD is marked by a slight increase in *A. formosa*, and *Cyclotella* species, and a decrease in *Aulacoseira* and *Eunotia* species. In Bluebell Pass Lake, the shift at 1930 AD is characterized by increasing *A. formosa*, *F. tenera*, *Cyclotella* species, and *Navicula* species and decreasing small benthic *Fragilaria* and *Achnanthes* species.

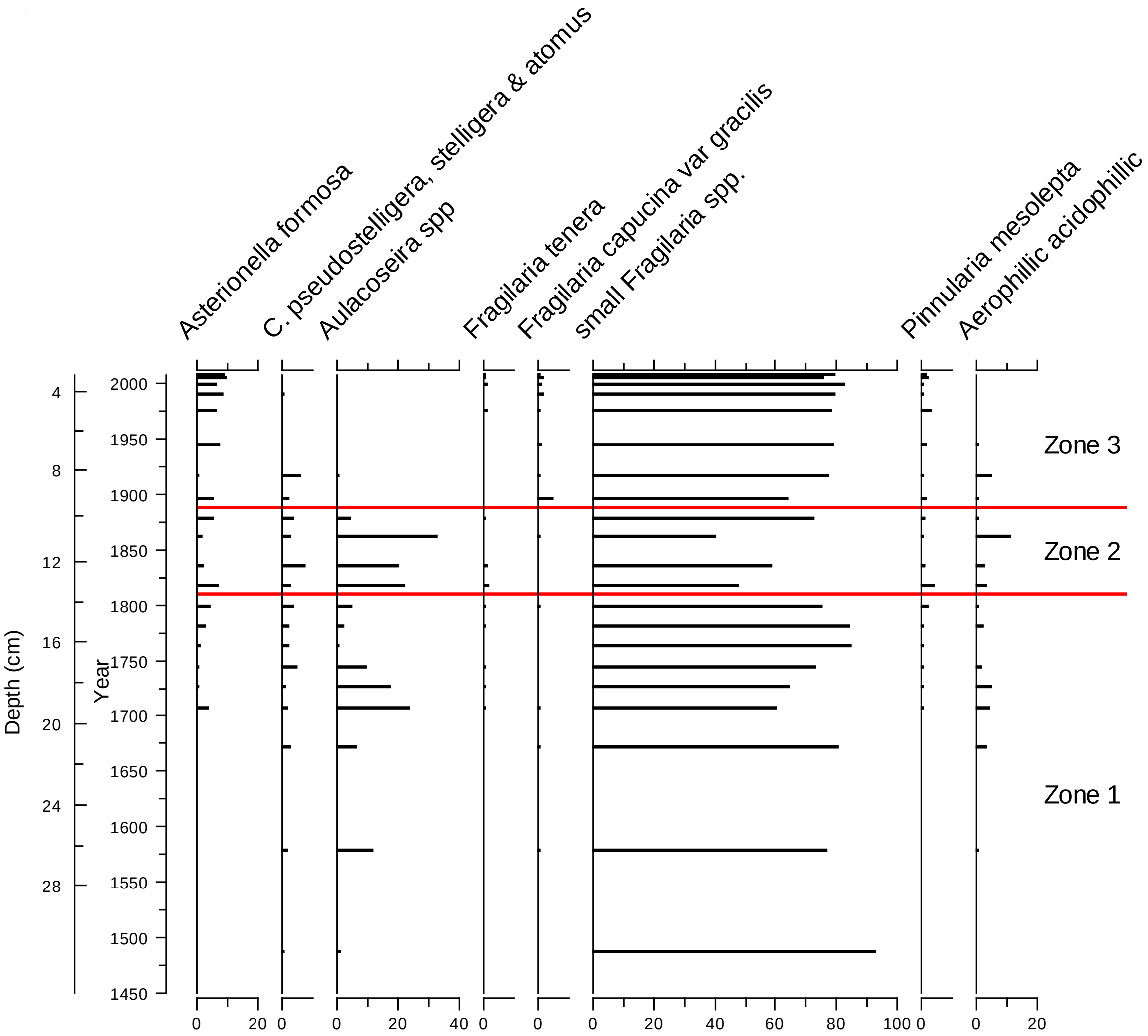

Figure 5.5. East Carrol Lake Diatom stratigraphy.

Three significant zones are separated by red lines. All data are expressed as relative frequency percentages of individual or grouped diatom taxa.

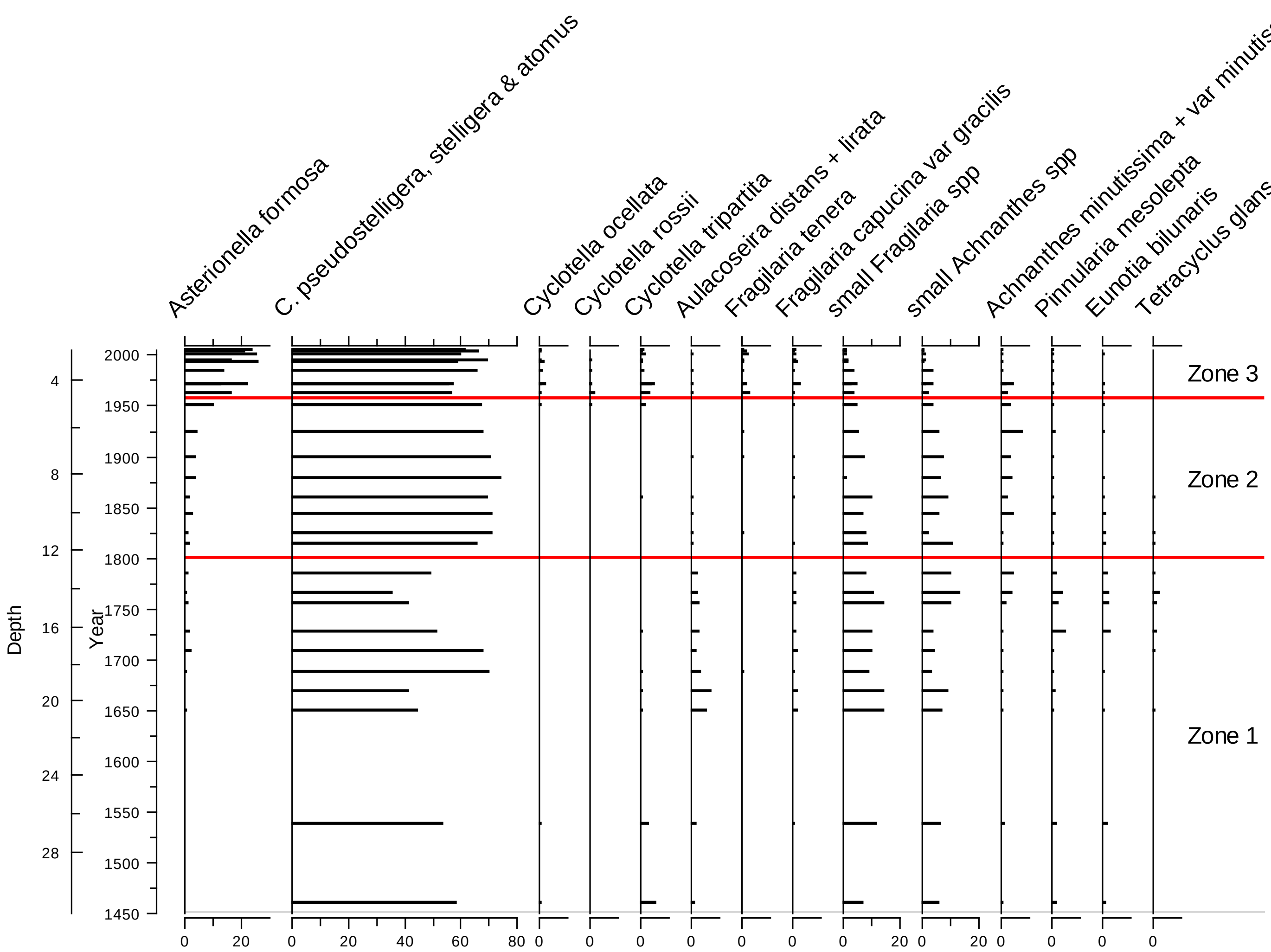

Figure 5.6. Taylor Lake diatom stratigraphy.

Three significant zones are separated by red lines. All data are expressed as relative frequency percentages of individual or grouped diatom taxa.

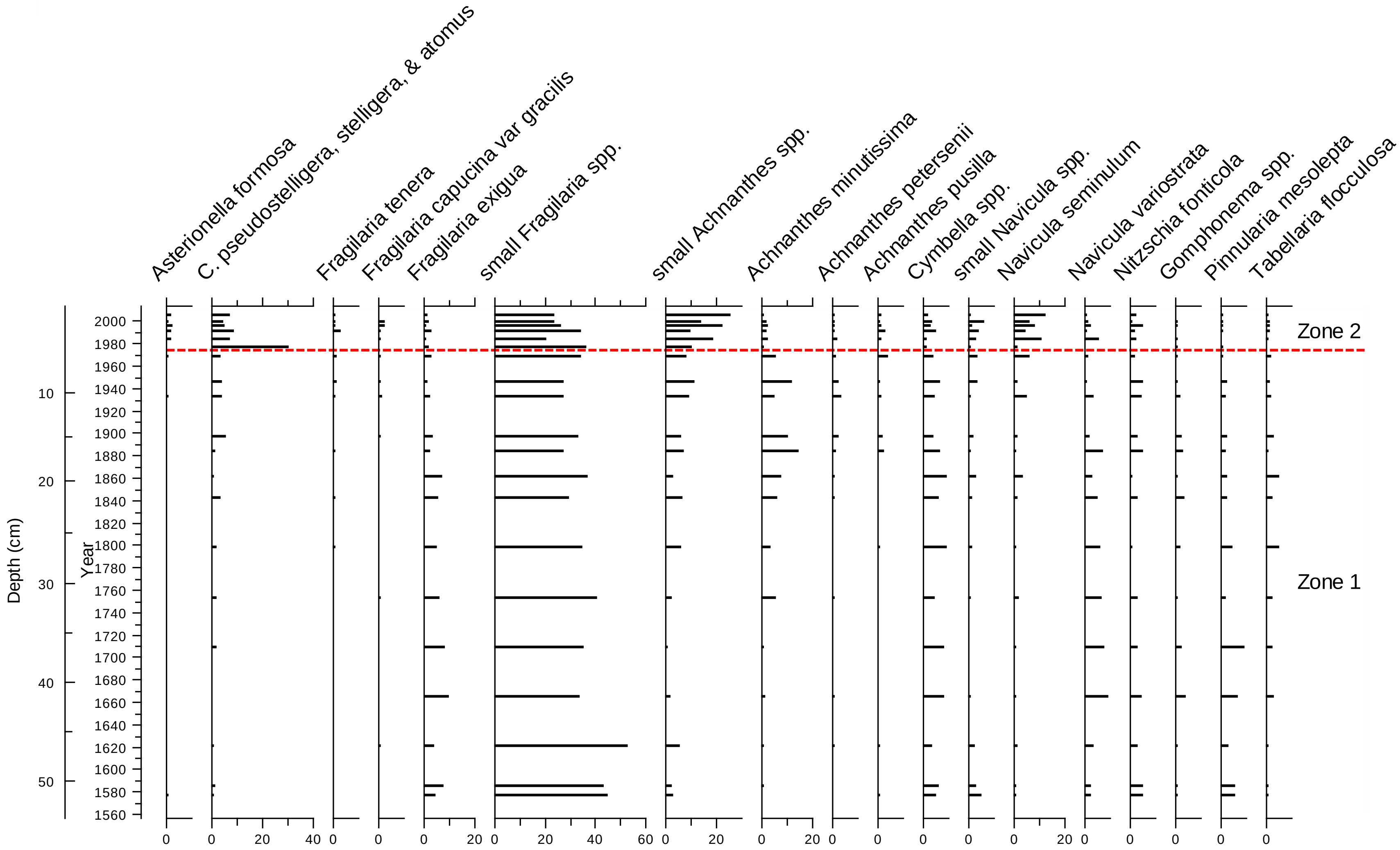

Figure 5.7. Denise Lake diatom stratigraphy.

The dashed red line denotes two non-significant zones. All data are expressed as relative frequency percentages of individual or grouped diatom taxa.

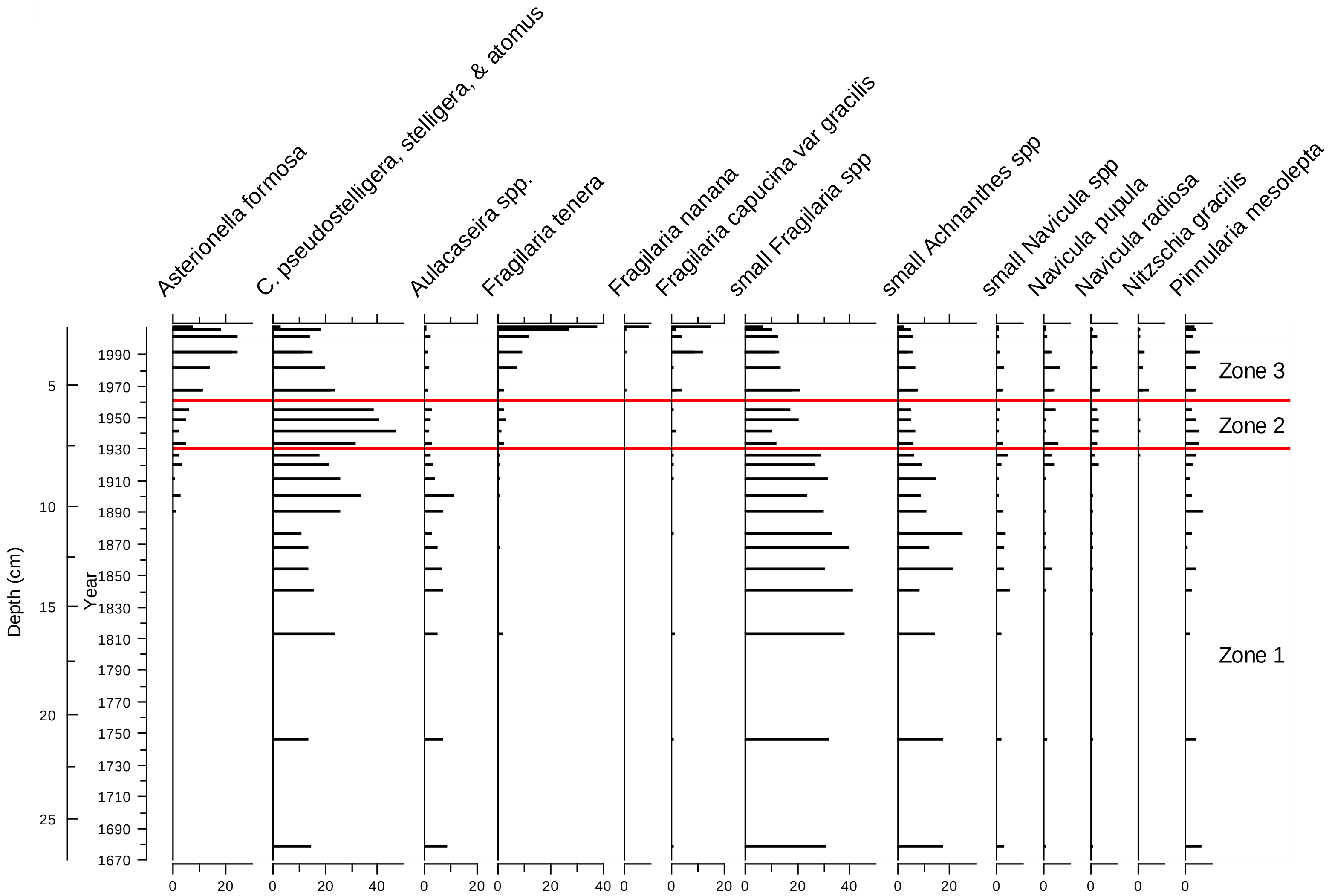

Figure 5.8. Bluebell Pass Lake diatom stratigraphy.

Three significant zones are separated by red lines. All data are expressed as relative frequency percentages of individual or grouped diatom taxa.

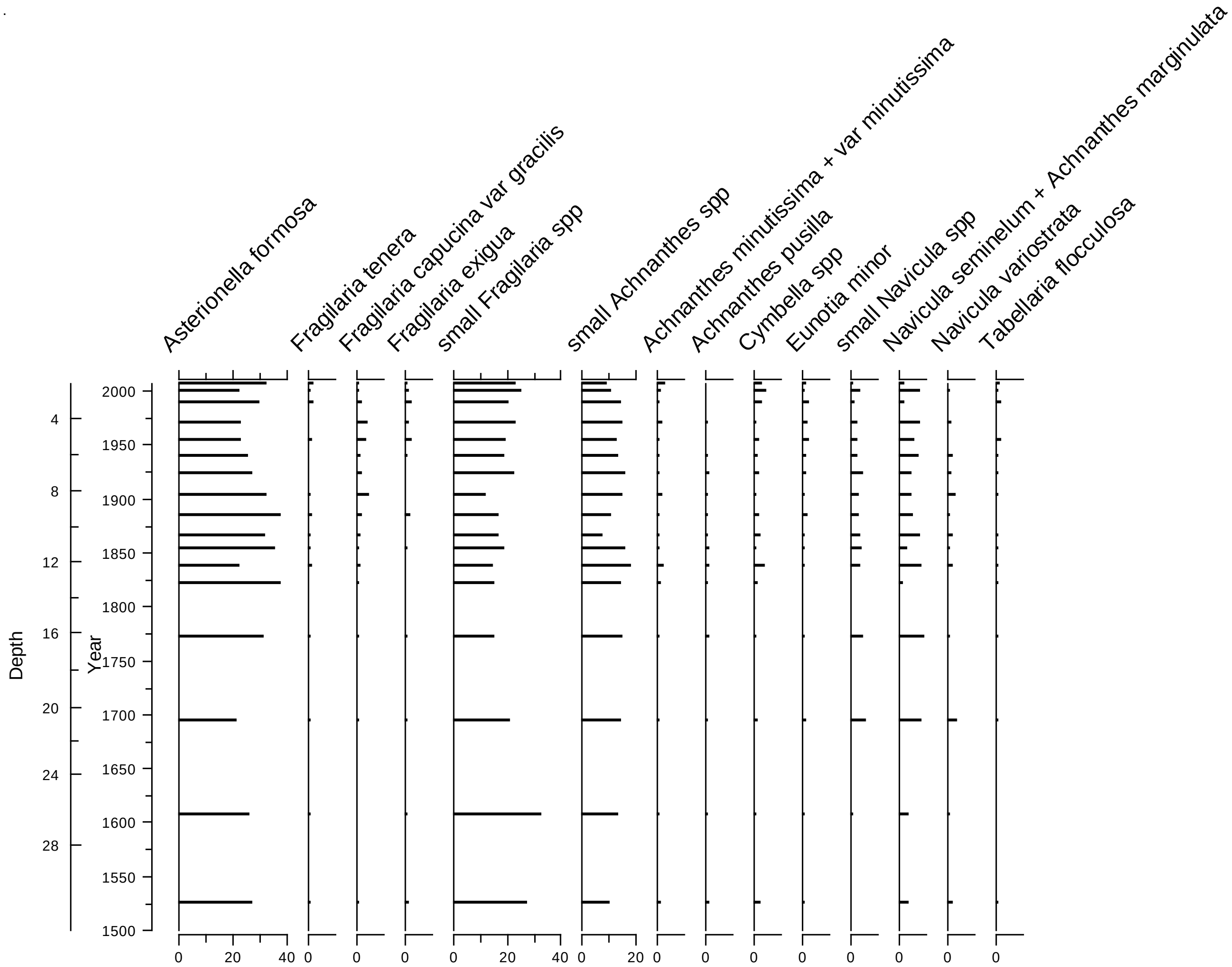

Figure 5.9. Upper Carrol Lake diatom stratigraphy.

All data are expressed as relative frequency percentages of individual or grouped diatom taxa.

