

Climatic and ecological change in Arctic Alaska over the last 32,000 years
inferred from lacustrine records and experiments

By

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A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in the Department of Earth, Environmental, and Planetary Sciences
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W.C. Daniels, P.M. Novis, M.B. Edlund (2016). The valid transfer of *Cyclotella bodanica* var. *intermedia* to *Lindavia* (Bacillariophyceae). *Notulae algarum* 14. ISSN 2009-8987.

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http://westerndiatoms.colorado.edu/taxa/species/cyclotella_bodanica_intermedia

B.T. De Stasio, M. B. Schrimpf, A. E. Beranek, W. C. Daniels, E. Hoyer (2010). *Dreissenid* driving tests:

going the “wrong” way in Green Bay, Lake Michigan? Verh. Intern. Verein. Limnol. 30(10): 1540-1544.

B.T. De Stasio, M. B. Schrimpf, A. E. Beranek, W. C. Daniels (2008). Increased Chlorophyll a, phytoplankton abundance, and cyanobacteria occurrence following invasion of Green Bay, Lake Michigan by *dreissenid* mussels. Aquatic invasions 3(1): 21-27.

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Abstract

Abstract of “Climatic and ecological change in Arctic Alaska over the last 32,000 years inferred from lacustrine records and experiments” by William C. Daniels, Ph.D., Brown University, May 2017

Continued development of organic geochemical proxies for paleoclimate reconstructions are proving invaluable for understanding climate dynamics and climate-ecosystem interactions. Here I investigate the utility of the leaf wax hydrogen isotope proxy (δD_{wax}) for inferring past changes in Arctic temperature and precipitation. I advance our understanding of the δD_{wax} proxy through field surveys and growth chamber experiments, quantifying the effect that vegetation D/H fractionation imparts on δD_{wax} in the tundra biome. These studies also improve constraints on the seasonality recorded by this proxy. Additionally, I present a paleotemperature reconstruction from sediments of Lake E5, one of few lakes in Alaska that contain sediments spanning the Last Glacial Maximum and Last Glacial Termination. The record, based on δD_{wax} , provides new insights on Arctic climate amplification in the region, characterizes abrupt temperature changes in Northern Alaska, and identifies the opening of the Bering Strait as a critical influence on deglacial climate. Furthermore, I demonstrate that the D/H offset between terrestrial and aquatic waxes is a useful indicator of precipitation changes in Arctic paleoclimate records. Lastly, through modern lake manipulations and analysis of the Lake E5 paleolimnology, I demonstrate that the aquatic ecosystem is extremely sensitive to both climatic and nutrient perturbations and explore the mechanisms behind this sensitivity. In summary, I demonstrate that δD_{wax} is a useful, but complex proxy in Arctic settings, and that paleoclimate reconstructions based on organic biomarkers provide an important context for understanding ecosystem-climate linkages.

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CHAPTER ONE

Introduction

William C. Daniels

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1.1 The importance of Paleoclimate in Alaska

Arctic climate is changing faster than anywhere on earth (Serreze et al., 2009). This phenomenon of “Arctic Amplification” is a robust feature in both geologic archives (Miller et al., 2010; Shakun and Carlson, 2010) and climate models (Manabe and Stouffer, 1980; Otto-Bliesner et al., 2006), and has been attributed to strong surface feedbacks from sea ice (Polyak et al., 2010 and references therein) and vegetation (Chapin et al., 2005), to changes in the strength of northward ocean heat transport (Thornalley et al., 2011), and to a smaller warming response of emitted blackbody radiation at the colder temperatures of the Arctic compared to low latitudes (Pithan and Mauritsen, 2014). These feedbacks, while most prominent in the Arctic, have important implications for the global climate system. Moreover, Arctic permafrost soils contain a vast quantity of organic carbon, 98 gigatonnes in North America alone (Ping et al., 2008), thus containing tremendous potential to amplify global warming should permafrost become destabilized by warming or disturbance in the future (ex. DeConto et al., 2012; Schuur et al., 2015). Accurately predicting future changes in Arctic and global climate depends on our mechanistic understanding of the climate and ecosystem dynamics of northern high latitudes.

Paleoclimate records are one of many essential tools for understanding climate sensitivity on equilibrium time scales in the Arctic, and are the principal focus of this thesis. Greenland ice cores have provided a foundational template of glacial-interglacial climate change in the Arctic. Greenland and the North Atlantic sector of the Arctic are regarded as the “center-of-action” for large-amplitude and abrupt climate change. Models have indicated, however, that the 10 °C warming which defines the LGM-

Holocene transition in Greenland is less substantial in other parts of the north (Otto-Bliesner et al., 2006). This finding has called into question if Greenland is representative of the pan-Arctic region (Shakun and Carlson, 2010), and has inspired research on the timing, severity, and mechanisms of deglacial climate change in other parts of the Arctic, particularly Alaska (ex. Hu et al., 2002; Briner and Kaufman, 2008). It is increasingly acknowledged that changes in the Western Arctic, such as varying tundra carbon balance and the opening of the Bering Strait, have large ramifications for global climate at glacial-interglacial timescales (Hu and Meehl, 2005; Hu et al., 2015; Crichton et al., 2016; Tesi et al., 2016) and result in geographically variable post-glacial climate evolution (Figure 1.1).

Arctic Alaska, defined here as the vast swath of land between the Brooks Range mountains and the Arctic Ocean, is an important region for testing theories on climate and ecosystem dynamics. Scientific endeavors in the region began in 1882 with the establishment of the US Naval Arctic Research Laboratory in Barrow, AK. They expanded in 1971 with the establishment of the International Biological Programme, and expanded again in 1975 with the establishment of the Toolik Lake Field Station (Hobbie and Kling, 2014). In addition to providing fundamental mechanistic-based ecological models, scientists have documented many changes associated with anthropogenic climate change in Alaska, such as increased permafrost temperatures of 1-3 °C (Hinzman et al., 2005 and references therein), increased disturbances by fire and thermokarst (Hu et al., 2010; Chipman et al., 2016), deepening soil active layers (Keller et al., 2010), altered bird migration patterns (Krause et al., 2016), and an expansion of shrubs (Sturm et al., 2001).

These changes highlight the sensitivity of this region to global climate change on relatively short time scales.

Numerous studies have shed light on the paleoclimate of Alaska as well. Paleoenvironmental reconstructions based on fossil pollen (ex. Livingstone, 1955; Eisner and Colinvaux, 1992; Abbott et al., 2010) and insects (Elias, 2000), as well as geomorphic evidence of glacier advance and floodplain alluviation (Hamilton, 2003; Briner and Kaufman, 2008; Mann et al., 2010) have revealed large changes in Alaska during the late Pleistocene and Holocene. These studies have provided important context for better understanding the peopling of the Americas (Goebel et al., 2008 and references therein) and the extinction of charismatic ice age megafauna (Mann et al., 2013; Mann et al., 2015), as well as guided our understanding of Alaska climate under vastly different set of boundary conditions. They do not, however, provide adequate quantitative reconstructions of climate necessary for understanding climate sensitivity of the region, and paleoclimate records show substantial disagreement in timing and magnitude of deglacial and Holocene climatic change (Figure 1.1). Thanks to recent advances in lacustrine paleoclimate proxies, particularly organic biomarkers, we are able to revisit this problem with new tools. In this thesis, I address the considerable uncertainty regarding the past climate of Arctic Alaska.

1.2 Water isotope perspectives on Arctic paleoclimate

Although paleoenvironmental reconstructions based on floral and faunal indicators have provided important insights into the history of Arctic Alaska, these methods largely fail to provide quantitative information on the past climate, due in part to the “no-modern-analog” problem and in part because the climate indicators are sensitive

to multiple environmental parameters (ex. Bartlein et al., 2011). Water isotopes have proven an invaluable alternative for reconstructing past temperature, hydrology, and atmospheric dynamics across the globe and at a range of timescales (ex. Pagani et al., 2006; Konecky et al., 2016; Puntisag et al., 2016). Water isotopes (D/H and $^{18}\text{O}/^{16}\text{O}$) not only provide a more direct view of past climatic/atmospheric conditions than traditional proxy systems, but they are cosmopolitan, being commonly recorded in ice sheets, cave deposits, tree rings, faunal fossils, marine or lacustrine carbonates, etc. Depending on the proxy, the water isotopes reflect ocean water, lake water, or precipitation isotopic signatures. In most settings, $\delta\text{D}_{\text{precipitation}}$ contains information on the atmospheric conditions (temperature and precipitation amount) at the time of rainfall (Dansgaard, 1964; Rozanski et al., 1993). At high latitudes, there is a strong correlation between air temperature and $\delta\text{D}_{\text{precipitation}}$, suggesting that $\delta\text{D}_{\text{precipitation}}$ could potentially be used as a paleothermometer (Dansgaard, 1964; Klein et al., 2016).

In Arctic Alaska where these water proxy systems are largely absent, organic “biomarkers”, including leaf waxes, are a viable recorder of D/H ratios (Sachse et al., 2012), and are therefore a central focus of this thesis. Leaf waxes (*n*-alkanes, *n*-acids, *n*-alcohols) are produced by terrestrial plants in a protective cuticle on leaf surfaces (Eglinton and Hamilton, 1967). These waxes are commonly deposited in sedimentary environments through wind and water ablation or whole-leaf transport, where they can be geologically stable for millions of years (Yang and Huang, 2003). As the hydrogen atoms used in the biosynthesis of leaf waxes are ultimately derived from rainfall, the leaf wax D/H ratios (hereafter $\delta\text{D}_{\text{wax}}$) reflect the $\delta\text{D}_{\text{precipitation}}$. Major and rapid advances in

compound specific isotope analytics have promoted vast exploration of this proxy system in paleoclimatology.

Indeed, a number of studies have demonstrated a remarkable correlation between δD_{wax} and $\delta D_{\text{precipitation}}$ (Sachse et al., 2006; Hou et al., 2008). In the Arctic, however, there remain certain challenges in the interpretation of δD_{wax} . First, vegetation imparts a significant fractionation (ϵ_{app}) between $\delta D_{\text{precipitation}}$ and δD_{wax} (Gao et al., 2014a). If vegetation assemblages change, then so too will the ϵ_{app} . Methods have been developed to account for this in tropical settings, but to a much lesser extent in the Arctic, and current reports have generated some confusion about the controls on ϵ_{app} at high latitudes (Yang et al., 2011; Shanahan et al., 2013). Secondly, pinpointing the seasonality of the proxy is extremely important in the high latitudes, where seasonal changes in temperature and rainfall are extreme (Porter et al., 2016). With continued advances in δD_{wax} calibrations, the proxy holds remarkable potential as a central tool in the future Arctic paleoclimatology.

To date, δD_{wax} has been used to examine some Holocene sections from the Arctic, but its utility on glacial-interglacial timescales remains largely unexplored. As such, efforts to apply δD_{wax} to long sediment archives should be coupled with lithologic and ecologic evidence for environmental reconstructions.

1.3 Thesis objective and overview

The overarching objective of this thesis is to improve our understanding of Arctic climate and ecosystem dynamics. The work falls into three general categories: 1) Calibration of organic geochemical proxies, specifically δD_{wax} , for reconstructing past

climate in Arctic environments; 2) Elucidation of the mechanisms and sensitivity of climate change in the Western Arctic through the generation of paleoclimate records based on δD_{wax} , sediment lithology, and sediment geochemistry; and, 3) Assessment of the Arctic lake ecosystem sensitivity to climate change through a combination of paleoecological and modern limnological methods. With the exception of results from one laboratory-based experiment, all the work presented was conducted at the Toolik Lake Research Natural Area (TLRNA) on the North Slope of Alaska (68.6 °N, 149.6 °W, Figure 1.1).

As described above, the δD_{wax} proxy is an invaluable tool for studying tropical paleohydrology (Tierney et al., 2015; Konecky et al., 2016) and Arctic paleotemperature and paleohydrology (Pagani et al., 2006; Thomas et al., 2012; Pautler et al., 2014). Translation of δD_{wax} measurements to $\delta D_{\text{precipitation}}$, however, is complicated by uncertainty in ϵ_{app} in the Arctic. Some reports from the Arctic as well as greenhouse experiments suggest that ϵ_{app} in the Arctic is anomalously small compared to mid- and low-latitude sites, as a result of 24-hour photosynthesis (Yang et al., 2009; Shanahan et al., 2013). These findings conflict with other research that does not support a latitude effect (Wilkie et al., 2012). I address this discrepancy in Chapters 1 and 2.

In Chapter 1, I investigate values of ϵ_{app} in Arctic Alaska based on field surveys of D/H ratios in soil water, plant waters, plants leaf waxes, and sedimentary leaf waxes. This study is the first work from the Arctic region that analyzes xylem waters of plants during the growing season, a critical step in constraining the $\delta D_{\text{source water}}$ for plants. The work investigates source water seasonality and biosynthetic fractionation factors for two of the most common tundra plants, *Betula nana* and *Eriophorum vaginatum*. Using a 24-

lake transect, I also correlate ϵ_{app} at the watershed scale with the plants within the watershed, demonstrating the local nature of wax transport while providing a means of correcting paleoclimate records for potential vegetation effects.

Chapter 2 investigates ϵ_{app} for tundra plants in more detail through a growth chamber experiment in which I test if continuous light imparts an effect on values of δD_{wax} . Results from this study, in conjunction with the results from Chapter 1, highlight the large differences in ϵ_{app} between plant types and refute the idea that 24-hour light cycle is a significant control on δD_{wax} .

In Chapters 3-5, I present results on Lake E5 in the TLRNA, addressing paleotemperature, paleohydrology, and paleoecology, respectively. In Chapter 3, I present a 32,000 year record of δD_{wax} from Lake E5. This record represents one of the longest continuous paleoclimate records from the Western Arctic, and one of few biomarker reconstructions from the region. I demonstrate that the observed δD_{wax} changes are most parsimoniously interpreted as a record of temperature change. While temperature change from the LGM to today mostly conforms to the pattern expected from changing insolation, I observe several periods of rapid climate warming, which are for the most part synchronous with abrupt events observed in the North Atlantic, but largely unobserved in Beringia (Figure 1.1). The amplitude of these events, however, is variably muted or accentuated in comparison to their N. Atlantic counterparts, thus illustrating that the Arctic Amplification observed across many parts of the Arctic is an inconsistent feature of Alaskan climate as a result of the complexity of ocean-atmosphere-land feedbacks in the region.

Little is known about the precipitation history of Alaska, other than that the North Slope was extremely arid during the LGM. In Chapter 4, I investigate the history of moisture balance in Northern Alaska by comparing D/H ratios of aquatic and terrestrial biomarkers in the Lake E5 stratigraphy. Results are in general agreement with the existing paradigm, but improve constraints on the timing of deglacial wettening and Holocene precipitation changes. The hydrogen-isotope inferred paleohydrology record is supported by numerous lines of lithologic and geochemical data, lending support to the applicability of the D/H method for reconstructing moisture changes.

Chapter 5 expands on the paleoecological history of Lake E5. The goals of Chapter 5 are two-fold: 1) To determine if organic carbon burial rate varies positively, negatively, or is unaffected by temperature. There is a paradox in recent literature in which theoretical predictions and field assessments for the relationship between temperature and organic carbon (OC) burial often disagree (Anderson et al., 2009; Yvon-Durocher et al., 2010; Heathcote et al., 2015; Rantala et al., 2016), thus hindering our ability to predict future changes in lacustrine carbon balance. The second goal here, related to the question of carbon burial, is if we can elucidate whether light or nutrients have been the primary limiting resource for whole-lake production in Lake E5. This theme is timely, as a growing body of literature is suggesting that boreal and arctic lakes are limited by Dissolved OC-interception of light (Karlsson et al., 2009; Karlsson et al., 2015), rather than nitrogen and phosphorus as traditionally viewed (Levine and Whalen, 2001). Overall, the carbon burial rate of the lake is negatively correlated with temperature, supporting the theoretical models of OC burial. However, over the

Holocene, I observe a trade-off between terrestrial and aquatic carbon burial in boreal and Arctic lakes that resulted in stable rates of OC burial despite long-term cooling.

Lastly, in Chapter 6, I focus on the modern limnology of lakes in the TLRNA. I investigate the importance of benthic substrates to whole-lake carbon balance, and analyze the response of benthic metabolism to a long-term nutrient manipulation experiment. The manipulations consisted of nitrogen and phosphorus addition over a span of fifteen years. Fertilization was carried out on Lake E5 and nearby lake E6, and two unmanipulated lakes served as references. These experiments are meant to mimic nutrient loading increases anticipated to result from both climate warming as well as atmospheric deposition and are the longest-duration, lowest-fertilization-rate experiments performed on entire lake systems in the Arctic. I demonstrate that benthic microalgae contributed upwards of 50% of the in-lake productivity prior to the fertilization, but a substantially smaller fraction by the end of the manipulation. The research also demonstrates that the oxygen levels in the Lake E5 hypolimnion are extremely sensitive to nutrient loading, as anoxia was observed after year 6 of the experiment. Results from this study are useful in interpreting the ecological changes described in Chapter 5.

In summary, this thesis calibrates and applies the leaf wax hydrogen isotope proxy in Arctic Alaska, and uses the resulting paleoclimate reconstructions to provide insight into understanding Arctic climate dynamics and ecological sensitivity to temperature or hydrologic variations.

1.4 Future work

There are numerous lines of inquiry that remain to be explored in the field of Arctic paleoclimatology. Here, I provide suggestions for future work and briefly outline

datasets that I have collected during my graduate school tenure but are not included in the dissertation.

The first suggestion for future work deals with further calibration of the leaf wax hydrogen isotope proxy for past precipitation. Application of vegetation correction factors to infer past $\delta D_{\text{precipitation}}$ relies on either pollen- or $^{13}\text{C}/^{12}\text{C}$ -inferred vegetation distributions. Unlike in the tropics, where the $^{13}\text{C}/^{12}\text{C}$ of leaf waxes are a useful indicator of the relative abundance of grass and trees and can therefore guide estimates of D/H fractionation (ϵ_{app}) (Konecky et al., 2016; Niedermeyer et al., 2016), nearly all plants in the Arctic use a C3 photosynthetic pathway. As such, the $^{13}\text{C}/^{12}\text{C}$ ratio is inadequate as an indicator of ϵ_{app} . I proposed a basis for determining ϵ_{app} in Chapter 1 that relies on fossil pollen assemblages, but this method could be improved further by comparing pollen spectra directly with estimates ϵ_{app} across a lake surface sediment transect. The results in Chapter 1 could thus be expanded and refined through pollen analysis.

In 2014, our Brown University research group cored seven lakes in the TLRNA. These lakes contain sediments from the Holocene, with basal dates averaging 11 ka. The lakes reside on different glacial substrates and likely underwent vastly different post-glacial ontogenetic shifts during the Holocene. As such, an inter-lake comparison will be useful to 1) validate biomarker proxy calibrations across watersheds and 2) assess how watershed traits interact with climate to impact aquatic ecosystems, as they do for terrestrial ecosystems (Oswald et al., 2003). To this end, I measured δD_{wax} on four lakes, and in collaboration with Dr. Sarah Ivory generated low-resolution pollen stratigraphy from each core. A biomarker synthesis of these four lakes should provide a robust assessment of Holocene climate dynamics. Furthermore, I measured sediment

geochemical and biotic (diatom) data from these lakes, which will inform the substrate-dependence of lake ecosystem changes. A complete assessment of carbon burial rates in these four lakes will expand the results presented in Chapter 5. C burial varies more across lakes (Hobbs et al., 2013) than through time within a given lake (Anderson et al., 2009, Chapter 5). Improved constraints C burial across a range of system types will guide scalable estimates of lacustrine OC burial in Alaska.

Secondly, the Lake E5 chronology is one of the most robust AMS ^{14}C -dated cores from northern Alaska. As such, the paleomagnetic data we gathered from Lake E5 may serve as a useful chronology reference point for other sediment records of comparable duration. Additional geochemical data on the Lake E5 sediments are available and likely contains clues on the sediment provenance. Such an analysis could prove of interest in better constraining glacial loess source and how loess deposition may have impacted terrestrial and aquatic ecosystems. Lastly, Lake E5 contains abundant zoologic indicators (data on *Daphnia ephippia* are available) which may prove interesting in future ecological research.

In general, data presented in this thesis provide solid evidence for abrupt climate changes in Alaska during the last deglaciation. As such changes were not observed previously, there remains a need to replicate this finding with biomarker proxies ($\delta\text{D}_{\text{wax}}$) at other locations. Other suitable archives from the region include: Ahaliorak Lake (Eisner and Colinvaux, 1990), Burial Lake (Finkenbinder et al., 2015), and the late Pleistocene loess sequences in central Alaska (Begét et al., 1990). Eventually, I would like to see a network of glacial-interglacial $\delta\text{D}_{\text{wax}}$ records develop in Alaska, as it has in

Africa, such that spatio-temporal dynamics in atmospheric circulation can be assessed in greater detail.

1.5 References

Abbott, M.B., Edwards, M.E. and Finney, B.P. (2010) A 40,000-yr record of environmental change from Burial Lake in Northwest Alaska. *Quatern. Res.* 74, 156-165.

Andersen, K.K., Azuma, N., Barnola, J.-M., Bigler, M., Biscaye, P., Caillon, N., Chappellaz, J., Clausen, H.B., Dahl-Jensen, D. and Fischer, H. (2004) High-resolution record of Northern Hemisphere climate extending into the last interglacial period. *Nature* 431, 147-151.

Anderson, N., D'andrea, W. and Fritz, S.C. (2009) Holocene carbon burial by lakes in SW Greenland. *Global Change Biol.* 15, 2590-2598.

Bartlein, P., Harrison, S., Brewer, S., Connor, S., Davis, B., Gajewski, K., Guiot, J., Harrison-Prentice, T., Henderson, A. and Peyron, O. (2011) Pollen-based continental climate reconstructions at 6 and 21 ka: a global synthesis. *Climate dynamics* 37, 775-802.

Begét, J.E., Stone, D.B. and Hawkins, D.B. (1990) Paleoclimatic forcing of magnetic susceptibility variations in Alaskan loess during the late Quaternary. *Geology* 18, 40-43.

Briner, J.P. and Kaufman, D.S. (2008) Late Pleistocene mountain glaciation in Alaska: key chronologies. *Journal of Quaternary Science* 23, 659-670.

Chapin, F., Sturm, M., Serreze, M., McFadden, J., Key, J., Lloyd, A., McGuire, A., Rupp, T., Lynch, A. and Schimel, J. (2005) Role of land-surface changes in Arctic summer warming. *Science* 310, 657-660.

Chipman, M.L., Kling, G.W., Lundstrom, C.C. and Hu, F.S. (2016) Multiple thermo-erosional episodes during the past six millennia: Implications for the response of Arctic permafrost to climate change. *Geology*, G37693. 37691.

Crichton, K.A., Bouttes, N., Roche, D.M., Chappellaz, J. and Krinner, G. (2016) Permafrost carbon as a missing link to explain CO₂ changes during the last deglaciation. *Nature Geosci* 9, 683-686.

- Dansgaard, W. (1964) Stable isotopes in precipitation. *Tellus* 16, 436-468.
- DeConto, R.M., Galeotti, S., Pagani, M., Tracy, D., Schaefer, K., Zhang, T., Pollard, D. and Beerling, D.J. (2012) Past extreme warming events linked to massive carbon release from thawing permafrost. *Nature* 484, 87-91.
- Eglinton, G. and Hamilton, R.J. (1967) Leaf epicuticular waxes. *Science* 156, 1322-1335.
- Eisner, W.R. and Colinvaux, P.A. (1990) A long pollen record from Ahaliorak Lake, Arctic Alaska. *Rev. Palaeobot. Palynol.* 63, 35-52.
- Eisner, W.R. and Colinvaux, P.A. (1992) Late Quaternary Pollen Records from Oil Lake and Feniak Lake, Alaska, U.S.A. *Arct. Alp. Res.* 24, 56-63.
- Elias, S.A. (2000) Late Pleistocene climates of Beringia, based on analysis of fossil beetles. *Quatern. Res.* 53, 229-235.
- Finkenbinder, M., Abbott, M., Finney, B., Stoner, J. and Dorfman, J. (2015) A multi-proxy reconstruction of environmental change spanning the last 37,000 years from Burial Lake, Arctic Alaska. *Quaternary Science Reviews* 126, 227-241.
- Gao, L., Edwards, E.J., Zeng, Y. and Huang, Y. (2014a) Major Evolutionary Trends in Hydrogen Isotope Fractionation of Vascular Plant Leaf Waxes. *PLoS ONE* 9, e112610.
- Goebel, T., Waters, M.R. and O'rourke, D.H. (2008) The late Pleistocene dispersal of modern humans in the Americas. *science* 319, 1497-1502.
- Heathcote A. J., Anderson N. J., Prairie Y. T., Engstrom D. R., and del Giorgio P. A. (2015) Large increases in carbon burial in northern lakes during the Anthropocene. *Nature Communications* 6, 10016.
- Hamilton, T.D. (2003) Surficial geology of the Dalton Highway (Itkillik-Sagavanirktok rivers) area, southern Arctic foothills, Alaska.
- Hinzman, L., Bettez, N., Bolton, W., Chapin, F., Dyurgerov, M., Fastie, C., Griffith, B., Hollister, R., Hope, A., Huntington, H., Jensen, A., Jia, G., Jorgenson, T., Kane, D., Klein, D., Kofinas, G., Lynch, A., Lloyd, A., McGuire, A., Nelson, F., Oechel, W., Osterkamp, T., Racine, C., Romanovsky, V., Stone, R., Stow, D., Sturm, M., Tweedie,

C., Vourlitis, G., Walker, M., Walker, D., Webber, P., Welker, J., Winker, K. and Yoshikawa, K. (2005) Evidence and Implications of Recent Climate Change in Northern Alaska and Other Arctic Regions. *Clim. Change* 72, 251-298.

Hobbie, J.E. and Kling, G.W. (2014) *Alaska's Changing Arctic: Ecological Consequences for Tundra, Streams, and Lakes*. Oxford University Press.

Hobbs, W.O., Engstrom, D.R., Scottler, S.P., Zimmer, K.D. and Cotner, J.B. (2013) Estimating modern carbon burial rates in lakes using a single sediment sample. *Limnol. Oceanogr.: Methods* 11, 316-326.

Hou, J., D'Andrea, W.J. and Huang, Y. (2008) Can sedimentary leaf waxes record D/H ratios of continental precipitation? Field, model, and experimental assessments. *Geochim. Cosmochim. Acta* 72, 3503-3517.

Hu, A. and Meehl, G.A. (2005) Bering Strait throughflow and the thermohaline circulation. *Geophys. Res. Lett.* 32.

Hu, A., Meehl, G.A., Han, W., Otto-Blietner, B., Abe-Ouchi, A. and Rosenbloom, N. (2015) Effects of the Bering Strait closure on AMOC and global climate under different background climates. *Prog. Oceanogr.* 132, 174-196.

Hu, F., Lee, B., Kaufman, D., Yoneji, S., Nelson, D. and Henne, P. (2002) Response of tundra ecosystem in southwestern Alaska to Younger-Dryas climatic oscillation. *Global Change Biol.* 8, 1156-1163.

Hu, F.S., Higuera, P.E., Walsh, J.E., Chapman, W.L., Duffy, P.A., Brubaker, L.B. and Chipman, M.L. (2010) Tundra burning in Alaska: Linkages to climatic change and sea ice retreat. *Journal of Geophysical Research* 115.

Irvine, F., Cwynier, L.C., Vermaire, J.C., and Rees, A.B. (2012) Midge-inferred temperature reconstructions and vegetation change over the last ~15,000 years from Trout Lake, northern Yukon Territory, eastern Beringia. *J. of Paleolimnology* 28 (1), 133-146.

Karlsson, J., Bergström, A.-K., Byström, P., Gudas, C., Rodríguez, P. and Hein, C.L. (2015) Terrestrial organic matter input suppresses biomass production in lake ecosystems. *Ecology*.