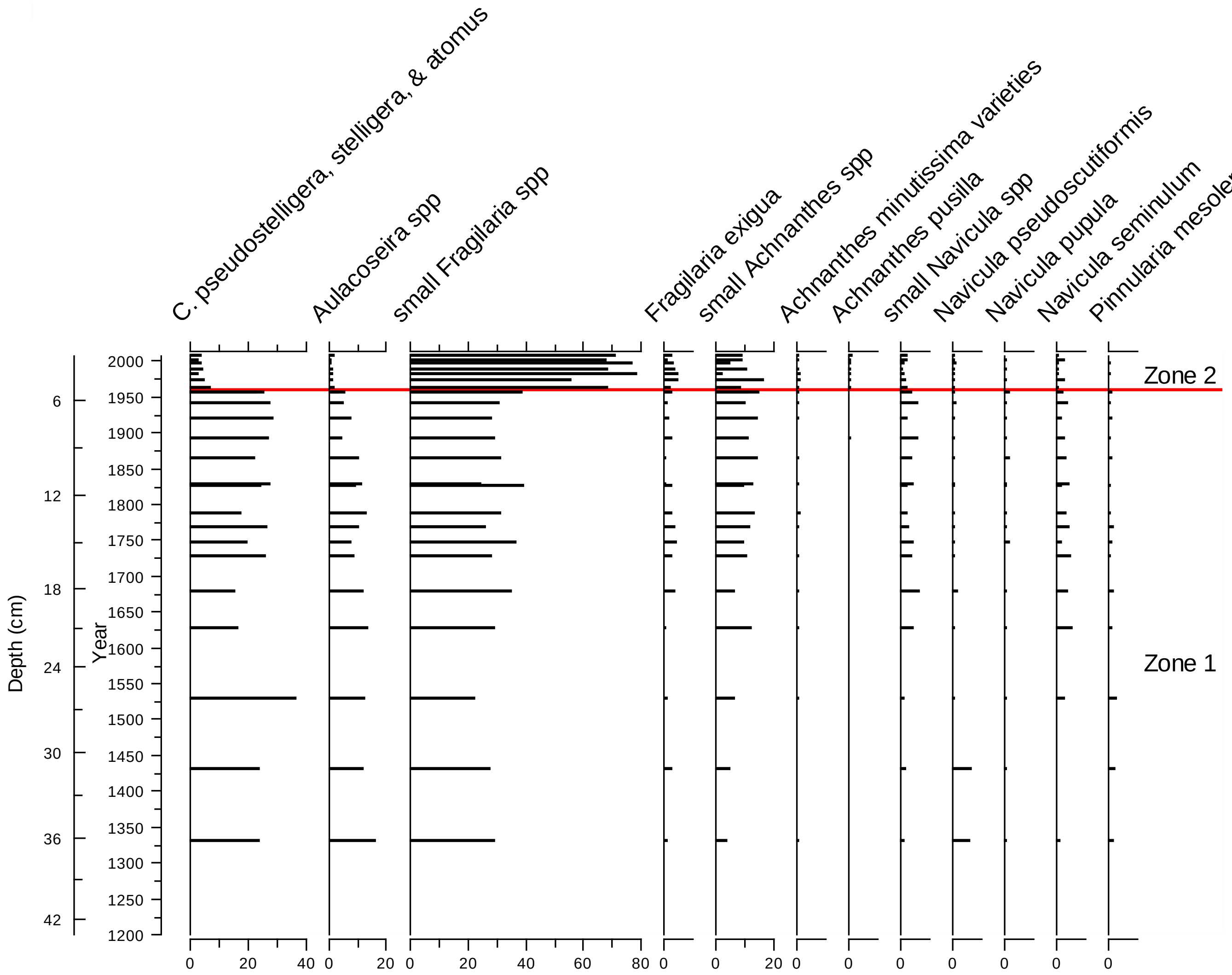

Figure 5.10. No Name Lake diatom stratigraphy.
Two significant zones are separated by a red line. All data are expressed as relative frequency percentages of individual or grouped diatom taxa.

In Figure 5.11A and B, the downcore samples are plotted as supplementary data on the calibration set CCA biplot (sites and environmental variables) in order to visualize the downcore changes in relation to the modern species environment relationships. On average, 85% of the diatoms in the six study lake sediment samples were represented in the calibration set. The bottom sediments of the six lakes are in or near the top right quadrant, which is indicative of greater abundances of small, benthic *Fragilaria* species (*F. brevistriata*, *F. construens* var. *venter*, *F. pinnata* and *F. pseudoconstruens*), small *Achnanthes* species, and *Aulacoseira* species (*A. lirata*, *A. perglaba*). This is a characteristic assemblage of oligotrophic alpine lakes (Lotter et al., 1997; Koinig et al., 1998).

Denise, Taylor, and Bluebell Pass Lakes (Figure 5.11A) exhibit directional changes towards the bottom right of the CCA plot, indicating a diatom community composition shift from a diverse benthic community towards greater dominance of planktonics such as *A. formosa* and *F. tenera* (see also Figures 5.6 to 5.8). The ordination also suggests a shift to deeper, and/ or less transparent, and/ or cooler conditions with lower NO_3^- concentrations. The remaining three lakes show changes that are less pronounced (No Name and East Carrol Lakes) or no changes at all (Upper Carrol Lake) (Figure 5.11B). The change in diatom community composition at East Carrol Lake is similar to that of Denise, Taylor, and Bluebell Pass Lakes such that *A. formosa* increases, and other planktonics like *C. stelligera, C. pseudostelligera, C. atomus* and *Aulacoseira* species disappear (see also Figures 5.5 to 5.8). However, on the CCA, East Carrol appears to undergo little change because despite the changes in planktonic diatoms, it has always been dominated (61-93%) by small *Fragilaria* species (Figure 5.5). No Name Lake exhibits an abrupt change toward the positive end of axis 2, during which planktonics such as *C. stelligera* and *Aulacoseira* species decrease and small benthic *Fragilaria* species increase (Figure 5.10).

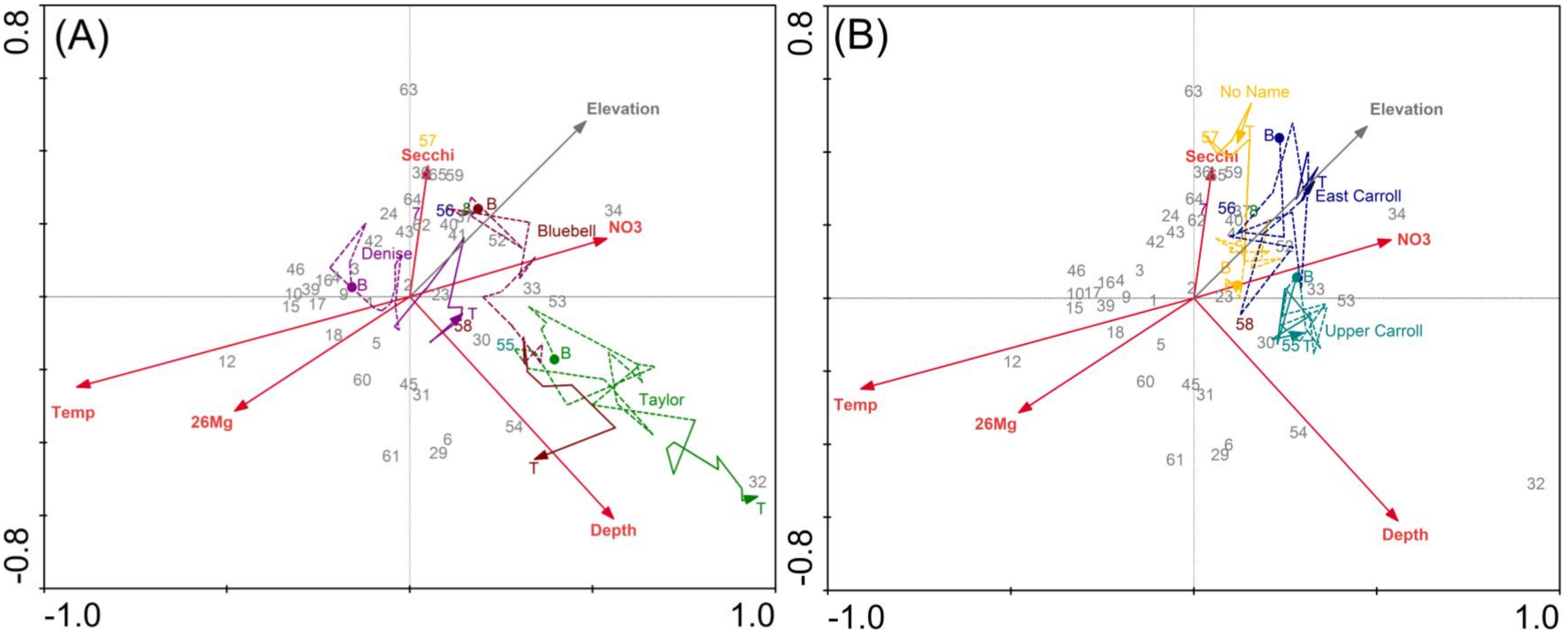

Figure 5.11 (A) and (B): Canonical Correspondence Analysis (CCAs) for Uinta Lake calibration set, with 6 lake sediment cores plotted as supplementary data.

The six study lake sediment cores are plotted from bottom (filled circle labeled “B”) to the top (arrowhead labeled “T”) of the core. Lines are dashed until chlorophyll *a* begins to increase (between 1937 and 1955 depending on the lake (Figure 5.12, also see Chapter 3) after which the points are connected by solid lines.

5.4.4.2 Species turnover

DCA axis 1 is significant for each study lake (Table 5.4), and therefore the differences between samples can be used to approximate ß-diversity or species turnover.

Table 5.4. Summary of the results of detrended correspondence analysis analysis (DCA) of the square root transformed diatom stratigraphies for all six lakes.

λ = eigenvalue, % = percentage of total inertia. Axes that have eigenvalues larger than expected under a simple broken-stick model are shown in bold.

Lake dataset	Total inertia		DCA axes			
			1	2	3	4
Bluebell Pass	1.392	λ	**0.170**	0.066	0.023	0.011
		%	**31.2**	12.14	4.2	2.0
Taylor	2.683	λ	**0.162**	0.045	0.031	0.014
		%	**30.5**	8.5	5.8	2.6
Denise	1.672	λ	**0.229**	**0.064**	0.02	0.010
		%	**31.4**	**8.8**	2.7	1.4
East Carrol	3.508	λ	**0.226**	0.076	0.039	0.017
		%	**33.6**	11.3	5.8	2.5
No Name	1.402	λ	**0.155**	0.057	0.032	0.012
		%	**29.1**	10.7	6.0	2.3
Upper Carrol	1.427	λ	**0.065**	0.028	0.009	0.006
		%	**24.9**	10.7	3.4	2.3

Pre-19th century values of DCA axis 1 sample scores are relatively stable, indicating that little assemblage turnover occurred (species compositions are similar between samples) (Figure 5.12). Beginning in the late 19th to early 20th century, DCA axis 1 values begin to decrease below pre-disturbance values[24] in East Carrol, Denise, Taylor, Bluebell Pass lakes, and to a small degree, in No Name Lake, indicating greater species turnover between samples. This early shift in ß-diversity post-dates the early CONISS zone in Taylor and East Carrol Lakes. The early CONISS zone at Taylor (1800) and East Carrol (1807) do coincide with increases in ß-diversity but the sample scores are still within the range of pre-disturbance variability, indicating that species composition were still typical of pre-disturbance conditions (Figure 5.12). By ~ 1950 AD, DCA axis 1 values are decreasing more rapidly in five of six lakes indicating an

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[24] These dates, ranging from 1883 to 1924, were determined based on when DCA axis sample scores continuously extend below pre-1850 values (mean ± 1 standard deviation). Pre-1850 sample scores are indicated in Figure 5.12.

increase in species turnover (Figure 5.12). The exception is Upper Carrol Lake, which has relatively noisy, but unchanging DCA axis 1 sample scores. The percent of planktonic species increases subtly towards present day in Denise, Taylor, and Bluebell Pass lakes (also the three lakes showing similar changes in the CCA, Figure 5.11). The timing of shifts in percentage of planktonics coincide with those in DCA axis 1 sample scores at Taylor, Bluebell, and Denise Lake, indicating that the shifts between benthic and planktonic diatoms largely account for changes in species turnover. DCA axis 1 sample scores show a similar shaped profile to δ^{15}N. Chlorophyll *a* appears to have an inverse pattern compared to DCA axis 1 sample scores and δ^{15}N, but the main change in chlorophyll *a* (1950 AD) lags behind the early (1877 - 1924 AD) shifts in DCA axis 1 and δ^{15}N. Temperatures in Heber begin to warm in the mid-1980s, which post-dates the changes in δ^{15}N, species turnover, and chlorophyll *a*.

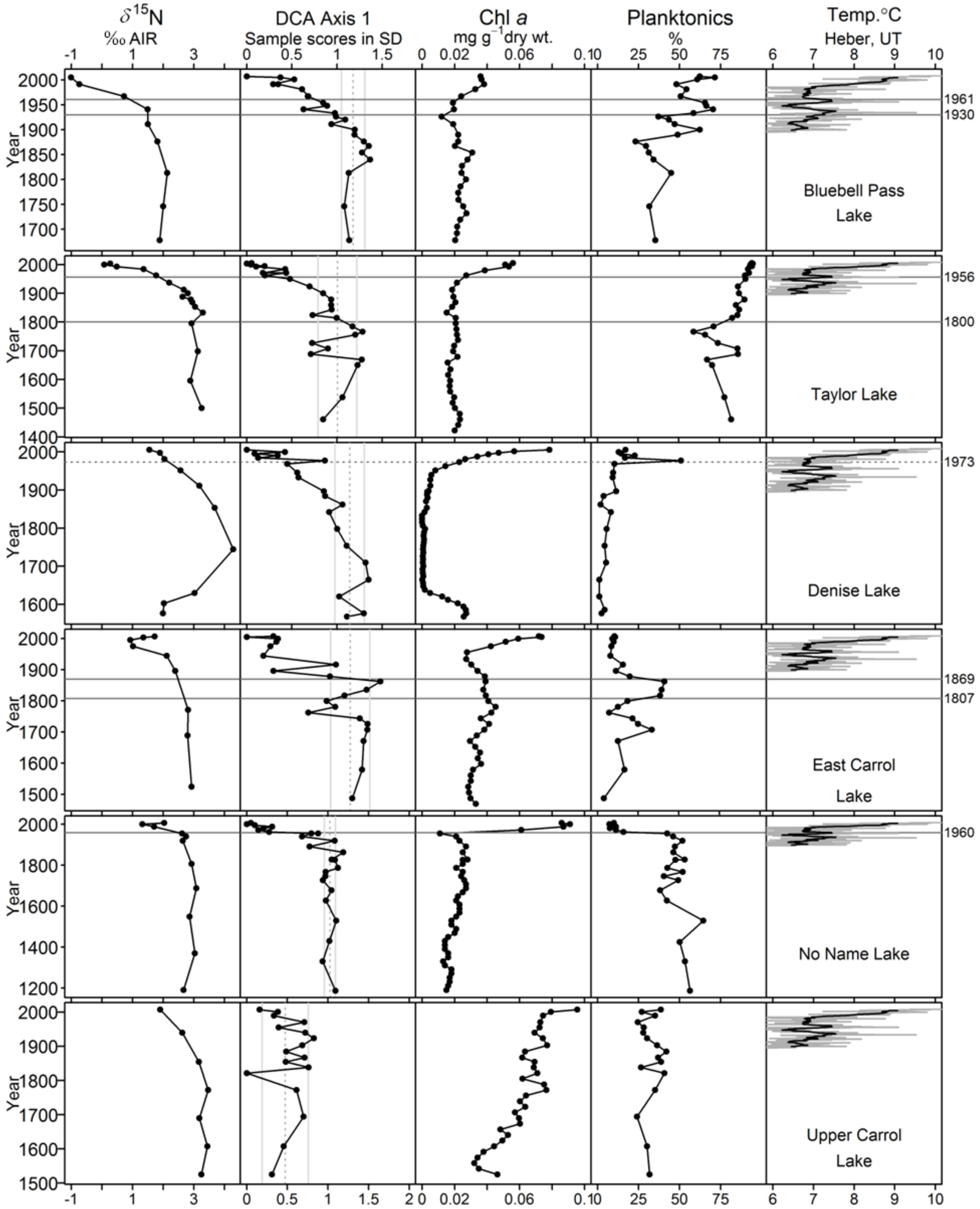

Figure 5.12. Comparison of Detrended Correspondence Analysis Axis 1 to δ^{15}N, Chlorophyll *a* family + derivatives (Hundey et al., (submitted)), and the mean annual temperature record for Heber, Utah (Western Regional Climate Center, http://www.wrcc.dri.edu).

The differences between samples in DCA axis 1 sample scores scale to ß-diversity or species turnover in SD units. Therefore, when DCA axis 1 appears invariant, species turnover is low, and when it changes rapidly, species turnover is high. The light gray vertical lines represent mean pre-1850 (*note continues*)

Figure 5.12 (Continued). sample scores (dotted) ±1 standard deviation (solid). In the temperature record, the gray line is the mean annual temperature and the black line is the 9-year running mean. Gray horizontal lines represent significant CONISS zone delineations as determined from each diatom stratigraphy (Figure 5.5- 5.10). Dotted gray horizontal lines are non-significant zone delineations. Sedimentary $\delta^{15}N$ data are indicative of changes in atmospheric nitrate deposition and chlorophyll *a* is indicative of primary production (Chapter 3).

5.5 Discussion

5.5.1 What is influencing diatom ecology at these sites?

The strongest evidence for the influence of nitrogen deposition on diatom community composition comes from the timing of an initial change in DCA axis 1 sample scores in the late 19th to early 20th century, and a second change in DCA axis 1 sample scores that coincides with the post-1950 CONISS zones (Figure 5.12). In Chapter 3 (this volume, also Hundey et al. (submitted)), we determined that the subtle decrease in $\delta^{15}N$ values ca. 1850 AD were likely due to increased nitrogen deposition as a result of land clearance, agricultural activities, and mining operations following the settlement of the Wasatch Front. The similarity of the shape of the DCA axis 1 sample scores to the $\delta^{15}N$ profiles in Bluebell Pass, Taylor, Denise and East Carrol lakes indicates that ß-diversity has increased (i.e., large shift in diatom species composition) in response to this early source of nutrient pollution. The initial shift (1877-1924 AD) in DCA axis 1 outside the range of pre-disturbance variability occurs just after the initial decrease in $\delta^{15}N$ (ca. 1850), indicating a lag in diatom response to increased nitrogen deposition. Overall primary production (see chlorophyll *a,* Figure 5.12) had not yet been affected. Beginning in the 1950s AD, $\delta^{15}N$ decreased more rapidly as agriculture activities intensified, synthetic fertilizers were produced, and population in the Wasatch Front increased rapidly (Figure 3.5, also Hundey et al. (submitted)). At this time both sedimentary $\delta^{15}N$ and DCA axis 1 decrease more rapidly and chlorophyll *a* increases at all but Upper Carrol Lake. The rapid change (steep slope) in DCA axis 1 sample scores indicates greater species turnover after 1950. CONISS zones from Bluebell Pass, Taylor, Denise, and No Name lakes also coincide with this shift (Figure 5.12). The increase in species turnover is similar to findings in alpine sites that are influenced by increased nitrogen deposition (Hobbs et al., 2010).

Evidence that warming is causing changes in the diatom ecology is less compelling. Arctic sites that are influenced by warming have also experienced increased ß-diversity (Smol et al., 2005; Hobbs et al., 2010). However, at the Uinta Mountain sites, the timing of changes in DCA axis 1 sample scores and the ca. 1950 CONISS zones both precede the most dramatic temperature warming at the nearby Heber climate station, which occurred post-1980 AD (Figure 5.12). A longer temperature record would be useful to compare historical temperature fluctuations with DCA axis 1 sample scores because the initial shift in ß-diversity occurs before temperature data are available. Unfortunately, an appropriate tree ring-based temperature reconstruction was not available. Ongoing work at Lakes and Reservoir Systems Research Facility at the University of Western Ontario on the association between temperature and diatom species composition on a seasonal basis will be useful in determining the relationship between diatoms and temperature in Uinta Mountain lakes.

Several changes in the diatom community composition provide further evidence that nitrogen deposition is affecting these sites. The increase in planktonics observed at Denise, Taylor, and Bluebell Pass lakes is expected with both warming and with nitrogen deposition, but similar to the changes in DCA axis 1 sample scores, the change in planktonics begins before recent climate warming (Figure 5.12). Furthermore, the increase in planktonics is largely due to the increase in long pennate species like *A. formosa* and *F. tenera*. *A. formosa* is a mesotrophic-eutrophic species that has been associated with higher N in high alpine environments (Saros et al., 2005; Michel et al., 2006), and it has increased in abundance in Bluebell Pass, Denise, Taylor and East Carrol lakes. Conversely, planktonic species like *C. stelligera* and *C. pseudostelligera* that reportedly do well in warmer lakes are instead associated with colder, higher elevation lakes in the Uinta Mountains (Figure 5.4). A recent increase in *Cyclotella* species is confirmed in the Denise Lake diatom stratigraphy (Figure 5.7), but at the other sites, the relative abundance of *Cyclotella* species is either unchanging (Taylor Lake) or decreasing

(East Carrol Lake, Bluebell Pass Lake, No Name Lake) during recent climate warming. In Upper Carrol Lake *Cyclotella* species are not present.

The CCA results also indicate, at least for Taylor, Bluebell, and Denise Lakes, a relationship between diatom community composition change and NO_3 (Figure 5.11A). NO_3^- is positively (though not significantly) related to elevation (Pearson Correlation: +0.122) and negatively correlated to temperature (Pearson Correlation: -0.645) – both of which are expected relationships given changing climatic conditions with increasing altitude (i.e., with increasing altitude, temperature decreases, and precipitation and wet deposition increase). *A. formosa,* a nitrophilous diatom, is associated with higher NO_3^- according to the CCA (Figure 5.3, [*As.for*]) and in the literature (Yang et al., 1996; Saros et al., 2005). The trends indicated by the arrows representing Taylor, Bluebell and Denise Lakes indicate increasing NO_3^- and *A. formosa*. Although the East Carrol Lake record shows little change in the CCA (Figure 5.11B), it nonetheless shows a response in diatom species composition that is indicative of increased nitrogen concentrations and similar to the responses observed in Denise, Taylor, and Bluebell Pass lakes (e.g., increasing species turnover (Figure 5.12), increased *A. formosa*, decreased *Cyclotella* and *Aulacoseira* species, Figure 5.5). The record appears invariant on the CCA because of the dominance of *F. construens* var. *venter, F. pinnata,* and *F. brevistriata* throughout the record, even though there is a shift in ß-diversity and changes in the planktonic diatoms.