- Karlsson, J., Byström, P., Ask, J., Ask, P., Persson, L. and Jansson, M. (2009) Light limitation of nutrient-poor lake ecosystems. *Nature* 460, 506-509.
- Keller, K., Blum, J.D. and Kling, G.W. (2010) Stream geochemistry as an indicator of increasing permafrost thaw depth in an arctic watershed. *Chem. Geol.* 273, 76-81.
- Klein, E., Nolan, M., McConnell, J., Sigl, M., Cherry, J., Young, J. and Welker, J. (2016) McCall Glacier record of Arctic climate change: Interpreting a northern Alaska ice core with regional water isotopes. *Quaternary Science Reviews* 131, 274-284.
- Konecky, B., Russell, J. and Bijaksana, S. (2016) Glacial aridity in central Indonesia coeval with intensified monsoon circulation. *Earth. Planet. Sci. Lett.* 437, 15-24.
- Krause, J.S., Pérez, J.H., Chmura, H.E., Sweet, S.K., Meddle, S.L., Hunt, K.E., Gough, L., Boelman, N. and Wingfield, J.C. (2016) The effect of extreme spring weather on body condition and stress physiology in Lapland longspurs and white-crowned sparrows breeding in the Arctic. *Gen. Comp. Endocrinol.* 237, 10-18.
- Kurek, J., Cwyner, L.C., Ager, T.A., Abbott, M.B., and Edwards, M.E. (2009) Late Quaternary paleoclimate of western Alaska inferred from fossil chironomids and its relation to vegetation histories. *Quat. Sci. Rev.* 28 (9), 799-811.
- Livingstone, D. (1955) Some pollen profiles from arctic Alaska. *Ecology*, 587-600.
- Manabe, S. and Stouffer, R.J. (1980) Sensitivity of a global climate model to an increase of CO₂ concentration in the atmosphere. *Journal of Geophysical Research: Oceans* 85, 5529-5554.
- Mann, D.H., Groves, P., Kunz, M.L., Reanier, R.E. and Gaglioti, B.V. (2013) Ice-age megafauna in Arctic Alaska: extinction, invasion, survival. *Quaternary Science Reviews* 70, 91-108.
- Mann, D.H., Groves, P., Reanier, R.E., Gaglioti, B.V., Kunz, M.L. and Shapiro, B. (2015) Life and extinction of megafauna in the ice-age Arctic. *Proceedings of the National Academy of Sciences* 112, 14301-14306.
- Mann, D.H., Groves, P., Reanier, R.E. and Kunz, M.L. (2010) Floodplains, permafrost, cottonwood trees, and peat: What happened the last time climate warmed suddenly in arctic Alaska? *Quaternary Science Reviews* 29, 3812-3830.

Melles, M., Brigham-Grette, J., Minyuk, P.S., Nowaczyk, N.R., Wennrich, V., DeConto, R.M., Anderson, P.M., Andreev, A.A., Coletti, A., Cook, T.L., Haltia-Hovi, E., Kukkonen, M., Lozhkin, A.V., Rosén, P., Tarasov, P., Vogel, H. and Wagner, B. (2012) 2.8 Million Years of Arctic Climate Change from Lake El'gygytgyn, NE Russia. *Science* 337, 315-320.

Miller, G.H., Alley, R.B., Brigham-Grette, J., Fitzpatrick, J.J., Polyak, L., Serreze, M.C. and White, J.W.C. (2010) Arctic amplification: can the past constrain the future? *Quaternary Science Reviews* 29, 1779-1790.

Niedermeyer, E.M., Forrest, M., Beckmann, B., Sessions, A.L., Mulch, A. and Schefuß, E. (2016) The stable hydrogen isotopic composition of sedimentary plant waxes as quantitative proxy for rainfall in the West African Sahel. *Geochim. Cosmochim. Acta* 184, 55-70.

Otto-Bliesner, B.L., Brady, E.C., Clauzet, G., Tomas, R., Levis, S. and Kothavala, Z. (2006) Last glacial maximum and Holocene climate in CCSM3. *J. Clim.* 19, 2526-2544.

Pagani, M., Pedentchouk, N., Huber, M., Sluijs, A., Schouten, S., Brinkhuis, H., Damsté, J.S.S. and Dickens, G.R. (2006) Arctic hydrology during global warming at the Palaeocene/Eocene thermal maximum. *Nature* 442, 671-675.

Pautler, B.G., Reichart, G.-J., Sanborn, P.T., Simpson, M.J. and Weijers, J.W. (2014) Comparison of soil derived tetraether membrane lipid distributions and plant-wax δD compositions for reconstruction of Canadian Arctic temperatures. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 404, 78-88.

Ping, C.-L., Michaelson, G.J., Jorgenson, M.T., Kimble, J.M., Epstein, H., Romanovsky, V.E. and Walker, D.A. (2008) High stocks of soil organic carbon in the North American Arctic region. *Nature Geosci* 1, 615-619.

Pithan, F. and Mauritsen, T. (2014) Arctic amplification dominated by temperature feedbacks in contemporary climate models. *Nature Geoscience*.

Polissar, P.J. and Freeman, K.H. (2010) Effects of aridity and vegetation on plant-wax δD in modern lake sediments. *Geochim. Cosmochim. Acta* 74, 5785-5797.

Polyak, L., Alley, R.B., Andrews, J.T., Brigham-Grette, J., Cronin, T.M., Darby, D.A., Dyke, A.S., Fitzpatrick, J.J., Funder, S. and Holland, M. (2010) History of sea ice in the Arctic. *Quaternary Science Reviews* 29, 1757-1778.

Porter, T.J., Froese, D.G., Feakins, S.J., Bindeman, I.N., Mahony, M.E., Pautler, B.G., Reichart, G.-J., Sanborn, P.T., Simpson, M.J. and Weijers, J.W.H. (2016) Multiple water isotope proxy reconstruction of extremely low last glacial temperatures in Eastern Beringia (Western Arctic). *Quaternary Science Reviews* 137, 113-125.

Praetorius, S.K., Mix, A.C., Walczak, M.H., Wolhowe, M.D., Addison, J.A., and Prahl, F.G. (2015) North Pacific deglacial hypoxic events linked to abrupt ocean warming. *Nature* 527 (7578), 362-366.

Puntsag, T., Mitchell, M.J., Campbell, J.L., Klein, E.S., Likens, G.E. and Welker, J.M. (2016) Arctic Vortex changes alter the sources and isotopic values of precipitation in northeastern US. *Scientific reports* 6.

Rantala, M.V., Luoto, T.P. and Nevalainen, L. (2016) Temperature controls organic carbon sequestration in a subarctic lake. *Scientific Reports* 6, 34780.

Rozanski, K., Araguás-Araguás, L. and Gonfiantini, R. (1993) Isotopic patterns in modern global precipitation. *Climate change in continental isotopic records*, 1-36.

Sachse, D., Billault, I., Bowen, G.J., Chikaraishi, Y., Dawson, T.E., Feakins, S.J., Freeman, K.H., Magill, C.R., McInerney, F.A. and Van der Meer, M.T. (2012) Molecular paleohydrology: interpreting the hydrogen-isotopic composition of lipid biomarkers from photosynthesizing organisms. *Annual Review of Earth and Planetary Sciences* 40, 221-249.

Sachse, D., Radke, J. and Gleixner, G. (2006) δD values of individual n-alkanes from terrestrial plants along a climatic gradient—Implications for the sedimentary biomarker record. *Org. Geochem.* 37, 469-483.

Schuur, E., McGuire, A., Schädel, C., Grosse, G., Harden, J., Hayes, D., Hugelius, G., Koven, C., Kuhry, P. and Lawrence, D. (2015) Climate change and the permafrost carbon feedback. *Nature* 520, 171-179.

Serreze, M., Barrett, A., Stroeve, J., Kindig, D. and Holland, M. (2009) The emergence of surface-based Arctic amplification. *The Cryosphere* 3, 11-19.

Shakun, J.D. and Carlson, A.E. (2010) A global perspective on Last Glacial Maximum to Holocene climate change. *Quaternary Science Reviews* 29, 1801-1816.

- Shanahan, T., Hughen, K., Ampel, L., Sauer, P. and Fornace, K. (2013) Environmental controls on the $^2\text{H}/^1\text{H}$ values of terrestrial leaf waxes in the Eastern Canadian Arctic. *Geochim. Cosmochim. Acta*.
- Sturm, M., Racine, C. and Tape, K. (2001) Climate change: increasing shrub abundance in the Arctic. *Nature* 411, 546-547.
- Tesi, T., Muschitiello, F., Smittenberg, R., Jakobsson, M., Vonk, J., Hill, P., Andersson, A., Kirchner, N., Noormets, R. and Dudarev, O. (2016) Massive remobilization of permafrost carbon during post-glacial warming. *Nature Communications* 7.
- Thomas, E.K., McGrane, S., Briner, J.P. and Huang, Y. (2012) Leaf wax $\delta^2\text{H}$ and varve-thickness climate proxies from proglacial lake sediments, Baffin Island, Arctic Canada. *J. Paleolimnol.*, 1-15.
- Thornalley, D.J., Barker, S., Broecker, W.S., Elderfield, H. and McCave, I.N. (2011) The deglacial evolution of North Atlantic deep convection. *science* 331, 202-205.
- Tierney, J.E., Ummenhofer, C.C. and deMenocal, P.B. (2015) Past and future rainfall in the Horn of Africa. *Science Advances* 1.
- Yang, H. and Huang, Y. (2003) Preservation of lipid hydrogen isotope ratios in Miocene lacustrine sediments and plant fossils at Clarkia, northern Idaho, USA. *Org. Geochem.* 34, 413-423.
- Yang, H., Liu, W., Leng, Q., Hren, M.T. and Pagani, M. (2011) Variation in n-alkane δD values from terrestrial plants at high latitude: Implications for paleoclimate reconstruction. *Org. Geochem.* 42, 283-288.
- Yang, H., Pagani, M., Briggs, D.E., Equiza, M., Jagels, R., Leng, Q. and LePage, B.A. (2009) Carbon and hydrogen isotope fractionation under continuous light: implications for paleoenvironmental interpretations of the High Arctic during Paleogene warming. *Oecologia* 160, 461-470.

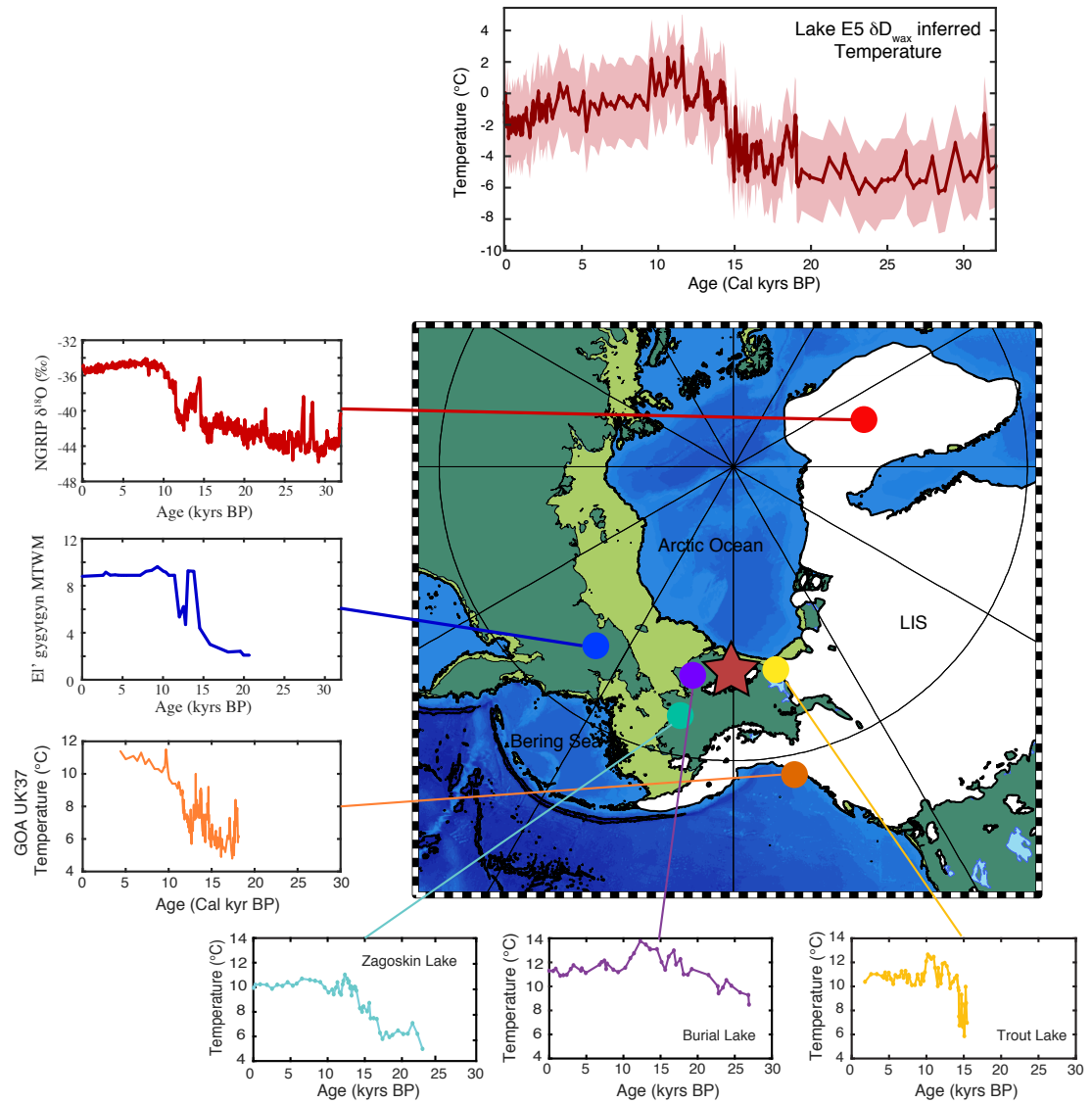


Figure 1.1. Map of the Arctic show key differences in geography at the LGM relative to today including the presence of the Laurentide Ice Sheet and changing shorelines due to sea level rise. Also shown are key paleoclimate records discussed in the text including the Lake E5 δD_{wax} -inferred temperature record presented here, the North Greenland ice core $\delta^{18}O$ (Anderson et al. 2004), Lake El'gygytgyn pollen-inferred temperature (Melles et al. 2012), Gulf of Alaska alkenone-inferred temperature (Praetorius et al. 2015), and chironomid-inferred July temperatures from Zagoskin Lake (Kurek et al. 2009), Burial Lake (Kurek et al. 2009), and Trout Lake (Irvine et al. 2012).

CHAPTER TWO

Leaf wax hydrogen isotope fractionation from synthesis to sedimentation in the Arctic tundra, North Slope, Alaska

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2.1 Abstract

Leaf wax hydrogen isotopes (δD_{wax}) are increasingly utilized in terrestrial paleoclimate research. Applications of this proxy must be grounded by studies of the modern controls on δD_{wax} , including the ecophysiological controls of isotope fractionation at both the plant and landscape scales. Several modern calibration studies suggest a considerably smaller apparent fractionation between source water and waxes (ϵ_{net}) at high latitudes relative to temperate or tropical locations, with major implications for paleoclimatic interpretations of sedimentary δD_{wax} . Here we investigate apparent fractionation in the Arctic by tracing the isotopic composition of leaf waxes from production in modern plants to deposition in lake sediments using isotopic observations of precipitation, soil and plant waters, living leaf waxes, and waxes in sediment traps in the Brooks Range foothills of northern Alaska. We also analyze a lake surface sediment transect to compare present-day vegetation assemblages to ϵ_{net} at the watershed scale. Source water and ϵ_{net} were determined for live specimens of *Eriophorum vaginatum* (cottongrass) and *Betula nana* (dwarf birch), two dominant tundra plants in the Brooks Range foothills. The δD of xylem water closely tracks that of surface soil water, and reflects a summer-biased precipitation source. Leaf water is enriched by $23 \pm 15\text{‰}$ relative to xylem water for *E. vaginatum* and by $41 \pm 19\text{‰}$ for *B. nana*. Evapotranspiration modeling indicates that this leaf water enrichment is consistent with the evaporative enrichment expected under the climate conditions of northern Alaska, and that 24-hour photosynthesis does not cause excessive leaf water isotope enrichment. The ϵ_{net} determined for our study species averages $-98 \pm 17\text{‰}$ for *B. nana* and $-162 \pm 26\text{‰}$ for

E. vaginatum, similar to the ϵ_{net} of related species in temperate and tropical regions, indicating that apparent fractionation does not differ strongly in the Arctic relative to other regions. Waxes of *E. vaginatum* are depleted by an average of 42‰ relative to waxes from *B. nana*, illustrating that the relative abundance of graminoids and shrubs is potentially an important control on $\delta\text{D}_{\text{wax}}$ in lake sediments and soils. This result is supported by $\delta\text{D}_{\text{wax}}$ data from surface sediments of 24 lakes where ϵ_{net} averages $-128 \pm 13\text{‰}$ for *n*-acids and $-130 \pm 8\text{‰}$ for *n*-alkanes, and watershed-scale ϵ_{net} co-varies with vegetation type across watersheds. These new determinations of plant source water seasonality and ϵ_{net} for the Arctic will improve the $\delta\text{D}_{\text{wax}}$ paleoclimate proxy at high latitudes.

Keywords Leaf waxes, Water isotopes, Biomarkers, Precipitation, Isotope fractionation, Arctic, Tundra, Sediment

2.2 Introduction

Hydrogen and oxygen isotope ratios in meteoric water (δD and $\delta^{18}\text{O}$) are well-established tracers of environmental processes (Dansgaard, 1964; Ehleringer and Dawson, 1992; Vachon et al., 2010; Welker, 2012). When preserved in the geologic record, these isotopes serve as robust tools for understanding paleoclimate (Feakins et al., 2012; Jasechko et al., 2015; Klein et al., 2016; Konecky et al., 2016). Hydrogen isotope signals of plant leaf waxes are an increasingly utilized proxy because they are abundant in many sediments (Huang et al., 2004; Sachse et al., 2004), are stable over long time periods (Yang and Huang, 2003), and their isotopic composition ($\delta\text{D}_{\text{wax}}$) primarily

reflects the δD of precipitation ($\delta D_{\text{precipitation}}$) (Sternberg, 1988; Sauer et al., 2001; Huang et al., 2004; Sachse et al., 2004; Sachse et al., 2010). The δD_{wax} is depleted by a fractionation factor (ϵ_{net}) relative to $\delta D_{\text{precipitation}}$ due to several isotope discriminating processes that occur between precipitation and leaf wax synthesis and deposition (Sachse et al., 2012). Accurate estimates of ϵ_{net} are fundamentally important to guide climatic interpretations of ancient δD_{wax} (Polissar and Freeman, 2010; Yang et al., 2011; Garcin et al., 2012; Feakins, 2013; Niedermeyer et al., 2016), and ideally, to quantitatively determine $\delta D_{\text{precipitation}}$ and climate variations in geological time.

Numerous analyses of δD_{wax} from lake sediments and living plants in temperate and tropical regions have begun to converge on average ϵ_{net} values of -100 to -130‰ (Sachse et al., 2004; Hou et al., 2008), with *n*-alkanes displaying slightly greater isotope discrimination than *n*-alkanoic acids (Chikaraishi and Naraoka, 2007b). Recent estimates of ϵ_{net} at high-latitude sites, however, are dramatically different. Shanahan et al. (2013) estimated ϵ_{net} of -61‰ using lake surface sediment samples from Baffin Island in the High Arctic (latitude: 63 to 73 °N) compared against mean annual precipitation isotopes compositions for source water estimated from the Online Isotopes in Precipitation Calculator (OIPC) geospatial model (Bowen and Revenaugh, 2003). Porter et al. (2016) produced similar ϵ_{net} values by comparing fossil waxes to adjacent fossil water (interpreted as mean annual precipitation formed simultaneously with the waxes) in loess sections in the Canadian sub-Arctic (latitude: 63.5 °N). Based on growth chamber experiments, these low ϵ_{net} values in high-latitude, continuous light environments have been suggested to result from plant stomata remaining open throughout the 24-hour sunlit

period, thus driving high daily rates of evapotranspiration and high leaf water isotope enrichment (Yang et al., 2009).

In contrast, in a study of lake sediment waxes in northern Siberia (latitude: 67°N), Wilkie et al. (2012) report ϵ_{net} of -101‰ with respect to estimates of mean annual precipitation isotope composition, and ϵ_{net} of -110‰ with respect to the isotopic composition of spring streamflow. Sachse et al. (2004) report ϵ_{net} of -100 to -135‰ for long chain *n*-alkanes from Arctic Europe using similar methods. These contrasting results raise the following questions: 1) is ϵ_{net} latitude-dependent? 2) is ϵ_{net} highly variable across high latitude biomes? and 3) are observations of small ϵ_{net} an artifact of relying on estimated, rather than measured, source water isotope compositions?

The apparent fractionation of Arctic δD_{wax} is of extreme importance to understanding past and current polar climate change. δD_{wax} records in polar regions have been interpreted as both summer and mean annual temperature change on time-scales from the Holocene to the Paleocene (Pagani et al., 2006; Feakins et al., 2012; Thomas et al., 2012; Pautler et al., 2014; Porter et al., 2016), with implications for the Earth's equilibrium climate sensitivity and future response to rising greenhouse gases. To illustrate, calculations of Paleocene/Eocene $\delta D_{\text{precipitation}}$ from ancient wax δD and an ϵ_{net} of -100‰ to -130‰ reveal extreme warmth and moisture convergence in the Arctic during the Paleocene/Eocene thermal maximum (PETM) (Pagani et al., 2006). If a smaller ϵ_{net} of -60‰ is used, however, the estimated $\delta D_{\text{precipitation}}$ during this time period was similar to modern $\delta D_{\text{precipitation}}$, and not strongly enriched, thus casting doubt on our understanding of Arctic climate during the PETM. Paleoclimate inferences for Antarctica during the mid-Miocene (Feakins et al., 2012) are likewise sensitive to whether an ϵ_{net} value of -100‰ or

-60‰ is used to calculate $\delta D_{\text{precipitation}}$. Similarly, two temperature anomaly estimates for the last glacial maximum in western Canada (Pautler et al., 2014; Porter et al., 2016), which rely on the same δD_{wax} data but different values of ϵ_{net} , differ by 14°C. Clearly, large deviations of ϵ_{net} , caused either by inaccurate assessment of plant source water δD values, by enhanced isotopic fractionation during 24-hour transpiration, or by large changes in vegetation assemblages, would complicate interpretations of polar δD_{wax} .

With the exception of the study by Wilkie et al. (2012), investigations of ϵ_{net} in the Arctic have thus far relied on estimated $\delta D_{\text{precipitation}}$ values from the OIPC model (Bowen and Revenaugh, 2003; Yang et al., 2011; Shanahan et al., 2013) or measurements of relict (frozen) water (Porter et al., 2016). Both of these methods could be insufficient for determining ϵ_{net} considering the complexity of precipitation seasonality, soil water dynamics, and plant water use dynamics (Alstad et al., 1999; Welker et al., 2005; Young et al., In press). Moreover, previous efforts to quantify the effects of 24-hour photosynthesis in greenhouse experiments used plants that do not grow in the Arctic, such as *Metasequoia* (redwood), and the hypothesized increase in leaf water isotopic values due to greater transpiration was not accompanied by leaf water isotopic measurements (Yang et al., 2009). Direct measurements of plant xylem and leaf waters in Arctic field conditions would provide a more robust estimate of plant source water isotope values (Welker, 2000; Leffler and Welker, 2013). To our knowledge, no previous study has traced Arctic D/H fractionation from precipitation to leaf wax production in living plant tissues, changes in δD_{wax} through the growing season, nor variations in δD_{wax} associated with native Arctic vegetation, ecosystem integration, and sedimentation.

Three ecophysiological controls are particularly important to estimating ϵ_{net} . First, the seasonal fluctuations in $\delta D_{\text{precipitation}}$ relative to the timing of wax synthesis by plants can lead to differences in source water isotope composition for different regions or plant types (Alstad et al., 1999; Vachon et al., 2010). Accurately determining seasonal changes in plant source water is especially important in the Arctic, where $\delta D_{\text{precipitation}}$ can change drastically through the year. Secondly, although the δD of xylem water (δD_{xylem}) generally reflects $\delta D_{\text{precipitation}}$ (White et al., 1985), the δD of leaf water (δD_{leaf}) is sensitive to factors that govern leaf water evaporation including relative humidity (Kahmen et al., 2013; Tipple et al., 2015), species effects (leaf morphology, canopy height, water use efficiency) (Sullivan and Welker, 2007), and possibly day length (Yang et al., 2009). Again, quantifying enrichment in δD_{leaf} in the Arctic could test the suggested strong fractionation resulting from 24-hour photosynthesis. Third, biosynthetic fractionation during leaf wax generation varies by plant type. Eudicots are typically characterized by ϵ_{net} value of -156 to -85‰ while monocotyledons have a larger fractionation ranging from -190 to -120‰ (Hou et al., 2007; Gao et al., 2014a; Liu et al., 2016). Fractionation values of arctic plants tend to fall into these ranges (Wilkie et al., 2012; Thomas, 2016), although there is also support for reduced fractionation at the plant-scale (Yang et al., 2011). Together, these effects may help explain the discrepancies in high-latitude estimates of ϵ_{net} , and also suggest that shifting vegetation communities can significantly alter values of ϵ_{net} .

The main objectives of this study are 1) to assess the importance of 24-hour daylight on D/H fractionation by determining ϵ_{net} at the plant and landscape scales in the Arctic tundra, and 2) to describe the environmental controls, especially vegetation

assemblages, on δD_{wax} . We report paired measurements of the δD of precipitation, soil water, xylem water, leaf water, and leaf waxes of two dominant plant taxa from the Alaskan Arctic that constrain the apparent fractionation in Arctic plants. We use sediment trap data to assess changes in δD_{wax} through the growing season, and a regional survey of leaf waxes preserved in lake surface sediment to estimate ϵ_{net} and evaluate whether local vegetation variations explain between-lake variation in ϵ_{net} . Together, these results provide a comprehensive framework for interpreting δD_{wax} in the Arctic tundra and illustrate the utility of combining plant-level and ecosystem-level studies of D/H fractionation.

2.3 Sites, samples, and methods

2.3.1 Site description

The study area is located in the northern foothills of the Brooks Range at the Toolik Lake Natural Research Area (68.5 °N, 149.5 °W; Figure 2.1). Annual temperature and precipitation average -8.5 °C and 312 mm, with roughly 60% of precipitation occurring during summer months (JJA; Figure 2.2) (Cherry et al., 2014). Summer relative humidity averages 75%. The soils are characterized by continuous permafrost with summer thaw depths ranging from 30 to 200 cm (Shaver et al., 2014). The growing season is characterized by an average date for first leaf appearance of June 3, with full spring green-up occurring in late-June and plant senescence occurring in late August and September (Toolik Environmental Data Center Team, 2016b).

Glacier activity emanating from the Brooks Range was spatially and temporally variable through the late Pleistocene, giving rise to three landscape surfaces of varying

age and vegetation in our study area (Figure 2.1) (Walker and Walker, 1996; Hamilton, 2003). These consist of the Sagavanirktok (>125 ka), Itkillik I (~60 ka), and the Itkillik II (~25 – 11.5 ka) surfaces. The Sagavanirktok surface is dominated by tussock tundra and *Sphagnum* spp. The Itkillik I surface is a mixture of tussock tundra and *Dryas* heath communities. The Itkillik II surface has shallower bedrock and substantial areas of *Dryas* heath. *Eriophorum vaginatum* is the primary tussock-forming graminoid, while the eudicot shrubs *Betula nana* and *Salix* spp. can be found on all glacial surfaces or along the riverbanks. Similar plant communities can be found around much of the Arctic (CAVM Team, 2003).

2.3.2 Sample collection

Vegetation and water isotopes

Precipitation isotopes were collected on a year-round event basis from 1993 to present (Klein et al., 2016). Not all events were measured, but in total, 254 precipitation events were measured for their isotopic composition. We calculated an amount-weighted mean annual precipitation isotope signature using binned monthly values of $\delta D_{\text{precipitation}}$ and monthly values of precipitation amount (Toolik LTER Environmental Data Center).

Soil water and vegetation samples were collected on August 6, 2013, July 7/8, 2014, and August 7/8, 2014 between 10:00 and 16:00. Sampling sites were located within the Imnaviat Creek watershed on the Saganavirktok glacial surface and the Toolik Lake watershed on the Itkillik I glacial surface. Both sites are characterized as moist acidic tundra. Soil water isotope profiles (δD_{soil}) were collected during each sampling.

Soil water was collected to a depth of 92.5 cm using two methods. First, we used soil probes fit with a 50 mL syringe to extract water from the thawed organic horizon—0, 5, 10, 15, or 20 cm soil depth. Water was pushed through a combusted GFF filter into plastic scintillation vials and frozen. Where soil was too dry or frozen to use this method we collected 5-10 cm³ soil from soil pits to be melted or distilled. Permafrost soil samples were provided from soil pits dug by Colin Ward, Jason Dubkowski, and Katherine Harrold of the ARC LTER (Ward and Cory, 2015).