The CCA could also be interpreted to be indicative of other environmental changes. For example, the records from Denise, Bluebell Pass, and Taylor lakes all show a substantial shift toward the bottom right of the CCA diagram (Figure 5.11A). This would seem to imply that Denise, Bluebell Pass, and Taylor lakes are getting deeper, but there is little evidence that the lakes are actually deeper today than in the recent past (e.g., submerged terrestrial vegetation, six Google Earth historical images from 1993 - 2011). If these lakes were increasing in depth we would expect the greatest change in No Name Lake as it is a closed-basin lake with an unvegetated ring of exposed rock and substantial lake level changes are evident in historical Google Earth images (Google Inc., 2013). However, minimal changes in lake level are indicated for No Name Lake based on the CCA, which instead indicates a change toward greater Secchi depth (Figure 5.11B).

Lake level fluctuations are also evident at Bluebell Pass and Taylor Lake on historical satellite images (Google Inc., 2013), although no overall trend toward decreasing or increasing lake levels is evident.

The change in diatom community composition from a shallow lake to a deep lake would be expected to be similar to a change from a lake that is more ice covered to one that is less ice covered; both a deeper lake (Wolin and Duthie, 2001) and a lake with less ice cover (Rühland et al., 2003; Smol et al., 2005) are expected to have more diatom habitats, stronger stratification, and increased abundance of planktonic algae. Perhaps the change in diatom community composition observed in recent lake sediments is indicative of reduced ice cover duration? The modern calibration set, however, would suggest that warmer lakes (negative side of axis 1, Figure 5.11A&B) have a different diatom community composition than the recent samples of the six study lakes (positive side of axis 1, Figure 5.11A&B). This is further indication that warming, and resulting changes in ice cover, are not a dominant influence on the changes in the six study lakes. However, duration of ice cover is related to temperature and snow cover, the latter being temporally and spatially variable in alpine areas (Cayan, 1996; Bales et al., 2006), so ice cover may not be positively related to temperature in alpine regions. For example, at Green Lake in the Colorado Front range, ice cover thickness steadily declined from 1980 to 2000 despite unchanging temperatures; these changes were attributed to increased snow cover, which insulated the lake ice and increased groundwater flow to the lake (Caine, 2002). Without ice cover data, it is inconclusive whether changing ice cover has played a role in diatom community composition at these sites.

5.5.2 What makes a lake less sensitive to nutrient deposition?

The results indicate that recent changes in diatom species composition and ß-diversity occur mainly in response to increased nitrogen availability. There is little evidence to support an influence of warming on lake ecology, although temperatures are expected to further increase in the western U.S.A. (Solomon et al., 2007) and may have synergistic effects with nutrient loading at these sites in the future. Although geographical proximity of the six study lakes would suggest that atmospheric delivery of nutrients should be similar at all six sites, the diatom stratigraphies (Figure 5.5 – 5.10), CCA biplots (Figure 5.11A and B), and ß-diversity indicate that there are substantial differences in the ecological response between lakes. The primary production profiles (Chapter 3, this volume, Hundey et al., (submitted)) provide further evidence that some lakes (Taylor Lake, Denise Lake, Bluebell Pass Lake, and East Carrol lakes) are more sensitive to the influence of nitrogen deposition than others (Upper Carrol and No Name lakes). For example, Taylor Lake appears sensitive; the DCA Axis 1 decreases rapidly indicating an increase in species turnover, there are distinct changes in the diatom stratigraphy around 1800 and 1950, and δ^{15}N decreases rapidly. Upper Carrol Lake, on the other hand, appears the least sensitive; the diatom stratigraphy and ß-diversity profile are fairly stable, the decrease in δ^{15}N is subtle, and there is only a gradual increase in chlorophyll *a* + derivatives (Figure 5.12).

Similar to the other lakes, the early part of the Upper Carrol Lake record consists of some diatom species typical of oligotrophic conditions: small *Achnanthes* species, *Aulacoseira* species, and small benthic *Fragilaria* species (Figure 5.9, Figure 5.3). However, unlike the other lakes, *A. formosa* is a dominant species (> 20 %) throughout the record which suggests nutrient concentrations that are naturally elevated relative to the other lakes. Furthermore, compared to the other study lakes, the diatom assemblages and species turnover are invariant over time. This stability could be linked to a couple of factors. First, Upper Carrol Lake has the highest through-flow, which would make it less sensitive to recent increases in nitrogen deposition. Lakes with permanent inflows are likely to be less dependent on snowmelt, which is variable year to year. For example, Nydick et al. (2003) showed that a permanent inflow in one lake in the Colorado Front Range (The Loch) provided sustained, high NO_3^- concentrations, whereas nearby lakes dominated by snowmelt had more variable NO_3^- inputs. Second, Upper Carrol Lake has the most vegetated catchment of the six lakes measured in both absolute area (134.1 ha) and by percent of catchment area (43.7 %). Increased terrestrial vegetation can reduce nutrient delivery because of increase uptake of nutrients by the terrestrial system as runoff passes through a vegetated landscape en route to a lake (Williams et al., 1997). In the case of Upper Carrol Lake, the area around the lake is covered by marsh vegetation and shrubs like *Salix planifolia* (shrub willow) and *Betula glandulosa* (dwarf birch), which have naturally elevated nutrient concentrations (Pathak et al., 2012), and could account for elevated nutrients throughout the lake sediment record.

ß-diversity increases rapidly in No Name Lake in around 1960 AD, but the changes in diatom species composition and on the CCA are different from the other lakes. No Name Lake has a typical oligotrophic diatom assemblage in the base sediments, similar to that of the other study lakes. However, unlike the other lakes, planktonics decrease, *A. formosa* never colonizes, and pioneering benthic species like *F. construens* var. *venter, F. pinnata,* and *F. brevistriata* rapidly increase in relative abundance (Figure 5.10). This change is reflected in the CCA (Figure 5.11B). It is hypothesized that a local event (landslide) occurred in the No Name Lake catchment in 1960 based on a large increase in sediment accumulation rate (Figure 3.3) that coincides with a light band in the sediment core (Figure 2.12D). It is suspected that this landslide event overrode the regional atmospheric deposition signal, although nitrogen deposition may still explain the increased primary production (Hundey et al., (submitted)).

The changes in diatom species composition and increasing species turnover in Bluebell Pass, Taylor, Denise, and East Carrol lakes indicate that these lakes are sensitive to increases in nitrogen deposition. The sensitivity of these sites could be linked to the proportion of talus within the catchment; the limited vegetation on these slopes could result in greater amounts of nitrogen from snow entering lakes (Campbell et al., 2000). As well, it has been speculated that the drainage of water through talus slopes can increase the amount of biologically active N that enters water bodies, as these slopes are potential sites of microbial nitrification (Williams et al., 1997; Campbell et al., 2000; Nydick et al., 2003). All four sensitive lakes have greater than 66% talus, bedrock and ice cover in the catchments (Table 5.2). At East Carrol, Taylor, and Bluebell Pass lakes, the talus slopes are immediately adjacent to the shore, with little vegetation buffer between. In contrast, Upper Carrol Lake is surrounded on all sides by vegetation (Figure 2.11E). These differences might be especially critical in spring, when nitrogen in snowmelt rapidly enters the lake from the talus slopes.

5.6 Conclusion

There are several compelling lines of evidence that show the influence of increased nitrogen deposition on Uinta Mountain lakes, including the coincident timing of changes in species composition and increased nutrient deposition, the similarity between DCA axis 1 and δ^{15}N profiles, and the widespread increase in the nitrophilous diatom *Asterionella formosa*. The timing of changes in diatom ecology precede recent warming trends leading me to presume that warming is not the initial trigger of ecological change. There is also little evidence of separate shifts in ß-diversity or diatom species composition that coincide with warming beginning in the mid-1980s AD. However, it is possible that recent and future climate warming could exacerbate the impacts of increased nutrients on these lakes, and that further warming may yet cause changes in lake ecology.

The lake ecosystem changes resulting from nitrogen deposition are not ubiquitous; by studying changes in diatom community composition in six high elevation lakes, we were able to determine that some lakes are more or less sensitive than others. Based on these findings, several factors could decrease a lake's sensitivity to increased nitrogen, including: 1) naturally high nutrient concentrations as a result of the amount and type of surrounding vegetation; 2) high through-flow resulting in greater stability in nutrient levels; and 3) local catchment disturbances that mask effects of longer-term and more regional environmental stressors. Lakes that are more sensitive to increased nitrogen deposition tend to have a high proportion of talus, and a minimal vegetation buffer between the talus slope and the lake.

With continued nitrogen deposition, we can expect further increases in productivity and changes in diatom community composition in the most sensitive lakes. These lakes could be approaching a tipping point and change to a new stable state as has occurred at other sites undergoing cultural eutrophication (Scheffer et al., 2001; Smith and Schindler, 2009). The resiliency of the unaffected lakes may also be surpassed, meaning that changes currently only observed in sensitive lakes may become even more widespread. Site selection (and the use of multiple study sites) in poorly understood environments is critical in order to determine whether changes are due to local or regional factors, or whether a lake is relatively sensitive (or insensitive) to change.

5.7 References

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Chapter 6

6 Conclusion

Mountain lakes are important as critical water resources for adjacent lowlands, key components of the larger recreational landscape, and as part of a unique ecosystem and reservoir of biodiversity (Beniston, 2003). Although local disturbances are minimal at these remote lakes, it is postulated that these systems could be threatened by atmospheric deposition of nutrients from anthropogenic sources such as synthetic fertilizers and fossil fuel burning. In this thesis, I investigated recent (within the last 200 years) trends in nutrient inputs and their resulting influence on primary production and diatom community composition in six high alpine lakes in the Uinta Mountains, U.S.A. The investigation had three primary goals: (1) to identify the timing and nature of changes in primary production and determine the potential drivers of changes in trophic status, including nutrient deposition and warming temperatures (Chapter 3); (2) to determine the proportional contributions of nitrates from different sources to the modern lake ecosystems (Chapter 4); and (3) to determine the diatom community responses to atmospheric fertilization and climate warming and investigate differences in lake sensitivity to these factors (Chapter 5). In this concluding chapter, I briefly summarize the cumulative findings from these three manuscripts and the combined contribution of the three papers to our understanding of alpine aquatic ecosystems in general. I also offer suggestions for improving our understanding of nutrient deposition and lake response in alpine environments and conclude with remarks about the challenges that remain for effective management and protection of these high elevation ecosystems.

6.1 Nutrient deposition and lake response in the Uinta Mountains

Five of the six high elevation lakes studied in the Uinta Mountains record an increase in primary production over the last 60 years. This change is synchronous with rapidly decreasing sedimentary δ^{15}N values, which suggests increasing atmospheric deposition of nitrogen (Chapter 3). Smaller, initial changes in diatom community composition and species turnover occur earlier (1850 AD) at some sites and coincide with more subtle increases in nitrogen deposition (Chapter 5). These changes are attributed to nitrogen deposition derived from intensive agriculture and fossil fuel production. Additional atmospheric contributions of phosphorus may be transported to these lakes as dust from increased phosphate mining and fertilizer. We confirmed the influence of atmospheric nitrate deposition at these sites by analysis of stable isotopes of nitrate in modern water and snow samples (Chapter 4). The results show that atmospherically-delivered nitrogen from fertilizers are currently the most important influence on nitrate concentrations at high elevation sites as they currently contribute ~35 % of nitrates to the study lakes and ~65 % to inflows. Additional anthropogenic components of atmospheric inputs of N originate as byproducts of fossil fuel combustion (~10%).

Grazing and fish stocking do not have a detectable influence on primary production or diatom species composition in Uinta Mountain lakes. The timing of increases in mean annual temperature in the Uinta Mountains in the 1980s occurs several decades later than the major shifts in primary production and diatom communities. This indicates that warming temperature was not the initial trigger for changes in primary production, although it may contribute to later biotic trends. Recent shifts in diatom community composition are also more indicative of increases in nitrogen (e.g., increased nitrophilous species) than warming (e.g., decreased small *Cyclotella* species). Nevertheless, warming is predicted to continue in the Western U.S., so it is possible that future warming may have synergistic effects with increasing nutrient inputs. Predicting these changes will require a greater understanding of the complex relationships between snow cover, temperature, and ice thickness/duration in the Uinta Mountains.

By analyzing primary production profiles from six high elevation lake sites, we determined not only that nitrogen deposition is increasing, but also that not all lakes are responding equally (Chapter 3). These differences in lake sensitivity to nutrient deposition were confirmed by our analysis of changes in diatom community composition (Chapter 5). The results suggest that elevated nutrient concentrations in lakes with greater through-flow, and/or naturally higher nutrient inputs from catchment vegetation can lead to decreased sensitivity to atmospheric nutrient inputs, whereas greater sensitivity is associated with catchments having a large percentage of surface covered with talus and/or little vegetation surrounding the lakes.

These results are timely because population in the western U.S.A.continues to increase and fossil fuel combustion and agricultural activities are on the rise. Temperatures in western North America are anticipated to increase by ~2.1 to 5.7 ˚C by the end of the 21st century (Solomon et al., 2007) and higher temperatures have been linked to increased algal production (Posch et al., 2012). I therefore predict that with warming there will be further reductions in alpine lake water quality in the near future. This has implications for water resource management because Uinta Mountain lakes are important water resources to the much drier adjacent lowlands (Beniston, 2003; Tingstad, 2010).

6.2 Contributions to the study of eutrophication in high elevation environments and future research directions

6.2.1 Combining approaches: benefits of paleolimnological study and triple isotope analysis of nitrates

This research is unique in combining paleolimnological techniques and isotope analysis of nitrates in modern water samples to determine the impacts of atmospheric nitrogen deposition to lake ecosystems. It is also one of the first studies to use the triple isotope approach to identify nitrate sources in alpine environments (see also Darrouzet-Nardi et al., 2012). This approach vastly improves our interpretation of the causes of recent increases in primary production by combining paleolimnological research (to determine the history of recent eutrophication) with identification and modeling of nitrate sources by triple isotope analysis of nitrates in modern samples. Several researchers have previously analyzed bulk sedimentary δ^{15}N (as in Chapter 3) to speculate about the source of nitrogen in high alpine environments (Baron et al., 2000; Wolfe et al., 2001; Holtgrieve et al., 2011) and indicated that the most parsimonious explanation for the decreased δ^{15}N values in Uinta Mountain lake sediments is an increase in nitrogen to remote lakes from anthropogenic N sources. However, the interpretation of this proxy is difficult because of overlapping source δ^{15}N values, internal lake N cycling (Teranes and

Bernasconi, 2000) and similar timing of other changes such as climate warming (Catalan et al., 2013). By analyzing triple isotope composition of nitrates in contemporary water and snow samples, I was able to determine the proportional contribution of modern nitrate sources, which also improves my confidence in my interpretation of the paleolimnological results. With the combination of the paleolimnological productivity data and the modern stable isotopic study of nitrates it is clear that primary production is increasing above natural variability and that fertilizer and fossil fuel-derived atmospheric nitrate is reaching these high elevation sites.

Continued use of this combined approach could prove extremely valuable in regions where the impact of nitrogen deposition has only been investigated using the paleolimnological record (e.g., the Colorado Front Range), as well as regions where nitrogen deposition has not yet been studied. Geographic expansion of the triple isotope nitrate analysis approach to other mountain regions will improve our understanding of spatial patterns of nitrate sources in environments that typically have scarce monitoring data. It would also prove extremely valuable to apply this combined approach to arctic regions where there has been debate regarding the role of warming versus (or combined with) nitrogen deposition (Smol and Douglas, 2007b; Hobbs et al., 2010; Holtgrieve et al., 2011; e.g., Catalan et al., 2013). Although nitrogen deposition in the arctic is among the lowest in the world (e.g., Galloway and Cowling, 2002; Smol and Douglas, 2007b, Figure 1.3) triple isotope analysis of nitrates on snow, inflow, and lake samples could be used to determine whether nitrates in arctic lakes primarily originate from soil nitrate, with only minor contributions from atmospherically oxidized nitrate and atmospherically delivered fertilizer. This critical information could give a better context to the post-1850 shifts in paleolimnological records of diatom community composition and ß-diversity at these sites (Smol et al., 2005).

6.2.2 Use of the multiproxy approach

The use of a multiproxy paleolimnological approach (e.g., analyzing several biological and geochemical variables in the same lake sediment cores) (H. H. Birks and Birks, 2006) has been critical to this research in the Uinta Mountains, where few actual measurements of limnological varaibles are available. Multiproxy studies will continue to be invaluable in alpine regions lacking monitoring data, especially with continuing concern over the potential for synergistic effects of nitrogen deposition and climate warming, which have often been discussed (e.g., Catalan et al., 2013) but are not yet understood.

6.2.3 Importance of multiple study lakes

Our ability to understand differences in lake sensitivity rests on our in-depth analysis of multiple study sites, without which our conclusions would have been very different. As an example, if we had studied the Upper Carrol Lake alone, we could conclude that nitrogen deposition has little influence on high elevation Uinta Mountain lakes, as Upper Carrol Lake has undergone little change in diatom ß-diversity, diatom community composition, and primary production. Instead, we were able to identify four sensitive lakes (Taylor, Bluebell, Denise, and East Carrol), one lake with little sensitivity to change (Upper Carrol Lake), and one in which the regional signal has been overridden by a local landslide event (No Name Lake). The use of multiple sites is especially important in dynamic and remote environments like the Uinta Mountains where local disturbances can have a marked impact.

Although the changes in primary production and lake ecology are obvious in lake sediment records, they are not yet visible to a recreational visitor. This kind of environmental problem is a challenge to water managers because people tend to respond to visible problems and symptoms (Smol, 2008). The “invisibility” of the changes is confounded because the causes of the changes are located hundreds of kilometers away. The lake sediment records provide an early warning system and bellwether of the effects of continued atmospheric fertilization and climate change that should help direct effective water resource management.

6.3 Concluding remarks

Humans have become a significant force in the earth system, altering the earth, water and air to the extent that many scientists argue we are now in the Anthropocene epoch (Crutzen and Stoermer, 2000), in which human impacts are a major driving force in the Earth System. Although the six study lakes investigated in this thesis are in a designated “Wilderness Area” (Wilderness Act, 1964) of the Uinta Mountains, which offers them increased protection from direct impacts of human activities, my research shows that they are not isolated from human impacts. These lakes are being significantly impacted by the long-distance transport of nutrients resulting in detectable changes in primary production and diatom community composition. These changes are caused in part by atmospheric nutrient deposition from fertilizer use and fossil fuel combustion. The timing of this research is critical, as population, agricultural activities, and urbanization are expected to continue to increase in the Wasatch Front, which will result in further increases in atmospheric nutrient deposition to high elevation Uinta Mountain lakes. The resulting increases in lake production may be compounded by continued warming predicted for the western U.S.A. (Solomon et al., 2007). It is my hope that by identifying these changes and the threats that they present to these fragile lakes, my research will contribute to protecting these important ecosystems.