We measured the δD_{xylem} , $\delta D_{\text{leaf water}}$, and δD_{wax} for two tundra plants, *Eriophorum vaginatum* (cottongrass) and *Betula nana* (dwarf birch). These species are two of the most dominant species in the Arctic tundra (Walker et al., 1994), together comprising over 30% of tussock tundra aboveground biomass (Chapin III et al., 1995). These species serve as model species for monocots (*E. vaginatum*) and dicots (*B. nana*). From the same sites where soil water was collected, one to three sets of roots, stems, and leaves from the same plant were collected with each effort. Live roots were separated from aboveground components and immediately cleaned of clinging soil and soil water. For *B. nana*, several 5 cm segments of stem were cut from each plant and composited. Likewise, >20 *B. nana* leaves were collected and composited to ensure sufficient leaf water yield for isotopic analyses and to homogenize variability among leaves. For *E. vaginatum*, stems were not distinguished from leaves, and approximately 20 leaves were composited for each plant. All plant parts were stored frozen in WhirlpakTM bags until processing.

Sedimentary waxes

To assess the ecosystem-integrated values of ϵ_{net} , we analyzed δD_{wax} from surface sediment samples from 24 lakes near Toolik Field Station (Figure 2.1). Surface sediments were collected from lake depocenters in 2011 and 2013 (Longo et al., 2016). To test if local (watershed-scale) differences in vegetation assemblages can affect the ϵ_{net} of lake sediments, we compared the ϵ_{net} with the relative abundance of major Arctic plant types for each lake's watershed using multiple linear regression. Vegetation distributions were derived from vegetation maps, which translate aerial photographs into nine discrete plant complexes, downloaded from the Alaska Geobotany Center (Walker and Maier, 2008)(Figure 2.1).

Sediments were also collected from sediment traps deployed in Toolik Lake and Lake E5 (ARC LTER). Sediment traps were deployed in May 2014 and collection vials were replaced 4 times during the summer giving 2-6 week resolution. Traps were deployed approximately 2 m above the lake floor.

2.3.3 Sample processing and analysis

Water isotopes

Water was extracted from plant tissues and bulk soils using cryogenic vacuum distillation (Gao et al., 2012). Soil and plant samples were heated under vacuum in extraction vials to 100 °C and the resulting vapor was collected in a vial in liquid nitrogen. Samples were immediately thawed and transferred into 4 mL vials, sealed with parafilm, and stored at 4 °C. For all soil water samples, 3 mg of activated charcoal (particle size <150 μm) was added to the samples to remove excessive dissolved organic matter. Samples reacted overnight and the charcoal was filtered using a GFF filter.

Precipitation, soil water, and plant water samples were analyzed for $\delta^{18}\text{O}$ and δD on a Picarro L1102-i cavity ring-down spectrometer at Brown University. Samples were analyzed with Picarro ChemCorrect software to test for the effects of organic contaminants and no samples were flagged as problematic. The 1σ analytical error determined from replicate standards was 0.09‰ for $\delta^{18}\text{O}$ and 0.57‰ for δD .

Biomarker processing

Lipids were extracted from leaf residues after removing leaf water. Approximately 100 mg of leaf material was sonicated for 15 minutes in dichloromethane:methanol (1:1 v/v), with three solvent rinses. Lipids were extracted from freeze dried surface sediments and sediment trap samples using a Dionex Accelerated Solvent Extractor (ASE) 350 with dichloromethane:methanol (9:1 v/v). Lipids were separated following the methods of Gao et al. (2011). The total lipid extract (TLE) was split into an acid and neutral fraction using aminopropyl silica gel chromatography with dichloromethane:isopropanol and 5% glacial acetic acid in ether as eluents. An internal standard (7 μg *cis*-eicosenoic acid) was then added to the acid fraction. Acids were derivatized overnight at 60 °C with acidified methanol of a known isotopic composition. δD values of individual *n*-acids were later corrected for the isotopic contribution incurred during methylation. Aliphatic compounds were isolated from the neutral fraction by silica gel chromatography with sequential elution by hexane (N1), dichloromethane (N2), and methanol (N4). The N1 fraction was spiked with an internal standard of hexamethylbenzene. A sample blank was analyzed with every batch.

The *n*-alkane and *n*-acid distributions of all samples were determined using Agilent 6890 gas chromatograph with a flame ionization detector (GC-FID). GC parameters were the same used by Gao et al. (2011). Compound-specific isotope ratios (δD_{wax}) of long chain (C_{22} - C_{31}) molecules were measured on a Thermo Finnigan Delta +XL isotope ratio mass spectrometer with a HP 6890 gas chromatograph and a high-temperature pyrolysis reactor for sample introduction. The GC was fit with a 30 m HP1-MS column. The heating protocol was as follows: injector was set to pulsed splitless mode at 320 °C; oven temperature was held at 70 °C for 1 minutes, then ramped by 25 °C min⁻¹ to 230 °C, then by 6°C min⁻¹ to 315 °C minutes. Pyrolysis reactor temperature was set to 1445 °C and the flow rate was held constant at 1.4 ml min⁻¹. H3+ factor was determined every other day and averaged 6.15 during the course of analyses. Samples were measured in at least duplicate. A standard mixture containing either C_{16} , C_{18} , C_{22} , C_{26} , and C_{28} *n*-acids or C_{25} , C_{27} , C_{29} , C_{30} , and C_{32} *n*-alkanes was analyzed between every six injections to monitor instrument accuracy. Uncertainty was calculated using the pooled standard deviation wherein $\sigma = \sqrt{\frac{\sum(n_i-1)*s_i^2}{\sum(n_i-1)}}$, where i=day for standards and i=sample for samples. The 1 σ uncertainties are reported in Table 2.S2.

Notation and Statistics

The isotopic composition of water and waxes is described in delta-notation, where $\delta D (\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$, $R = \frac{D}{H}$, and the standard is Vienna standard mean ocean water (VSMOW). Hydrogen isotope enrichment factors, ϵ , were calculated

between two reservoirs A and B as $\varepsilon_{A-B} = \left[\frac{\delta D_A + 1000}{\delta D_B + 1000} - 1 \right] * 1000$. Statistical analyses were performed in R.

2.4 Results

2.4.1 Plant source water

The $\delta D_{\text{precipitation}}$ is most enriched during summer and most depleted during winter (Figure 2.2), with a precipitation-weighted mean annual value of $-166 \pm 16.4\text{‰}$. The mean annual $\delta D_{\text{precipitation}}$ determined by the Online Isotope in Precipitation Calculator is -159‰ , just slightly enriched relative to observations (Bowen and Revenaugh, 2003; Bowen, 2015). OIPC modeled monthly values are also somewhat enriched, with a RMSE of 32‰ relative to observations.

In July the surface (0-1cm) δD_{soil} averages -161.5‰ , not significantly different than mean annual precipitation ($p=0.27$) whereas in August, surface δD_{soil} is more enriched than annual precipitation with values averaging -142‰ ($p=0.0003$), suggesting that summer rainfall is the primary source of soil moisture by late summer (Figure 2.3). Vertical profiles in δD_{soil} also differ between months. In July, there is a negative depletion at intermediate (10-30 cm) depth to values more negative than the permafrost, possibly a result of residual winter precipitation. In contrast, there is a steady D-depletion with depth in August. Permafrost δD_{soil} is assumed to be constant and has a value of -162 ± 6 , the same as mean annual precipitation ($p=0.54$). Soil water isotopes fall on the local meteoric water line (LMWL), indicating little effect of soil evaporation (Figure 2.4). As such, the progressive enrichment of surface soil water isotopes from

July to August likely reflects an increasing contribution of summer rains to the soil water pool.

Xylem water isotopes also fall on the LMWL (Figure 2.4), indicating there is little to no fractionation during plant uptake, consistent with previous studies (Ehleringer and Dawson, 1992). Overall, there is no difference in δD_{xylem} between *E. vaginatum* and *B. nana* ($p = 0.084$). The δD_{xylem} increases from -160 ± 8 to -147 ± 9 between July and August, thus tracking the increase in soil water isotopes (Figure 2.5).

Evaporative enrichment increases δD and $\delta^{18}O$ values of leaf water relative to xylem water. The δD_{leaf} is enriched relative to δD_{xylem} by $40 \pm 17\text{‰}$ in *B. nana* and $22 \pm 16\text{‰}$ in *E. vaginatum* (Figs. 2.4, 2.5). The intersection between the leaf water δD - $\delta^{18}O$ line and the LMWL can be used to infer the isotopic composition of source water for plant uptake (Polissar and Freeman, 2010), and occurs at $\delta^{18}O = -19\text{‰}$ and $\delta D = -148\text{‰}$. This composition is between the July and August xylem water measurements.

2.4.2 Leaf waxes

Modern plant waxes

Leaves from both species contain *n*-acids from C_{20} to C_{30} and *n*-alkanes from C_{23} to C_{33} . The *n*-acids show a strong even-over-odd predominance for both *B. nana* and *E. vaginatum*, and vice versa for *n*-alkanes (Figure 2.6). For *B. nana*, even chain *n*-acids are roughly equally distributed from C_{22} to C_{28} , whereas the *n*-alkane distribution has two peaks at C_{27} and C_{31} . For C_{20} - C_{30} *n*-acids, average chain length (ACL) is 24.5 ± 0.7 and the carbon preference index (CPI) is 14.2 ± 2.8 , while for *n*-alkanes, the C_{20} - C_{33} ACL and CPI average 28.7 ± 0.4 and 7.4 ± 3.1 , respectively. *E. vaginatum* lipids are unimodally

distributed and dominated by C_{26} *n*-acid and C_{31} *n*-alkane. ACL and CPI average 24.8 ± 0.5 and 6.3 ± 1.5 for *n*-acids and 30.1 ± 0.7 and 32.3 ± 8.1 for *n*-alkanes. No difference in ACL was observed between sampling months for either species ($p = 0.59$ for *E. vaginatum* and $p = 0.16$ for *B. nana*). While the two species have similar concentrations of total *n*-alkanes, *B. nana* leaves contained significantly more *n*-acids than *E. vaginatum* on a mass basis.

For isotopic analyses, we focus on the most abundant long chain *n*-acids (C_{22} - C_{30}) and *n*-alkanes (C_{25} - C_{31}). There are systematic differences in the δD of these different homologues. For *E. vaginatum*, δD_{wax} ranges from -307‰ for C_{31} *n*-alkane to -262‰ for C_{22} *n*-acid (Table 2.1). For *B. nana*, δD_{wax} ranges from -267‰ in C_{22} *n*-acid to -226‰ for C_{29} *n*-alkane. Overall, ϵ_{net} was more negative for leaf waxes of *E. vaginatum* (range of all homologues = -130.9 to -183.4‰) compared to *B. nana* (-82.7 to -127.7‰) (Table 2.1). The difference in fractionation between the two species decreases with decreasing chain length (Figure 2.7).

Sedimentary waxes

In Lake E5, the flux of both *n*-acids (C_{20} - C_{30}) and *n*-alkanes (C_{23} - C_{33}) in sediment traps peak in June, during and shortly after the spring thaw (Figure 2.8). The *n*-acids exhibit a unimodal distribution with a peak at the C_{24} homologue. ACL and CPI values of 23.3 ± 0.7 and 2.7 ± 1.3 , respectively. The *n*-alkanes are bimodal with peaks at C_{20} and C_{27} . They are typically in lower abundance than the *n*-acids, and have ACL and CPI values of 25.2 ± 1.5 and 3.1 ± 2.9 , respectively. The low abundance of waxes required that sediment trap replicates be composited into early and late summer samples for

isotope analysis. In Lake E5, $\delta D_{C_{28}\text{-acid}}$ varies by 15‰ throughout the summer, ranging from -256‰ in May/June and August/September to -243‰ in July (Figure 2.8). The flux-weighted input of C_{28} *n*-acid during the summer has a δD value -253.7‰, which is indistinguishable from the C_{28} *n*-acid in Lake E5 surface sediment of -254.8‰. In Toolik Lake, wax abundance was too low for isotope analysis.

Like sediment trap samples, C_{24} *n*-acid is the most abundant wax homologues in surface sediments from all lakes; the ACL for *n*-acids is 24.8 ± 0.8 and the CPI is 5.2 ± 1.0 consistent with a terrestrial plant wax origin. The C_{27} to C_{29} are the most abundant *n*-alkanes and present in roughly equal abundances. The ACL and CPI for *n*-alkanes average 27.2 ± 0.4 and 5.0 ± 0.8 , respectively. The δD_{wax} of lipids in surface sediments averages $-261.8 \pm 9.9\text{‰}$ for all measured homologues and has a range of 49‰ (Table 2.S1), similar to values from the sediment traps.

2.4.3 Vegetation effects on apparent fractionation

To calculate a watershed-scale ϵ_{net} , we compared the δD_{wax} of lake surface sediments to the average δD_{xylem} in our plant samples (-153‰). In the 24 study lakes, average ϵ_{net} is $-128.5 \pm 11.7\text{‰}$ for all lipid homologues, and ranges from -113‰ in C_{30} *n*-acid to -136‰ in C_{22} *n*-acid. Values of ϵ_{net} are slightly more negative for shorter chain lengths (Figure 2.7). Isotopic differences between study lakes arise from edaphic differences, evaporative enrichment, and differing plant distributions. The relative abundance of dry tundra vegetation is positively correlated with ϵ_{net} , whereas the abundance of moist and shrub tundra vegetation is negatively correlated with ϵ_{net} (Figure 2.9, Table 2.S2).

2.5 Discussion

2.5.1 Apparent fractionation in the Arctic is similar to temperate and tropical settings

A pressing question in the application of leaf wax hydrogen isotopes for paleoclimate reconstructions is whether apparent D/H fractionation is affected by enhanced transpiration in polar regions due to 24-hour photosynthesis, as suggested by previous studies (Yang et al., 2011; Shanahan et al., 2013; Porter et al., 2016), or, if there is little effect of latitude on ϵ_{net} as recently suggested by Liu et al. (2016). Our study site is within the Arctic circle, at a similar latitude to previous studies on Arctic leaf wax fractionation. We find that ϵ_{net} of Arctic *n*-alkanes and *n*-acids are similar to mid- and low-latitude locations (Sachse et al., 2004; Hou et al., 2007; Garcin et al., 2012), suggesting that the effect of 24-hour photosynthesis is of limited importance and that the fundamental controls on ϵ_{net} in the Arctic are similar to those in temperate and tropical regions.

At the scale of individual plants, our measurements of ϵ_{net} are similar to results from regions both with and without a summer diurnal light cycle. For example, in Massachusetts, USA, Hou et al. (2007) found that ϵ_{net} of waxes from eudicot trees ranged from -156 to -85‰ whereas waxes from graminoids showed greater fractionation, ranging from -206 to -148‰. In comparison, ϵ_{net} values in our study range from -127.7 to -82.7‰ for various lipid homologues from the eudicot *B. nana* and from -183.4 to -130.9‰ for waxes from the graminoid *E. vaginatum*. Our results are also in close agreement with other Arctic measurements from living plants – Wilkie et al. (2012)

report ϵ_{net} values ranging from -135.4 to -96.7‰ for leaf waxes in Siberia, and Thomas (2016) report an ϵ_{net} of -117‰ for C_{27} *n*-alkanes of dominant shrub taxa in western Greenland.

Ecosystem-scale ϵ_{net} inferred from waxes in lake sediments averages -128.5‰ across all the measured *n*-acid and *n*-alkane homologues. This value is intermediate between our estimates of ϵ_{net} from *B. nana* and *E. vaginatum*, and is similar to an estimate of -110.5‰ in Arctic Siberia (Wilkie et al., 2012). Our estimate is also within the range of many mid- and low-latitude sites (Huang et al., 2004; Hou et al., 2008) and agrees quite well with an ϵ_{net} estimate of -128‰ for long chain *n*-alkanes found in high latitude lakes of Europe (Sachse et al., 2004). However, our estimate differs substantially from reports of -60‰ in the sub-Arctic and Arctic (Shanahan et al., 2013; Porter et al., 2016).

We postulate that the large discrepancy in ϵ_{net} between our study and previous Arctic field studies derives from differences in the assumed seasonality and estimated isotope compositions of plant source waters. Some prior studies that found small Arctic ϵ_{net} use source water δD values estimated to represent mean annual $\delta\text{D}_{\text{precipitation}}$ (Yang et al., 2011; Shanahan et al., 2013; Porter et al., 2016). For the Baffin Island study (Shanahan et al., 2013), this assumption is compounded with the use of estimated rather than measured $\delta\text{D}_{\text{precipitation}}$ values, as well as low humidity and a predominance of dicotyledonous species (forbs) in their study area, all of which might reduce apparent D/H fractionation. In Central Canada, Porter et al. (2016) calculated ϵ_{net} of -59‰ by comparing fossil waxes to mean annual precipitation preserved in pore ice. However, it is unclear whether pore ice records water frozen in situ at the same time and in the same season as that when the plant waxes were formed. Moreover, application of this ϵ_{net} value

to δD_{wax} of modern soils in their study area (Pautler et al., 2014) results in an underestimation of modern mean annual $\delta D_{\text{precipitation}}$ by 28‰ and a resulting underestimation of modern mean annual temperature by 13°C (Porter et al., 2016). While it is possible that source water for plants can come from snowmelt (Alstad et al., 1999; Leffler and Welker, 2013), the ground is often frozen during the season of snow melt. It is more likely that the fossil pore water isotopes used by Porter et al. (2016) reflect cold season (D-depleted) precipitation rather than precipitation during the plant growing season (D-enriched) (Blok et al., 2015).

Low apparent fractionation values have been previously explained by the 24-hour sunlit conditions that characterize the Arctic summer, which allow photosynthesis throughout the 24-hour day that might drive strong isotopic fractionation of leaf waters due to 24-hour evaporation. This hypothesis is supported by greenhouse experiments that indicate ϵ_{net} values from -87 to -62‰ for plants grown in 24-hour light conditions (Yang et al., 2009). These values are difficult to explain. It is possible that the exceptionally small fractionation values that Yang et al. (2009) observed partly resulted from their choice of study species – *Metasequoia*, *Larix*, and *Taxodium* are expected to exhibit relatively small ϵ_{net} values based on their evolutionary lineages (Gao et al., 2014a). Thus, in cases where arctic forests are dominated by these conifers, a reduced fractionation value may be appropriate for calculating ancient $\delta D_{\text{precipitation}}$ from ancient δD_{wax} . Nonetheless, for modern arctic tundra plants, our data argue against a 24-hour photosynthesis effect of leaf water isotopes.

Direct observations of $\epsilon_{\text{leaf-xylem}}$ do not indicate that continuous daylight has a large impact on δD_{wax} . Although evaporative enrichment at the leaf surface increases

δD_{leaf} relative to δD_{xylem} (Roden and Ehleringer, 1999; Tipple et al., 2015), the magnitude of this enrichment observed at Toolik (40‰ and 21‰ for *B. nana* and *E. vaginatum*, respectively) is within the range of isoscape model predictions for Alaska (Kahmen et al., 2013). The observed enrichment of leaf water over xylem water is also similar to field and growth chamber observations in temperate environments with diurnal light cycles and similar relative humidity (Massachusetts and New York) where Gao et al. (2014a) found that $\epsilon_{\text{leaf-xylem}}$ is slightly greater for shrubs and trees ($34 \pm 13\%$) than graminoids ($20 \pm 11\%$). We hypothesize that the species difference in δD_{leaf} may result from differences in plant height and leaf physiology, with *B. nana* somewhat taller and more susceptible to leaf water enrichment due to a longer flow path of water during transpiration (Gao and Huang, 2013). Regardless of the differences between plant types, both plant water isotope measurements show little effect of continuous daylight on leaf water isotopes.

While leaf water measurements are useful for assessing the importance of evaporative enrichment, leaf waters can display large diurnal isotope variations (Flanagan and Ehleringer, 1991) which were not captured in our sampling scheme. To circumvent the uncertainties of spot sampling, we further tested the effect of changing leaf transpiration on the isotope values of leaf water using the modified Craig-Gordon model for leaf water (Flanagan and Ehleringer, 1991; Tipple et al., 2015). This model calculates the isotopic composition of water at the site of evaporation, rather than water in the bulk leaf tissue, which can also contain a fraction of unevaporated xylem water. Nevertheless, the model can qualitatively describe the potential impact of diurnal or continuous transpiration on leaf water isotope enrichment. Using average JJA meteorological

conditions from Toolik Field Station (Toolik Environmental Data Center Team, 2016b), and atmospheric vapor δD at Toolik (Klein et al., 2015), we modeled δD_{leaf} for the range of transpiration rates of Arctic grasses (Gebauer et al., 1998). We find that δD_{leaf} decreases with increasing transpiration rates, but the overall variation is small, less than 1‰ (Figure 2.10). These model results support the findings of Sullivan and Welker (2007), who demonstrated that, for arctic willow (*Salix arctica*), increasing transpiration results in lower, not higher, leaf water $\delta^{18}O$. Furthermore, findings of Roden and Ehleringer (1999) indicate that leaf water at the site of evaporation reaches isotopic equilibrium within two hours under constant evaporation, and so prolonged (24 hour) transpiration should not lead to anomalously enriched leaf water isotope values. Thus, our modeling and prior observational data suggest that 24-hour transpiration in the Arctic would, if anything, decrease δD_{leaf} and thereby make ϵ_{net} more negative, rather than the opposite.

Model results also suggest a relatively small humidity effect on leaf water isotopes. For a 1% increase in relative humidity, δD_{leaf} decreases by 0.33‰ (Figure 2.10). Based on the $\delta D_{\text{precipitation}}$ -temperature relationship of $3.1\text{‰}^{\circ}\text{C}^{-1}$ reported by Porter et al. (2016), this equates to approximately a 1 °C inferred temperature change per 10% change in relative humidity. As such, the effect of humidity change on δD_{wax} interpretations may be relatively insignificant in the Arctic.

The ϵ_{net} values for leaf waxes from *E. vaginatum* and *B. nana* align well with previous studies that find waxes in graminoids are D-depleted relative to those from forbs, shrubs, and trees (Sachse et al., 2012; Gao et al., 2014a; Liu et al., 2016) and that waxes in monocots are depleted relative to eudicots (Gao et al., 2014a). Interestingly,

however, fractionation values for the shorter chain length n -acids (C_{24} and C_{26}) were similar for our two study species. This result suggests that shorter chain lengths may be more resilient to vegetation effects in the geologic record. However, the relative abundance of these molecules is low in the vegetation samples compared to the sediment samples (Figure 2.6) indicating that other organisms, such as *Sphagnum* moss (Nichols et al., 2009), contribute the bulk of C_{24} n -acid to lake sediments.

Overall, we suggest that apparent D/H fractionation of Arctic plants is similar to that of plants in temperate and tropical latitudes. It is possible that D/H fractionation in this study is overestimated (more negative than true δ_{net}), due to seasonally biased sampling of waxes and source waters. To evaluate this, we consider a wider range of possible source water δD values. For sedimentary waxes in Toolik and the surrounding lakes, if the plant source water is equal to the mean annual $\delta D_{\text{precipitation}}$ (-166‰) rather than summer xylem water (-153‰), ϵ_{net} ranges from -99‰ for C_{30} n -acid to -122‰ for C_{22} and C_{24} n -acids. This is still similar to ϵ_{net} in non-polar regions (Sachse et al., 2004; Hou et al., 2008) and very different from the small values observed at Baffin Island and Central Canada (Shanahan et al., 2013; Porter et al., 2016). To generate ϵ_{net} as small as -60‰ at our site, it is necessary to invoke source water δD values of -213‰ . Such a strong winter-biased source water isotope value is unlikely considering that δD_{xylem} during the growing season averaged -153‰ , that 60% of annual precipitation occurs in the three summer months, and that most of the snowmelt is lost as runoff during the spring thaw (Woo, 2012).

2.5.2 Constraining the seasonality of δD_{wax} signals in the Arctic

It is challenging to accurately identify the isotope value of the source water involved in plant wax synthesis in the Arctic because of the extreme seasonal changes in $\delta D_{\text{precipitation}}$. For our location, we estimate the δD of source water used for plant growth averages -153‰ , based upon both direct measurements of xylem water as well as the intersection between the leaf evaporation line with the LMWL (Figure 2.5). Although soil and xylem water collections occurred during peak seasonal warmth and peak $\delta D_{\text{precipitation}}$, their isotopic composition was intermediate between the mean annual amount-weighted $\delta D_{\text{precipitation}}$ (-166‰) and the summer $\delta D_{\text{precipitation}}$ (JJA average = $-136 \pm 25\text{‰}$.) In regions of continuous permafrost, soil infiltration of snowmelt is variable, but generally inhibited during cold months by the impermeability of soil ice (Woo, 2012). As a result, considerable snowmelt is theoretically lost as surface runoff and the spring/summer soil water during the period of leaf flush is mostly composed of spring (May and June) precipitation. The predominance of growing-season precipitation over cold-season precipitation in surface soil waters is evident in both July and August, as the δD_{soil} is isotopically similar to spring and summer rains (Figure 2.4). Nevertheless, δD_{soil} increases from July to August, and, D-depleted water is present at intermediate soil depths in July, both of which suggest that complete replacement of remnant fall, winter, and spring precipitation requires several weeks to months and that cold-season precipitation may be available for plant growth. The seasonal change in δD_{soil} profiles seems to have a stronger influence on the δD_{xylem} of *Betula nana*, which as a shrub has a deeper rooting depth than the sedge *Eriophorum vaginatum* (Figure 2.4). Indeed, there are indications that snowmelt can contribute over 30% of source water to plants (Ebbs

2016 MS Thesis). Nevertheless, xylem water isotope measurements in this study and another study in Greenland (Sullivan and Welker, 2007) indicate that arctic plants primarily utilize water from the shallow, thawed soil zones, where soil water is isotopically similar to growing season precipitation events (Figure 2.3).

Despite the enrichment of xylem water in August relative to July, δD_{wax} of plants did not change between months (Figure 2.4). Biosynthetic changes during the growing season have been shown to depress mid-summer D/H ratios in plant waxes (Sessions, 2006), and may partially offset the increasing δD_{xylem} . Alternatively, summer changes in δD_{wax} of plants may lag δD_{xylem} because leaf wax turnover occurs on a timescale of weeks to months (Gao et al., 2012).

Sediment trap results provide additional insight into seasonal variations in the source water that plants use for biosynthesis. Since the highest flux of waxes to the sediment occurs during the spring freshet, it appears that waxes entering the lake are primarily produced during previous years and are flushed from soil and leaf litter by snowmelt. Like $\delta D_{\text{precipitation}}$, sediment trap δD_{wax} is most D-enriched in July (Figure 2.8), implying that there is indeed seasonal regeneration of leaf waxes and that the regeneration records changes in source water isotope composition. As such, a considerable proportion of the mid-summer wax flux appears to originate from waxes produced in mid-summer. The amplitude of the δD_{wax} change throughout the summer (15‰) is greater than we observed in the monthly change in δD_{wax} of living plants, which is surprising, but may be because we did not measure δD_{wax} of plants in the earliest part of the growing season (May or June). Based on the combined flux and isotope data, we conclude that the waxes are primarily sourced during the early growing season rather

than peak summer, consistent with the idea that leaf flush is the main wax-forming period. In either case, these sediment trap data together with soil water profiles, suggest that the source water for leaf wax production is precipitation falling during the growing season, particularly during spring (May to June).

Our observations support the hypothesis that δD of long chain *n*-acids and *n*-alkanes records a summer-biased mean annual precipitation isotope signal in the Arctic. Wilkie et al. (2012) found that the isotopic composition of spring precipitation and streamwater is a good representation of plant source water during the growing season in Siberia. In their study the streamwater isotope values were intermediate between mean annual and summer precipitation values, and the resulting value of ϵ_{net} was approximately -105‰. We find strong evidence that plants use summer precipitation in the Toolik region, as well as fall and winter precipitation stored in the soil as ice. However, we note that the average composition of plant source waters is similar to $\delta D_{\text{precipitation}}$ during spring (May and June). The use of summer precipitation by plants was also observed in Arctic Svalbard, where the δD of plant annual growth rings is more strongly correlated with summer $\delta D_{\text{precipitation}}$ than with either winter $\delta D_{\text{precipitation}}$ or with the amount of snow accumulation during winter (Blok et al., 2015). These findings have important implications for the interpretation of δD_{wax} records of Arctic paleoclimate, given the potential importance of seasonality in governing high-latitude climate change (Denton et al., 2005).

2.5.3 Constraining landscape-scale vegetation effects on sedimentary δD_{wax}

Surface sediment δD_{wax} can vary by up to 44‰ across our 24 study lakes for a given *n*-acid or *n*-alkane homologue. This range is substantial, especially if δD_{wax} is to be used for reconstructing paleotemperature. The relationship between temperature and $\delta D_{\text{precipitation}}$ across northern North America is $\sim 3.1\text{‰ }^{\circ}\text{C}^{-1}$ (Porter et al., 2016), and thus the δD_{wax} variability across study lakes equates to a temperature range of 14°C. We tested the hypothesis that the variation of δD_{wax} values between lakes results from differences in vegetation assemblages within watersheds. Quantifying this effect in the absence of a climatic and $\delta D_{\text{precipitation}}$ gradient is important because in Alaska and around the Arctic, deglacial and modern climate warming have been accompanied by vegetation changes, especially an expansion of shrub vegetation (Livingstone, 1955; Tape et al., 2012), which could alter the ecosystem value of ϵ_{net} .

The different glacial landscapes in the Toolik Lake area support well-characterized vegetation assemblages with varying relative abundances of monocot and eudicot plants over a very small area (Walker et al., 1994), allowing a test of whether catchment-scale differences in vegetation affect δD_{wax} independent of climatic influences. Dry tundra and heath tundra predominantly support dicotyledonous forbs and shrubs, whereas wetland areas and moist tundra contain a mix of shrubs, forbs, monocotyledonous graminoids, and *Sphagnum* moss, with graminoids and mosses dominating the biomass (Walker et al., 1994). Based on the ϵ_{net} difference between *E. vaginatum* and *B. nana*, we expect waxes in lakes surrounded predominantly by

graminoids (sedges and grasses) to be isotopically depleted compared to waxes in lakes surrounded by dry tundra or heath.

We combine the eudicot-dominant vegetation types described by Walker et al. (1994) (dry tundra, barren tundra, snowbed complex) into the class of ‘dry tundra’, which can then be used as an indication of the relative abundance of eudicots relative to the more monocot-rich moist tundra vegetation types. We find that the relative abundance of dry tundra vegetation around a lake is positively correlated with ϵ_{net} of sedimentary lipids for some, but not all, lipid homologues (Figure 2.9; Table 2.S2). The positive relationship of ϵ_{net} with dry tundra could be caused by greater soil evaporation in the shallow soils of dry tundra; however, our soil water isotope measurements suggest little evaporation of soil waters (Figure 2.4). Rather, we suggest that the predominance of eudicots on the dry tundra influences the δD_{wax} we observe in lake sediments via the lower ϵ_{net} values that characterize eudicot vegetation.

Watershed scale effects should be most prominent if waxes are primarily transported through runoff, and least prominent if aeolian transport prevails, as the latter should result in exchange of waxes between watersheds. While waxes can be transported via wind over long ranges as aerosols (Conte and Weber, 2002; Gao et al., 2014b) or particulates (Fahnestock et al., 2000), the large range in sediment δD_{wax} observed among our study lakes suggests that hydraulic transport causes the lake sediment δD_{wax} signal to primarily record watershed scale effects of vegetation and soil. Local transport is further substantiated by the seasonal pattern in wax transport and deposition observed in the lake sediment traps. Approximately 65% of the total *n*-acids (C_{20} - C_{30}) were deposited between May 16 and July 1, during the spring freshet for Arctic lakes. The most likely

explanation for this peak is that waxes are transported by runoff during the period of high snowmelt and mass movement. As the summer progresses and snowmelt-derived inputs decline, long-distance aerosol waxes may become more important relative to local hydraulic inputs. Since the late summer wax flux is small, however, watershed scale heterogeneity is preserved in lake sediments.

Overall, the range in the ecosystem scale ϵ_{net} between lakes is substantially smaller than the potential range based on end-member monocot and eudicot fractionations that we found at the plant scale. The reduced range could be due to some aerosol transport homogenizing the isotope signal between lakes, or simply because within each watershed, plant communities contain a mixture of monocot and eudicot species. Nonetheless, the impact of vegetation assemblages is consistent with expectations based on fractionation among plant types. These data stress the importance of considering independent estimates of paleovegetation, such as pollen (Feakins, 2013) or plant macrofossils (Nichols et al., 2014) when quantitatively determining Arctic $\delta D_{\text{precipitation}}$ based on sediment or soil δD_{wax} measurements.

2.6 Conclusions

Specific knowledge of the D/H fractionation between precipitation and plant waxes is critical for quantitatively interpreting geologic records of δD_{wax} . Results from the Arctic have so far been conflicting. Here we assessed the effects of uptake, transpiration, biosynthesis, and landscape integration as controls on ϵ_{net} in Arctic Alaska, as well as provide estimates of ϵ_{net} under different vegetation regimes.

We find that ϵ_{net} of two of the most abundant plants in the Arctic tundra, *B. nana* and *E. vaginatum*, are similar to shrubs and grasses in non-Arctic sites. This finding is substantiated by direct observations of leaf water isotope enrichment and ϵ_{net} at the plant-scale as well as ϵ_{net} at the ecosystem-scale. Likewise, modeled leaf water shows no particularly strong enrichment in a continuous light regime. We propose that the effect of prolonged, 24-hour photosynthesis during the Arctic summer on the isotopic composition of waxes is small in the low Arctic tundra despite 24-hour day lengths.

We take advantage of the strong edaphic control on vegetation assemblages in the Brooks Range foothills to produce the first analysis of a vegetation effect on ϵ_{net} in the absence of a climatic gradient. Across 24 lakes within 10 km of each other, ϵ_{net} varied by 44‰. This result suggests that 1) wax transport between watersheds as aerosols is small compared to the hydraulic transport within watersheds and 2) variation in plant assemblages between watersheds plays a significant role in the observed ϵ_{net} . Using vegetation maps, we demonstrate a positive correlation between the abundance of dry tundra (eudicots) and ϵ_{net} for long-chain *n*-acids and *n*-alkanes. The relationship illustrates the necessity of correcting δD_{wax} changes for changes in vegetation, and serves as a guide for such corrections. We propose that for sedimentary records of δD_{wax} , a sliding scale of ϵ_{net} can be appropriately applied if the relative abundance of eudicots is known.

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2.8 References

Alstad, K., Welker, J., Williams, S. and Trlica, M. (1999) Carbon and water relations of *Salix monticola* in response to winter browsing and changes in surface water hydrology: an isotopic study using $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. *Oecologia* 120, 375-385.

Blok, D., Weijers, S., Welker, J.M., Cooper, E.J., Michelsen, A., Löffler, J. and Elberling, B. (2015) Deepened winter snow increases stem growth and alters stem $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in evergreen dwarf shrub *Cassiope tetragona* in high-arctic Svalbard tundra. *Environmental Research Letters* 10, 044008.

Bowen, G. (2015) The Online Isotopes in Precipitation Calculator, version 2.2. <http://www.waterisotopes.org>.

Bowen, G.J. and Revenaugh, J. (2003) Interpolating the isotopic composition of modern meteoric precipitation. *Water Resour. Res.* 39, 1299.

CAVM Team (2003) Circumpolar Arctic Vegetation Map. Scale 1:7,500,000. Conservation of Arctic Flora and Fauna (CAFF) Map No. 1. U.S. Fish and Wildlife Service, Anchorage, Alaska.

Chapin III, F.S., Shaver, G.R., Giblin, A.E., Nadelhoffer, K.J. and Laundre, J.A. (1995) Responses of arctic tundra to experimental and observed changes in climate. *Ecology* 76, 694-711.

Cherry, J.E., Déry, S.J., Stieglitz, M. and Pan, F.-f. (2014) Meteorology and climate of Toolik Lake and the north slope of Alaska: Past, present and future. *Alaska's changing Arctic: Ecological consequences for tundra, streams, and lakes*. Oxford Univ. Press.

Chikaraishi, Y. and Naraoka, H. (2007) $\delta^{13}\text{C}$ and δD relationships among three n-alkyl compound classes (n-alkanoic acid, n-alkane and n-alkanol) of terrestrial higher plants. *Org. Geochem.* 38, 198-215.

Conte, M.H. and Weber, J.C. (2002) Plant biomarkers in aerosols record isotopic discrimination of terrestrial photosynthesis. *Nature* 417, 639-641.

Dansgaard, W. (1964) Stable isotopes in precipitation. *Tellus* 16, 436-468.

Denton, G., Alley, R., Comer, G. and Broecker, W. (2005) The role of seasonality in abrupt climate change. *Quaternary Science Reviews* 24, 1159-1182.

Ehleringer, J. and Dawson, T. (1992) Water uptake by plants: perspectives from stable isotope composition. *Plant, Cell Environ.* 15, 1073-1082.

Fahnestock, J., Povirk, K. and Welker, J. (2000) Abiotic and biotic effects of increased litter accumulation in arctic tundra. *Ecography* 23, 623-631.

Feakins, S.J. (2013) Pollen-corrected leaf wax D/H reconstructions of northeast African hydrological changes during the late Miocene. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 374, 62-71.

Feakins, S.J., Warny, S. and Lee, J.-E. (2012) Hydrologic cycling over Antarctica during the middle Miocene warming. *Nature Geoscience* 5, 557-560.

Flanagan, L.B. and Ehleringer, J.R. (1991) Effects of Mild Water Stress and Diurnal Changes in Temperature and Humidity on the Stable Oxygen and Hydrogen Isotopic Composition of Leaf Water in *Cornus stolonifera* L. *Plant Physiol.* 97, 298-305.

Gao, L., Burnier, A. and Huang, Y. (2012) Quantifying instantaneous regeneration rates of plant leaf waxes using stable hydrogen isotope labeling. *Rapid Commun. Mass Spectrom.* 26, 115-122.

Gao, L., Edwards, E.J., Zeng, Y. and Huang, Y. (2014a) Major Evolutionary Trends in Hydrogen Isotope Fractionation of Vascular Plant Leaf Waxes. *PLoS ONE* 9, e112610.

Gao, L., Hou, J., Toney, J., MacDonald, D. and Huang, Y. (2011) Mathematical modeling of the aquatic macrophyte inputs of mid-chain n-alkyl lipids to lake sediments:

implications for interpreting compound specific hydrogen isotopic records. *Geochimica et Cosmochimica Acta* 75, 3781-3791.

Gao, L. and Huang, Y. (2013) Inverse gradients in leaf wax δD and $\delta^{13}C$ values along grass blades of *Miscanthus sinensis*: Implications for leaf wax reproduction and plant physiology. *Oecologia* 172, 347-357.

Gao, L., Zheng, M., Fraser, M. and Huang, Y. (2014b) Comparable hydrogen isotopic fractionation of plant leaf wax n-alkanoic acids in arid and humid subtropical ecosystems. *Geochem. Geophys. Geosyst.* 15, 361-373.

Garcin, Y., Schwab, V.F., Gleixner, G., Kahmen, A., Todou, G., Séné, O., Onana, J.-M., Achoundong, G. and Sachse, D. (2012) Hydrogen isotope ratios of lacustrine sedimentary n-alkanes as proxies of tropical African hydrology: insights from a calibration transect across Cameroon. *Geochim. Cosmochim. Acta* 79, 106-126.

Gebauer, R., Reynolds, J. and Tenhunen, J. (1998) Diurnal patterns of CO₂ and H₂O exchange of the Arctic sedges *Eriophorum angustifolium* and *E. vaginatum* (Cyperaceae). *Am. J. Bot.* 85, 592-592.

Hamilton, T.D. (2003) Surficial geology of the Dalton Highway (Itkillik-Sagavanirktok rivers) area, southern Arctic foothills, Alaska.

Hou, J., D'Andrea, W.J. and Huang, Y. (2008) Can sedimentary leaf waxes record D/H ratios of continental precipitation? Field, model, and experimental assessments. *Geochim. Cosmochim. Acta* 72, 3503-3517.

Hou, J., D'Andrea, W.J., MacDonald, D. and Huang, Y. (2007) Hydrogen isotopic variability in leaf waxes among terrestrial and aquatic plants around Blood Pond, Massachusetts (USA). *Org. Geochem.* 38, 977-984.

Huang, Y., Shuman, B., Wang, Y. and Webb, T. (2004) Hydrogen isotope ratios of individual lipids in lake sediments as novel tracers of climatic and environmental change: a surface sediment test. *J. Paleolimnol.* 31, 363-375.

Jasechko, S., Lechler, A., Pausata, F., Fawcett, P., Gleeson, T., Cendón, D., Galewsky, J., LeGrande, A., Risi, C. and Sharp, Z. (2015) Glacial–interglacial shifts in global and regional precipitation $\delta^{18}O$. *Clim. Past Discuss* 11, 831-872.

Kahmen, A., Hoffmann, B., Schefuß, E., Arndt, S.K., Cernusak, L.A., West, J.B. and Sachse, D. (2013) Leaf water deuterium enrichment shapes leaf wax n-alkane δD values of angiosperm plants II: Observational evidence and global implications. *Geochim. Cosmochim. Acta* 111, 50-63.

Klein, E., Nolan, M., McConnell, J., Sigl, M., Cherry, J., Young, J. and Welker, J. (2016) McCall Glacier record of Arctic climate change: Interpreting a northern Alaska ice core with regional water isotopes. *Quaternary Science Reviews* 131, 274-284.

Klein, E.S., Cherry, J.E., Young, J., Noone, D., Leffler, A.J. and Welker, J.M. (2015) Arctic cyclone water vapor isotopes support past sea ice retreat recorded in Greenland ice. *Scientific Reports* 5, 10295.

Konecky, B., Russell, J. and Bijaksana, S. (2016) Glacial aridity in central Indonesia coeval with intensified monsoon circulation. *Earth. Planet. Sci. Lett.* 437, 15-24.

Leffler, A.J. and Welker, J.M. (2013) Long-term increases in snow pack elevate leaf N and photosynthesis in *Salix arctica*: responses to a snow fence experiment in the High Arctic of NW Greenland. *Environmental Research Letters* 8, 025023.

Liu, J., Liu, W., An, Z. and Yang, H. (2016) Different hydrogen isotope fractionations during lipid formation in higher plants: Implications for paleohydrology reconstruction at a global scale. *Scientific Reports* 6, 19711.

Livingstone, D. (1955) Some pollen profiles from arctic Alaska. *Ecology*, 587-600.

Longo, W.M., Theroux, S., Giblin, A.E., Zheng, Y., Dillon, J.T. and Huang, Y. (2016) Temperature calibration and phylogenetically distinct distributions for freshwater alkenones: Evidence from northern Alaskan lakes. *Geochim. Cosmochim. Acta* 180, 177-196.

Nichols, J.E., Peteet, D.M., Moy, C.M., Castañeda, I.S., McGeachy, A. and Perez, M. (2014) Impacts of climate and vegetation change on carbon accumulation in a south-central Alaskan peatland assessed with novel organic geochemical techniques. *The Holocene* 24, 1146-1155.

Nichols, J.E., Walcott, M., Bradley, R., Pilcher, J. and Huang, Y. (2009) Quantitative assessment of precipitation seasonality and summer surface wetness using ombrotrophic sediments from an Arctic Norwegian peatland. *Quatern. Res.* 72, 443-451.

Niedermeyer, E.M., Forrest, M., Beckmann, B., Sessions, A.L., Mulch, A. and Schefuß, E. (2016) The stable hydrogen isotopic composition of sedimentary plant waxes as quantitative proxy for rainfall in the West African Sahel. *Geochim. Cosmochim. Acta* 184, 55-70.

Pagani, M., Pedentchouk, N., Huber, M., Sluijs, A., Schouten, S., Brinkhuis, H., Damsté, J.S.S. and Dickens, G.R. (2006) Arctic hydrology during global warming at the Palaeocene/Eocene thermal maximum. *Nature* 442, 671-675.

Pautler, B.G., Reichart, G.-J., Sanborn, P.T., Simpson, M.J. and Weijers, J.W. (2014) Comparison of soil derived tetraether membrane lipid distributions and plant-wax δD compositions for reconstruction of Canadian Arctic temperatures. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 404, 78-88.

Polissar, P.J. and Freeman, K.H. (2010) Effects of aridity and vegetation on plant-wax δD in modern lake sediments. *Geochim. Cosmochim. Acta* 74, 5785-5797.

Porter, T.J., Froese, D.G., Feakins, S.J., Bindeman, I.N., Mahony, M.E., Pautler, B.G., Reichart, G.-J., Sanborn, P.T., Simpson, M.J. and Weijers, J.W.H. (2016) Multiple water isotope proxy reconstruction of extremely low last glacial temperatures in Eastern Beringia (Western Arctic). *Quaternary Science Reviews* 137, 113-125.

Roden, J.S. and Ehleringer, J.R. (1999) Observations of hydrogen and oxygen isotopes in leaf water confirm the Craig-Gordon model under wide-ranging environmental conditions. *Plant Physiol.* 120, 1165-1174.

Sachse, D., Billault, I., Bowen, G.J., Chikaraishi, Y., Dawson, T.E., Feakins, S.J., Freeman, K.H., Magill, C.R., McInerney, F.A. and Van der Meer, M.T. (2012) Molecular paleohydrology: interpreting the hydrogen-isotopic composition of lipid biomarkers from photosynthesizing organisms. *Annual Review of Earth and Planetary Sciences* 40, 221-249.

Sachse, D., Gleixner, G., Wilkes, H. and Kahmen, A. (2010) Leaf wax n-alkane δD values of field-grown barley reflect leaf water δD values at the time of leaf formation. *Geochim. Cosmochim. Acta* 74, 6741-6750.

Sachse, D., Radke, J. and Gleixner, G. (2004) Hydrogen isotope ratios of recent lacustrine sedimentary n-alkanes record modern climate variability. *Geochim. Cosmochim. Acta* 68, 4877-4889.

Sauer, P.E., Eglinton, T.I., Hayes, J.M., Schimmelmann, A. and Sessions, A.L. (2001) Compound-specific D/H ratios of lipid biomarkers from sediments as a proxy for environmental and climatic conditions. *Geochim. Cosmochim. Acta* 65, 213-222.

Sessions, A.L. (2006) Seasonal changes in D/H fractionation accompanying lipid biosynthesis in *Spartina alterniflora*. *Geochim. Cosmochim. Acta* 70, 2153-2162.

Shanahan, T., Hughen, K., Ampel, L., Sauer, P. and Fornace, K. (2013) Environmental controls on the $^2\text{H}/^1\text{H}$ values of terrestrial leaf waxes in the Eastern Canadian Arctic. *Geochim. Cosmochim. Acta*.

Shaver, G.R., Laundre, J.A., Bret-Harte, M.S., Chapin III, F.S., Mercado-Díaz, J.A., Giblin, A.E., Gough, L., Gould, W.A., Hobbie, S.E. and Kling, G.W. (2014) Terrestrial Ecosystems at Toolik Lake, Alaska. *Alaska's Changing Arctic: Ecological Consequences for Tundra, Streams and Lakes*, Oxford University Press, New York, 90-142.

Sternberg, L.d.S.L. (1988) D/H ratios of environmental water recorded by D/H ratios of plant lipids. *Nature* 333, 59-61.

Sullivan, P.F. and Welker, J.M. (2007) Variation in leaf physiology of *Salix arctica* within and across ecosystems in the High Arctic: test of a dual isotope ($\Delta^{13}\text{C}$ and $\Delta^{18}\text{O}$) conceptual model. *Oecologia* 151, 372-386.

Tape, K.D., Hallinger, M., Welker, J.M. and Ruess, R.W. (2012) Landscape heterogeneity of shrub expansion in Arctic Alaska. *Ecosystems* 15, 711-724.

Thomas, e.K. (2016) A major increase in winter snowfall during the middle Holocene on western Greenland caused by reduced sea ice in Baffin Bay and the Labrador Sea.

Thomas, E.K., McGrane, S., Briner, J.P. and Huang, Y. (2012) Leaf wax $\delta^2\text{H}$ and varve-thickness climate proxies from proglacial lake sediments, Baffin Island, Arctic Canada. *J. Paleolimnol.*, 1-15.

Tipple, B.J., Berke, M.A., Hambach, B., Roden, J.S. and Ehleringer, J.R. (2015) Predicting leaf wax n-alkane $2\text{H}/1\text{H}$ ratios: controlled water source and humidity experiments with hydroponically grown trees confirm predictions of Craig-Gordon model. *Plant, Cell Environ.* 38, 1035-1047.

Toolik Environmental Data Center Team (2016) Plant phenological monitoring program at Toolik, Alaska. Toolik Field Station, Institute of Arctic Biology, University of Alaska Fairbanks.

Vachon, R., Welker, J., White, J. and Vaughn, B. (2010) Monthly precipitation isoscapes ($\delta^{18}\text{O}$) of the United States: Connections with surface temperatures, moisture source conditions, and air mass trajectories. *Journal of Geophysical Research: Atmospheres* 115.

Walker, D. and Walker, M. (1996) Terrain and vegetation of the Imnavait Creek watershed, Landscape Function and Disturbance in Arctic Tundra. Springer, pp. 73-108.

Walker, D.A. and Maier, H.A. (2008) Vegetation in the vicinity of the Toolik Field Station, Alaska. University of Alaska. Institute of Arctic Biology.

Walker, M.D., Walker, D.A. and Auerbach, N.A. (1994) Plant communities of a tussock tundra landscape in the Brooks Range Foothills, Alaska. *Journal of Vegetation Science* 5, 843-866.

Ward, C.P. and Cory, R.M. (2015) Chemical composition of dissolved organic matter draining permafrost soils. *Geochim. Cosmochim. Acta* 167, 63-79.

Welker, J. (2000) Isotopic ($\delta^{18}\text{O}$) characteristics of weekly precipitation collected across the USA: an initial analysis with application to water source studies. *Hydrological Processes* 14, 1449-1464.

Welker, J.M. (2012) ENSO effects on $\delta^{18}\text{O}$, $\delta^2\text{H}$ and d-excess values in precipitation across the US using a high-density, long-term network (USNIP). *Rapid Commun. Mass Spectrom.* 26, 1893-1898.

Welker, J.M., Rayback, S. and Henry, G.H. (2005) Arctic and North Atlantic Oscillation phase changes are recorded in the isotopes ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of *Cassiope tetragona* plants. *Global Change Biol.* 11, 997-1002.

White, J.W., Cook, E.R. and Lawrence, J.R. (1985) The DH ratios of sap in trees: Implications for water sources and tree ring DH ratios. *Geochim. Cosmochim. Acta* 49, 237-246.

Wilkie, K., Chaplignin, B., Meyer, H., Burns, S., Petsch, S. and Brigham-Grette, J. (2012) Modern isotope hydrology and controls on δD of plant leaf waxes at Lake El'gygytgyn, NE Russia. *Climate of the Past Discussions* 8, 3719-3764.

Woo, M.-k. (2012) *Permafrost hydrology*. Springer Science & Business Media.

Yang, H. and Huang, Y. (2003) Preservation of lipid hydrogen isotope ratios in Miocene lacustrine sediments and plant fossils at Clarkia, northern Idaho, USA. *Org. Geochem.* 34, 413-423.

Yang, H., Liu, W., Leng, Q., Hren, M.T. and Pagani, M. (2011) Variation in n-alkane δD values from terrestrial plants at high latitude: Implications for paleoclimate reconstruction. *Org. Geochem.* 42, 283-288.

Yang, H., Pagani, M., Briggs, D.E., Equiza, M., Jagels, R., Leng, Q. and LePage, B.A. (2009) Carbon and hydrogen isotope fractionation under continuous light: implications for paleoenvironmental interpretations of the High Arctic during Paleogene warming. *Oecologia* 160, 461-470.

Young, J., Olga, K. and Welker, J.M. (In press) Thawing seasonal ground ice: an important water source for boreal forest plants in interior Alaska. *Ecohydrology*.

2.9 Figures and Tables

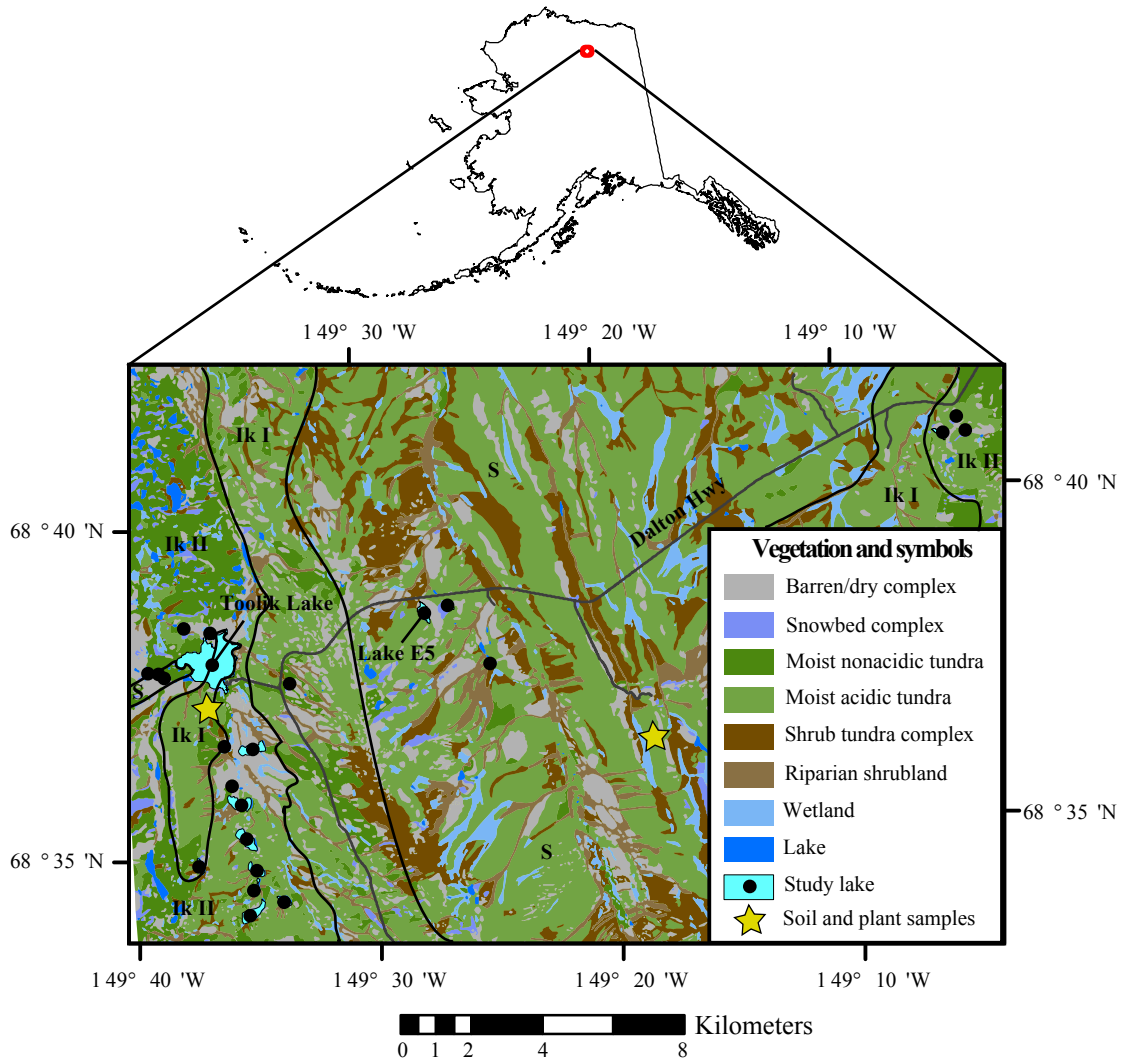


Figure 2.1 Map of study lakes (black) and plant sampling locations (yellow stars) used in this study. The basemap shows the diversity of plant communities in the study area and a generalization of the glacial ages referenced in the text (<http://www.arcticatlas.org/>). The glacial geology abbreviations are: S: Saganavirktok drift and outwash (> 125 ka), Ik-I: Itkillik I drift and outwash (50-125 ka), Ik-II: Itkillik II drift and outwash (11-25 ka). Sediment traps were deployed in Lake E5 and Toolik Lake, designated on the map.