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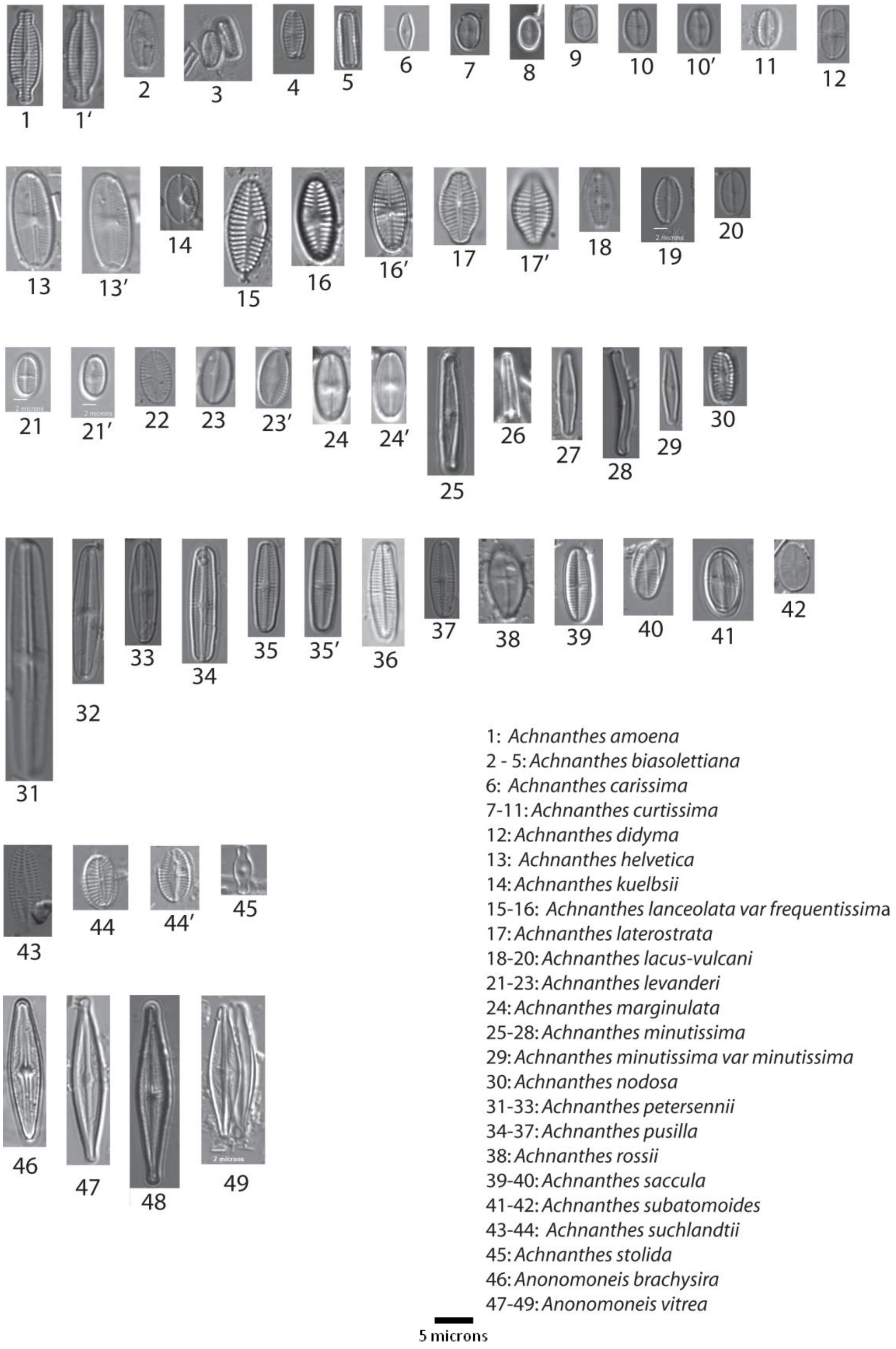
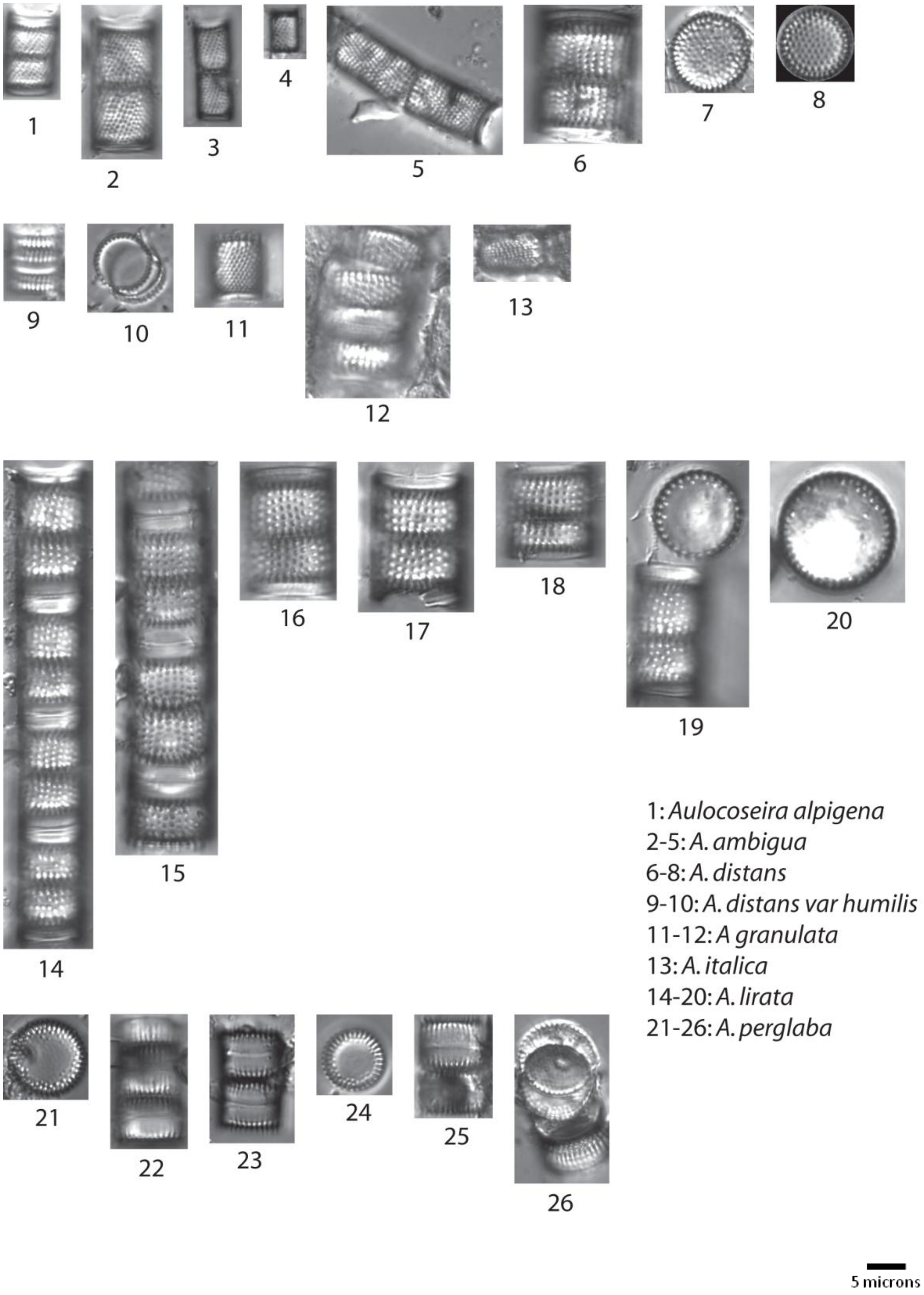


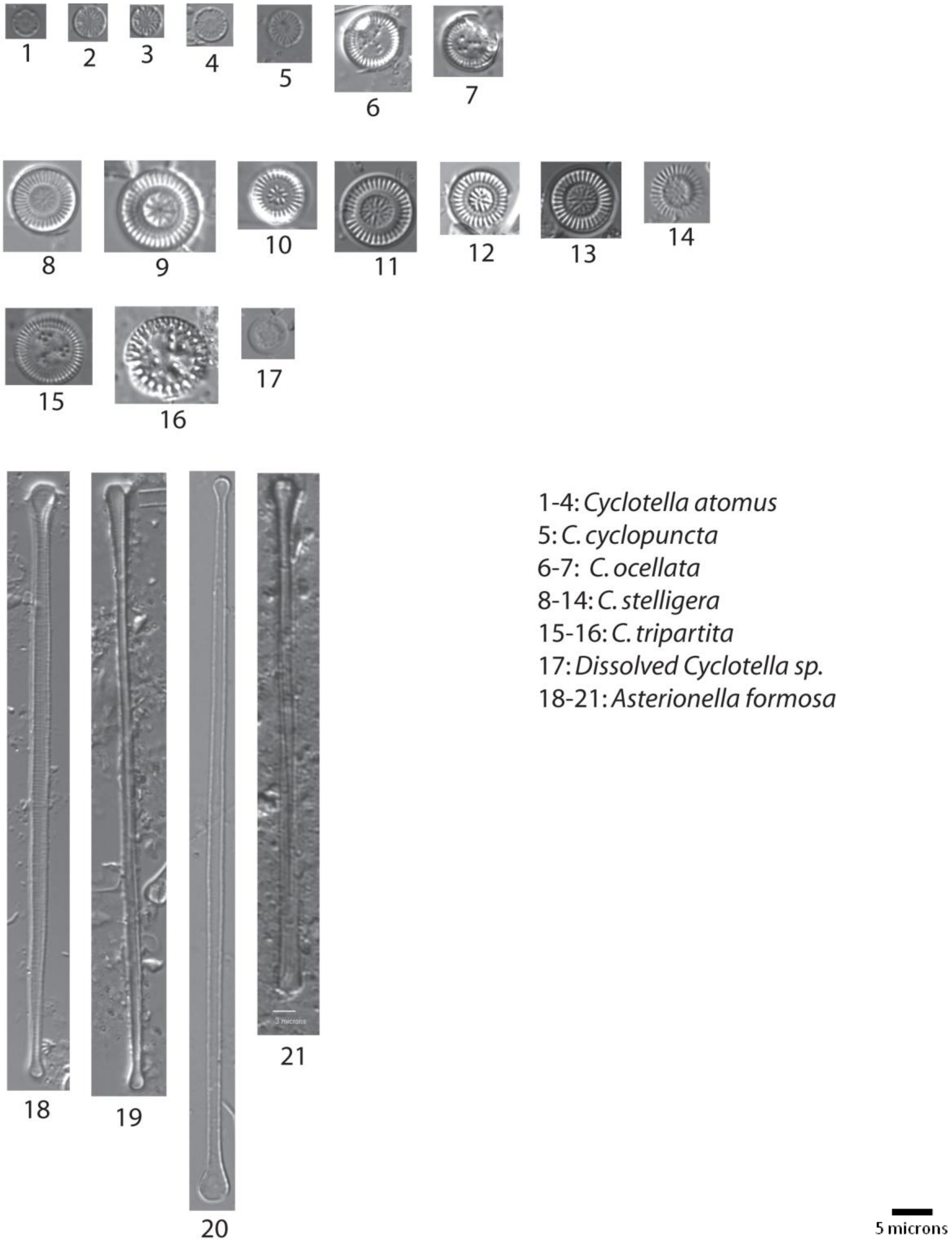
1: *Achnanthes amoena*
2 - 5: *Achnanthes biasolettiana*
6: *Achnanthes carissima*
7-11: *Achnanthes curtissima*
12: *Achnanthes didyma*
13: *Achnanthes helvetica*
14: *Achnanthes kuelbsii*
15-16: *Achnanthes lanceolata var frequentissim*a
17: *Achnanthes laterostrata*
18-20: *Achnanthes lacus-vulcani*
21-23: *Achnanthes levanderi*
24: *Achnanthes marginulata*
25-28: *Achnanthes minutissima*
29: *Achnanthes minutissima var minutissima*
30: *Achnanthes nodosa*
31-33: *Achnanthes petersennii*
34-37: *Achnanthes pusilla*
38: *Achnanthes rossii*
39-40: *Achnanthes saccula*
41-42: *Achnanthes subatomoides*
43-44: *Achnanthes suchlandtii*
45: *Achnanthes stolida*
46: *Anonomoneis brachysira*
47-49: *Anonomoneis vitrea*

Plate 1. *Achnanthes* and *Anomonoeis* species.



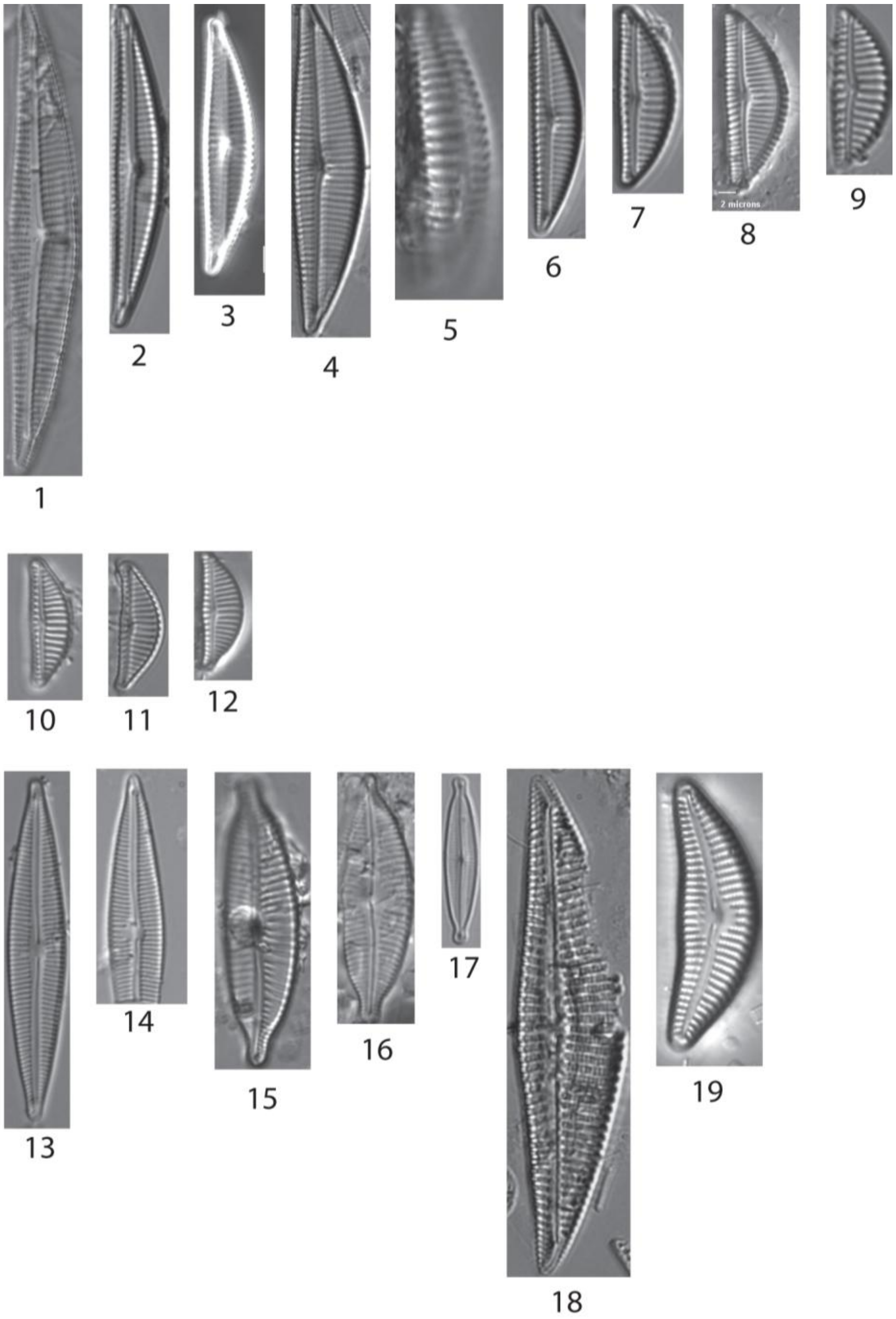
1: *Aulocoseira alpigena*
2-5: *A. ambigua*
6-8: *A. distans*
9-10: *A. distans var humilis*
11-12: *A granulata*
13: *A. italica*
14-20: *A. lirata*
21-26: *A. perglaba*

Plate 2. *Aulacoseira* species.



1-4: *Cyclotella atomus*
5: *C. cyclopuncta*
6-7: *C. ocellata*
8-14: *C. stelligera*
15-16: *C. tripartita*
17: *Dissolved Cyclotella sp.*
18-21: *Asterionella formosa*

Plate 3. *Cyclotella* and *Asterionella* species.



1-3: *Cymbella gracilis*
4: *C. hebridica*
5-9: *C. silesiaca*
10-12: *C. minuta*
13-14: *C. cesatii*
15-16: *C. cuspidata*
17: *C. amphicephela*
18: *C. mesiana*
19: *C. cistula*

Plate 4. *Cymbella* species.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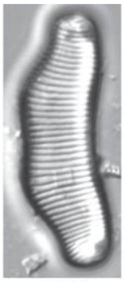
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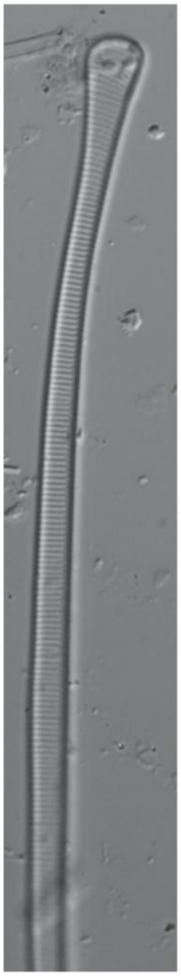
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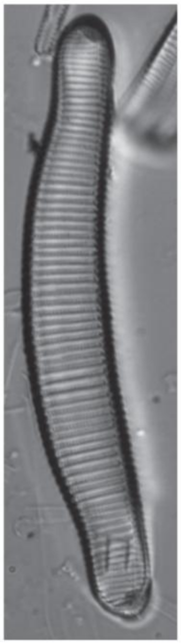
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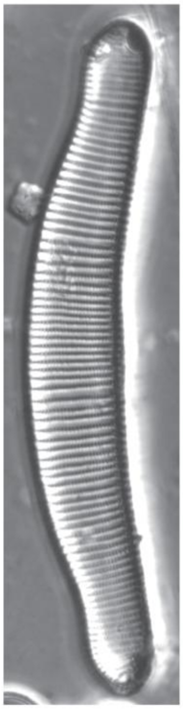
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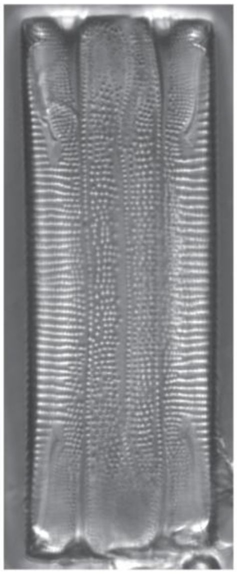
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1-3: *Eunotia minor*
4-5: *E. musicicola var tridentula*
6: *E. intermedia*
7: *E. arcus*
8-9: *E. rhynocephela var satelles*
10: *E. curcumborealis*
11: *E. glacialis*
12: *E. monodon*
13-15: *E. soleirolii*
16-18: *E. serra var diadema*