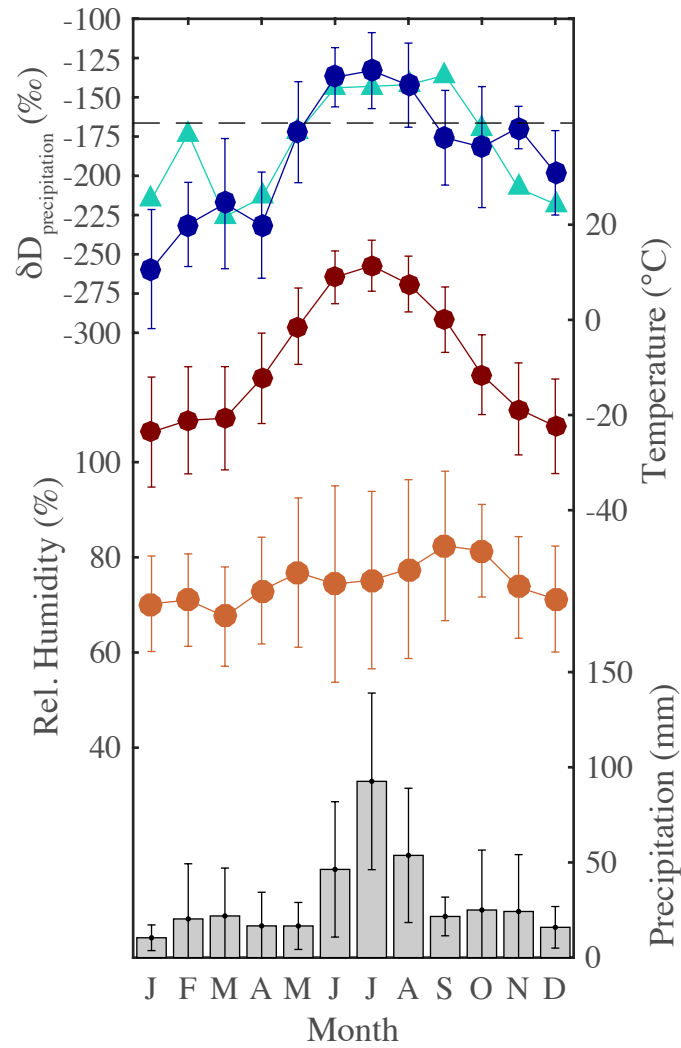


Figure 2.2 Climatology and $\delta D_{\text{precipitation}}$ at Toolik Lake including monthly precipitation isotopes (blue – precipitation event measurements; green – OIPC estimate; the horizontal dashed line is the weighted mean annual $\delta D_{\text{precipitation}}$ value of -166 ‰), air temperature (red), relative humidity (orange), and precipitation (gray bars) (source: Toolik Environmental Data Center; accessed Nov. 2015).

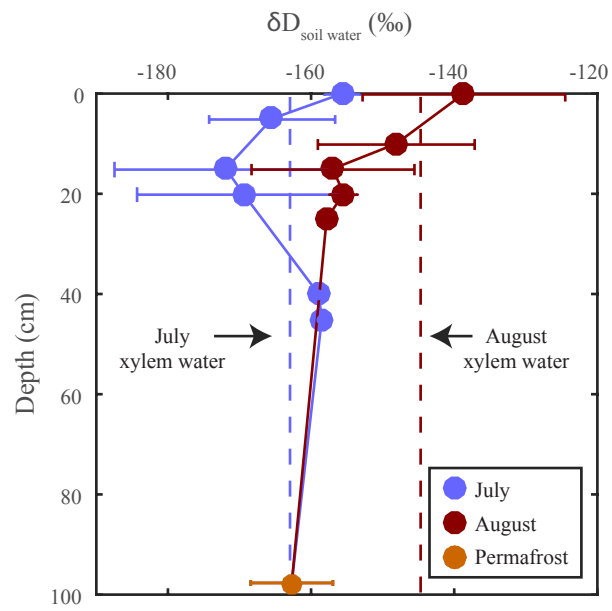


Figure 2.3 δD_{soil} water profiles from July and August. The deep permafrost was sampled in July and is assumed to be constant throughout the year. Error bars are 1s standard deviation from multiple samples; no error bar indicates $n=1$. Dashed vertical lines are plant xylem waters (*E. vaginatum* and *B. nana* combined) sampled at the same time as soil water.

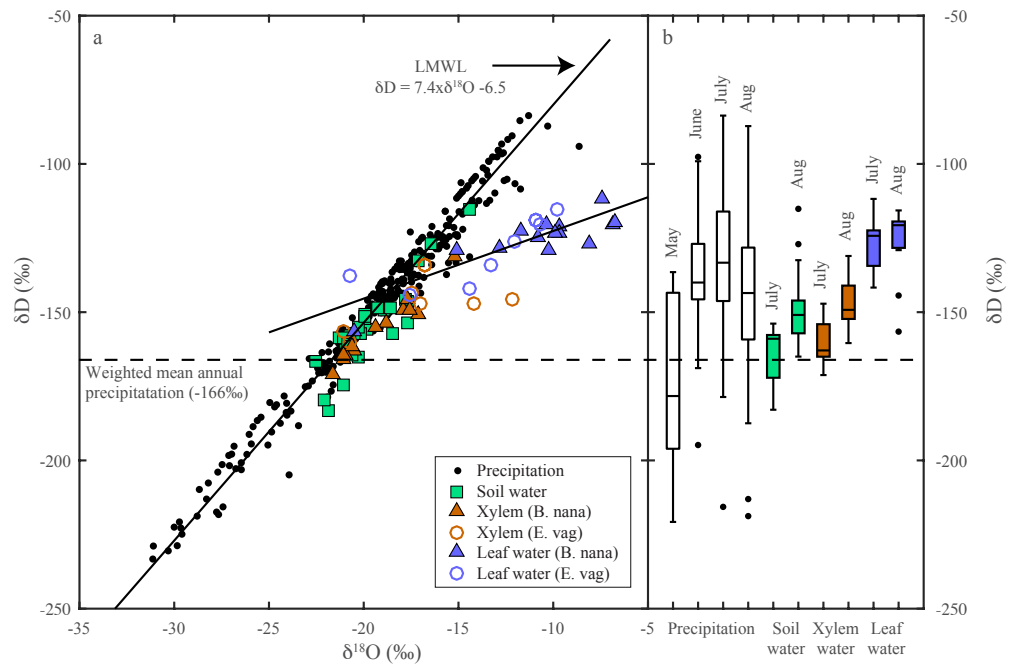


Figure 2.4 Panel a: The relationship between δD and $\delta^{18}O$ at Toolik Lake for precipitation (black points), soil water (green squares), plant xylem water of *B. nana* (red triangles) and *E. vaginatum* (red circles), and leaf water of *B. nana* (blue triangles) and *E. vaginatum* (blue circles). Nine precipitation isotope measurements were more depleted than shown in the figure, reaching δD values as low as -316 ‰, but are truncated for clarity. These lower values do not diverge systematically from the LMWL. Panel b: Summary figure of monthly $\delta D_{\text{precipitation}}$, δD_{soil} , δD_{xylem} , and δD_{leaf} . Xylem and leaf water plots combine data from both study species. Boxes represent median, 25th and 75th percentiles, and whiskers extend to most extreme non-outliers.

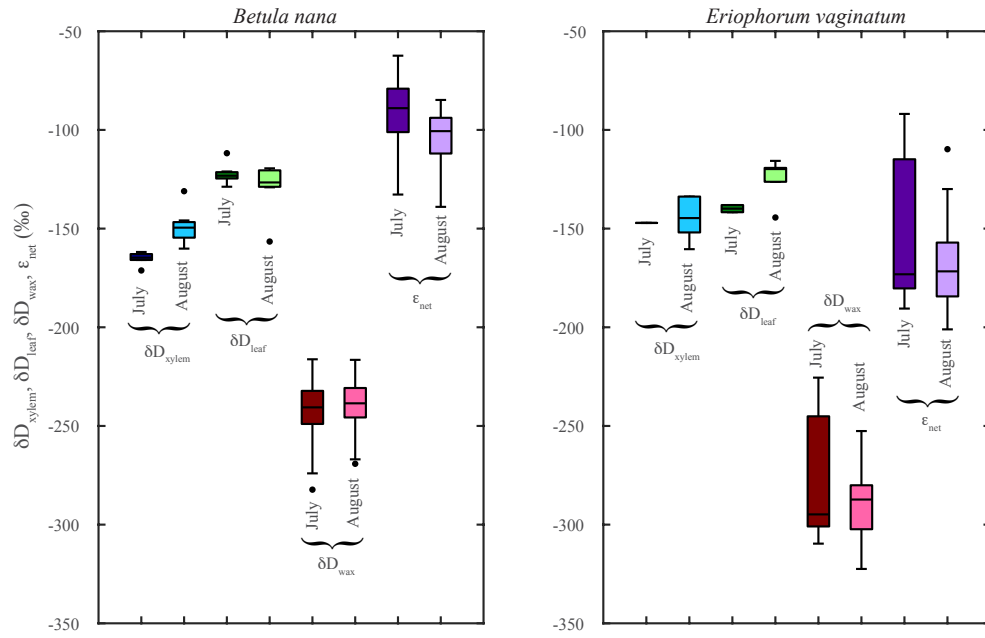


Figure 2.5 Hydrogen isotope ratios of plant water and leaf waxes, and the net apparent fractionation between xylem water and leaf waxes for *Betula nana* and *Eriophorum vaginatum* in July and August. The month effect is not significant for values of ϵ_{net} , but is significant for xylem water in *Betula nana* and leaf water in *Eriophorum vaginatum*.

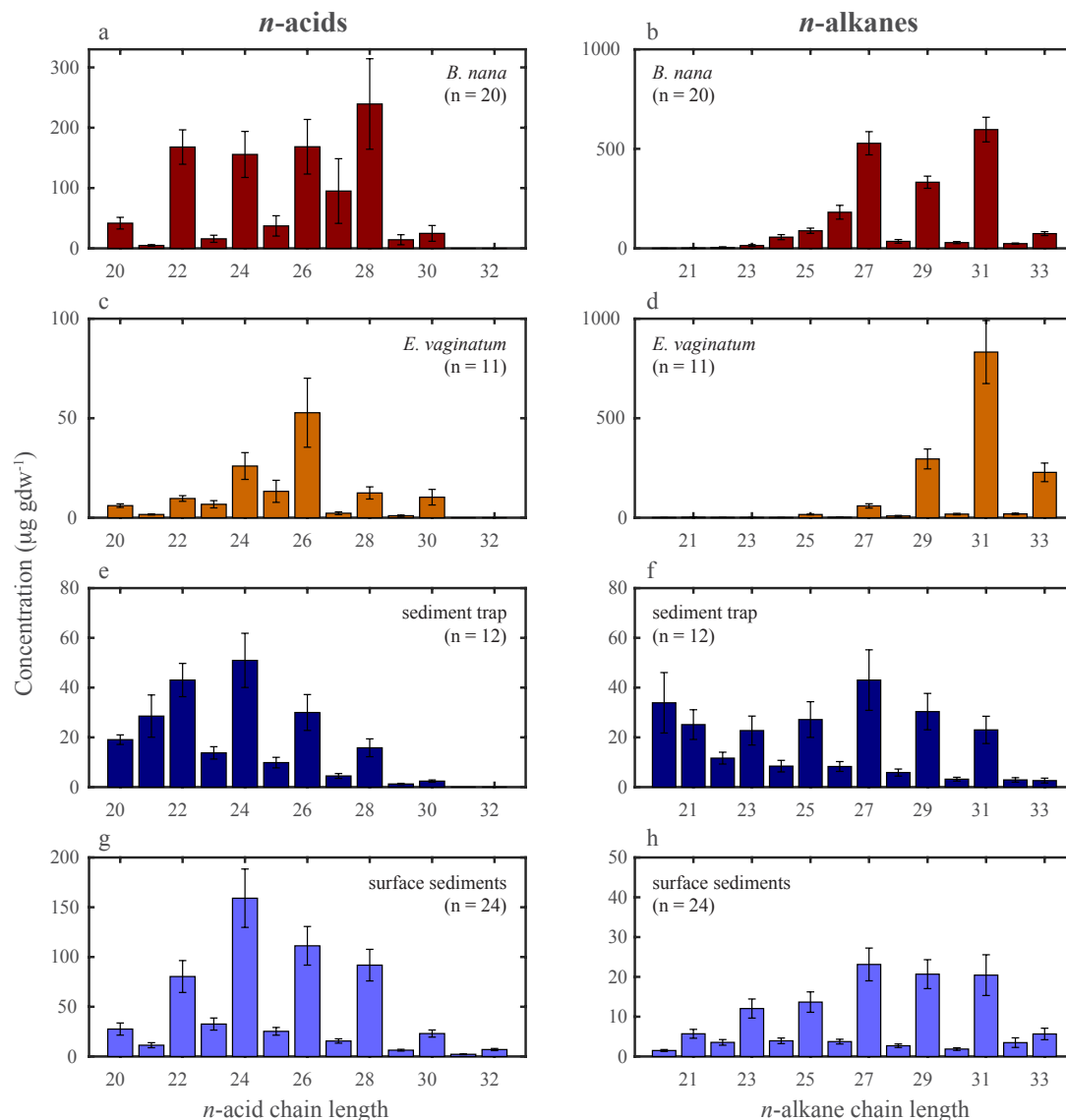


Figure 2.6 Concentration of long chain *n*-acids (C₂₀-C₃₂) and *n*-alkanes (C₂₀-C₃₃) in live specimens of *Betula nana* (panels a and b), *Eriophorum vaginatum* (panels c and d), sediment trap samples in Lake E5 (panels e and f), and surface sediments from lakes around Toolik Field Station (panels g and h). For plant samples, concentrations are given relative to grams of dry leaf material, and for sediments it is relative to grams of dry sediment. Error bars represent standard error of the mean.

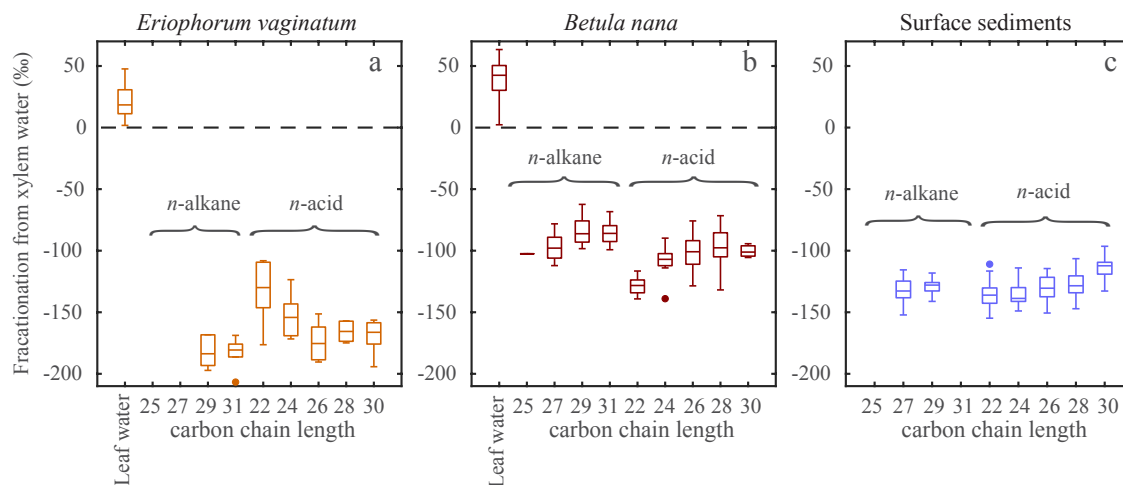


Figure 2.7 Net apparent D/H fractionation (ϵ_{net}) for a) *Eriophorum vaginatum* (C3 monocot; $n = 8$), b) *Betula nana* (C3 shrub; $n = 12$), and c) lake surface sediments ($n = 24$). For plant samples, fractionation is calculated relative to paired xylem water measurements, while for surface sediments, source water is set to the average of all xylem water measurements (-153‰). Boxes represent median, 25th and 75th percentiles, and whiskers extend to most extreme non-outliers.

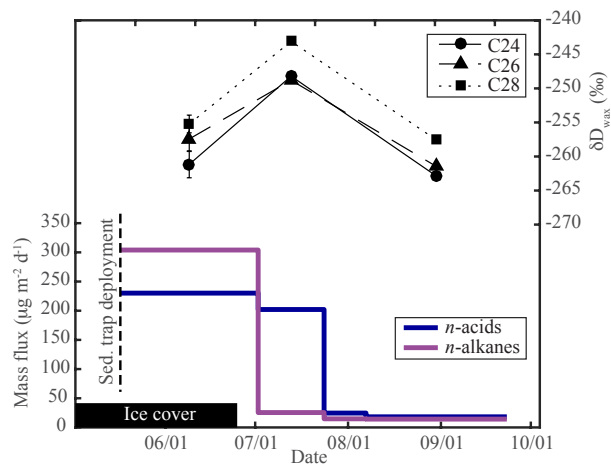


Figure 2.8 *n*-acid and *n*-alkane fluxes and δD_{wax} , measured in sediment traps deployed in Lake E5 in 2014. Each point represents an average of 14-46 days of sediment collection. D/H ratios were measured on *n*-acids only, and are not available for the third collection because of insufficient sample mass. δD_{wax} error bars are standard deviation of 3 sediment traps, but traps were composited prior to analysis for the later sampling dates.

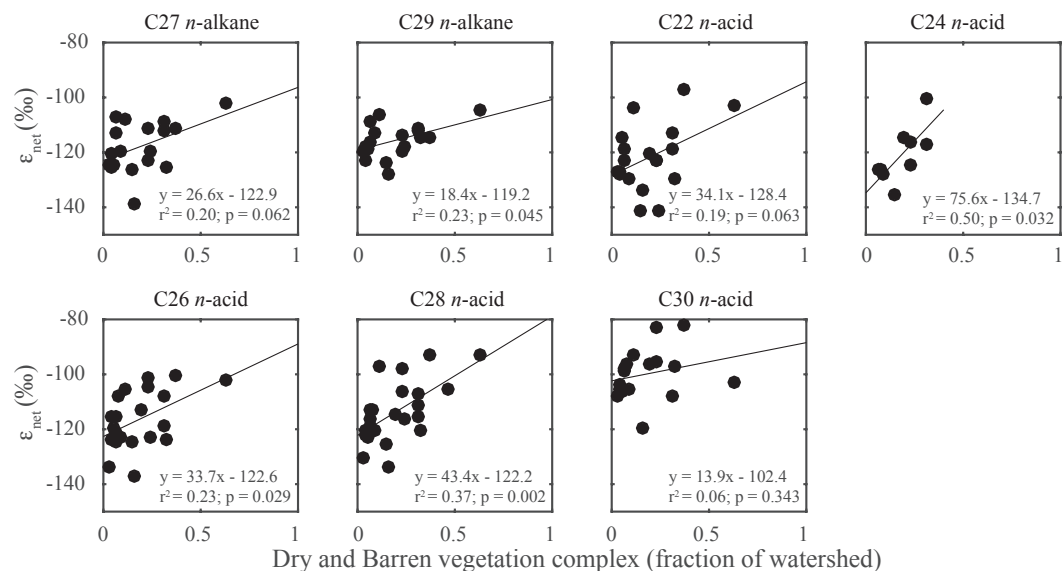


Figure 2.9 Relationship between surface sediment ϵ_{net} and the relative area of each watershed comprised of dry or barren tundra (Alaska Geobotany Center, <http://www.arcticatlas.org/>). Dry and barren tundra are dominated by shrubs and forbs and serve to represent the proportion of dicots contributing waxes to lakes (Walker et al., 1994). Some samples contain insufficient lipids for isotopic analysis and so fewer than 24 data points are shown.

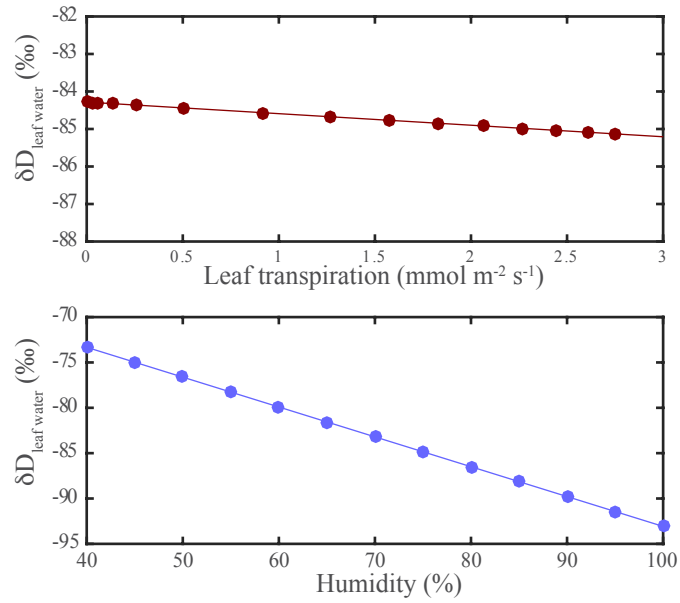


Figure 2.10 Modeled leaf water isotopes under varying a) transpiration and b) humidity conditions. The model used in this sensitivity analysis was developed by Tipple et al. (2015) and uses JJA meteorological inputs from Toolik Lake Field Station (Toolik Environmental Data Center Team, 2016b), an initial source water isotope value of -153‰ (this study), and atmospheric vapor δD measured at Toolik Lake (Klein et al., 2015).

	<i>n</i> -acids					<i>n</i> -alkanes			
	C ₂₂	C ₂₄	C ₂₆	C ₂₈	C ₃₀	C ₂₅	C ₂₇	C ₂₉	C ₃₁
<i>Betula nana</i>									
$\delta D_{\text{wax}} (1\sigma)$	-267 (7)	-248 (7)	-241 (5)	-238 (7)	-244 (11)	-244 (7)	-238 (6)	-227 (6)	-231 (6)
$\epsilon_{\text{net}} (1\sigma)$	-128 (8)	-108 (12)	-101 (14)	-97 (16)	-100 (6)	-102 (-)	-97 (10)	-83 (12)	-85 (10)
<i>Eriophorum vaginatum</i>									
$\delta D_{\text{wax}} (1\sigma)$	-267 (20)	-272 (21)	-282 (27)	-278 (13)	-296 (12)	-	-	-303 (8)	-308 (8)
$\epsilon_{\text{net}} (1\sigma)$	-137 (28)	-148 (27)	-164 (36)	-160 (20)	-172 (12)	-	-	-183 (9)	-187 (8)

Table 2.1 δD_{wax} and ϵ_{app} of leaf waxes on living plants. Fractionation is calculated using paired xylem water measurements for each set of leaf measurements. Dashes mean not measured.

Lake Name	Lat.	Long.	<i>n</i> -acids					<i>n</i> -alkanes	
			C22	C24	C26	C28	C30	C27	C29
E1	68.626	-149.554	-260	-	-265	-262	-256	-259	-259
E5	68.643	-149.458	-268	-263	-253	-255	-246	-258	-261
E6	68.644	-149.439	-268	-270	-250	-248	-235	-269	-266
FOG1	68.684	-149.079	-268	-	-267	-263	-248	-255	-257
FOG2	68.679	-149.089	-265	-264	-	-259	-	-257	-259
FOG4	68.680	-149.072	-284	-	-269	-263	-	-266	-264
GALBRAITH	68.460	-149.420	-267	-262	-260	-262	-246	-	-
I1	68.569	-149.588	-279	-277	-257	-256	-243	-261	-260
I2	68.571	-149.566	-	-271	-256	-260	-246	-	-
I3	68.575	-149.581	-272	-	-278	-275	-256	-270	-265
I4	68.580	-149.583	-272	-	-269	-268	-254	-266	-264
I5	68.587	-149.590	-272	-	-262	-266	-253	-271	-268
I6	68.597	-149.593	-262	-	-266	-268	-255	-270	-265
I6HW	68.581	-149.619	-265	-271	-262	-260	-248	-260	-263
I7	68.601	-149.593	-284	-279	-270	-270	-	-271	-269
I8	68.610	-149.582	-274	-273	-268	-267	-254	-265	-260
ISWAMP	68.611	-149.597	-278	-	-281	-278	-265	-282	-273
N1	68.640	-149.604	-253	-	-254	-247	-243	-256	-255
N2	68.641	-149.622	-252	-	-251	-244	-251	-251	-253
S11	68.631	-149.648	-	-250	-256	-255	-	-	-
S6	68.630	-149.639	-247	-	-250	-243	-235	-259	-261
S7	68.630	-149.643	-274	-	-269	-267	-247	-270	-261
TLK	68.632	-149.602	-	-	-	-254	-	-	-
UCL	68.629	-149.413	-	-	-270	-265	-	-	-
Average δD_{wax} (1σ)			-268 (10)	-268 (9)	-263 (9)	-261 (9)	-249 (8)	-264 (8)	-262 (5)
Average ϵ_{net} (1σ)			-136 (12)	-136 (10)	-130 (10)	-127 (11)	-113 (9)	-131 (9)	-129 (6)

Table 2.2 δD_{wax} and ϵ_{app} of lake surface sediments. Fractionation is calculated using a source water value of -153‰ based on xylem water observations for the two plant species. Dashes mean not measured.

2.10 Supplemental Material

<i>n</i> -acids			<i>n</i> -alkanes		
C22	standards	1.72			
	Samples	1.77			
C24	Standards	-	C25	Standards	1.60
	Samples	2.06		Samples	1.73
C26	Standards	1.03	C27	Standards	1.17
	Samples	1.55		Samples	2.11
C28	Standards	1.71	C29	Standards	2.42
	Samples	2.33		Samples	3.00
C30	Standards	-	C31	Standards	-
	Samples	1.08		Samples	1.33

Table 2.S1: Summary of analytical uncertainties (pooled standard deviation as described in the text) in δD_{wax} measurements.

	<i>n</i> -acid					<i>n</i> -alkane	
	C22	C24	C26	C28	C30	C27	C29
Barren Complex	-165.0				-85.2		
Dry tundra complex	49.5	93.3	42.6	50.3		21.1	14.3
Snowbed complex					39.3		
moist non-acidic complex		64.0	-29.5	-33.1			
MAT complex							
Shrub tundra complex	-73.5	-105.6			-111.8	-65.5	-45.8
Riparian shrubland complex	220.9	116.1					
wetland complex							
Intercept	-135.3	-143.1	-120.3	-119.4	-96.9	-119.2	-116.5
AIC	88.5	29.1	94.8	99.5	70.9	76.4	59.4
r-squared	0.542	0.910	0.352	0.506	0.482	0.390	0.439
p	0.020	0.023	0.020	0.001	0.031	0.025	0.013

Table 2.S2. Multiple regression coefficients describing the relationship between relative abundance of various vegetation classes and δ_{app} across lake watersheds.

CHAPTER THREE

Arctic leaf wax D/H ratios are unaffected by continuous light in greenhouse experiments

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3.1 Abstract

Quantitative reconstructions of climate using leaf wax D/H ratios (δD_{wax}) require correcting for vegetation effects on the net apparent fractionation (ϵ_{app}) between water and waxes. Previous work on Arctic leaf waxes has suggested that daytime length has a strong impact on δD_{wax} and ϵ_{app} , though this finding remains controversial. We tested the effect of day length on ϵ_{app} in greenhouse experiments in order to test whether Arctic plants systematically fractionate hydrogen isotopes differently under Arctic environmental conditions. Two of the most common plants of the Arctic tundra were grown under conditions of continuous light, simulating Arctic summer, and diurnal light to simulate mid-latitude summer. We found that the ϵ_{app} of *Eriophorum vaginatum* (tussock cottongrass) was about 60‰ more negative than that of *Betula nana* (dwarf birch), consistent with field studies of the same species. No difference in δD_{wax} was observed between light treatments, suggesting that day length does not affect leaf wax D/H ratios of Arctic plants. There is, however, a species*light interaction effect, indicating that physiological (i.e. stomatal conductance) adaptation to differing light regimes varies between plant types. We modeled the sensitivity of the isotopic composition of leaf waters to variations in stomatal conductance for a range of leaf morphologies to assess the potential impact of light exposure. The model shows that the δD_{lw} varies by up to 40‰ under our greenhouse conditions over a range of reasonable stomatal conductance, but cannot explain the light-species interaction, possibly because the model does not capture non-light controls on conductance, such as water availability. Differences in the diurnal patterns of transpiration rate among Arctic plants further call into question if the light cycle could be a unifying control on δD_{wax} at high latitudes.

These greenhouse results suggest that ϵ_{app} is not consistently affected by day length and that small values of ϵ_{app} from high latitudes reported previously do not result from the Arctic light cycle but rather other, more geographically limited environmental conditions.

Keywords Leaf waxes, hydrogen isotope ratios, Continuous Light, Greenhouse Experiment, Leaf physiology, Isotope fractionation

3.2 Introduction

Hydrogen isotope ratios of terrestrial leaf waxes (δD_{wax}) are a powerful paleoclimate proxy, as waxes are abundant in sedimentary archives, geochemically stable, and δD_{wax} principally reflects changes in the isotope composition of rainfall (δD_{precip}) (Huang et al., 2004; Sachse et al., 2004; Hou et al., 2008; Garcin et al., 2012). Yet, δD_{wax} not only depends on the isotopic composition of source water, but also on the net apparent fractionation (ϵ_{app}) between meteoric water and waxes. Apparent fractionation can vary due to changes in the degree of evaporative enrichment of leaf waters (δD_{lw}) and different species-specific biosynthetic isotope fractionations (Roden and Ehleringer, 1999; Polissar and Freeman, 2010; Gao et al., 2014a). As ϵ_{app} is sensitive to environmental factors and vegetation types, variations in ϵ_{app} must be considered in paleoclimate reconstruction, and can provide additional insights in the interpretation of δD_{wax} (Polissar and Freeman, 2010; Feakins, 2013; Konecky et al., 2016).