Plate 5. ***Eunotia*** **species (previous page)**

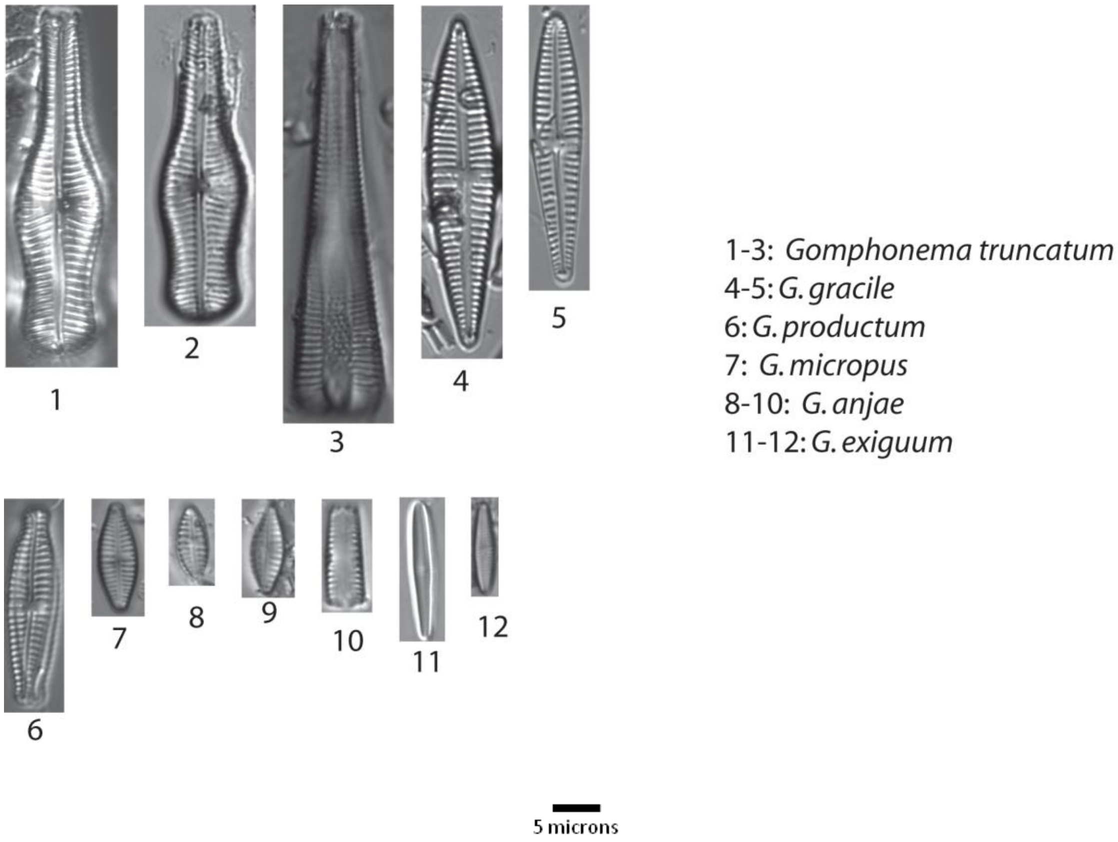
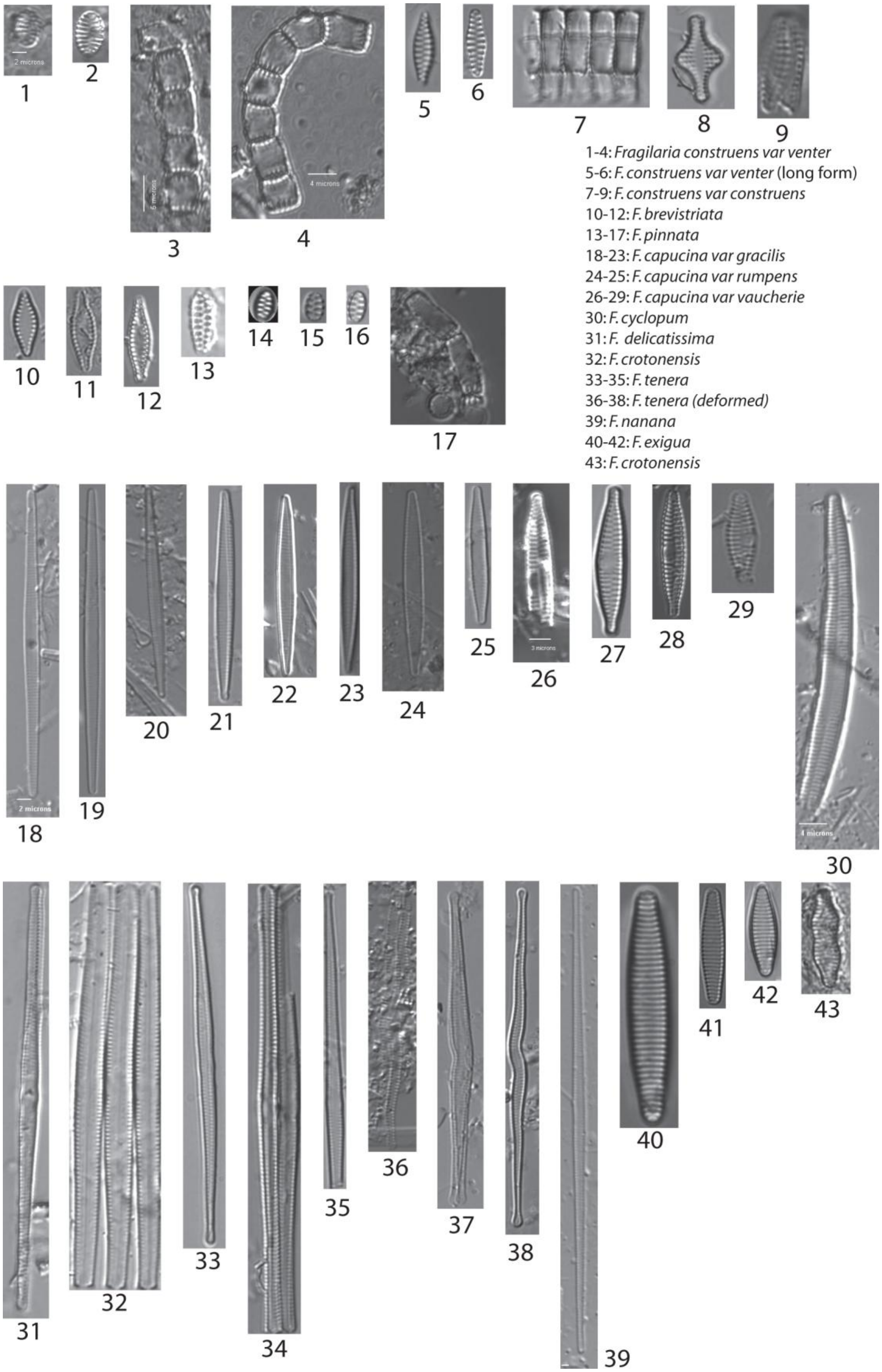
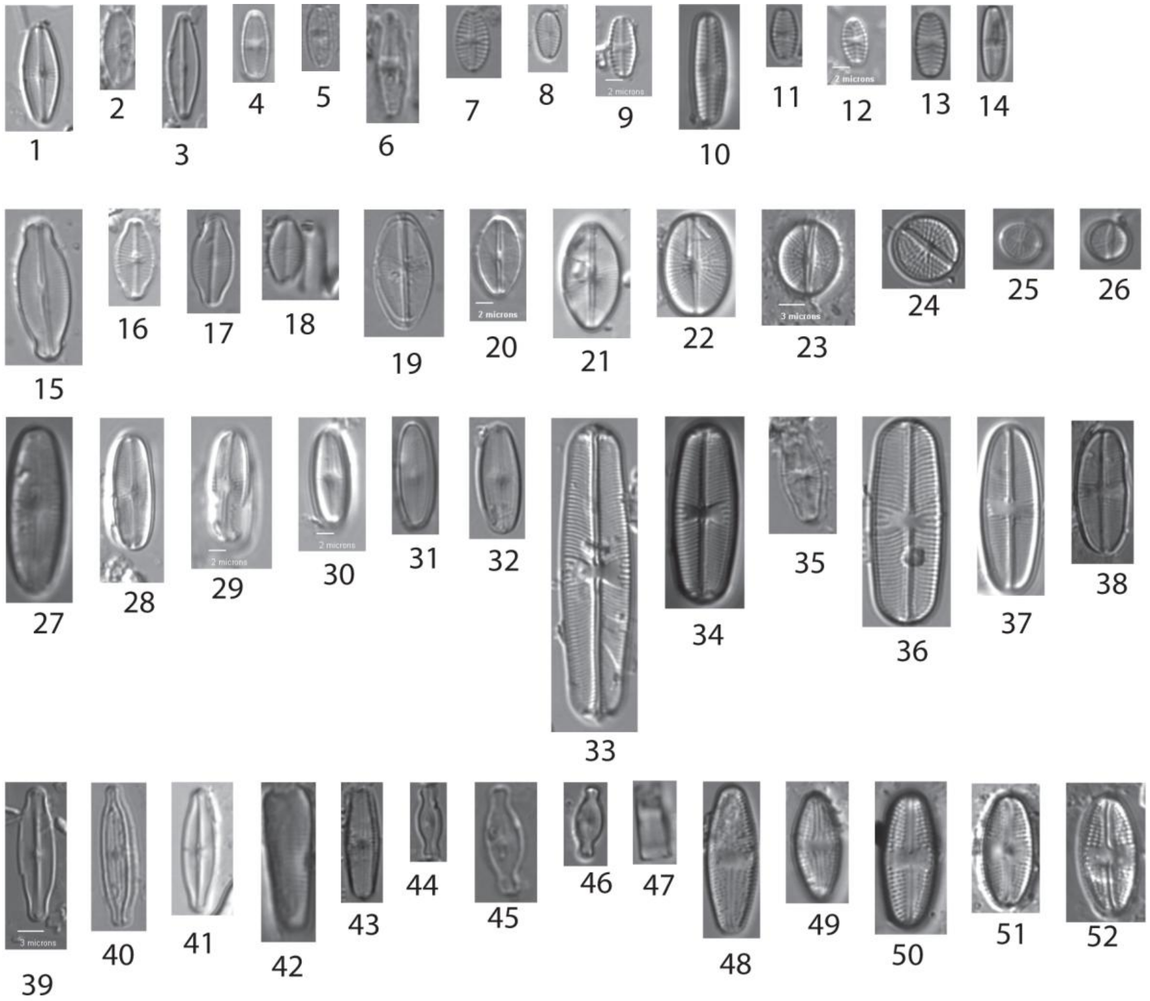


Plate 6. ***Gomphonema*** **species.**



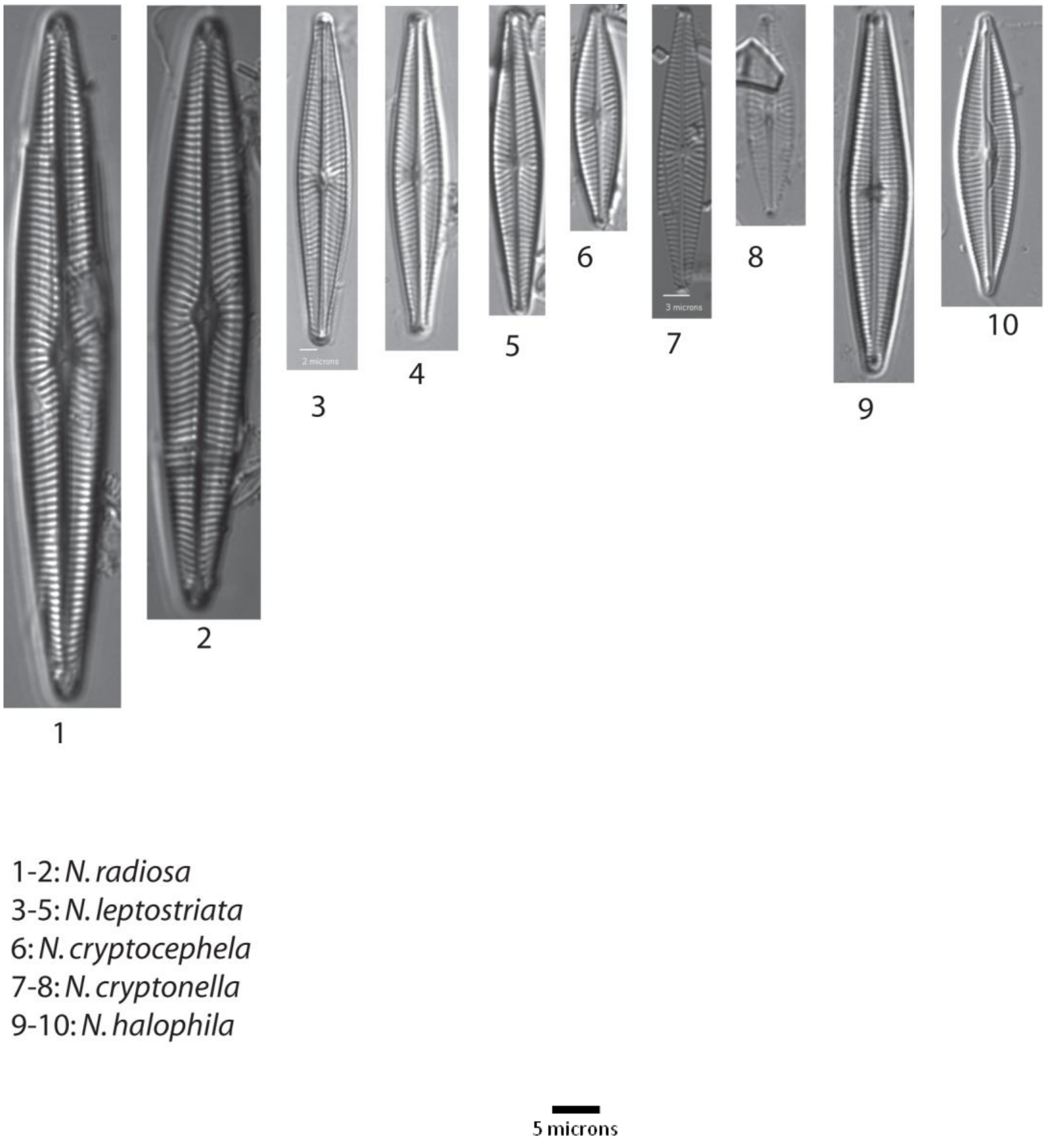
1-4: *Fragilaria construens var venter*
5-6: *F. construens var venter* (long form)
7-9: *F. construens var construens*
10-12: *F. brevistriata*
13-17: *F. pinnata*
18-23: *F. capucina var gracilis*
24-25: *F. capucina var rumpens*
26-29: *F. capucina var vaucherie*
30: *F. cyclopum*
31: *F. delicatissima*
32: *F. crotonensis*
33-35: *F. tenera*
36-38: *F. tenera (deformed)*
39: *F. nanana*
40-42: *F. exigua*
43: *F. crotonensis*

Plate 7. *Fragilaria* species (previous page)



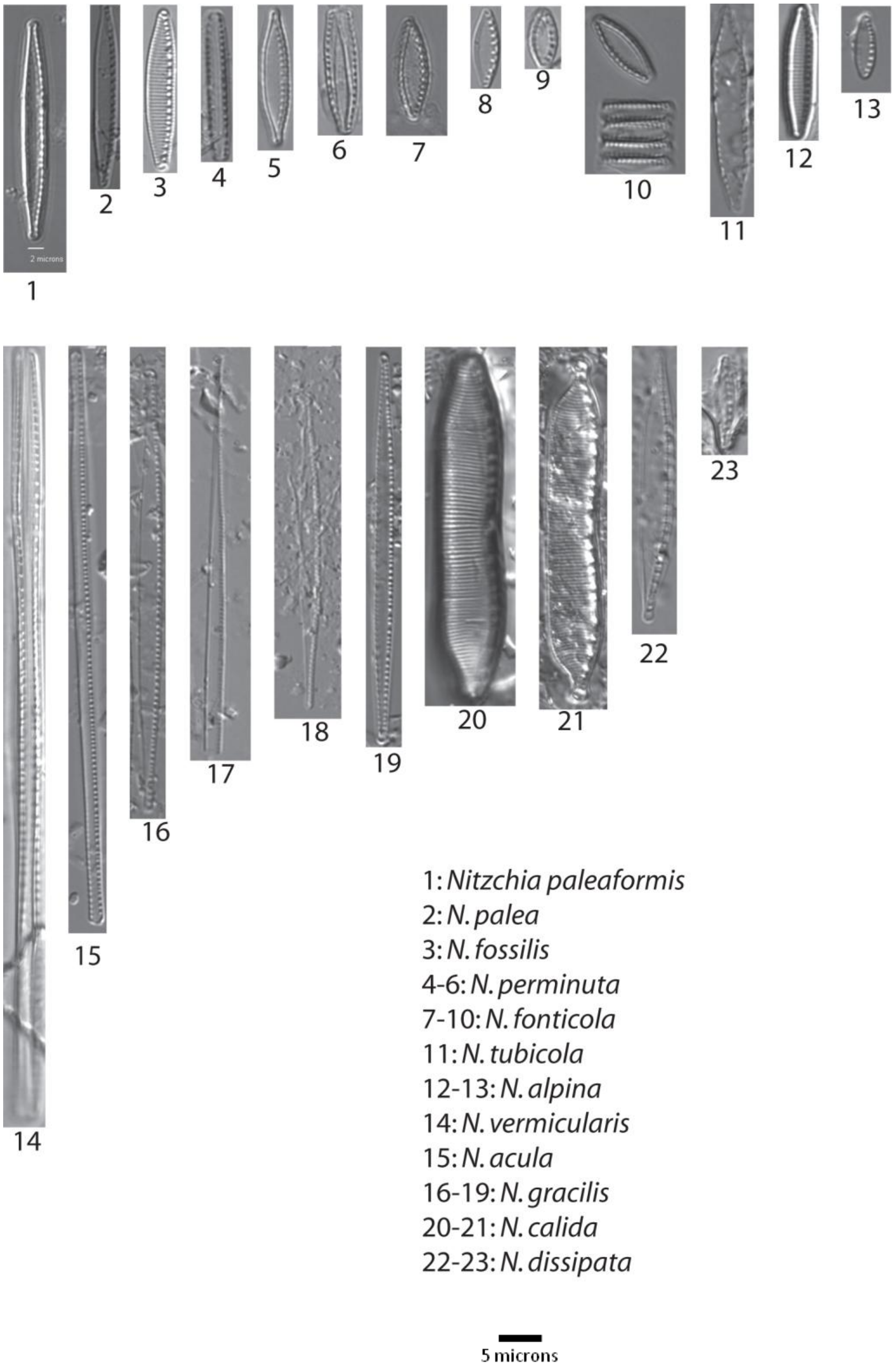
1-2: *Navicula bahusiensis*
3: *N. miniscula*
4-6: *N. minima*
7-8: *N. subminiscula*
9-13: *N. seminelum*
14: *N. harderii*
15: *N. detenta*
16-18: *N. modica*
19-20: *N. utermoehli*
21: *N. cocconeiformis*
22-26: *N. pseudocutiformis*
27-32: *N. variostrata*
33-34: *N. pupula*
35: *N. pupula var pupula*
36: *N. laevissima*
37-38: *N. lapidosa*
39: *N. difficillima*
40-41: *N. bryophila*
42-43: *N. digitilus*
44-47: *N. schmassmannii*
48-50: *N. mutica*
51-52: *N. saxophila*

Plate 8. *Navicula* species.



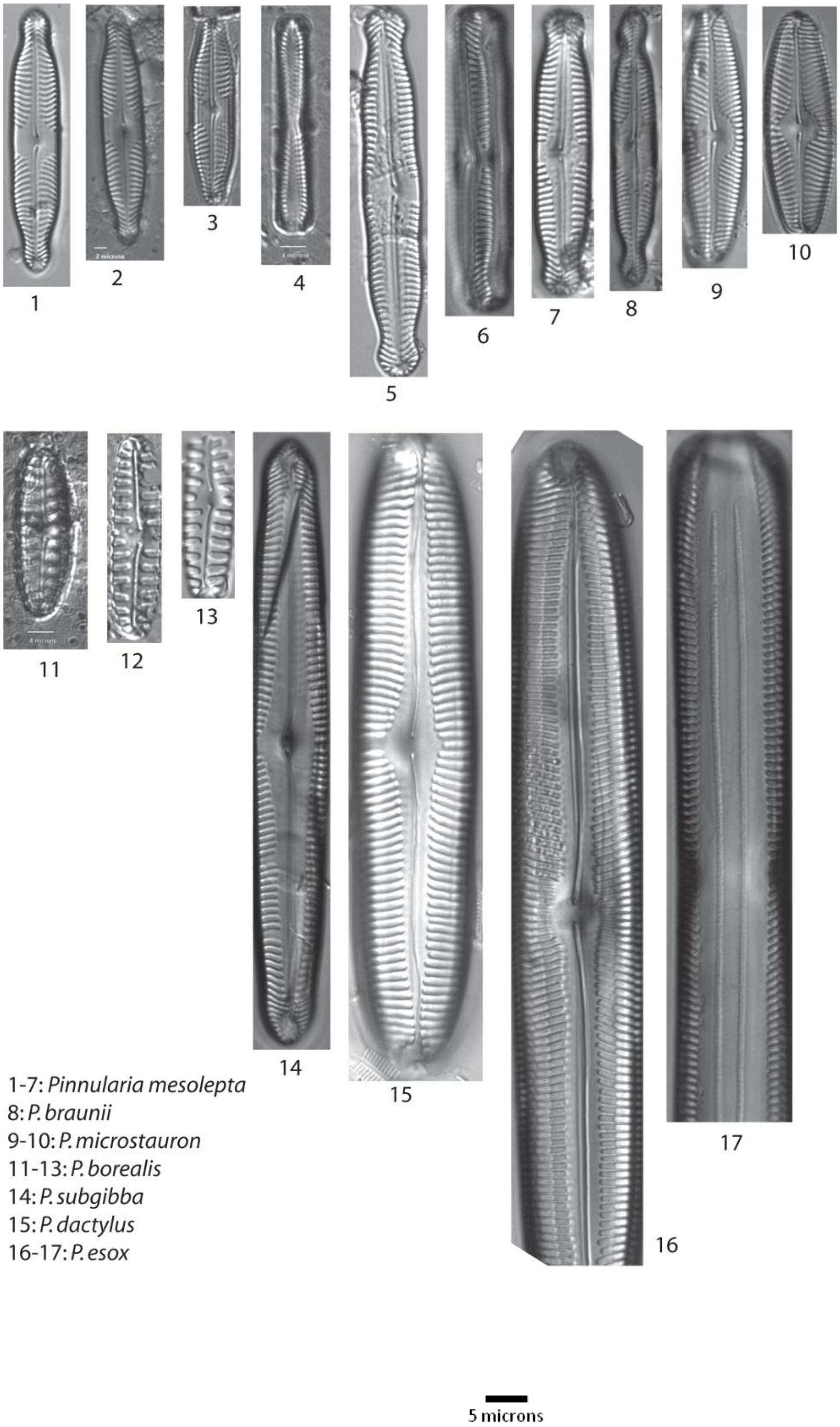
1-2: *N. radiosa*
3-5: *N. leptostriata*
6: *N. cryptocephela*
7-8: *N. cryptonella*
9-10: *N. halophila*

Plate 9. *Navicula* species.



1: *Nitzchia paleaformis*
2: *N. palea*
3: *N. fossilis*
4-6: *N. perminuta*
7-10: *N. fonticola*
11: *N. tubicola*
12-13: *N. alpina*
14: *N. vermicularis*
15: *N. acula*
16-19: *N. gracilis*
20-21: *N. calida*
22-23: *N. dissipata*

Plate 10. *Nitzschia* species.



1-7: *Pinnularia mesolepta*
8: *P. braunii*
9-10: *P. microstauron*
11-13: *P. borealis*
14: *P. subgibba*
15: *P. dactylus*
16-17: *P. esox*

Plate 11. *Pinnularia* species.

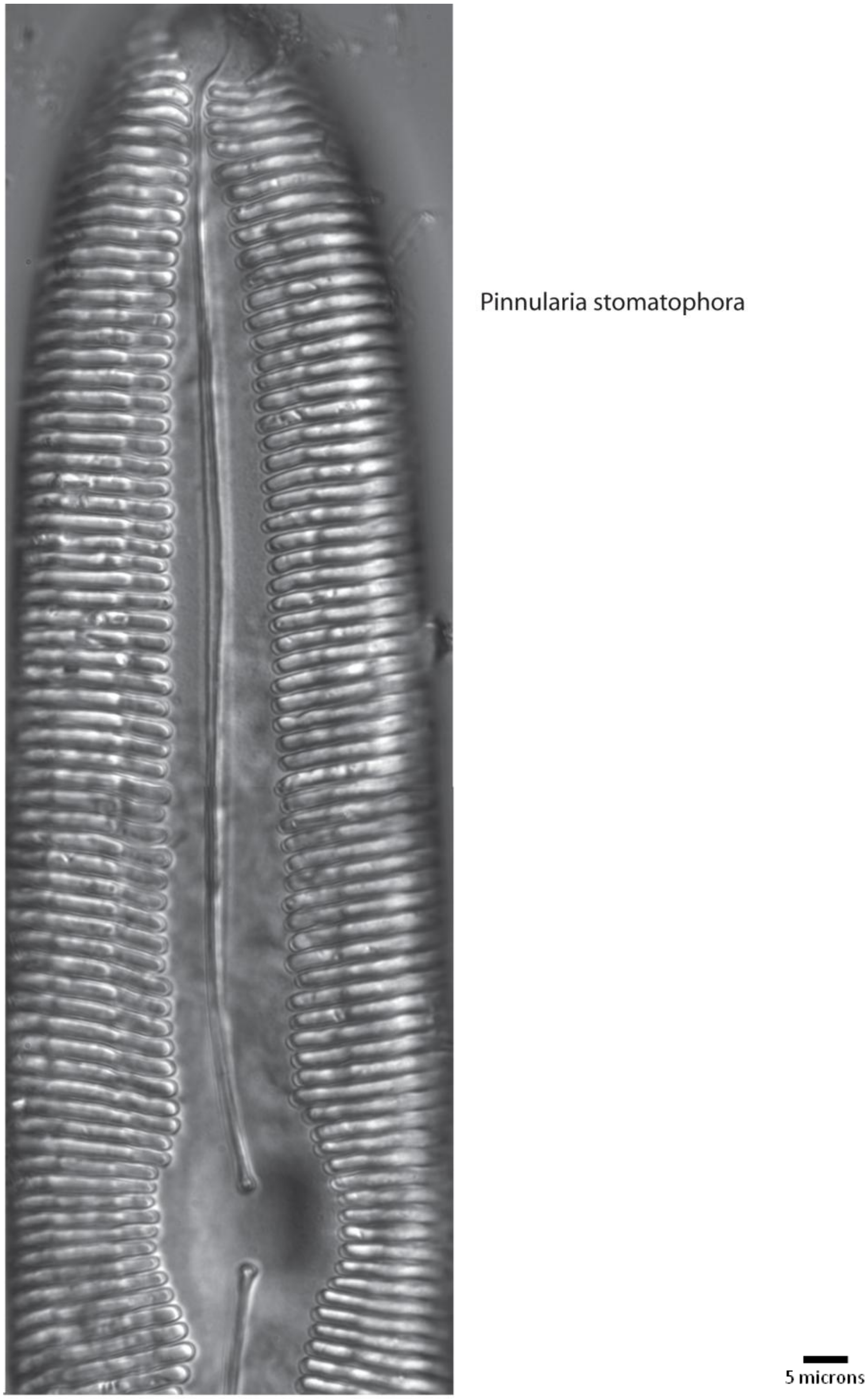
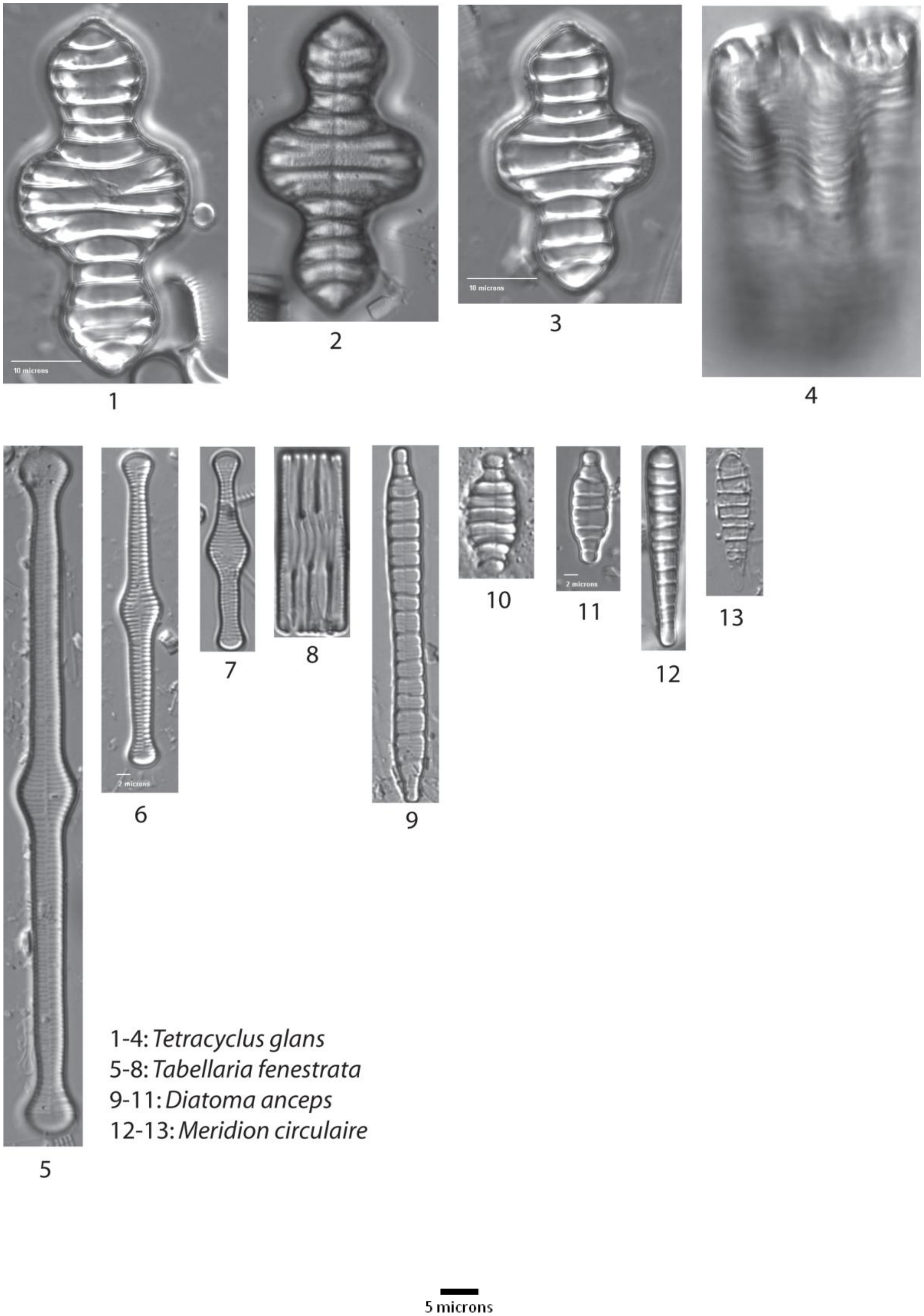
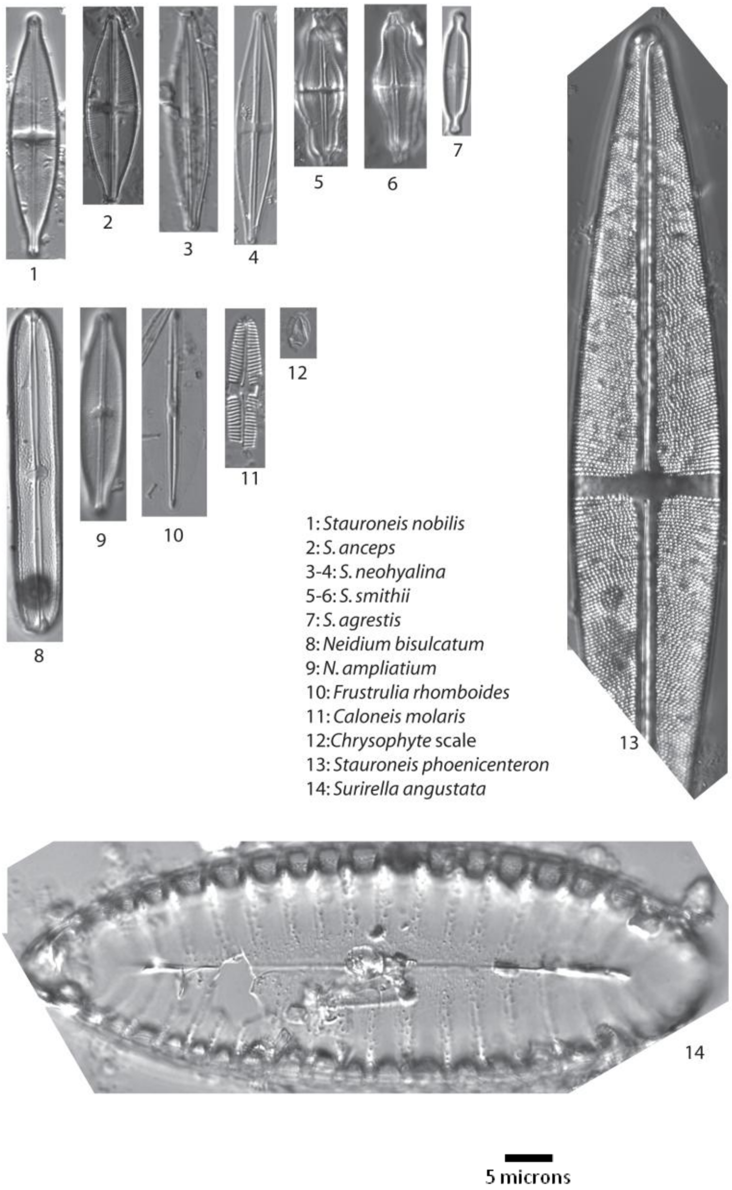


Plate 12. ***Pinnularia*** **species.**



1-4: *Tetracyclus glans*
5-8: *Tabellaria fenestrata*
9-11: *Diatoma anceps*
12-13: *Meridion circulaire*

Plate 13. ***Tetracyclus, Tabellaria, Diatoma,*** **and** ***Meridion*** **species.**



1: *Stauroneis nobilis*
2: *S. anceps*
3-4: *S. neohyalina*
5-6: *S. smithii*
7: *S. agrestis*
8: *Neidium bisulcatum*
9: *N. ampliatium*
10: *Frustrulia rhomboides*
11: *Caloneis molaris*
12: *Chrysophyte* scale
13: *Stauroneis phoenicenteron*
14: *Surirella angustata*

Plate 14. *Stauroneis, Neidium, Frustrulia,* and *Surirella* diatom species, and a *Chrysophyte* scale.

Appendices

Appendix A. Water sample data from triple isotope analysis of nitrates.

Date MM/YY	Sample Name	Sample Type	Latitude (N)	Longitude (W)	Elev. (m)	δ^{15}N ‰ AIR	δ^{18}O ‰ VSMOW	Δ^{17}O ‰ VSMOW	NO_3^- (μM)	NH_4^+ (μM)
03/09	Chepeta	snow	40.76	110.016	3228	+1.5	+75.08	+30.68	7.85	5.78
03/09	Trial Lk	snow	40.68	110.95	3046	+0.6	+71.74	+25.28	4.38	4.64
03/09	Spirit Lk	snow	40.83	110.0	3116	+2.1	+74.14	+29.24	10.14	7.43
03/09	Lakefork	snow	40.6	110.43	3174	+3.4	+73.81	+28.54	7.50	6.57
04/11	Lakefork	snow	40.5955	110.4339	3094	+1.8	+55.00	+20.18	10.00	6.0
04/11	Grizzly Ridge	snow	40.7489	109.5051	2914	–1.2	+48.60	+15.04	15.79	3.4
07/09	UN58SNOW	snow	40.7117	110.3923	3611	–0.8	+62.50	+20.04	2.59	4.64
08/09	UN08SNOW	snow	40.7904	110.0954	3486	–0.0	+67.00	+20.31	2.01	8.07
07/08	UN08IN1A	snowmelt	40.7904	110.0953	3483	+2.7	+52.51	+17.11	1.86	3.00
07/08	UN08IN1B	snowmelt	40.7904	110.0952	3469	–3.7	+35.82	+12.68	4.31	0.79
07/08	UN08IN1C	inflow	40.7899	110.0935	3428	–1.2	+11.86	+5.82	19.78	0.78
07/08	UN08IN1D	inflow	40.7902	110.0939	3435	–2.0	+14.65	+7.40	14.79	0.71
07/08	UN08IN2	inflow	40.7888	110.0939	3429	–3.3	+13.37	+6.15	28.47	0.64
07/08	UN08IN3	inflow	40.7876	110.0931	3426	–1.4	+7.33	+4.40	9.20	1.21
07/08	UN07IN	inflow	40.7820	110.0872	3408	–1.3	–4.66	+0.52	2.88	0.64
07/08	UN55IN1	inflow	40.7226	110.3564	3403	–0.7	+9.46	+4.49	14.69	0.57
07/08	UN56IN1	inflow	40.7198	110.3451	3428	–2.0	+11.42	+4.95	41.39	0.57
07/08	UN58IN1A	inflow	40.7006	110.3881	3366	–2.6	+17.07	+7.16	47.18	0.64
07/08	UN58IN1B	inflow	40.7009	110.3877	3354	–2.8	+17.78	+6.89	46.50	0.71
08/09	UN08IN1A	inflow	40.7907	110.0943	3447	–0.9	+11.23	+5.40	19.92	0.92
08/09	UN08IN1B	inflow	40.7902	110.0938	3434	–1.3	+11.34	+5.50	19.42	0.64
08/09	UN08IN1C	inflow	40.7921	110.0948	3456	–2.1	+15.26	+6.90	15.14	0.57
08/09	UN08IN2	inflow	40.7888	110.0939	3432	–1.6	+12.34	+5.91	55.97	0.86
08/09	UN08IN3	inflow	40.7876	110.0931	3426	–0.9	+10.35	+4.75	38.98	0.57
08/09	UN07IN1	inflow	40.7820	110.0872	3408	–1.3	–2.42	+1.77	6.20	1.14
07/09	UN55IN1A	inflow	40.7226	110.3564	3403	–1.1	+13.04	+5.89	19.42	1.00
07/09	UN55IN1B	inflow	40.7230	110.3576	3415	+1.0	+13.14	+5.13	8.21	4.36
07/09	UN56IN1A	inflow	40.7203	110.3444	3435	–2.0	+13.10	+5.08	45.12	0.50
07/09	UN56IN1B	inflow	40.7198	110.3451	3428	–1.6	+13.12	+4.85	44.48	0.71
07/09	UN58IN1A	inflow	40.7006	110.3881	3366	–1.7	+15.91	+6.82	44.55	0.79
07/09	UN58IN1B	inflow	40.7006	110.3881	3364	–2.0	+16.23	+6.33	45.19	0.57
07/09	UN58IN1C	inflow	40.7009	110.3877	3353	–2.7	+15.62	+6.56	44.55	0.64
07/08	UN32	lake	40.8114	110.0380	3393	+2.4	+12.26	+4.70	7.35	0.50
07/08	UN08A	lake	40.7884	110.0926	3424	+0.4	+15.60	+2.63	1.83	0.93
07/08	UN55	lake	40.7215	110.3545	3400	–1.1	+24.40		0.39	0.50
07/08	UN58	lake	40.7017	110.3866	3400	+0.0	+21.60		0.76	0.50
07/09	UN56	lake	40.7187	110.3449	3424	+0.4	+14.62	+3.81	0.78	1.57
08/09	UN08b	lake	40.7884	110.0926	3425	+0.9	+17.96		0.21	0.79
08/09	UN07	lake	40.7818	110.0860	3404	+2.3	+12.37		0.59	1.21
09/12	UN55	lake	40.7215	110.3545	3400	+1.5	+9.58	+8.04	0.87	1.43
05/12	UN08	lake	40.7884	110.0926	3424	+0.8	+21.86	+7.52	1.57	0.64
07/11	GSLH2O	GSL	40.7357	112.2107	1281	+10.4	+16.25	+4.66	3.06	

Appendix B. Detailed coupled cadmium azide reduction lab methods.

The chemical procedure for determining δ^{15}N-, δ^{18}O- and Δ^{17}O-NO_3^- involves two main steps - the conversion of nitrate to nitrite using activated cadmium, and the conversion of nitrite to N_2O using a 1:1 molar solution of sodium azide and acetic acid (Russell and Longstaffe, in prep). Chemical procedures are carried out in a fume hood designated for nitrate isotope analysis preparation in order to avoid contamination.

Prior to analyses, frozen samples were thawed in a hot water bath and filtered using a 0.45 µM syringe filter. Samples, standards (USGS-35, USGS-34, USGS-32, IAEA-NO-3 and GSI-NO-3) and blanks are prepared to meet a set of consistent chemical conditions to ensure that the same fractionation affects all standards and samples.

- 40 mL volume
- Nitrate concentration is diluted to 1.24 ppm (maximum for samples)
- Sodium chloride concentration is set to 0.5± 0.04 M NaCl
- pH is set to 8.5 ± 0.05

The cadmium is activated by transferring 2 % $CuSO_4$ solution through the column. The samples are pumped at a rate of ~5 mL/minute through the cadmium column (3 mm Tygon® tubing filled with cadmium) to convert nitrate to nitrite. Before each sample or standard, 15 mL of blank solution (0.5 M NaCl) is flushed through the column, and the first 15 mL of sample is discarded, thus eliminating any potential for memory effects. The samples and standards are collected in 15 mL Falcon tubes and immediately frozen. Following nitrate reduction, sample, standard, and blank nitrate concentrations are measured by spectrophotometry (O'Dell, 1993) and the necessary volume of solution (up to a maximum of 7.5 mL) is calculated in order to decant 60 nmol of nitrate into a Labco Exetainer (4) vial. Two Exetainer® vials per sample (one for analysis of N_20 and one for analysis of N_2 and O_2) are prepared and sealed with a septa-lined cap. Samples are mixed and placed in the refrigerator at 4°C until the next step.

A solution of 1:1 acetic acid and sodium azide is prepared in the fume hood. Exactly 0.8 mL of the mixture is injected into each sample vial through its septum cap using a syringe with a needle. This step serves to reduce nitrite to nitrous oxide. Samples are placed in a 30 ˚C bath for 30 minutes, after which 0.3 mL of NaOH is injected into each vial to stop the reaction. The isotopic ratios of the resulting N_2O are measured the following day using a Thermo Finnigan Delta^{plus} XL accessorized with a Gas Bench II and CTC CombiPal autosampler, as described by Russell and Longstaffe (in prep).

Appendix C. Isotope ratio corrections.

δ^{15}N corrections

An explanation of the conversion from isotope mass ratios into raw δ^{15}N values can be found in McIlvin and Altabet (2005).

The intent is to measure the ratio of $^{15}N/^{14}N$, which is achieved by measuring mass 45/ mass 44 of N_2O gas. However, there are two isotopologues with the mass number 45, $^{15}N^{14}N^{16}O$ (what we intend to measure) and $^{14}N^{14}N^{17}O$. This interference occurs even when Δ^{17}O values are zero due to mass-dependent fractionation. Therefore, a "Craig correction" (Craig, 1957) is applied by the computer software (ISODAT) to account for the artificially high δ^{15}N due to mass interference as described in McIlvin and Altabet (2005). This correction is based on the δ^{18}O value, which is proportional to δ^{17}O, assuming mass-dependent fractionation.

In most of our samples, δ^{17}O is larger than would be expected based on the mass-dependent relationship with δ^{18}O (i.e., $\Delta^{17}O > 0$), for which the Craig correction does not account. To correct for this effect, we apply a Δ^{17}O dependent correction:

$$\delta^{15}N_{NO3\ 17corr} = \delta^{15}N_{NO3cal} - x_{corr} \times \Delta^{17}O_{spl} \qquad \text{A1}$$

where $\delta^{15}N_{NO3\ 17corr}$ is the corrected value reported in this paper (herein $\delta^{15}N_{NO3}$) and $\delta^{15}N_{NO3cal}$ is calibrated result produced using standards. The value of x_{corr} is based on:

$$x_{corr} = (\delta^{15}N_{N2O\ USGS\text{-}35cal} - \delta^{15}N_{USGS35True})/\Delta^{17}O_{USGS35cal} \qquad \text{A2}$$

where $\delta^{15}N_{N2O\ USGS35cal}$, $\delta^{15}N_{USGS35True}$ and $\Delta^{17}O_{USGS35cal}$ are the calibrated (cal) and true values of USGS-35 nitrate. In our case, x_{corr} = 0.1 ‰, meaning that δ^{15}N is inflated by 0.1 ‰ for every 1 ‰ increase in Δ^{17}O. Thus, for snow samples with Δ^{17}O values upwards of +30 ‰, this effect causes uncorrected δ^{15}N values to be higher by 3 ‰ than the true result. In the case of four lake water samples, we could not correct for the mass overlap between $^{15}N^{14}N^{16}O$ and $^{14}N^{14}N^{17}O$ because the nitrate concentrations were too low to measure Δ^{17}O accurately. In these cases, uncorrected $\delta^{15}N\text{-}NO_3^-$ values were used.

Although the mix of uncorrected and corrected nitrogen isotopic ratios is not ideal, the correction would likely have been minor because the lakes tend to have low $\Delta^{17}O\text{-}NO_3^-$ values (mean lake $\Delta^{17}O = +5.3$ ‰).

$\delta^{18}O$ corrections

$\delta^{18}O$ is calculated from the ratio of masses 46/44 ($^{14}N^{14}N^{18}O/^{14}N^{14}N^{16}O$). An explanation of the conversion from isotope mass ratios into raw $\delta^{15}N$ and $\delta^{18}O$ values can be found in McIlvin and Altabet (2005).