To this end, there are numerous surveys of δD_{wax} in modern vegetation and sediments in tropical and temperate regions in order to quantify ϵ_{app} . These studies have generally found that ϵ_{app} of sedimentary waxes ranges from -100 to -150‰ (Garcin et al.,

2012; Sachse et al., 2012), with ϵ_{app} of dicotyledonous plants averaging -100 and that of monocots averaging -140‰ or less (Gao et al., 2014a; Liu et al., 2016). Reports from the Arctic, however, suggest much smaller ϵ_{app} . Waxes preserved in lake surface sediments from Baffin Island (Shanahan et al., 2013) and from western Canada (Porter et al., 2016) indicate ϵ_{app} of -60‰. Similarly, some Arctic plants from arid regions such as Baffin Island and Greenland appear to also exhibit less fractionation (Yang et al., 2011). Although these studies have led to suggestions of widespread low apparent fractionation values in the Arctic, all of these studies relied on modeled precipitation isotopic ratios for calculating fractionation factors, which, if incorrect, could bias ϵ_{app} . Indeed, a recent global synthesis of plant leaf wax isotopes shows no such latitude effect on ϵ_{app} (Liu et al., 2016). Furthermore, studies of lake sediments in Siberia (Wilkie et al., 2012), Alaska (Daniels et al., in revision), and northern Europe (Sachse et al., 2004) have demonstrated ϵ_{app} values that are similar to those of the mid-latitudes. Thus, it is uncertain if and why Arctic plant D/H fractionation differs from mid- and low-latitude plants, and, if so, what values of ϵ_{app} are appropriate for estimating ancient δD_{precip} based on measurements of δD_{wax} .

The principal hypothesis to explain small ϵ_{app} values in the Arctic posits that continuous daylight leads to increased/prolonged transpiration, and thereby enhanced evaporative D-enrichment of leaf water (Yang et al., 2009; Yang et al., 2011). A greenhouse experiment testing this hypothesis found an ϵ_{app} difference between continuous-light and diurnal-light treatments (Yang et al., 2009). The species studied in that experiment, *Taxodium sp.*, *Metasequoia sp.*, and *Larix sp.*, however, have not been found in the Arctic since the Eocene. Since transpiration and isotopic responses to light

may differ between species, it remains uncertain whether the light environment is a viable explanation for low ϵ_{app} values for modern Arctic plants. Additionally, the experimental conditions used may not be an appropriate for testing the effect of light duration on δD_{wax} . In their greenhouse experiment, the daily variation in temperature and humidity were substantially greater in the diurnal light treatment than in the continuous light treatment (Equiza et al., 2006a); it is therefore difficult to attribute the δD_{wax} response they observed to light alone. Moreover, in maintaining saturated soil conditions, Yang et al. (2009) did not consider the potential for moisture availability as a second factor influencing leaf physiological response to light (Vourlitis and Oechel, 1999). An analogous experimental growth study using modern tundra plants could constrain the sensitivity of the modern tundra vegetation to a 24-hour light effect.

Theoretically, the diurnal light cycle could affect δD_{lw} and δD_{wax} by two mechanisms. First, plants control their stomatal opening and transpiration rates partly in response to available light. Modeling studies of δD_{lw} illustrate that it is sensitive to transpiration rate (Roden and Ehleringer, 1999; Tipple et al., 2015), although in these studies, humidity was the dominant control on δD_{lw} and light was not explicitly tested. Moreover, plants have a variety of stomatal conductance strategies and it is not immediately obvious whether transpiration by Arctic plants is in fact higher or lower compared to the same plants grown in a diurnal light environment. This question is particularly challenging considering a diurnal light pattern exists even in mid-summer in the Arctic. In Alaskan field studies, Gebauer et al. (1998) observed a day/night photon flux difference in mid-summer of 800 to 1500 $\mu\text{mol m}^{-2} \text{s}^{-1}$. Diurnal patterns in photosynthesis and stomatal conductance were not apparently tied to light availability,

but varied by species, leaf temperature and vapor pressure deficits (Gebauer et al., 1998). Thus Arctic species may vary their stomatal conductance to limit water loss in a 24-hour light environment. Nitrogen limitation (Shaver and Chapin, 1980) combined with photosynthetic downregulation under continuous light (Van Gestel et al., 2005; Equiza et al., 2006b) may further limit the effect of continuous light on δD_{lw} .

Secondly, and relatedly, the water pool from which waxes are synthesized, which is found in leaf mesophyll cells, is a mixture of unevaporated xylem water flowing from the leaf meristem and evaporated leaf water diffusing into the leaf from the leaf surface (Barbour et al., 2004). The ratio of these two sources is described by the pecclet effect, and varies as a function of leaf morphology and transpiration rates. The pecclet effect describes steady-state leaf water dynamics, as might be expected in a continuous light environment, but it remains unexplored how rapid changes in light, such as those occurring over a diurnal cycle, and thereby changing transpiration rates, impacts the relative contribution of evaporated and unevaporated water to the mesophyll cells.

In summary, empirical results from Arctic field studies are inconclusive as to whether the Arctic light environment affects the D/H composition of leaf waxes. Previous greenhouse studies support the importance of 24-hour light to δD_{wax} , but used plants that do not grown in the Arctic and greenhouse conditions that differ substantially from Arctic field conditions and cannot attribute ϵ_{app} differences to a single variable. Recent field studies suggesting that Arctic plants have ϵ_{app} values similar to their temperate counterparts argue against a strong effect of the light cycle in the Arctic. There remains a need to model transpiration and leaf water enrichment under varying light conditions to examine the mechanisms behind a potential 24-hour daylight effect of leaf

water and wax isotopes. Here we present new empirical results from a growth chamber experiment using Arctic plants to test the effects of 24-hour sunlight on leaf wax isotopes, as well as results from models examining how evaporative enrichment and leaf water circulation could influence δD_{wax} and ϵ_{app} under different light environments.

3.3 Methods

3.3.1 Growth experiment

To assess the effect of the daily light cycle on the isotopic composition of leaf waxes, we performed a controlled growth chamber experiment at Brown University. We examined the common arctic and alpine tundra plants, the graminoid, *Eriophorum vaginatum* var. *spissum* (common name: tussock cottongrass) and the deciduous shrub, *Betula nana* (common name: dwarf birch). These two species together represent approximately 40% of above ground biomass in tussock tundra of Northern Alaska (Chapin III et al., 1995), and are important components of tundra ecosystems across northern Eurasia and Canada (Walker et al., 2005). The plants were grown for three months in either continuous light or diurnal light. At the end of this growth period, we compared leaf wax hydrogen isotopes between the two treatments to determine the magnitude of the continuous light effect on δD_{wax} .

Sixteen specimens of *E. vaginatum* and ten specimens of *B. nana* were obtained in individual pots from the Welker's Grove Nursery in Connecticut. Plants were divided equally into two treatments, one with a diurnal light cycle (DL), and one with continuous light (CL) (Figure 3.1). The light levels were chosen to mimic natural patterns of light in temperate and high-latitude environments, and a PAR sensor (photosynthetically active

radiation) was used to measure light levels at hourly intervals. PAR varied between 0 and 350 $\mu\text{moles photons m}^{-2} \text{ s}^{-1}$ in the DL chamber and between 215 and 250 $\mu\text{moles photons m}^{-2} \text{ s}^{-1}$ in the CL chamber. Temperatures varied between 10 and 15 °C on a diel cycle to mimic Arctic conditions. Plants were grown in loamy peat and were watered on average every 5 days during the experiment, to minimize water stress while keeping the soil from becoming anoxic, using a constant-isotope water source (δD and $\delta^{18}\text{O}$ of the irrigation water was $-39.0 \pm 0.2 \text{ ‰}$ and $-6.1 \pm 0.04 \text{ ‰}$ relative to VSMOW). In the study of Yang et al. (2009), plants were provided unlimited water from a drip irrigation system (Equiza et al., 2006a), so our watering protocol may provide a more realistic natural simulation than their greenhouse experiment. To ensure we measured waxes produced only during the growth period, we trimmed the *E. vaginatum* specimens to approximately 2 cm length at the onset of the experiment. For *B. Nana*, we pruned branches and leaves, and marked remaining leaves so that they could be avoided in later harvesting.

After 3 months of growth, new *E. vaginatum* growth (entire tillers) and new *B. Nana* leaves were harvested, composited for each specimen, and freeze-dried for isotopic analysis. Leaf waxes were extracted and purified using standard procedures (Gao et al., 2014). The *n*-acids were derivatized to fatty acid methyl esters (FAMES) using acidified methanol of known isotopic composition. The molecular composition of straight chain *n*-acids and *n*-alkanes were measured using a gas chromatograph equipped with a flame ionization detector (GC-FID). Hydrogen isotope ratios were determined using a Finnigan Delta Plus isotope-ratio mass spectrometer (IRMS) with the same GC configuration as in GC-FID analysis. Samples were run in triplicate and an external standard containing either FAMES or alkanes of known isotopic composition was run every 6 injections. The

δD values of FAMES were mathematically corrected for the methyl groups added during derivatization.

Statistical comparisons were made using a 2-way ANOVA in R, with species and light treatment as independent factors. Statistical analyses were conducted independently for each lipid homologue. Data met the assumptions of homoscedasticity and normality and no data required transformations. Where ANOVA found statistical differences at the $p=0.05$ level, pairwise comparisons were performed using a Student's t-test using bonferonni's correction for multiple comparisons.

3.3.2 Model sensitivity test

We also perform a model sensitivity test to evaluate the potential effect of 24-hour daylight on the δD of leaf water. The model calculates steady state values of δD_{lw} , and is applicable for understanding the potential effect of diurnal light cycles on δD_{wax} , since estimates of daytime and nighttime stomatal conductances are available in literature. We adapt a commonly used leaf water $\delta^{18}O$ model to predict δD_{lw} under various leaf morphologic and physiologic characteristics (Roden and Ehleringer, 1999; Barbour et al., 2004; Tipple et al., 2015). The basis of the model is a modified version of the Craig-Gordon evaporation model (Flanagan et al., 1991) which accounts for kinetic fractionation through both stomatal pores and across the leaf boundary layer. The model approximates the enrichment of evaporated water over source water (Δ_e) using equations 1-3 (Barbour et al., 2004):

$$1) \Delta_e = \varepsilon^* + \varepsilon_k + (\Delta_v - \varepsilon_k) \frac{e_a}{e_i}$$

$$2) \varepsilon^* = \exp\left(\frac{24844}{T^2} - \frac{76.248}{T} 0.052612\right) - 1$$

$$3) \varepsilon_k = \frac{25r_s + 17r_b}{r_s + r_b}$$

where ε^* is the equilibrium fractionation between HD¹⁶O and H₂¹⁶O, ε_k is the diffusive fractionation through the leaf boundary layer, Δ_v is the isotopic difference between external water vapor and source water, and e_a and e_i are the external and internal vapor pressures, respectively. We modified the values of these parameters from Barbour et al. (2004) to describe the fractionation and diffusivities of HD¹⁶O rather than H₂¹⁸O. ε^* is described for HD¹⁶O/H₂¹⁶O by Majoube (1971) as a function of temperature (T, in kelvin). ε_k comprises fractionation through the stomata (ε_s) and through the boundary layer (ε_b). ε_s has an H/D fractionation of 1.025 while ε_b is calculated as ε_s to the two-thirds power, or 1.017.

The isotopic composition of mesophyll water, which is relevant to biosynthesized material, is a mixture of evaporated leaf water and unevaporated leaf water. The relative fraction of each component can be estimated empirically; however, advances in the understanding of water movement through leaves indicates that a peclet-based model of the relative contribution of each pool can improve estimates of leaf water $\delta^{18}\text{O}$ and leaf cellulose $\delta^{18}\text{O}$ (Barbour et al., 2004). The peclet number describes the ratio of advected xylem water to evaporated water diffused from the leaf surface to the site of biosynthesis, and is described by the equation,

$$4) \wp = \frac{L \cdot E}{C \cdot D}$$

where L is the effective path length (m), E is the rate of transpiration ($\text{mmol m}^{-2} \text{s}^{-1}$), C is the molar density of water ($55.6 \times 10^3 \text{ mol m}^{-3}$), and D is the diffusivity of DH^{16}O in water. D is set to $1.78 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ (Mills, 1973), a slight decrease compared to the parameter for $\delta^{18}\text{O}$ ($3.4 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$). The resulting offset (Δ_{lw}) between the isotopic composition of the evaporated water at the leaf surface and the bulk leaf water is thus described as,

$$5) \Delta_{\text{lw}} = \frac{\Delta_e(1 - e^{-\wp})}{\wp}$$

We use this model to explore how leaf physiology (described by L) and environmental conditions (relative humidity) influence the sensitivity of δD_{lw} to different illumination regimes. In this exercise, stomatal conductance serves as a proxy for illumination conditions, as this is the main mechanism connecting light cycles to δD_{wax} (Yang et al., 2009). We model pecelet number and δD_{lw} as a function of stomatal conductance, effective path length (L), and relative humidity (rH).

3.4 Results

3.4.1 Greenhouse experiment

We observed production of new foliar biomass over the three-month growth period in both study species and treatments. The cut *E. vaginatum* grew to approximately 20 cm in length. *B. Nana* showed less growth, but new leaves were nonetheless apparent

and were targeted for isotope sampling. No quantitative information on growth is available.

For both species, *n*-acids show a strong even over odd predominance for *n*-acids, and the opposite for *n*-alkanes (Figure 3.2; Table 3.1). *B. Nana* has a higher concentration of waxes, except for the C₃₀ and C₃₂ *n*-acid homologues, for which *E. vaginatum* has more. Both species also produce a small amount of short-chain (C₁₆ and C₁₈) *n*-acids, but no corresponding short-chain *n*-alkanes are evident. The average chain length (ACL) was determined for the C₂₀-C₃₂ *n*-acids and C₂₁-C₃₂ *n*-alkanes. ACL for BN is 25.9 ± 0.4 for *n*-acids and 28.8 ± 0.4 for *n*-alkanes. ACL for *E. vaginatum* is 26.5 ± 0.5 for *n*-acids and 28.5 ± 0.2 for *n*-alkanes. No difference is observed in the wax distributions of either plant in response to light treatments.

δD_{wax} ranges from -207‰ to -135‰ across all species, treatments and leaf wax homologues. Pooled standard deviation of replicate standards and samples averages 2.6‰ across all homologues (Table 3.2). After correcting for an irrigation water δD value of -39‰, ϵ_{app} varies from -100 to -176 (Figure 3.3, Table 3.3). There is no effect of light treatment on δD_{wax} for any leaf wax homologue (Two-way ANOVA results in Table 3.4). A strong species effect is apparent, however, with *E. vaginatum* waxes being more depleted than *B. Nana* for every homologue (Table 3.4). Interestingly, we observe a light-species interaction effect for most waxes ($p < 0.05$ for all homologues except C₂₃ *n*-alkane and C₂₄ *n*-acid), whereby waxes in the CL chambers are slightly (5-11 ‰) more D-enriched than the DL treatment for *E. vaginatum*, but CL waxes are slightly (3-13 ‰) more D-depleted for *B. Nana*.

3.4.2 Leaf water model sensitivity analysis

The species*light interaction effect on δD_{wax} observed in the greenhouse experiment suggests that leaf physiological differences between *B. nana* and *E. vaginatum* could lead to opposite responses to light treatments for the two species. Assuming that biosynthetic fractionation remains constant for each species across light treatments, variable δD_{lw} is the most likely explanation for a species*light interaction. We investigate this possibility with a sensitivity analysis using a modified version of the Craig-Gordon model (Equations 1-4) in which the environmental parameters are representative of our growth chamber environments with $\delta D_{\text{SourceWater}} = -39\text{‰}$, $rH = 80\%$, and leaf temperature = 13 °C. The enrichment over source water is also a function of δD_{vapor} , which is unconstrained in our study, and was prescribed to -121‰ assuming equilibrium fractionation between the $\delta D_{\text{SourceWater}}$ (-39‰) and δD of vapor at the average incubation temperature (13 °C) (Majoube, 1971). The patterns of sensitivity are robust across different values of δD_{vapor} .

The Craig-Gordon leaf water model estimates that, at the site of evaporation, leaf water isotopes are 32‰ enriched over irrigation water under the conditions of our growth experiment, resulting in a δD_{lw} of -7‰ . After accounting for evaporated and unevaporated water mixing within the leaf (i.e. the pecllet number), the sensitivity of δD_{lw} to stomatal conductance varies strongly as a function of L (Figure 3.4). Bearing in mind that stomatal conductance should respond positively to continuous light, this implies that differences in leaf morphology and physiology should strongly impact plant responses to the light environment. At high stomatal conductance and high pecllet number (i.e. large leaves or mixing path length), modeled δD_{lw} is only slightly enriched relative to the

source water because relatively depleted xylem water dominates sites of wax synthesis within leaf mesophyll. In low L cases, δD_{lw} is insensitive to transpiration rates but shows consistently large D-enrichment relative to source water. δD_{lw} is most sensitive to stomatal conductance for high L plants. As such, we might expect the largest leaves (high L) to be most responsive to a 24-hour light effect on δD_{lw} or δD_{wax} , if stomatal conductance varies as a function of the light cycle.

Song et al. (2013) showed that the effective path length can also vary as a function of gas exchange rates across the stomata. As transpiration rate increases, L decreases due to a shift to more direct, extracellular, flowpaths of water through the leaf. The Peclet number decreases accordingly. In the model case where L varies with transpiration rate (dark red lines of Figure 3.4), the Peclet number is low and δD_{lw} is insensitive to stomatal conductance. It is important to note that in the model calculations, evapotranspiration and stomatal conductance are positively correlated, whereas in field studies from the Arctic this is not always the case (Gebauer et al., 1998).

3.5 Discussion

3.5.1 D/H fractionation under varying light in growth experiments

All plants regulate their evapotranspiration rates to maximize the ratio of CO_2 uptake to water loss by controlling their stomatal conductance (Farquhar et al., 1989). There is also a rich body of evidence that stomatal opening/closure responds directly to light (Darwin, 1898). Previous studies have demonstrated a persistent circadian rhythm of stomatal conductance for plants transferred from a DL environment into either a continuously dark or continuously light environment (Kerr et al., 1985; Hennessey and

Field, 1991). Despite the continued diurnal stomatal regulation in these studies, both of which focused on bean plants, other studies have shown that transpiration rates of onions and gymnosperms lose a diurnal cycle in continuous light environments, with plants continuously photosynthesizing and transpiring over a 24-hour cycle (Van Gestel et al., 2005; Yang et al., 2009). These studies, however, show slightly lower rates of transpiration during “night” hours or during cooler periods. The driver of these circadian rhythms is unknown, although the strength of circadian rhythms in gas exchange appears to vary between species, pointing to an underlying genetic control (Van Gestel et al., 2005). Chemical responses to continuous light also differ between species. For example, Van Gestel et al. (2005) showed that photosynthetic down-regulation in response to continuous light occurs in the onion *Allium fistulosum*, but not in the closely-related onion *A. cepa*, and suggested differential resource allocation strategies between the two plants as the cause of the photosynthetic response difference.

Few studies on the diurnal patterns of transpiration in continuous light have focused on the isotopic changes of leaf biomass. Prior work (Yang et al., 2009; 2011) suggested a 15-40‰ effect of CL on plant water isotopic compositions, but used plants that today do not inhabit CL environments (Figure 3.5). Our greenhouse experiments demonstrate that the effect of daily light cycles on the net apparent fractionation between irrigation water and leaf waxes is negligible for two of the most common plants that live in the Arctic today.

The magnitude of D/H fractionation observed for *B. Nana* and *E. vaginatum* in our greenhouse studies agree almost perfectly with field studies of the same species conducted in the Alaskan Arctic (Daniels et al., In Review). Comprehensive analyses of

the isotopic composition of soil water, leaf water, and waxes showed that, in the field, *B. nana* had an ϵ_{app} of -100 to -110 ‰ for various homologues, compared to -100 -115‰ for our greenhouse specimens. Likewise, ϵ_{app} of waxes from *E. vaginatum* were -155 to -170‰ in the Alaska field study and -160 to -170‰ in our growth experiment. These ϵ_{app} values for *B. nana* are consistent with ϵ_{app} of *n*-alkanes measured on a related species, *B. pubescens*, across a wide range of latitudes (Sachse et al., 2006). Indeed, our greenhouse experiments yield ϵ_{app} values that are similar to those from studies of plants within the same families and growth forms grown in DL environments (Gao et al., 2014), indicating that our study is broadly representative for these two species in a range of environmental conditions. This is noteworthy, as the maximum PAR in our greenhouse experiment was approximately 50% of the maximum natural light in the Arctic due to space and resource constraints in the growth chamber. The consistency of ϵ_{app} values observed for these plants, in the field and in experiments, and across very different light cycles and intensities strongly suggests that light is not a strong control on ϵ_{app} .

The discrepancies between these results and those of (Yang et al., 2009) are difficult to explain, but may emanate from different experimental conditions and/or plant species used in the two studies. An important experimental difference may be the differing irrigation protocol. To mimic Eocene Arctic conditions, Yang et al. (2009) kept soils saturated throughout the growth phase in both treatments such that water stress did not limit transpiration, and was not a critical factor governing δD_{lw} (Equiza et al., 2006a; Yang et al., 2009). This condition may not be representative of the modern Arctic environment in which water limitation may occasionally limit the ability for plants to fully utilize light continuously. In our study, plants in DL and CL treatments received the

same amount of water every five days. We did not monitor soil water saturation, but the intermittent watering could have induced occasional stomatal closure due to water stress in the CL chamber, such that the CL and DL stomatal conductances were not significantly different. That said, none of the plants showed outward signs of water stress at any time in the growth chamber experiment and so other factors are more likely to cause the differing results of our experiment from those of Yang et al. (2009, 2011). A second important experimental difference may be that in our study, the CL and DL treatments experienced the same daily temperature and humidity cycles, controlled by the growth chambers, whereas in the previous study, the two treatments experienced different temperature cycles (Equiza et al., 2006a). Since these are two critical variables controlling leaf physiology and are known to influence the δD_{lw} , they may have been as or more important than light in the treatment effect reported by (Yang et al., 2009).

Although neither *B. nana* nor *E. vaginatum* showed a statistically significant effect of CL versus DL, the opposite direction of change in δD_{wax} between our two study species is surprising. For *E. vaginatum*, CL waxes are slightly more enriched relative to DL waxes, but CL waxes are more depleted for *B. nana*. Our model results imply that this discrepancy could result from a stomatal control on δD_{lw} involving decreased conductance for *E. vaginatum* under CL conditions and increased conductance for *B. nana*. These responses most likely originate from genetic differences, as neither species showed any sign of water stress.

The species*light interaction suggests that the plants' isotopic response to different light cycles may be species-specific. Thus, the differing results between Yang et al. (2009) and our study may simply be a function of the different species studied.

Indeed, the *Metasequoia*, *Larix*, and *Taxodium* grown by Yang et al. exhibited differences between species in carbon allocation and photosynthesis rates to DL versus CL light treatments (Equiza et al., 2006a; Equiza et al., 2006b). Our leaf water model shows that the continuous transpiration observed by Yang et al. (2009) should be accompanied by more negative values of δD_{lw} due to enhanced flux of D-depleted xylem water to the meristem. It is unclear why Yang et al. observed the opposite effect, but it may reflect the complex biochemical reactions linking light availability and wax production, or that their experimental conditions were not conducive for analyzing the light effect on δD_{wax} .

Lastly, we note that our results are consistent with the idea that species that are more basal in their evolutionary histories tend to show smaller ϵ_{app} than later-derived plants (Gao et al., 2014a). The two gymnosperms grown by Yang et al. (2009), *Larix* and *Metasequoia*, had ϵ_{app} values from -50 to -80‰ in the DL treatment, substantially smaller than the angiosperms *B. nana* (-110 ‰) and the *E. vaginatum* (-150 ‰) grown here. Likewise, monocots are known to fractionate more strongly than eudicots (Gao et al., 2014a), a result evident in our experiments. While these differences do not directly explain the response of *Larix* and *Metasequoia* to changes in light conditions, the large differences in ϵ_{app} between our study and that of Yang et al. are not unexpected. The between species difference in ϵ_{app} eclipses leaf water enrichment effects, pointing to a need to further quantify ϵ_{app} for a broader range of species in order better constrain vegetation effects on paleoclimate reconstructions using δD_{wax} .

3.5.2 Application to Field Studies

How applicable are these growth experiments to understanding the isotopic composition of leaf waxes in the Arctic? While it is true that light is available continuously during polar summer, daily rhythms of temperature, plant photosynthesis, soil moisture, and even light availability do exist at high latitude sites, which may lead to diurnal patterns of gas exchange in plants. For example, at Toolik Field Station in Alaska (69°N latitude), hourly PAR measurements during the summer solstice from 1999 to 2013 show a strong daily cycle from 30 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ at ‘night’ up to 980 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ at midday. Additionally, diurnal temperature change plays an important role in controlling soil moisture in the Arctic, as shallow soils water is susceptible to freezing during the “dark” hours.

For *Betula sp.* and *Eriophorum sp.*, the relationship between light, stomatal conductance, and transpiration is either ill-defined or thought to be a function of other environmental factors such as temperature (Gebauer et al., 1998). Indeed, Jagels and Day (2000) indicate that stomatal conductance and evapotranspiration can be as much a function of temperature, water availability, and species as it can be of light. Moreover, diurnal studies from the Arctic show day/night differences in transpiration despite continuously available PAR. Gebauer et al. (1998) found that transpiration rates decrease during “night” in the arctic sedge *Eriophorum*, similar to results from Bliss (1960) for *Betula* and *Salix* shrub specimens in northern Alaska. Diel patterns in evapotranspiration have also been observed in eddy flux measurements in the tundra and are attributed to a stomatal conductance control (Vourlitis and Oechel, 1999). These measurements have also demonstrated that conductance is most sensitive to vapor pressure deficit and water

stress in the tundra. These results show that in the field, under continuous light, many Arctic plants experience diurnal cycles in key physiologic processes that would influence the isotopic compositions of their leaf waters. In light of these studies, it is not surprising that continuous light does not necessarily alter the isotopic composition of Arctic plant waxes relative to the light cycle they experience in temperate regions. By extension, species effects and non-light environmental effects (e.g. rH) are likely more important factors governing ϵ_{app} in different environments (Sachse et al., 2006; Yang et al., 2011; Wilkie et al., 2012; Shanahan et al., 2013; Porter et al., 2016; Thomas, 2016).

Our greenhouse experiments, together with these field studies, do not support a 24-hour light effect to explain widespread small ϵ_{app} in the Arctic. Rather, other factors must explain the differences across Arctic sites, particularly with regards to the small fractionation inferred at Baffin Island (Shanahan et al., 2013) and central Canada (Porter et al., 2016). We cannot rule out inaccuracies in the estimates of dD of source water, which are difficult to constrain and strongly influence the field estimates of ϵ_{app} . Shanahan et al. (2013) relied upon modeled, rather than measured, source water isotopic composition. Additionally, these authors used modeled mean annual dD_{precipitation} despite evidence that Arctic plants derive much of their biosynthetic water from spring and summer rains (Wilkie et al., 2012). This seasonality difference would contribute to the observations of reduced fractionation. Likewise, Porter et al. (2016) compared the D/H of fossil waxes to fossil (permafrost) water to estimate ϵ_{app} but the seasonality and time-integrated nature of the fossil water is not strictly known, thus limiting the robustness of the calculated ϵ_{app} . Alternatively, the difference could arise from climatic or vegetation differences. Relative humidity has been frequently identified as a critical meteorological

influence on ϵ_{app} through its control on leaf evaporation. At present, however, Baffin Island and the North Slope of Alaska have comparable rH values (average 74% and 75%, respectively), and so rH is unlikely to explain the difference between sites. Rather, if these prior field estimates of ϵ_{app} are correct, our greenhouse experiments implicate differences in vegetation type as an important control on the response of Arctic plants to continuous light. These differences are difficult to constrain in calibration studies based upon sedimentary leaf waxes (e.g. Shanahan et al., 2013), but may explain a considerable portion of the discrepancies in estimates of Arctic ϵ_{app} . As such, future work should aim to constrain values of ϵ_{app} at both the whole-ecosystem scale for a range of biomes and climatic regions and also at the scale of individual plants. A focus on the seasonality of source water isotopes and plant growth, together with a growing database of species-specific fractionation values will prove especially useful in future paleoclimate applications of δD_{wax} .