$\delta^{18}O$ values must be adjusted during each analytical run to account for oxygen isotopic exchange between the $\delta^{18}O$ of nitrate and water during the reduction to nitrous oxide, following the equation of McIlvin and Altabet (2005):

$$\delta^{18}O_{NO3corr} = \delta^{18}O_{NO3} - (1-(1/m_{stds}))\times(\delta^{18}O_{H2Ospl} - \delta^{18}O_{H2Ostd}) \qquad \text{A3}$$

where $\delta^{18}O_{H2Ospl}$ and $\delta^{18}O_{H2Ostd}$ are the oxygen isotope values of the water containing the nitrate samples and the water used for standard mixtures, respectively. This correction is important because of potential differences in $\delta^{18}O$ from laboratory water and sample water.

$\Delta^{17}O$ Corrections

Oxygen (O_2) and nitrogen (N_2) gas isotope ratios were collected by monitoring masses 32, 33, and 34, and 28, 29, and 30, respectively. Raw $\delta^{15}N$, $\delta^{18}O$ and $\delta^{17}O$ values are calculated by mass spectrometry software as described in Kaiser et al. (2006).

The $\Delta^{17}O$ value is calculated using raw δ- values by rearranging the Terrestrial Fractionation Line (Matsuhisa et al., 1978):

$$\Delta^{17}O_{sample} = \delta^{17}O - 0.52 \times \delta^{18}O \qquad \text{A4}$$

Appendix D. Average ammonium and nitrate concentrations and triple isotope compositions.

Table D.1. Nitrate and ammonium concentrations for all samples. This listing includes those samples that did not have sufficiently high nitrate concentrations for triple isotope analysis.

		NO_3^- (μM)	NH_4^+ (μM)
Snow	Mean	4.9	4.5
n=14	Median	2.3	5.1
	Minimum	1.1	1.1
	Maximum	15.7	8.1
Lakes	Mean	0.7	0.9
n=23	Median	0.28	0.8
	Minimum	0.01	0.5
	Maximum	7.4	1.9
Inflows	Mean	25.5	1.0
n=25	Median	19.8	0.7
	Minimum	0.1	0.5
	Maximum	56	4.4
All Uinta Samples	Mean	10.4	1.7
n=70	Median	1.8	0.9
	Minimum	0.01	0.5
	Maximum	56.0	8.1
Great Salt Lake, n = 1		3.1	-

Table D.2. Summary of concentrations and triple isotope compositions of nitrate for samples selected for the study.

*for lake Δ^{17}O, n =5, due to low concentrations of nitrate. Similarly, for all Uinta samples, N = 37 for Δ^{17}O due to missing values for the same 4 samples.

		NO_3^- (μM)	NH_4^+ (μM)	δ^{15}N (‰)	δ^{18}O (‰)	Δ^{17}O (‰)
Snow	Mean	7.5	5.8	+0.9	+66.0	+23.7
	Median	7.7	5.9	+1.1	+69.4	+22.8
n=8	Minimum	2.0	3.4	–1.2	+48.6	+15.0
	Maximum	15.8	8.1	+3.4	+75.1	+30.7
Lakes	Mean	1.6	0.9	+0.83	+16.7	+5.3
	Median	0.8	0.8	+0.9	+15.6	+4.7
n=9*	Minimum	0.2	0.5	–1.1	+9.6	+2.6
	Maximum	7.4	1.6	+2.4	+24.4	+8.0
Inflows	Mean	26.6	1.0	–1.5	+14.4	+6.2
	Median	19.9	0.7	–1.6	+13.1	+5.9
n=24	Minimum	1.9	0.5	–3.7	–4.7	+0.5
	Maximum	56.0	4.4	+2.6	+52.5	+17.1
All Uinta	Mean	17.4	1.9	–0.5	+25.0	+9.9
Samples	Median	10	0.8	–1.12	+15.3	+6.3
	Minimum	0.2	0.5	–3.7	–4.7	+0.5
n=41*	Maximum	56.0	8.1	+3.4	+75.1	+30.7
Great Salt Lake, n=1		3.1		+10.4	+16.3	+4.7

Appendix E. Uinta Mountain samples and the terrestrial fractionation line.

The calculation of Δ^{17}O and the concept of the Terrestrial Fractionation Line (TFL) are illustrated by plotting δ^{17}O versus δ^{18}O for the Uinta Mountain data (Figure A5.1). The lake, inflow and snow sample isotopic compositions are elevated above the TFL (this 'vertical' difference is described by Δ^{17}O), indicating the presence of nitrate that has had atmospheric reactions with ozone. The TFL has a slope of 0.52, whereas the regression equation of the sample points from the Uinta Mountains is $\delta^{17}O = 0.85(\delta^{18}O) + 0.81$ (Figure E.1). Therefore, δ^{17}O is ~85 % of the δ^{18}O values, rather than ~52% as expected for terrestrial sources and processes. The lake samples deviate somewhat from this relationship, possibly because (i) the concentration of nitrates in these samples is particularly low, so measurements are likely to be less precise and (ii) given the low nitrate concentrations in these systems, even a small change in nitrate inputs could result in a large change in stable isotope composition. A third possibility is that a process not affecting snowmelt and inflows occurs in this lake – a yet unidentified source of nitrate to the lake water or the influence of processes that have more time to occur in lake water, such as assimilation.

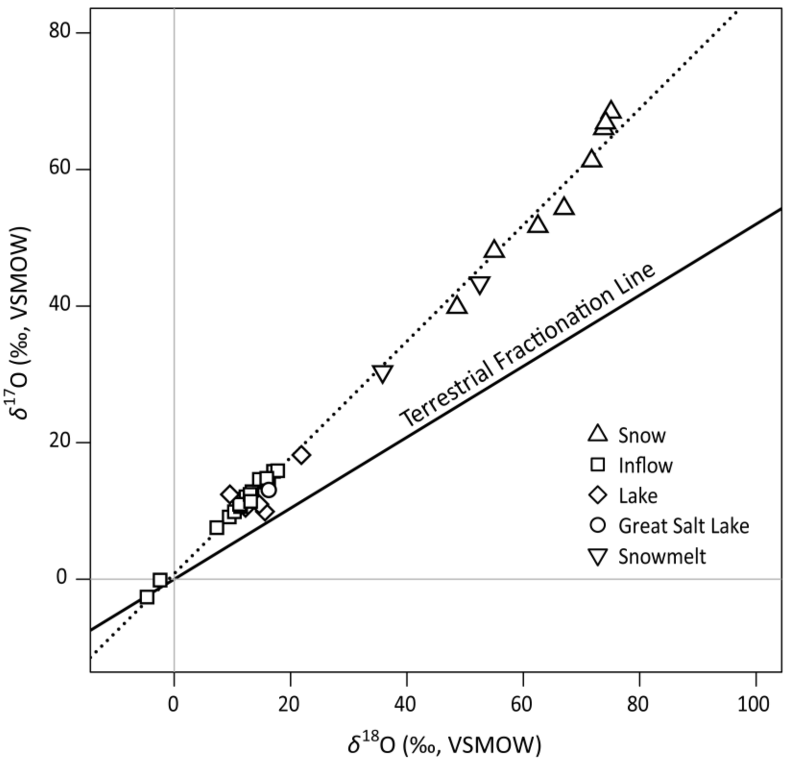


Figure E.1 Sample $\delta^{18}O$ and $\delta^{17}O$ relative to the Terrestrial Fractionation Line.

Appendix F. Calibration set data.

Those sites excluded from the calibration subset due to high alkalinity (>10 Mg L^{-1} CaCO$_3^-$) are shaded gray.

Lake	LAT °N	LONG °W	Elev. (m)	Secchi (m)	Depth (m)	Temp °C	pH	Alkalinity Mg L^{-1} CaCO$_3^-$	NO$_3$ ppm	SO$_4$ ppm	^{26}Mg ppm	^{27}Al ppb	^{29}Si ppm	^{39}K ppm	^{44}Ca ppm	^{55}Mn ppb	^{88}Sr ppb	^{7}Li ppb	^{52}Cr ppb	^{59}Co ppb	^{60}Ni ppb	^{65}Cu ppb	^{66}Zn ppb	^{75}As ppb	DOC ppm	DIC ppm	^{54}Fe ppb
1	40.68	110.87	3021	4.04	8.1	16.9	7.3	3.0	0.00	2.10	0.48	49.2	0.44	0.26	1.5	0.56	8.26	0.00	0.32	0.05	0.54	2.12	37.92	0.32	4.33	1.33	36.93
2	40.68	110.87	3048	5.26	10.7	16.3	7.4	3.0	0.00	1.13	0.40	13.6	0.00	0.33	1.3	0.37	7.69	0.00	0.29	0.00	0.16	0.47	1.73	0.31	7.05	1.16	0.00
3	40.67	110.89	3133	1.83	1.8	16.2	7.1	3.0	0.00	0.57	0.30	60.3	0.29	0.09	1.2	1.80	7.43	0.00	0.35	0.07	0.22	0.64	1.43	0.28	11.11	1.24	0.00
4	40.67	110.89	3087	2.02	2.0	17.0	6.9	3.0	0.00	0.89	0.39	65.4	0.33	0.43	1.5	4.06	8.85	0.00	0.38	0.15	0.31	0.92	2.64	0.38	3.59	1.32	62.62
5	40.66	110.90	2975	5.19	11.6	18.5	6.8	4.0	0.00	0.99	0.39	47.5	0.54	0.29	1.5	0.39	8.49	0.00	0.32	0.04	0.29	0.66	1.74	0.30	6.39	1.09	34.19
6	40.74	110.03	3158	3.86	15.7	16.6	7.2	3.0	0.00	1.13	0.36	87.8	0.69	0.36	1.6	4.35	8.74	0.82	0.39	0.05	0.35	0.39	0.64	0.32	6.44	1.09	68.77
Denise	40.77	110.09	3399	2.36	2.4	13.6	7.5	3.0	0.01	0.60	0.23	13.7	0.56	0.23	1.1	1.42	5.86	0.00	0.33	0.03	0.00	0.35	0.86	0.19	4.87	1.29	33.11
Taylor	40.79	110.09	3414	5.42	9.7	13.5	7.5	4.0	0.00	0.60	0.21	13.6	0.60	0.29	1.0	1.36	5.52	0.00	0.23	0.00	0.00	0.24	1.08	0.18	8.35	1.29	24.37
9	40.78	110.02	3231	1.12	1.1	16.4	7.5	3.0	0.00	0.88	0.36	43.1	0.00	0.12	1.5	1.11	8.31	1.06	0.43	0.04	0.38	0.59	1.44	0.41	2.11	1.01	0.00
10	40.72	110.03	2990	2.73	2.7	18.8	7.2	5.0	0.00	1.22	0.52	94.0	0.53	0.64	2.5	3.67	13.13	0.00	0.56	0.05	0.40	0.67	1.51	0.31	1.42	1.66	83.99
11	40.70	109.54	2652	1.50	1.5	19.1	9.1	72.4	0.00	0.00	5.11	2.7	4.54	2.88	25.3	6.65	92.74	3.97	1.62	0.11	0.82	0.36	1.61	0.99	7.77	20.64	146.8
12	40.74	109.73	2938	1.61	1.6	21.0	7.1	3.0	0.00	1.40	0.76	93.5	0.00	0.60	1.9	7.25	11.13	0.00	0.66	0.08	0.50	0.95	1.97	0.58	8.39	1.12	67.86
13	40.88	110.81	2719	1.53	1.5	18.3	7.3	13.0	0.00	4.19	1.55	49.2	0.31	0.63	5.2	4.48	23.99	0.00	0.67	0.09	0.76	0.99	4.58	0.74	10.37	4.02	179.7
15	40.79	110.90	2987	2.30	2.3	18.7	7.9	7.3	0.00	0.87	0.55	62.8	0.80	0.20	1.9	1.55	13.41	0.77	0.45	0.07	0.37	0.45	0.55	0.36	15.10	2.18	76.19
16	40.65	110.97	2987	2.25	2.3	17.5	7.1	4.0	0.00	0.77	0.44	59.4	0.00	0.30	1.7	2.47	10.38	0.00	0.52	0.16	0.33	0.90	0.87	0.46	0.34	1.30	99.82
17	40.64	110.97	2950	2.10	2.1	18.0	7.0	4.0	0.00	0.90	0.43	62.3	0.00	0.28	1.8	1.35	11.15	0.00	0.42	0.11	0.50	0.92	2.47	0.40	5.76	1.43	64.54
18	40.61	110.98	2850	4.56	9.0	19.1	7.6	6.0	0.00	0.80	0.56	27.2	0.14	0.47	2.7	0.74	13.86	0.88	0.43	0.03	0.66	2.16	73.71	0.45	6.52	1.84	63.74
19	40.96	110.39	2841	1.86	4.0	16.0	7.7	35.3	0.00	2.81	2.25	3.5	2.97	0.89	9.9	24.02	34.42	0.00	0.51	0.04	1.11	1.06	3.48	0.62	6.55	12.86	425.5
20	41.00	110.38	2778	4.30	5.0	16.9	8.3	76.4	0.01	2.32	6.11	2.3	3.87	0.94	33.4	4.15	82.25	2.10	0.99	0.04	1.03	0.92	9.52	0.53	6.54	29.11	55.62
21	40.97	110.31	2717	1.74	1.7	16.4	9.2	74.0	0.00	1.26	11.61	7.0	5.45	1.71	9.3	3.31	24.59	0.00	0.75	0.02	0.58	0.73	2.53	0.66	10.56	21.27	90.90
22	40.98	110.32	2737	2.00	2.0	17.2	8.4	20.4	0.00	0.76	1.39	33.4	0.22	2.46	3.2	3.74	25.27	0.00	0.34	0.03	0.63	1.10	5.91	0.85	11.67	4.68	132.8
23	40.73	110.89	3304	2.78	7.1	14.3	9.5	4.1	0.00	0.61	0.13	10.3	0.00	0.12	0.5	0.52	4.05	0.00	0.09	0.00	0.00	0.83	0.41	0.41	12.36	1.05	28.32

Lake	LAT °N	LONG °W	Elev. (m)	Secchi (m)	Depth (m)	Temp °C	pH	Alkalinity mg L^{-1} $CaCO_3$-	NO_3 ppm	SO_4 ppm	^{26}Mg ppm	^{27}Al ppb	^{29}Si ppm	^{39}K ppm	^{44}Ca ppm	^{55}Mn ppb	^{88}Sr ppb	^{7}Li ppb	^{52}Cr ppb	^{59}Co ppb	^{60}Ni ppb	^{65}Cu ppb	^{66}Zn ppb	^{75}As ppb	DOC ppm	DIC ppm	^{54}Fe ppb
24	40.73	110.90	3197	3.84	4.0	15.7	8.5	3.8	0.00	0.75	0.20	9.1	0.29	0.12	0.8	1.23	6.49	0.00	0.12	0.00	0.00	0.91	0.56	0.25	22.39	1.11	0.00
29	40.68	110.93	3033	2.00	13.0	15.0	8.4	4.3	0.00	0.44	0.55	21.9	0.20	0.46	2.2	1.47	12.49	0.00	0.11	0.02	0.21	0.35	0.71	0.30	4.78	2.81	40.78
30	40.68	110.89	3034	1.23	8.0	11.8	7.4	3.1	0.01	0.70	0.34	87.1	0.80	0.21	1.4	2.52	7.80	0.23	0.17	0.00	0.31	0.62	1.99	0.55	3.60	1.80	54.90
31	40.65	110.90	2960	2.11	10.2	14.7	7.4	3.7	0.00	1.31	0.60	55.6	0.49	0.31	1.7	1.46	9.81	0.22	0.16	0.04	0.28	0.67	1.50	0.20	4.37	2.01	70.89
32	40.82	110.04	3392	1.41	22.3	4.6	7.2	2.2	0.15	0.75	0.29	5.8	0.36	0.26	1.4	7.18	7.04	0.07	0.00	0.03	0.16	0.17	1.01	0.17	0.91	1.61	0.00
33	40.79	110.03	3354	2.90	10.7	10.1	7.4	3.0	0.01	0.83	0.34	28.6	0.36	0.25	1.7	1.61	8.50	0.22	0.14	0.02	0.22	0.28	1.78	0.23	3.94	2.01	40.66
34	40.70	110.08	3239	2.50	5.4	9.7	7.6	1.9	0.50	0.94	0.26	6.8	0.63	0.19	1.5	0.71	6.80	0.09	0.07	0.00	0.08	0.21	0.76	0.12	0.41	1.01	0.00
36	40.67	109.91	3071	5.20	6.5	13.9	7.1	2.8	0.00	0.80	0.37	16.8	0.07	0.37	1.2	3.70	5.73	0.16	0.13	0.00	0.14	0.18	0.87	0.36	5.90	1.70	0.00
37	40.73	110.47	3416	3.69	6.9	11.9	7.5	1.0	0.00	0.95	0.38	13.1	0.83	0.17	1.1	0.44	5.99	0.14	0.10	0.01	0.20	0.44	7.86	0.10	1.63	1.64	0.00
39	40.43	110.47	3322	1.76	1.8	17.7	7.1	2.7	0.01	1.07	0.46	84.6	0.10	0.24	1.6	1.29	8.89	0.31	0.28	0.08	0.40	0.81	4.31	0.35	7.81	1.82	28.48
40	40.69	110.45	3473	3.25	5.8	12.3	7.2	3.2	0	1.73	0.38	7.6	0.90	0.20	1.3	0.45	10.10	0.13	0.09	0.01	0.14	0.50	3.61	0.07	1.24	1.67	0.00
41	40.76	110.46	3552	1.40	3.1	11.3	6.9	3.7	0.04	1.18	0.39	8.0	1.57	0.23	1.2	0.90	7.09	0.22	0.11	0.02	0.20	0.66	6.42	0.09	0.97	1.59	0.00
42	40.76	110.45	3560	2.37	2.4	15.1	7.5	1.9	0.00	1.73	0.37	9.5	0.85	0.23	1.3	1.15	10.37	0.20	0.10	0.01	0.15	0.60	13.93	0.07	0.82	1.53	0.00
43	40.75	110.45	3458	2.59	3.6	13.8	7.2	3.1	0.00	1.27	0.36	6.8	0.60	0.22	1.3	0.95	7.98	0.15	0.08	0.00	0.14	0.46	2.15	0.13	1.43	1.76	0.00
45	40.73	110.88	3164	1.90	8.2	16.2	7.9	2.9	0.01	0.54	0.26	28.5	0.70	0.13	1.2	0.57	6.28	0.22	0.07	0.02	0.21	0.39	0.99	0.25	2.97	1.77	11.16
46	40.72	110.87	3115	3.05	3.1	17.6	7.3	3.1	0.01	0.84	0.82	66.2	0.21	0.31	3.4	2.17	19.13	0.32	0.13	0.06	0.34	0.61	20.03	0.39	6.12	2.01	37.92
47	40.94	110.62	2827	4.65	7.3	19.0	9.1	123.0	0.00	0.38	12.32	6.0	1.06	0.62	22.7	5.56	41.74	1.08	0.21	0.09	0.47	0.36	4.13	0.77	10.57	31.11	82.56
48	40.92	110.54	2811	0.30	1.1	20.8	9.1	30.0	0.01	4.12	2.69	51.2	0.55	1.44	8.2	13.85	30.44	1.41	0.32	0.19	0.64	0.91	1.98	1.93	30.33	10.22	188.5
49	40.93	110.19	2813	7.22	13.8	17.6	8.7	167.0	0.00	0.02	6.40	1.8	0.21	8.08	21.7	2.33	114.30	1.23	0.17	0.07	0.42	0.18	1.62	0.38	14.10	26.74	0.00
50	40.93	110.20	2804	3.50	10.5	17.9	8.7	64.0	0.00	0.95	2.94	13.2	0.09	2.96	7.7	1.43	39.93	0.54	0.19	0.04	0.30	0.40	6.35	0.42	15.80	9.1	32.21
51	40.93	110.20	2848	3.75	4.6	17.8	8.9	84.0	0.00	2.30	4.28	5.1	0.11	4.58	11.5	3.50	61.15	1.02	0.14	0.05	0.31	0.23	3.72	0.55	15.55	13.55	23.80
52	40.83	110.00	3200	1.10	2.6	11.1	8.2	3.5	0.22	0.96	0.37	13.8	1.62	0.31	1.7	0.99	8.62	0.28	0.06	0.02	0.18	0.21	2.48	0.15	1.31	1.96	2.12
53	40.83	110.02	3188	0.88	6.2	10.0	7.7	3.4	0.30	1.15	0.40	11.7	1.29	0.40	1.9	0.56	9.18	0.37	0.10	0.07	0.13	0.20	1.12	0.19	0.99	1.78	6.63
54	40.83	110.02	3186	3.60	16.8	13.5	7.7	3.9	0.05	1.09	0.44	23.0	0.14	0.40	2.0	3.07	10.55	0.27	0.00	0.03	0.17	0.19	1.36	0.16	1.99	2.19	29.89
Upper Carrol	40.72	110.35	3395	3.95	13.8	12.9	7.7	2.4	0.01	0.74	0.29	12.9	0.55	0.19	1.3	0.65	6.58	0.16	0.06	0.05	0.17	0.29	1.67	0.10	1.53	1.60	9.36
East Carrol	40.72	110.35	3423	3.45	5.3	12.9	8.0	1.9	0.03	1.01	0.32	8.8	0.30	0.24	1.7	1.79	8.00	0.15	0.00	0.02	0.00	0.22	0.82	0.20	1.14	1.79	2.29
No Name	40.71	110.38	3355	5.17	5.2	13.6	7.7	1.9	0.00	0.76	0.27	9.9	0.00	0.19	1.4	2.18	6.67	0.00	0.00	0.02	0.00	0.30	1.51	0.16	1.93	1.73	1.77

Lake	LAT °N	LONG °W	Elev. (m)	Secchi (m)	Depth (m)	Temp °C	pH	Alkalinity Mg L^{-1} $CaCO_3^-$	NO_3 ppm	SO_4 ppm	^{26}Mg ppm	^{27}Al ppb	^{29}Si ppm	^{39}K ppm	^{44}Ca ppm	^{55}Mn ppb	^{88}Sr ppb	^{7}Li ppb	^{52}Cr ppb	^{59}Co ppb	^{60}Ni ppb	^{65}Cu ppb	^{66}Zn ppb	^{75}As ppb	DOC ppm	DIC ppm	^{54}Fe ppb
Bluebell Pass	40.70	110.39	3342	1.95	7.7	13.1	7.5	2.5	0.02	0.77	0.28	12.0	0.00	0.36	1.5	0.98	6.71	0.11	0.08	0.01	0.11	0.23	0.78	0.14	2.17	2.85	10.88
59	40.69	110.38	3297	4.66	4.7	14.4	7.4	2.3	0.13	0.95	0.25	11.9	0.00	0.16	1.4	0.45	6.51	0.10	0.06	0.00	0.00	0.19	0.56	0.14	0.91	1.31	0.00
60	40.75	109.74	3018	1.09	6.4	15.4	8.1	5.6	0.01	1.17	0.82	101.9	0.28	0.66	3.4	1.64	15.58	0.30	0.38	0.06	0.67	1.10	22.03	0.44	15.21	3.87	78.65
61	40.71	109.72	2950	2.01	12.1	16.0	7.8	5.6	0.00	1.26	0.82	68.7	0.17	0.67	3.1	1.44	15.60	0.21	0.32	0.03	0.42	0.53	2.22	0.33	12.72	2.84	41.21
62	40.77	109.81	3239	3.10	4.9	12.7	8.0	5.2	0.00	0.85	0.57	26.7	0.82	0.35	2.1	1.61	8.87	0.44	0.16	0.03	0.38	0.91	40.72	0.12	2.53	2.62	23.79
63	40.81	110.24	3392	7.00	7.0	12.8	7.6	8.4	0.00	1.55	0.81	10.7	1.55	0.16	2.0	1.12	10.24	0.33	0.11	0.02	0.14	0.35	1.15	0.10	1.66	2.86	27.09
64	40.81	110.24	3419	3.50	4.9	12.4	7.0	5.0	0.00	0.79	0.70	12.9	0.29	0.26	1.4	1.54	7.36	0.25	0.00	0.03	0.21	0.48	2.09	0.20	2.56	2.42	109.9
65	40.82	110.25	3456	3.56	3.6	12.9	6.8	2.2	0.00	0.61	0.24	16.6	0.00	0.25	1.0	1.48	4.87	0.00	0.08	0.01	0.00	0.36	1.27	0.20	1.87	2.06	17.43
Min	**40.43**	**109.54**	**2651.76**	**0.30**	**1.1**	**4.6**	**6.8**	**1.0**	**0.00**	**0.00**	**0.13**	**0.0**	**0.00**	**0.09**	**0.5**	**0.37**	**4.05**	**0.00**	**0.00**	**0.00**	**0.00**	**0.17**	**0.41**	**0.07**	**0.34**	**1.01**	**0.00**
Max	**41.00**	**110.98**	**3559.76**	**7.22**	**22.3**	**21.0**	**9.5**	**167.0**	**0.50**	**7.35**	**12.32**	**117.8**	**5.45**	**8.08**	**33.4**	**24.02**	**114.30**	**4.28**	**1.62**	**0.19**	**1.11**	**2.16**	**296.9**	**1.93**	**30.33**	**29.11**	**425.50**
Median	**40.74**	**110.38**	**3145.54**	**2.76**	**5.2**	**15.3**	**7.5**	**3.5**	**0.00**	**0.95**	**0.44**	**13.7**	**0.36**	**0.30**	**1.7**	**1.54**	**9.04**	**0.16**	**0.17**	**0.03**	**0.29**	**0.48**	**1.87**	**0.31**	**4.82**	**1.31**	**29.19**
Mean	**40.76**	**110.39**	**3132.94**	**3.06**	**6.4**	**15.1**	**7.7**	**15.6**	**0.03**	**1.29**	**1.33**	**31.0**	**0.69**	**0.71**	**4.1**	**2.78**	**17.01**	**0.41**	**0.27**	**0.04**	**0.31**	**0.59**	**10.62**	**0.35**	**6.39**	**4.85**	**45.48**
StDev	**0.11**	**0.38**	**243.67**	**1.59**	**4.6**	**3.0**	**0.7**	**31.4**	**0.08**	**1.18**	**2.40**	**30.5**	**1.04**	**1.25**	**6.4**	**3.69**	**21.09**	**0.80**	**0.27**	**0.04**	**0.25**	**0.40**	**38.78**	**0.29**	**5.92**	**7.80**	**66.28**

Appendix G. Species codes and authorities

Species code	**Species name**	**Authority**
Ac.bio	*Achnanthes bioretii*	Germain 1957
Ac.car	*Achnanthes carissima*	Lange-Bertalot 1990
Ac.chl	*Achnanthes chlidanos*	Hohn & Hellerman 1963
Ac.cur	*Achnanthes curtissima*	J.R. Carter 1963
Ac.did	*Achnanthes didyma*	Hustedt 1933
Ac.hel	*Achnanthes helvetica*	(Hustedt) Lange-Bertalot in LB & K 1989
Ac.hol	*Achnanthes holsatica*	Hustedt 1936
Ac.kue	*Achnanthes kuelbsii*	Lange-Bertalot 1989
Ac.lan+	*Achnanthes lanceolata* ssp. *lanceolata* var. *lanceolata*[1] + *A. lanceolata* spp. *frequentissima*[2].	1. (Brébisson) Grunow, 2.
Ac.mar	*Achnanthes marginulata*	Grunow in Cleve & Grunow 1880
Ac.min+	*Achnanthes minutissima*[1] + *Achnanthes minutissima* var. *minutissima*[2]	Kützing 1833
Ac.pet	*Achnanthes petersenii*	Hustedt 1937
Ac.pus	*Achnanthes pusilla*	Grunow in Cleve & Grunow 1880
Ac.sto+Na.sch	*Achnanthes stolida*[1] + *Navicula schassmannii*[2]	1. (Krasske) Krasske 1949, 2. Hust. 1937
Ac.sub	*Achnanthes subatomoides*	(Hust.) Lange-Bertalot & Archibald in Krammer & Lange-Bertalot 1985
Am.kri	*Amphipleura kriegerana*	(Krasske) Hustedt 1954
Am.ova	*Amphora ovalis*	(Kützing) Kützing 1844
Au.alp	*Aulacoseira alpigena*	
Au.gra	*Aulacoseira granulata*	(Ehrenberg) Simonson 1979
Au.lir+	*Aulacoseira lirata* + *Aulacoseira distans*	(Ehrenberg) R. Ross in Hartley 1986
Au.per	*Aulacoseira perglaba*	
As.for	*Asterionella formosa*	Hassall 1850

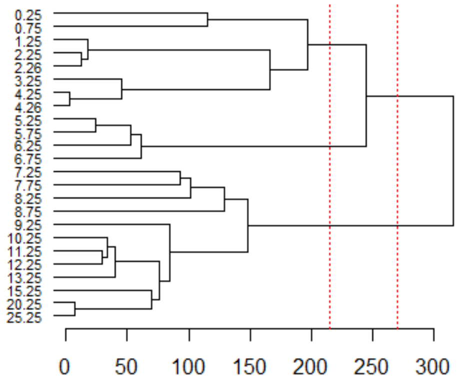
Species code	**Species name**	**Authority**
B.int	*Brachysira intermedia*	(Østrup) Lange-Bertalot 1994
B.neo	*Brachysira neoexilis*	Lange-Bertalot 1994
Cyc.ste.pse.ato	*Cyclotella stelligera*^{1} + *Cyclotella pseudostelligera*^{2} + *Cyclotella atomus*^{3}	1. Cleve & Grunow 1880, 2. Hustedt 1950, 3. Hustedt 1937
Cym.des	*Cymbella descripta*	(Hustedt) Krammer & Lange-Bertalot 1985
Cym.gae	*Cymbella gaeumannii*	Meister 1934
Cym.gra	*Cymbella gracilis*	(Rabenhorst) Cleve 1894
Cym.inc	*Cymbella incerta*	Grunow in Cleve & Moller 1878
Cym.mic	*Cymbella microcephela*	Grunow (in Van Heurck) 1880
Cym.min	*Cymbella minuta*	Hilse ex. Rabenhorst 1862
Cym.sil	*Cymbella silesiaca*	Bleisch ex Rabenhorst 1864
D.anc	*Diatoma anceps*	(Ehrenberg) Kirchner 1878
E.bil	*Eunotia bilunaris*	(Ehrenberg) F.W. Mills 1934
E.min+	*Eunotia incisa*^{1} + *Eunotia minor*^{2}	Gregory 1854, 2. (Kützing) Grunow in Van Heurck 1881.
E.mus	*Eunotia muscicola* var *tridentula*	Nörpel & Lange-Bertalot 1993
E.pra	*Eunotia praerupta*	Ehrenberg 1843
F.pin.con.bre	*Fragilaria brevistriata*^{1} + *F. construens* var *construens*^{2} + *F construents var venter*^{3} + *F. pinnata*^{4}	1. Grunow in Van Heurck 1885, 2., 3. (Ehrenberg) Grunow in Van Heurck 1881, 4. Ehrenberg 1843
Fra.capcap	*Fragilaria capucina* var *capucina*	(Kützing) Lange-Bertalot 1991
Fra.capgra	*Fragilaria capucina* var *gracilis*	(Østrup) Hustedt 1950
Fra.del	*Fragilaria delicatissima*	(W. Smith) Lange-Bertalot 1991
Fra.ten	*Fragilaria tenera*	Lange-Bertalot 1980
Fra.vir	*Fragilaria virescens*	Ralfs 1843
Fru.rho+	*Frustulia rhomboides*^{1} + *Frustulia rhomboides* var *crassinervia*^{2}	1. (Ehrenberg) De Toni 1891, 2. (Brébisson ex W. Smith) Ross
G.acu	*Gomphonema acuminatum*	Ehrenberg 1832

Species code	**Species name**	**Authority**
G.ang	*Gomphonema angustatum*	(Kützing) Rabenhorst 1864
G.par	*Gomphonema parvulum*	(Kützing) Kützing 1849
G.tru	*Gomphonema truncatum*	Ehrenberg 1832
G.unid	*Gomphonema unidentified*	
Na.bry	*Navicula bryophila*	J. B. Petersen 1928
Na.coc	*Navicula cocconeiformis*	Gregory Ex Greville 1855
Na.crycep	*Navicula cryptocephela*	Kützing 1844
Na.cryten	*Navicula cryptotenella*	Lange-Bertalot 1985
Na.exp	*Navicula expecta*	S.L. VanLandingham 1975
Na.lae	*Navicula laevissima*	Kützing 1844
Na.lep	*Navicula leptostriata*	Jørgensen 1948
Na.lae	*Navicula laevissima*	Kützing 1844
Na.lep	*Navicula leptostriata*	Jorgensen 1948
Na.pse+	*Navicula pseudoscutiformis*[1] + *Navicula scutiformis*[2]	1. Hustedt 1930, 2. Grunow ex A. Schmidt et al. 1881
Na.pseve	*Navicula pseudoventralis*	Hustedt 1953
Na.pup	*Navicula pupula*	Kützing1844
Na.rad	*Navicula radiosa*	Kützing 1844
Na.sem	*Navicula seminulum*	Grunow 1860
Ne.amp	*Neidium ampliatum*	(Ehrenberg) Krammer 1985
Ne.dub	*Neidium dubium*	(Ehrenberg) Cleve 1894
Ni.bry	*Nitzschia bryophila*	(Hustedt) Hustedt 1943
Ni.fon	*Nitzschia fonticola*	Grunow in Van Heurck 1881
Ni.fle	*Nitzschia flexoides*	Geitler 1968
Ni.gra	*Nitzschia gracilis*	Hantzsch 1860
Ni.pal	*Nitzschia palea*	(Kützing) W. Smith 1856

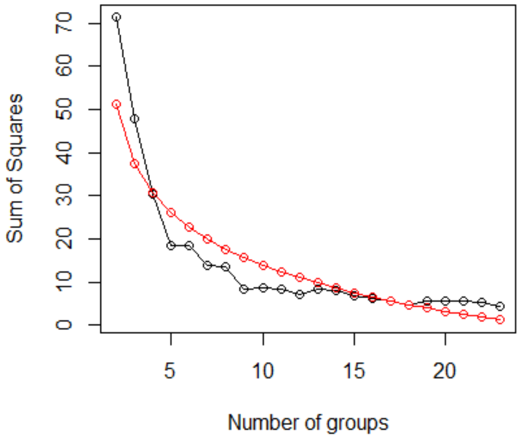
Species code	**Species Name**	**Authority**
Ni.per	*Nitzschia perminuta*	(Grunow in Van Heurck) Peragallo 1903
Ni.unid	*Nitzschia unid*	
P.mes	*Pinnularia mesolepta*	(Ehrenberg) W. Sm. 1853
P.mic	*Pinnularia microstauron*	(Ehrenberg) Cleve 1891
P.sub	*Pinnularia subgibba*	Krammer 1992
S.anc	*Stauroneis anceps*	Ehrenberg 1843
S.neo	*Stauroneis neohyalina*	Lange-Bertalot and Krammer 1996
Ta.flo	*Tabellaria flocculosa*	(Roth) Kützing 1844

Appendix H. CONISS dendrograms and broken stick models.

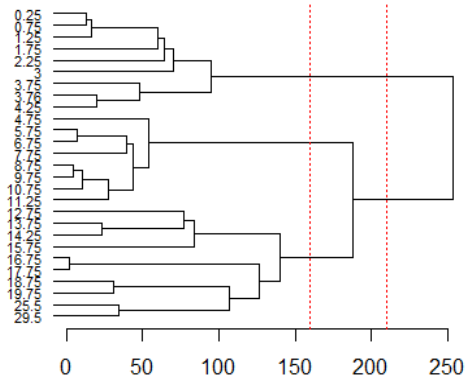
CONISS Dendrogram, Bluebell Pass Lake



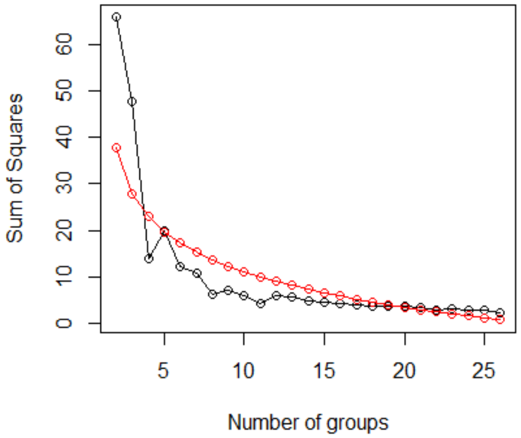
CONISS Broken Stick, Bluebell Pass Lake



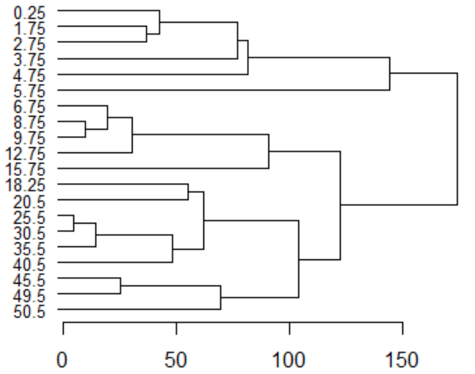
CONISS Dendrogram, Taylor Lake



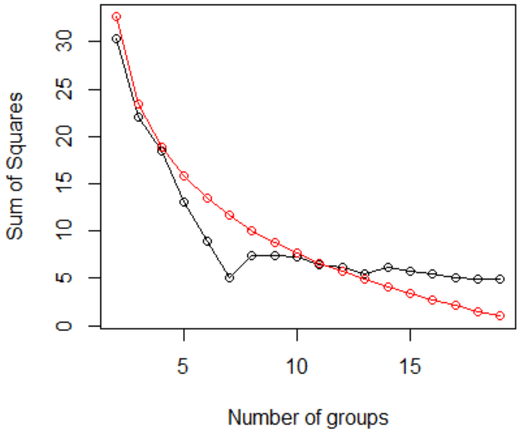
CONISS Broken Stick Plot, Taylor Lake



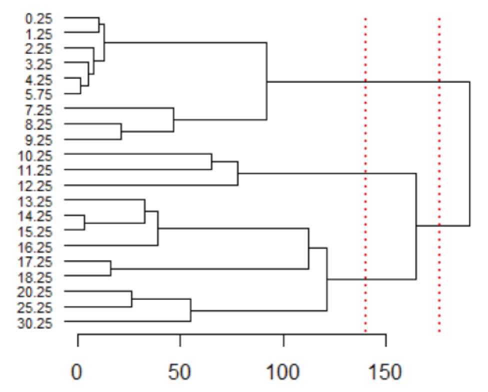
CONISS Dendrogram, Denise Lake



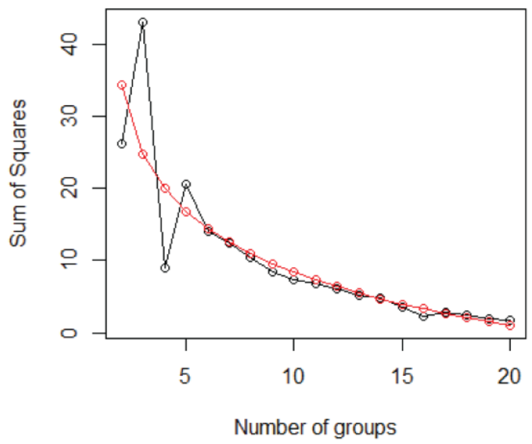
CONISS Broken Stick Plot, Denise Lake



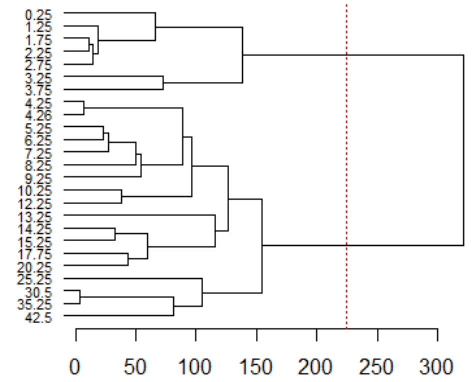
CONISS Dendrogram, East Carrol Lake



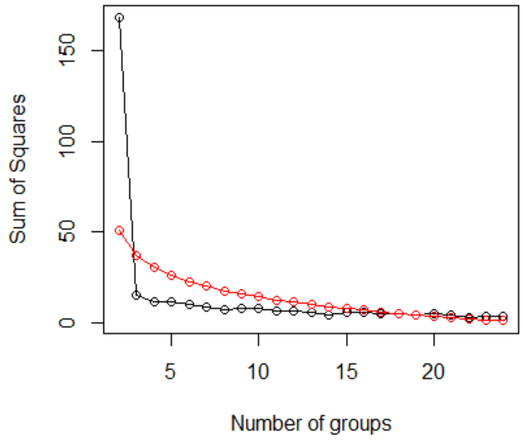
CONISS Broken Stick, East Carrol Lake



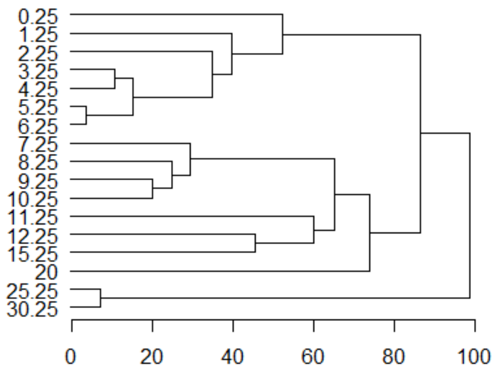
CONISS Dendrogram, No Name Lake



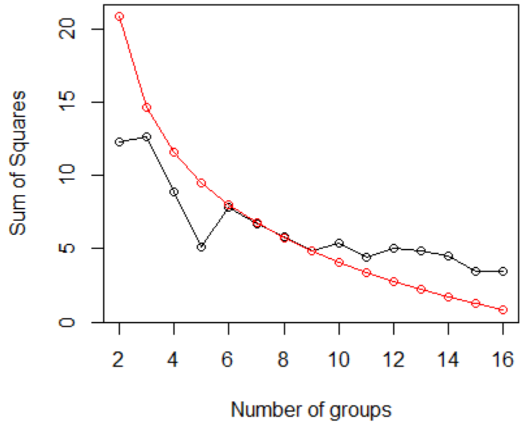
CONISS Broken Stick Plot, No Name Lake



CONISS Dendrogram, Upper Carrol Lake



CONISS Broken Stick, Upper Carrol Lake



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Hundey, E.J., and P.E. Ashmore (2009). Length scale of braided river morphology, *Water Resources Research*, 45, W08409, doi:10.1029/2008WR007521.