3.6 Conclusion

Our results establish that day length is a poor explanation for the small apparent hydrogen isotopic fractionations sometimes observed between leaf wax lipids and source water in high-latitude northern locations. Instead, vegetation differences between sites is a more important factor governing δD_{wax} across the modern Arctic. Our modeling exercises confirm that intraspecies variations in leaf morphology and physiology may regulate plants' responses to varying light, which may explain divergent results from previous growth experiments. These results will guide reconstructions of $\delta D_{\text{precipitation}}$ across vast areas of tundra where *B. nana* and *E. vaginatum* have dominated plant communities for millennia.

3.7 Acknowledgements

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3.8 References

Barbour, M.M., Roden, J.S., Farquhar, G.D. and Ehleringer, J.R. (2004) Expressing leaf water and cellulose oxygen isotope ratios as enrichment above source water reveals evidence of a Péclet effect. *Oecologia* 138, 426-435.

Bliss, L. (1960) Transpiration rates of arctic and alpine shrubs. *Ecology* 41, 386-389.

Chapin III, F.S., Shaver, G.R., Giblin, A.E., Nadelhoffer, K.J. and Laundre, J.A. (1995) Responses of arctic tundra to experimental and observed changes in climate. *Ecology* 76, 694-711.

Darwin, F. (1898) Observations on Stomata. *Proceedings of the Royal Society of London* 63, 413-417.

Equiza, M.A., Day, M.E. and Jagels, R. (2006a) Physiological responses of three deciduous conifers (*Metasequoia glyptostroboides*, *Taxodium distichum* and *Larix laricina*) to continuous light: adaptive implications for the early Tertiary polar summer. *Tree Physiology* 26, 353-364.

Equiza, M.A., Day, M.E., Jagels, R. and Li, X. (2006b) Photosynthetic downregulation in the conifer *Metasequoia glyptostroboides* growing under continuous light: the significance of carbohydrate sinks and paleoecophysiological implications. *Botany* 84, 1453-1461.

Farquhar, G., Hubick, K., Condon, A. and Richards, R. (1989) Carbon isotope fractionation and plant water-use efficiency, *Stable isotopes in ecological research*. Springer, pp. 21-40.

Feakins, S.J. (2013) Pollen-corrected leaf wax D/H reconstructions of northeast African hydrological changes during the late Miocene. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 374, 62-71.

Flanagan, L.B., Comstock, J.P. and Ehleringer, J.R. (1991) Comparison of modeled and observed environmental influences on the stable oxygen and hydrogen isotope composition of leaf water in *Phaseolus vulgaris* L. *Plant Physiol.* 96, 588-596.

Gao, L., Edwards, E.J., Zeng, Y. and Huang, Y. (2014) Major Evolutionary Trends in Hydrogen Isotope Fractionation of Vascular Plant Leaf Waxes. *PLoS ONE* 9, e112610.

Garcin, Y., Schwab, V.F., Gleixner, G., Kahmen, A., Todou, G., Séné, O., Onana, J.-M., Achoundong, G. and Sachse, D. (2012) Hydrogen isotope ratios of lacustrine sedimentary n-alkanes as proxies of tropical African hydrology: insights from a calibration transect across Cameroon. *Geochim. Cosmochim. Acta* 79, 106-126.

Gebauer, R., Reynolds, J. and Tenhunen, J. (1998) Diurnal patterns of CO₂ and H₂O exchange of the Arctic sedges *Eriophorum angustifolium* and *E. vaginatum* (Cyperaceae). *Am. J. Bot.* 85, 592-592.

Hennessey, T.L. and Field, C.B. (1991) Circadian rhythms in photosynthesis oscillations in carbon assimilation and stomatal conductance under constant conditions. *Plant Physiol.* 96, 831-836.

Hou, J., D'Andrea, W.J. and Huang, Y. (2008) Can sedimentary leaf waxes record D/H ratios of continental precipitation? Field, model, and experimental assessments. *Geochim. Cosmochim. Acta* 72, 3503-3517.

Huang, Y., Shuman, B., Wang, Y. and Webb, T. (2004) Hydrogen isotope ratios of individual lipids in lake sediments as novel tracers of climatic and environmental change: a surface sediment test. *J. Paleolimnol.* 31, 363-375.

Kerr, P.S., Rufty, T.W. and Huber, S.C. (1985) Endogenous rhythms in photosynthesis, sucrose phosphate synthase activity, and stomatal resistance in leaves of soybean (*Glycine max* [L.] Merr.). *Plant Physiol.* 77, 275-280.

Konecky, B., Russell, J. and Bijaksana, S. (2016) Glacial aridity in central Indonesia coeval with intensified monsoon circulation. *Earth. Planet. Sci. Lett.* 437, 15-24.

Liu, J., Liu, W., An, Z. and Yang, H. (2016) Different hydrogen isotope fractionations during lipid formation in higher plants: Implications for paleohydrology reconstruction at a global scale. *Scientific Reports* 6, 19711.

Majoube, M. (1971) Oxygen-18 and deuterium fractionation between water and steam. *J. Chim. Phys. Phys.-Chim. Biol.* 68, 1423-+.

Mills, R. (1973) Self-diffusion in normal and heavy water in the range 1-45. deg. *The Journal of Physical Chemistry* 77, 685-688.

Polissar, P.J. and Freeman, K.H. (2010) Effects of aridity and vegetation on plant-wax δD in modern lake sediments. *Geochim. Cosmochim. Acta* 74, 5785-5797.

Porter, T.J., Froese, D.G., Feakins, S.J., Bindeman, I.N., Mahony, M.E., Pautler, B.G., Reichart, G.-J., Sanborn, P.T., Simpson, M.J. and Weijers, J.W.H. (2016) Multiple water isotope proxy reconstruction of extremely low last glacial temperatures in Eastern Beringia (Western Arctic). *Quaternary Science Reviews* 137, 113-125.

Roden, J.S. and Ehleringer, J.R. (1999) Observations of hydrogen and oxygen isotopes in leaf water confirm the Craig-Gordon model under wide-ranging environmental conditions. *Plant Physiol.* 120, 1165-1174.

Sachse, D., Billault, I., Bowen, G.J., Chikaraishi, Y., Dawson, T.E., Feakins, S.J., Freeman, K.H., Magill, C.R., McInerney, F.A. and Van der Meer, M.T. (2012) Molecular paleohydrology: interpreting the hydrogen-isotopic composition of lipid biomarkers from photosynthesizing organisms. *Annual Review of Earth and Planetary Sciences* 40, 221-249.

Sachse, D., Radke, J. and Gleixner, G. (2004) Hydrogen isotope ratios of recent lacustrine sedimentary n-alkanes record modern climate variability. *Geochim. Cosmochim. Acta* 68, 4877-4889.

Sachse, D., Radke, J. and Gleixner, G. (2006) δD values of individual n-alkanes from terrestrial plants along a climatic gradient—Implications for the sedimentary biomarker record. *Org. Geochem.* 37, 469-483.

Shanahan, T., Huguen, K., Ampel, L., Sauer, P. and Fornace, K. (2013) Environmental controls on the $\delta^2 H$ values of terrestrial leaf waxes in the Eastern Canadian Arctic. *Geochim. Cosmochim. Acta*.

Shaver, G. and Chapin, F.S. (1980) Response to fertilization by various plant growth forms in an Alaskan tundra: nutrient accumulation and growth. *Ecology* 61, 662-675.

Song, X., Barbour, M.M., Farquhar, G.D., Vann, D.R. and Helliker, B.R. (2013) Transpiration rate relates to within-and across-species variations in effective path length in a leaf water model of oxygen isotope enrichment. *Plant, Cell Environ.* 36, 1338-1351.

Thomas, e.K. (2016) A major increase in winter snowfall during the middle Holocene on western Greenland caused by reduced sea ice in Baffin Bay and the Labrador Sea.

Tipple, B.J., Berke, M.A., Hambach, B., Roden, J.S. and Ehleringer, J.R. (2015) Predicting leaf wax n-alkane 2H/1H ratios: controlled water source and humidity experiments with hydroponically grown trees confirm predictions of Craig–Gordon model. *Plant, Cell Environ.* 38, 1035-1047.

Van Gestel, N.C., Nesbit, A.D., Gordon, E.P., Green, C., Paré, P.W., Thompson, L., Peffley, E.B. and Tissue, D.T. (2005) Continuous light may induce photosynthetic downregulation in onion—consequences for growth and biomass partitioning. *Physiol. Plant.* 125, 235-246.

Vourlitis, G.L. and Oechel, W.C. (1999) Eddy covariance measurements of CO₂ and energy fluxes of an Alaskan tussock tundra ecosystem. *Ecology* 80, 686-701.

Walker, D.A., Raynolds, M.K., Daniëls, F.J., Einarsson, E., Elvebakk, A., Gould, W.A., Katenin, A.E., Kholod, S.S., Markon, C.J. and Melnikov, E.S. (2005) The circumpolar Arctic vegetation map. *Journal of Vegetation Science* 16, 267-282.

Wilkie, K., Chaplgin, B., Meyer, H., Burns, S., Petsch, S. and Brigham-Grette, J. (2012) Modern isotope hydrology and controls on δD of plant leaf waxes at Lake El'gygytyn, NE Russia. *Climate of the Past Discussions* 8, 3719-3764.

Yang, H., Liu, W., Leng, Q., Hren, M.T. and Pagani, M. (2011) Variation in n-alkane δD values from terrestrial plants at high latitude: Implications for paleoclimate reconstruction. *Org. Geochem.* 42, 283-288.

Yang, H., Pagani, M., Briggs, D.E., Equiza, M., Jagels, R., Leng, Q. and LePage, B.A. (2009) Carbon and hydrogen isotope fractionation under continuous light: implications for paleoenvironmental interpretations of the High Arctic during Paleogene warming. *Oecologia* 160, 461-470.

3.9 Figures and Tables

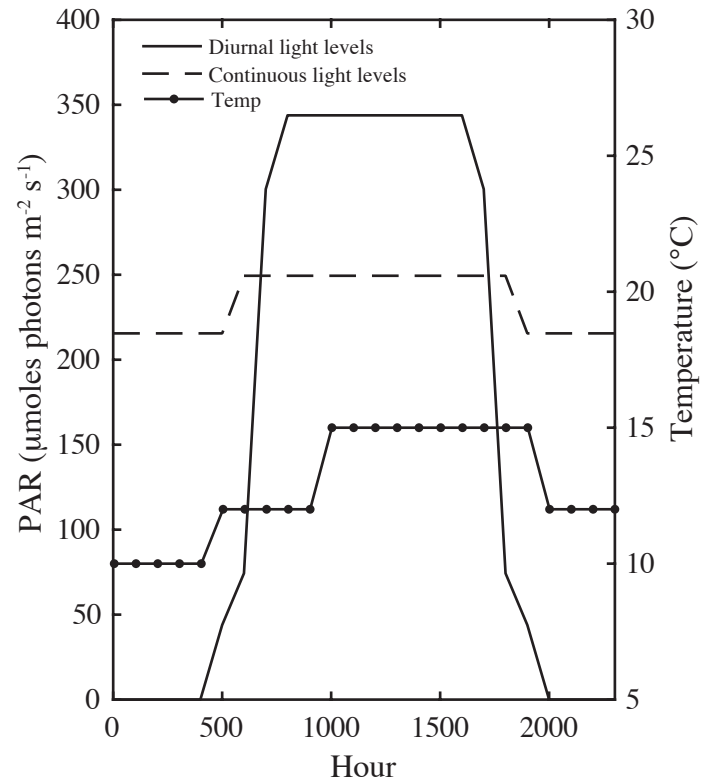


Figure 3.1 Growth chamber light and temperature conditions.

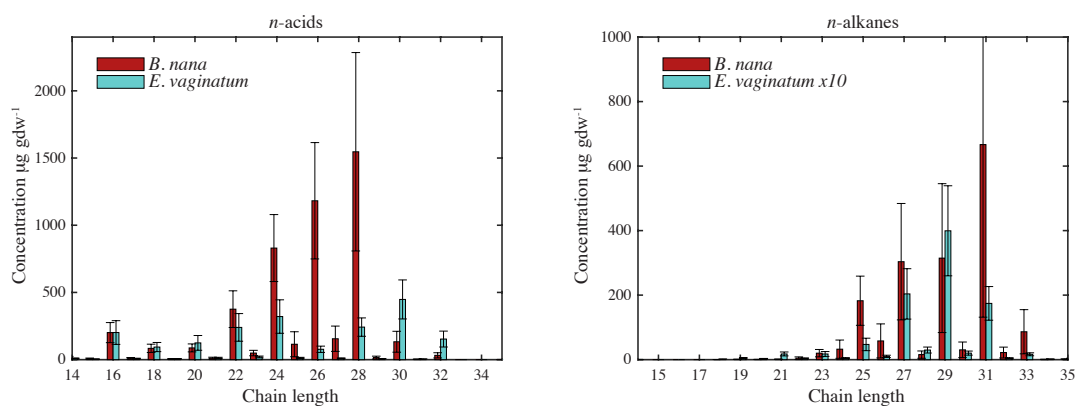


Figure 3.2 The *n*-alkane and *n*-acid distributions for BN and EV. No differences in wax distributions were observed between light treatments, and so data represent an average of both treatments. Note scale difference between *n*-acids and *n*-alkanes.

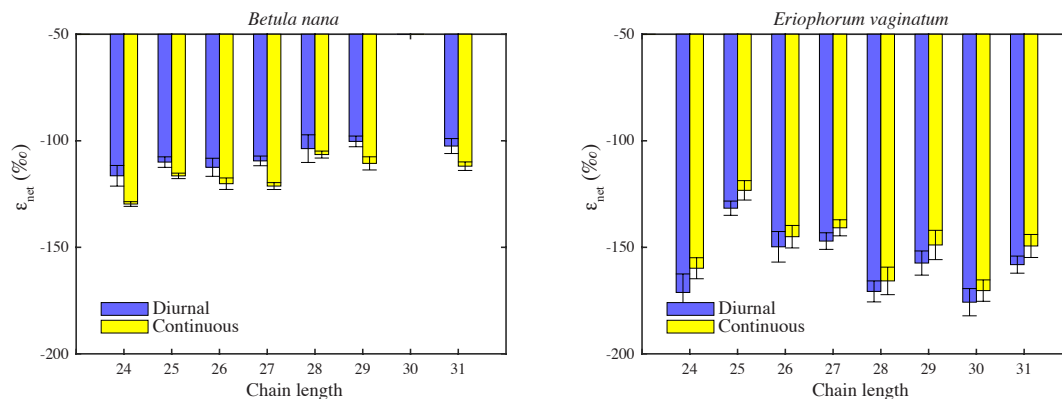


Figure 3.3 Net apparent fractionation between irrigation water (-39.0‰) and leaf waxes under different diurnal light patterns for a) BN and b) EV. Even chain length homologues are n -acids and odd chain lengths are n -alkanes.

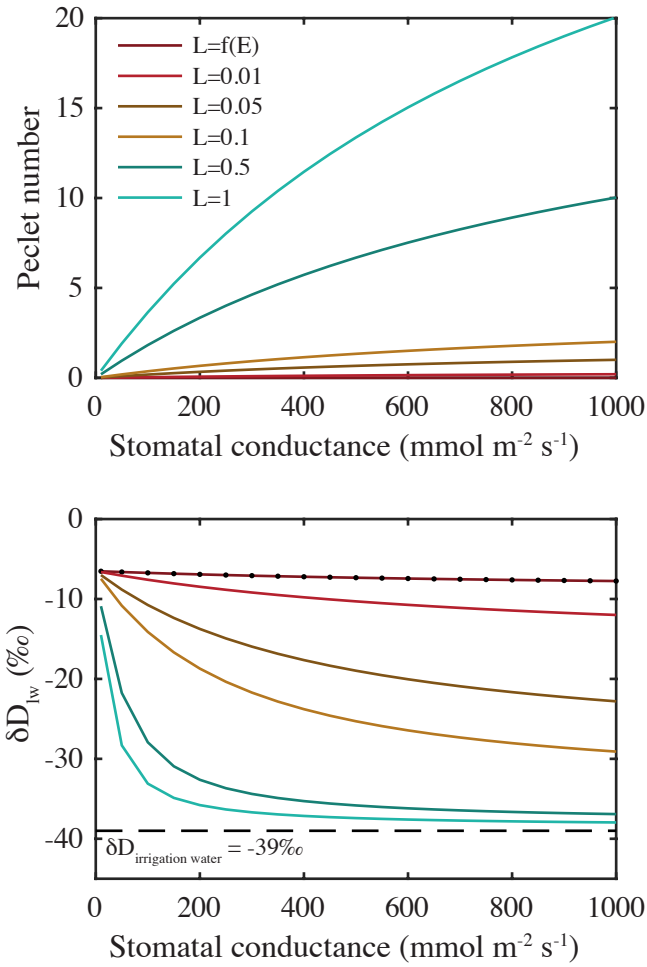


Figure 3.4 Modeled values of the peclet number (a) and leaf water D/H ratios (b), as a function of stomatal conductance and leaf effective path length (L). L is shown in units of meters, and in the first case, L is calculated as a function of transpiration rate (E, $\text{mmol m}^{-2} \text{s}^{-1}$) with the equation $L = 2.36 \times 10^{-5} \cdot E^{-1.2}$ following Song et al. (2013).

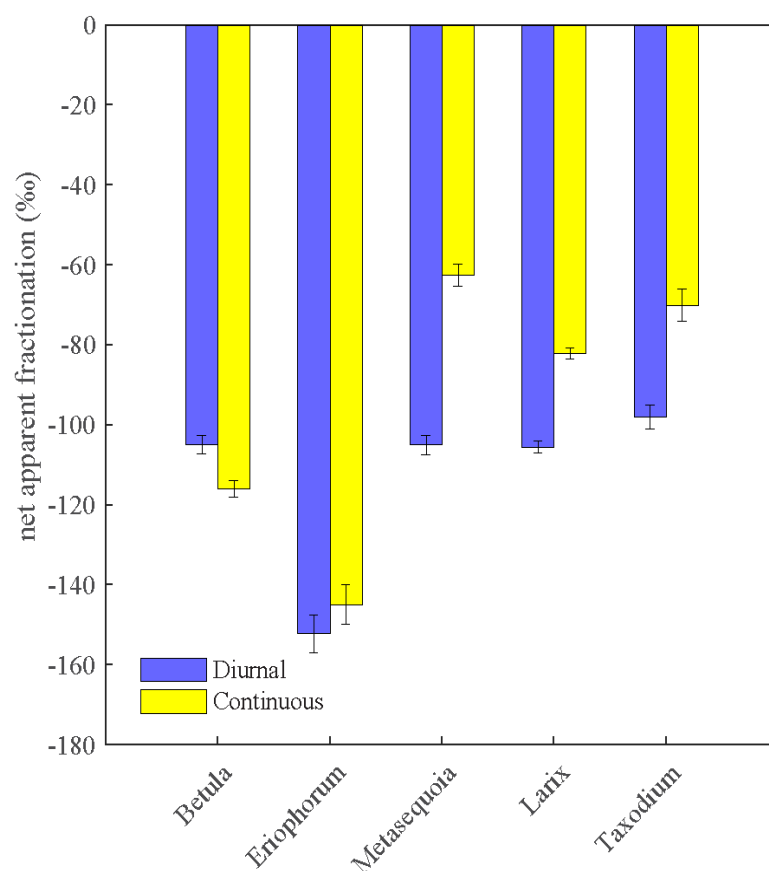


Figure 3.5 A comparison of net apparent fractionation (ϵ_{app}) of five plant species grown under diurnal and continuous light conditions. Data for *Metasequoia*, *Larix*, and *Taxodium* are from Yang et al. (2009). Data represent numerical averages of C_{27} and C_{29} *n*-alkanes.

	FAME		ALKANE	
	C ₂₀ -C ₃₂ CPI	C ₂₀ -C ₃₂ ACL	C ₂₁ -C ₃₃ CPI	C ₂₁ -C ₃₃ CPI
<i>B. nana</i> avg	15.8 ± 2.7 (9)	25.9 ± 0.4 (10)	11.9 ± 3.7 (10)	28.8 ± 0.4 (10)
<i>E. vaginatum</i> avg	23.7 ± 4.3 (18)	26.5 ± 0.5 (18)	11.7 ± 0.7 (18)	28.5 ± 0.2 (18)

Table 3.1 Summary information on chain length distributions for *E. vaginatum* and *B. nana*.

	<i>n</i> -acids				<i>n</i> -alkanes			
	C ₂₄	C ₂₆	C ₂₈	C ₃₀	C ₂₅	C ₂₇	C ₂₉	C ₃₁
Standards		2.8 (41)	2.7 (43)		1.9 (22)	1.2 (23)	1.5 (24)	
Samples	2.3 (97)	3.1 (98)	3.0 (107)	2.0 (62)	3.2 (52)	1.8 (57)	3.6 (80)	4.9 (81)

Table 3.2 Pooled standard deviation (1σ) estimates on δD_{wax} analytical measurements. Error is calculated at daily time steps and the pooled standard deviation s is calculated as

$\sigma = \sqrt{\frac{\sum((N_i - 1) * s_i^2)}{\sum N_i}}$, where N_i is the number of replicate standards for each day i, or the number of replicate injections for each sample i.

	<i>B. nana</i> (n=5)		<i>E. vaginatum</i> (n=9)	
<i>n</i> -acids	DL	CL	DL	CL
C ₂₄	-116.4 ± 4.8	-129.7 ± 1.1	-171.2 ± 8.7	-159.8 ± 4.9
C ₂₆	-112.4 ± 4.2	-120.1 ± 2.7	-149.8 ± 7.2	-145 ± 5.3
C ₂₈	-103.7 ± 6.5	-106.5 ± 1.6	-170.7 ± 4.9	-165.8 ± 6.5
C ₃₀			-175.8 ± 6.4	-170.3 ± 5
<i>n</i> -alkanes				
C ₂₅	-110 ± 2.5	-116.5 ± 1.3	-131.6 ± 3.3	-123.3 ± 4.6
C ₂₇	-109.4 ± 2.3	-121.3 ± 1.6	-147.1 ± 3.9	-140.8 ± 3.8
C ₂₉	-100.3 ± 2.5	-110.6 ± 3.1	-157.4 ± 5.7	-148.9 ± 6.9
C ₃₁	-102.5 ± 3.5	-111.9 ± 2	-158.1 ± 4	-149.4 ± 5.4

Table 3.3 Net apparent fractionation for *B. nana* and *E. vaginatum* under different light conditions. DL = Diurnal Light; CL = Continuous Light. Fractionations are calculated relative to irrigation water with a δD value of -39‰.

Effect		<i>n</i> -alkanes				<i>n</i> -acids				
		C ₂₅	C ₂₇	C ₂₉	C ₃₁	C ₁₆	C ₂₂	C ₂₄	C ₂₇	C ₂₈
Light	SS	4	50	5	1	300	465	6	14	7
	Df	1	1	1	1	1	1	1	1	1
	F	0.5	4.5	0.2	0.04	13.8	8.3	0.2	0.5	0.3
	p	0.51	0.045	0.67	0.84	0.002	0.008	0.71	0.51	0.62
Species	SS	898	5263	14306	13630	327	5461	11332	6219	25644
	Df	1	1	1	1	1	1	1	1	1
	F	99.0	474.1	493.3	786.5	15.0	97.7	298.6	202.9	870.5
	p	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Species X Light	SS	245	523	556	521	38	1588	952	249	96
	Df	1	1	1	1	1	1	1	1	1
	F	27.0	47.2	19.2	30.1	1.8	28.4	25.1	8.1	3.2
	p	<0.01	<0.01	<0.01	<0.01	0.20	<0.01	<0.01	<0.01	0.08
Resid.	SS	127	266	667	399	370	1341	873	735	737
	DF	14	24	23	23	17	24	23	24	24

Table 3.4 Statistical results from a two-way ANOVA, testing the effects of light treatment and species on values of ϵ_{app} .

CHAPTER FOUR

Amplification of climate change in the Western Arctic depends on the changing boundary conditions

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4.1 Abstract

Abrupt climate fluctuations during the last deglaciation have been studied extensively in the North Atlantic region and are thought to have ramifications at the global scale. Paleoclimate data from Alaska, however, are inconclusive both with regards to glacial-interglacial temperature change as well as the presence or absence of such rapid warming or cooling, calling into question the mechanisms and consistency of “Arctic Amplification” in the Western Arctic. We investigated temperature change in the Western Arctic from the last glacial maximum (LGM) to present using a lacustrine record of leaf wax hydrogen isotope ratios (δD_{wax}) from Northern Alaska. Past temperature changes were coherent with changes in summer insolation, but are superimposed by a series of rapid warming events that encompass most of the deglacial warming. These events are largely synchronous with abrupt events in the North Atlantic, but are variably amplified or muted in comparison, depending on the mean climate state. Hydrogen-isotope inferred warming of 1.4 ± 0.5 °C between the preindustrial and present day indicates that under Holocene boundary conditions, Alaskan temperature is highly sensitive to greenhouse gas radiative forcing, possibly due to feedbacks including decreased surface albedo associated with shrub expansion, reduced sea ice, or enhanced advection of subpolar air into the region.

Keywords Lacustrine paleoclimate, Alaska, Arctic Amplification, biomarkers, leaf wax hydrogen isotopes, Bering Strait

4.2 Main Text

During the last glacial termination, the North Atlantic experienced some of the most extreme temperature changes known in recent geologic time. This includes up to 10 °C of warming from the LGM to the Holocene Thermal Maximum (HTM), and high-amplitude abrupt changes such as Heinrich event 1 (H1), the Bølling-Allerød (BA), and the Younger Dryas (YD) (Johnsen et al., 1992; Grootes et al., 1993; Severinghaus and Brook, 1999). The amplitude and rate of these changes is linked to changes in strength of the Atlantic meridional overturning circulation (AMOC) and feedbacks from sea ice (Broecker et al., 1989; Li et al., 2005; Bradley and England, 2008) that cause Arctic temperature changes to be larger than anywhere else on earth – a phenomenon known as “Arctic amplification” (Miller et al., 2010; Shakun and Carlson, 2010). Future climate changes across the Arctic are also predicted to eclipse those in lower latitudes. Although the amplitude and rate of past temperature changes are well-known from the North Atlantic, they are very poorly constrained in other parts of the Arctic due to a dearth of long, continuous paleoclimate archives. One such region is Arctic Alaska, where there is controversial evidence for possible Arctic warming during the LGM (Bartlein et al., 2011), and limited evidence for millennial-scale changes during the glacial termination (Kokorowski et al., 2008). These records would suggest that the amplification of climate change in Arctic Alaska is muted, which is surprising in light of modern observations of significant warming in places such as Fairbanks, AK and Barrow, AK (Hinzman et al., 2005).

Various changes in atmospheric circulation, ocean heat transport, and surface conditions could either enhance or weaken climate change in Arctic Alaska compared to

the North Atlantic. Climate models predict that the Laurentide Ice Sheet (LIS) may have orographically steered warm air into Alaska during the LGM (Figure 4.1), thereby maintaining relatively mild temperatures (Broccoli and Manabe, 1987; Otto-Bliesner et al., 2006); however, different climate models predict different, and often opposite, temperature changes in Arctic Alaska in response to changes in LIS height, calling this mechanism into question. Nevertheless, in this scenario, melting of the LIS during the last glacial termination may have diminished the role of warm southerlies entering Alaska, partially offsetting deglacial warming. Secondly, strengthening of Pacific Meridional Overturning Circulation (PMOC) during collapses in AMOC could have enhanced heat transport to the North Pacific (Hu et al., 2007; Okazaki et al., 2010), possibly minimizing or even reversing abrupt cooling in the North Pacific relative to the North Atlantic. The importance of Pacific heat transport is sensitive to the open/closed status of the Bering Strait, and would have been stronger prior to the land bridge submergence (Hu et al., 2015) between 13.4 ka and 12.2 ka (Keigwin et al., 2006; England and Furze, 2008). Existing evidence for rapid climate change in Alaska is equivocal both prior to and after the submergence of the Bering Land Bridge. Even the largest climate oscillation, the Bølling-Allerød/ Younger Dryas reversal, is consistently observed only in Southern Alaska (Engstrom et al., 1990; Kokorowski et al., 2008), although highly discontinuous evidence for winter-time cooling exists for Northern Alaska (Meyer et al., 2010).

Lastly, changes in surface albedo may have played an important role in deglacial climate change (Bartlein et al., 2015). The transition from grassland to shrub tundra between 15 and 10 ka (Abbott et al., 2010) would have increased the energy balance of

the Alaska land surface by 2-3 W m⁻² (Lynch et al., 1999), similar to ongoing changes today (Chapin et al., 2005). Such an effect was irrelevant in the North Atlantic, where upstream ice sheets persisted on Greenland and Eastern Canada into the Holocene. At present, the re-expansion of shrubs in Alaska tundra is thought to be a principal amplifier of climatic warming relative to low latitudes (Chapin et al., 2005). Another important surface feedback, sea ice, is geographically variable in the Western Arctic, exhibits large changes on glacial-interglacial and shorter timescales (McKay et al., 2008; Caissie et al., 2010), and is known to influence climate over Beringia (Hu et al., 2010).

To determine the dynamics of past and recent temperature change in Arctic Alaska during and since the LGM, we generated a continuous record of the hydrogen isotopic composition of precipitation ($\delta D_{\text{precipitation}}$) from ~32 ka to the present from a sediment core from Lake E5 (68.643 °N, 149.458 °W, Figure 4.1). Lake E5 is one of the only lakes in the Arctic Alaska known to contain sediments extending through the LGM (Eisner and Colinvaux, 1992) (Figure 4.2, Table 4.S1). We examine the hydrogen isotope ratios of terrestrial leaf waxes (C₂₈ *n*-acids; hereafter δD_{wax} ; Materials and Methods and Figure 4.S1 and Tables 4.1 and 4.S2). In the Alaskan tundra, terrestrial plants use unevaporated growing-season precipitation for leaf wax biosynthesis (Daniels et al., in review), and so δD_{wax} records changes in growing season (May-August) $\delta D_{\text{precipitation}}$. Instrumental monitoring demonstrates a strong positive relationship between $\delta D_{\text{precipitation}}$ and temperature at Lake E5 (Figure 4.S2), highlighting the sensitivity of δD_{wax} as a quantitative proxy for air temperature (Thomas et al., 2012; Klein et al., 2016). Although changes in moisture source and transport can also affect the $\delta D_{\text{precipitation}}$ -T slope, observational data show that the relationship is stable across multiple sites in Alaska

(Figure 4.S2), as well as temporally, as evident in isotope-enabled climate model simulations of the past 20 ka (Figure 4.S3). We therefore estimate changes in temperature from changes in δD_{wax} using the modern relationship, after accounting for vegetation effects on D/H fractionation and the $\sim 8 \text{ ‰}$ global ice-volume effect on the oceanic D/H reservoir (Schrag et al., 1996; Lisiecki and Raymo, 2005; Konecky et al., 2016).

The δD_{wax} at Lake E5 varies from -286 ‰ to -245 ‰ and exhibits a distinct glacial-interglacial structure (Figure 4.3), with ice volume-corrected LGM waxes are $20.7 \pm 7.3 \text{ ‰}$ more depleted than during the Holocene (Table 4.1). Because of the difference in D/H fractionation (ϵ_{app}) between plant types (Gao et al., 2014a), changes in plant communities likely contributed to the observed change in δD_{wax} . Of particular importance were the transition from grassland-dominated ecosystems during the LGM to the shrub tundra of the Holocene, and the transient expansion of *Cyperaceae* sedges from 16-11 ka (Eisner and Colinvaux, 1992; Abbott et al., 2010). We account for these effects using pollen-based inferences to inform estimates of ϵ_{app} based upon calibrations developed in the Alaskan Arctic (Daniels et al., in review). We calculated binned values of $\delta D_{\text{precipitation}}$ and temperature from discrete time intervals, and performed pairwise statistical comparisons among intervals to determine significant differences (Table 4.1).

We estimate that LGM temperature was $-4.7 \pm 3.8 \text{ °C}$, a 4.1 °C temperature depression compared to present day ($p < 0.001$), and 2.6 °C colder than pre-industrial time ($p < 0.001$). A cooling of 4.1 °C in Arctic Alaska is colder than previous estimates based on pollen and fossil beetle assemblages, which show LGM temperatures of $+2$ to -2 °C relative to modern (Elias, 2000; Bartlein et al., 2011). This cooling, however, is much

smaller than temperature changes estimated for other parts of the Arctic, which range from -9 and -21 °C (Severinghaus and Brook, 1999; Shakun and Carlson, 2010; Porter et al., 2016). We attribute the moderate LGM cooling primarily to steering of warm southerlies into Alaska as simulated by many climate models (Broccoli and Manabe, 1987; Otto-Bliesner et al., 2006). Interestingly, LGM temperature was 8-9 °C colder than present at Lake El'gygytgyn in Western Beringia (Melles et al., 2012), revealing a strong East-West gradient in climate change, and illustrating that the upstream effects of the LIS could be limited to the Alaska region. This contributes to a growing body of evidence for mild conditions in Eastern Beringia, perhaps important to human migration from northeastern Asia to North America during the LGM (Goebel et al., 2008).

Temperatures rose from the LGM to an early Holocene thermal maximum (HTM) that was 3.2 ± 0.6 °C warmer than pre-industrial, before cooling over the Holocene to a minimum during pre-industrial time. The temperature record thus closely resembles summer insolation, as anticipated in light of the $>50 \text{ W m}^{-2}$ change in insolation over the last ~21 ka. During the last deglaciation we observe several intervals of abrupt warming and cooling, which despite the large error envelopes (average $1\sigma \pm 3.9$ °C), correspond in timing with both regional and global abrupt environmental changes.

Rapid warming of approximately 4 °C occurred at 19 ka, corresponding with rapid glacier retreat in the nearby Brooks Range mountains (Pendleton et al., 2015) and the initiation of peatland development in some parts of Alaska (Jones and Yu, 2010). This initial post-LGM warming lasted approximately two thousand years, and could have resulted from the initial rise in greenhouse gasses (Schilt et al., 2010), and/or increasing summer insolation. However, this period of relative warmth is absent or small in the

Greenland ice cores (Seierstad et al., 2014), suggesting that regional influences amplified the event in Alaska. Using ventilation ages in the North Pacific, Okazaki et al. (2010) showed that PMOC initiated at 19.5 ka, during or just prior to Heinrich Event 1 (H1). PMOC intensification was possibly a direct result of the H1 AMOC collapse (Hu et al., 2015), and may have raised temperatures of the Bering Sea by upwards of 3 °C (Okazaki et al., 2010). The PMOC persisted through Heinrich 1, but began to wane by approximately 17 ka. Results from cores in the Bering Sea are more equivocal (Caissie et al., 2010), but show a reduction in sea ice at 19 ka. Thus, the timing and potential regional impact of greater ocean heat transport in the Pacific could explain the amplified warming from 19 to 17 ka in Arctic Alaska and the notable absence of Heinrich 1 cooling.

Additional abrupt warming events at 14.8 and 11.6 ka in the Lake E5 record correspond with the onset of the Bølling interstadial and the termination of the Younger Dryas, thereby confirming links between the continental climate of Northern Alaska and AMOC. However, the amplitude of warming is approximately 2 °C for each of these step changes, much smaller than the ~9 °C changes estimated in the North Atlantic (Severinghaus and Brook, 1999). As these events were driven by the reestablishment of AMOC, it appears that the increase in heat to the North Atlantic was retained in that region, with probable heat sinks associated with melting of the Laurentide, Greenland, and Barents ice caps. The waning influence of the LIS on atmospheric circulation may have helped buffer the amplitude of these events as well, while land surface changes would have amplified them. The two abrupt warmings are critical to Arctic Alaskan climate evolution and they encompass most of the deglacial warming, and are associated

with considerable environmental change, including a shift from herb steppe tundra to deciduous shrub tundra at 14 ka (Abbott et al., 2010), the formation of thermokarst lakes at 14.5 and 11 ka (Jones and Yu, 2010), and the initiation of peat formation at many locations (Jones and Yu, 2010). The Younger Dryas is characterized by summer coolings of approximately 2 °C.

The contrast between the absent/warm H1 and cool YD suggests that coupling between Arctic Alaska and North Atlantic climate is stronger during the late-deglacial relative to the early deglacial time intervals. We tested this idea using idealized freshwater hosing experiments in the Community Climate System Model 3 by simulating AMOC collapse under a variety of boundary conditions (Methods and Figure 4.4). Results show that under glacial boundary conditions, AMOC collapse results in a temperature decrease of 2-4 °C in Alaska when the Bering Strait is open (BSO), similar to the amplitude we observe during the Younger Dryas. However, the amplitude of cooling is only 1-2 °C when the Bering Strait is closed (BSC)(Figure 4.4). Under present-day (1990 A.D.) boundary conditions, the temperature sensitivity to freshwater forcing is approximately double that of the glacial simulations for both BSO and BSC scenarios. Thus while the flooding of the Bering Strait alone could explain the differences between H1 and YD in Alaska, we expect the Pacific-Atlantic coupling to strengthen most significantly during interglacial climates due to boundary conditions other than the opening of the Bering Strait, including the melting of the Laurentide Ice Sheet and increasing atmospheric greenhouse gas concentrations. Moreover, the proxy and model results both highlight the reduced amplitude in YD temperature change relative to the 9 °C observed cooling at Greenland (Severinghaus and Brook, 1999).

Between the warming at 14.8 ka and the YD, there is a warming of approximately 2 °C in Lake E5 from 13.5 to 12.8 ka. This positive excursion agrees in timing with the Allerød oscillation in the North Atlantic region but plays a more prominent role in the deglacial warming of Arctic Alaska. Rising seas and the submergence of the Bering land bridge likely played a role (Bartlein et al., 2015) in driving temperature change at this time. Model simulations suggest that, aside from its effects on North Atlantic-western Arctic coupling, the opening of the Bering Strait itself can induce a 0.5-1.5 °C warming over Arctic Alaska (Figure 4.4). In these simulations, only Bering Strait throughflow was altered, and so we can attribute the modeled warming to northward heat transport through the strait in the BSO scenarios. The timing of the Bering land bridge submergence is not precisely known, but may have occurred as early as 13.4 ka (Keigwin et al., 2006), within the error of the warming event in the Lake E5 record.

The most prominent feature of the Holocene is a $\delta D_{\text{precipitation}}$ maximum between ~11.6 ka (the termination of the YD) until 9.5 ka (Figure 4.3). Temperature during this Holocene Thermal Maximum (HTM) was 5.9 ± 0.5 °C warmer than the LGM ($p < 0.0001$), 3.2 ± 0.6 °C warmer than the pre-industrial era ($p < 0.001$), and 1.8 ± 0.6 °C warmer than present ($p < 0.001$). The termination of the HTM occurs abruptly, with ~2 °C of cooling at 9.5 ka. After this initial cooling, temperature declined gradually, being driven by declining northern hemisphere summer insolation. In light of the substantial HTM-PI temperature change relative to the HTM-LGM change, it is apparent that in the absence of an ice sheet influence, climate of Alaska is highly sensitive to insolation changes, probably a result of important land surface feedbacks. Nonetheless, a local maximum at ~5 ka corresponds with a reduction in Chukchi sea ice concentrations

(McKay et al., 2008), which may have contributed to warming over northern Alaska (Klein et al., 2016). Cooling intensified from 4 to 0.1 ka, with temperature decreasing by 0.58 °C per thousand years. Temperatures were somewhat more stable during the pre-industrial period from 2-0.1 ka, but still cooling at a rate of ~0.39 °C per thousand years, consistent with glacier readvances in the Brooks range (Badding et al., 2013) and similar to the average Neoglacial cooling of 0.22 °C per thousand years reported across the Arctic (Kaufman et al., 2009).

Our analysis contextualizes ongoing Arctic warming in the prism of climate changes of the past ~32 kyr. Modern leaf waxes from the surface sediment of Lake E5 are D-enriched relative to the pre-industrial average by 5.7 ± 1.0 ‰. This equates to a warming of 1.4 ± 0.5 °C in the Anthropocene (here defined as 1890 CE to 2014), and a rate of 5.5 °C per thousand years. This temperature increase contrasts strongly with the long-term cooling of the late Holocene, and agrees well with the sparse instrumental records that exist from Northern Alaska during the last century (Hinzman et al., 2005) as well as the 1.4 °C pan-Arctic temperature increase for the last century seen in geologic archives (Kaufman et al., 2009). The modern climate warming seen in both instrumental and proxy data is amplified compared to the global average (Alley et al., 2003; Hinzman et al., 2005; Serreze et al., 2009). This contrasts with deglacial warming, which was muted at our site relative to both the Arctic and the global signal. To explain this amplification, we propose a combination of factors which affected Alaska as seen in this paleoclimate record, namely the contraction of winter and summer sea ice in the adjacent Chukchi Sea (Serreze et al., 2007; Stroeve et al., 2012) and the expansion of shrubs into low tundra biomes (Sturm et al., 2001; Chapin et al., 2005). These positive feedbacks

also likely affected deglacial warming; but were likely offset by negative feedbacks associated with the collapse of the Laurentide Ice Sheet. As temperatures in the North Pacific also impact the climate of Alaska, we cannot exclude the possibility that the shifts from the negative phase to the positive phase of the Pacific Decadal Oscillation during the past millennium and again in the mid-1900's (MacDonald and Case, 2005) has further contributed to warming at this time scale.

Our new Lake E5 record of Arctic Alaska temperature highlights the diverse origins and feedbacks of abrupt climate changes in Alaska during the last glacial termination, and the variable sensitivity of the region to climate forcing. The muted LGM-Holocene temperature change relative to records from the North Atlantic and Siberia implies that the Arctic amplification of temperature change varies regionally and may be strongly dependent on the mean climate state. Likewise, identification of the Bølling-Allerød/Younger Dryas climate reversal at Lake E5 indicates that AMOC initiation and collapse impacted the climate of Alaska, but the impact on summer temperature was weak relative to temperature fluctuations in the North Atlantic due to competing influences on Arctic Alaskan climate. In contrast, other climate events seem to be amplified in Alaska, including the warming at 19 ka (synchronous or leading the H1 stadial) and warming at 13.5 ka, associated with the Bering Strait flooding and expansion of shrubs. The 19 ka warming in Alaska likely contributed to the formation of high-latitude peatlands (Jones and Yu, 2010), possibly contributing to the deglacial rise in greenhouse gasses. At present, without the buffering capacity of the LIS and changing shoreline configuration, the post-industrial amplification of climate warming seen across the Arctic is also occurring in northern Alaska.

4.3 Methods

Study site and core collection

Lake E5 (68.643°N, -149.458°E) is in the northern foothills of the Brooks Range Mountains in Alaska's North Slope and is part of the Arctic Long Term Ecologic Research program. The lake is situated on glacial deposits dating to the Saganavirktok glaciation (780-125 ka). The lake's maximum depth is 12 m and the lake is typically ice-free from early June to mid-September. Overlapping cores were obtained using a Bolivia and a modified Livingstone square-rod piston corer through the ice from the deepest point in the lake in May, 2014, and a gravity core was retrieved from a boat in 2012 to capture an intact sediment water interface. The gravity core was sectioned in the field and all cores were transported to Brown University.

Core Chronology

The composite core is 4.8 m long and has a basal date of $32,086 \pm 2197$ (2s) calibrated years before present. An age model was constructed from ^{210}Pb and 16 radiocarbon dates (Table 4.S1) modeled using Clam version 2.2 (Blaauw, 2010; Reimer et al., 2013). Several intervals (205-213 cm, 235-237 cm, 258.5-264 cm, 266-268 cm, 271-273.5 cm, 285-288 cm, 289.5-295.5 cm, 325-326 cm, 330-332 cm, 332.5-333 cm) were deposited instantaneously and are modeled as slump events in the Clam software. Radiocarbon ages of macrofossils from two of these layers are approximately 35,000 ^{14}C yr bp, suggesting they contain aged terrestrial fragments and are likely derived from mass

wasting events and shoreline failures related to either rising lake levels or thermokarst activity. As such, leaf wax isotope measurements were omitted from these intervals.

dD_{wax} measurements

Lipids were extracted from 1-5 g of dry sediment using a Dionex accelerated solvent extractor with 9:1 dichloromethane:methanol. Total lipid extracts were separated using aminopropyl silica gel chromatography with 2:1 dichloromethane:isopropanol and 4% acetic acid in ether as eluents. Acid fractions were then methylated overnight at 60 °C in acidified methanol of known isotopic composition. Further purification of fatty acid methyl esters (FAMES) was performed with silica gel chromatography with dichloromethane and hexane as eluents. FAMES were analyzed on GC-FID for quantification prior to isotope analysis.

Hydrogen isotope ratios of FAMES were analyzed on a Thermo Finnegan Delta XL GC-IRMS at Brown University. Each sample was injected at least twice, and is reported relative to VSMOW. The average sample 1 σ uncertainty of $\delta D_{\text{C}_{28}\text{-FAME}}$ is 1.3‰ (n=336). Standards run after every 6 sample injections had a 1 σ uncertainty of 1.4‰ (n=172). δD_{wax} values are mathematically corrected for the added methyl groups from derivatization. δD_{wax} is also corrected for the global ice-volume effect on ocean D/H ratios (Konecky et al., 2016). This correction accounts for the approximately 8‰ increase in the oceanic reservoir during the LGM relative to the Holocene, and so the correction contributes ~8 ‰ to the glacial-interglacial structure in this record.

Climate model simulations

We use the CCSM3 global circulation model to test the effect of Bering Strait opening/closure and other glacial/interglacial boundary conditions on Beringian temperature and on Beringian sensitivity to global freshwater forcing events. The model has fully-coupled atmosphere and ocean components at T42x1 resolution. Boundary conditions are provided by Hu et al. (2015) and include changes to the Laurentide Ice Sheet, orbital forcing, and atmospheric greenhouse gas concentrations. Equilibrium surface temperatures were averaged over 100 years under 15 ka boundary conditions with an open and closed Bering Strait, and under present-day (1990 A.D.) boundary conditions with an open and closed Bering Strait. Additionally, we used the same model configurations to test the effect of freshwater addition to the North Atlantic on Beringian climate. Under the four scenarios described above (15 ka open/closed, 0 ka open/close), freshwater was gradually added to the North Atlantic until the AMOC collapsed, at which point we averaged surface temperatures for the succeeding 100 years.

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4.5 References

Abbott, M.B., Edwards, M.E. and Finney, B.P. (2010) A 40,000-yr record of environmental change from Burial Lake in Northwest Alaska. *Quatern. Res.* 74, 156-165.

Alley, R.B., Marotzke, J., Nordhaus, W.D., Overpeck, J.T., Peteet, D.M., Pielke, R.A., Pierrehumbert, R., Rhines, P., Stocker, T. and Talley, L. (2003) Abrupt climate change. *science* 299, 2005-2010.

Andersen, K.K., Azuma, N., Barnola, J.-M., Bigler, M., Biscaye, P., Caillon, N., Chappellaz, J., Clausen, H.B., Dahl-Jensen, D. and Fischer, H. (2004) High-resolution record of Northern Hemisphere climate extending into the last interglacial period. *Nature* 431, 147-151.

Badding, M.E., Briner, J.P. and Kaufman, D.S. (2013) ^{10}Be ages of late Pleistocene deglaciation and Neoglaciation in the north-central Brooks Range, Arctic Alaska. *Journal of Quaternary Science* 28, 95-102.

Bartlein, P., Edwards, M., Hostetler, S., Shafer, S., Anderson, P., Brubaker, L. and Lozhkin, A. (2015) Early-Holocene warming in Beringia and its mediation by sea-level and vegetation changes. *Climate of the Past Discussions* 11, 873-932.

Bartlein, P., Harrison, S., Brewer, S., Connor, S., Davis, B., Gajewski, K., Guiot, J., Harrison-Prentice, T., Henderson, A. and Peyron, O. (2011) Pollen-based continental climate reconstructions at 6 and 21 ka: a global synthesis. *Climate dynamics* 37, 775-802.

Blaauw, M. (2010) Methods and code for 'classical' age-modelling of radiocarbon sequences. *quaternary geochronology* 5, 512-518.

Bradley, R.S. and England, J.H. (2008) The Younger Dryas and the sea of ancient ice. *Quatern. Res.* 70, 1-10.

Broccoli, A.J. and Manabe, S. (1987) The effects of the Laurentide ice sheet on North American climate during the last glacial maximum. *Geographie physique et Quaternaire* 41, 9.

Broecker, W.S., Kennett, J.P., Flower, B.P., Teller, J.T., Trumbore, S., Bonani, G. and Wolfli, W. (1989) Routing of meltwater from the Laurentide Ice Sheet during the Younger Dryas cold episode.

- Caissie, B.E., Brigham-Grette, J., Lawrence, K.T., Herbert, T.D. and Cook, M.S. (2010) Last Glacial Maximum to Holocene sea surface conditions at Umnak Plateau, Bering Sea, as inferred from diatom, alkenone, and stable isotope records. *Paleoceanography* 25, PA1206.
- Chapin, F., Sturm, M., Serreze, M., McFadden, J., Key, J., Lloyd, A., McGuire, A., Rupp, T., Lynch, A. and Schimel, J. (2005) Role of land-surface changes in Arctic summer warming. *Science* 310, 657-660.
- Eisner, W.R. and Colinvaux, P.A. (1992) Late Quaternary Pollen Records from Oil Lake and Feniak Lake, Alaska, U.S.A. *Arct. Alp. Res.* 24, 56-63.
- Elias, S.A. (2000) Late Pleistocene climates of Beringia, based on analysis of fossil beetles. *Quatern. Res.* 53, 229-235.
- England, J.H. and Furze, M.F. (2008) New evidence from the western Canadian Arctic Archipelago for the resubmergence of Bering Strait. *Quatern. Res.* 70, 60-67.
- Engstrom, D., Hansen, B. and Wright, H. (1990) A possible Younger Dryas record in southeastern Alaska. *Science* 250, 1383-1385.
- Gao, L., Edwards, E.J., Zeng, Y. and Huang, Y. (2014) Major Evolutionary Trends in Hydrogen Isotope Fractionation of Vascular Plant Leaf Waxes. *PLoS ONE* 9, e112610.
- Goebel, T., Waters, M.R. and O'rourke, D.H. (2008) The late Pleistocene dispersal of modern humans in the Americas. *science* 319, 1497-1502.
- Grootes, P., Stuiver, M., White, J., Johnson, S. and Jouzel, J. (1993) Comparison of oxygen isotope records from the GISP2 and GRIP Greenland ice cores. *Nature* 366, 3.
- Hinzman, L., Bettez, N., Bolton, W., Chapin, F., Dyurgerov, M., Fastie, C., Griffith, B., Hollister, R., Hope, A., Huntington, H., Jensen, A., Jia, G., Jorgenson, T., Kane, D., Klein, D., Kofinas, G., Lynch, A., Lloyd, A., McGuire, A., Nelson, F., Oechel, W., Osterkamp, T., Racine, C., Romanovsky, V., Stone, R., Stow, D., Sturm, M., Tweedie, C., Vourlitis, G., Walker, M., Walker, D., Webber, P., Welker, J., Winker, K. and Yoshikawa, K. (2005) Evidence and Implications of Recent Climate Change in Northern Alaska and Other Arctic Regions. *Clim. Change* 72, 251-298.

- Hu, A., Meehl, G.A. and Han, W. (2007) Role of the Bering Strait in the thermohaline circulation and abrupt climate change. *Geophys. Res. Lett.* 34.
- Hu, A., Meehl, G.A., Han, W., Otto-Blietner, B., Abe-Ouchi, A. and Rosenbloom, N. (2015) Effects of the Bering Strait closure on AMOC and global climate under different background climates. *Prog. Oceanogr.* 132, 174-196.
- Hu, F.S., Higuera, P.E., Walsh, J.E., Chapman, W.L., Duffy, P.A., Brubaker, L.B. and Chipman, M.L. (2010) Tundra burning in Alaska: Linkages to climatic change and sea ice retreat. *Journal of Geophysical Research* 115.
- Johnsen, S.J., Clausen, H.B., Dansgaard, W., Fuhrer, K., Gundestrup, N., Hammer, C.U., Iversen, P., Jouzel, J., Stauffer, B. and Steffensen, J.P. (1992) Irregular glacial interstadials recorded in a new Greenland ice core. *Nature* 359, 3.
- Jones, M.C. and Yu, Z. (2010) Rapid deglacial and early Holocene expansion of peatlands in Alaska. *Proceedings of the National Academy of Sciences* 107, 7347-7352.
- Kaufman, D.S., Schneider, D.P., McKay, N.P., Ammann, C.M., Bradley, R.S., Briffa, K.R., Miller, G.H., Otto-Blietner, B.L., Overpeck, J.T. and Vinther, B.M. (2009) Recent warming reverses long-term arctic cooling. *Science* 325, 1236-1239.
- Keigwin, L.D., Donnelly, J.P., Cook, M.S., Driscoll, N.W. and Brigham-Grette, J. (2006) Rapid sea-level rise and Holocene climate in the Chukchi Sea. *Geology* 34, 861-864.
- Klein, E., Nolan, M., McConnell, J., Sigl, M., Cherry, J., Young, J. and Welker, J. (2016) McCall Glacier record of Arctic climate change: Interpreting a northern Alaska ice core with regional water isotopes. *Quaternary Science Reviews* 131, 274-284.
- Kokorowski, H., Anderson, P., Mock, C. and Lozhkin, A. (2008) A re-evaluation and spatial analysis of evidence for a Younger Dryas climatic reversal in Beringia. *Quaternary Science Reviews* 27, 1710-1722.
- Konecky, B., Russell, J. and Bijaksana, S. (2016) Glacial aridity in central Indonesia coeval with intensified monsoon circulation. *Earth. Planet. Sci. Lett.* 437, 15-24.
- Li, C., Battisti, D.S., Schrag, D.P. and Tziperman, E. (2005) Abrupt climate shifts in Greenland due to displacements of the sea ice edge. *Geophys. Res. Lett.* 32.

Lisiecki, L.E. and Raymo, M.E. (2005) A Pliocene-Pleistocene stack of 57 globally distributed benthic $\delta^{18}\text{O}$ records. *Paleoceanography* 20.

Lynch, A., Chapin III, F., Hinzman, L., Wu, W., Lilly, E., Vourlitis, G. and Kim, E. (1999) Surface energy balance on the arctic tundra: Measurements and models. *J. Clim.* 12.

Melles, M., Brigham-Grette, J., Minyuk, P.S., Nowaczyk, N.R., Wennrich, V., DeConto, R.M., Anderson, P.M., Andreev, A.A., Coletti, A., Cook, T.L., Haltia-Hovi, E., Kukkonen, M., Lozhkin, A.V., Rosén, P., Tarasov, P., Vogel, H. and Wagner, B. (2012) 2.8 Million Years of Arctic Climate Change from Lake El'gygytyn, NE Russia. *Science* 337, 315-320.

Miller, G.H., Alley, R.B., Brigham-Grette, J., Fitzpatrick, J.J., Polyak, L., Serreze, M.C. and White, J.W.C. (2010) Arctic amplification: can the past constrain the future? *Quaternary Science Reviews* 29, 1779-1790.

Okazaki, Y., Timmermann, A., Menviel, L., Harada, N., Abe-Ouchi, A., Chikamoto, M., Mouchet, A. and Asahi, H. (2010) Deepwater formation in the North Pacific during the last glacial termination. *Science* 329, 200-204.

Otto-Bliesner, B.L., Brady, E.C., Clauzet, G., Tomas, R., Levis, S. and Kothavala, Z. (2006) Last glacial maximum and Holocene climate in CCSM3. *J. Clim.* 19, 2526-2544.

Pendleton, S.L., Ceperley, E.G., Briner, J.P., Kaufman, D.S. and Zimmerman, S. (2015) Rapid and early deglaciation in the central Brooks Range, Arctic Alaska. *Geology* 43, 419-422.

Porter, T.J., Froese, D.G., Feakins, S.J., Bindeman, I.N., Mahony, M.E., Pautler, B.G., Reichert, G.-J., Sanborn, P.T., Simpson, M.J. and Weijers, J.W.H. (2016) Multiple water isotope proxy reconstruction of extremely low last glacial temperatures in Eastern Beringia (Western Arctic). *Quaternary Science Reviews* 137, 113-125.

Reimer, P.J., Bard, E., Bayliss, A., Beck, J.W., Blackwell, P.G., Bronk Ramsey, C., Buck, C.E., Cheng, H., Edwards, R.L. and Friedrich, M. (2013) IntCal13 and Marine13 radiocarbon age calibration curves 0-50,000 years cal BP.

Schilt, A., Baumgartner, M., Schwander, J., Buiron, D., Capron, E., Chappellaz, J., Loulergue, L., Schüpbach, S., Spahni, R., Fischer, H. and Stocker, T.F. (2010)

Atmospheric nitrous oxide during the last 140,000 years. *Earth. Planet. Sci. Lett.* 300, 33-43.

Schrag, D.P., Hampt, G. and Murray, D.W. (1996) Pore Fluid Constraints on the Temperature and Oxygen Isotopic Composition of the Glacial Ocean. *Science* 272, 1930.

Seierstad, I.K., Abbott, P.M., Bigler, M., Blunier, T., Bourne, A.J., Brook, E., Buchardt, S.L., Buizert, C., Clausen, H.B. and Cook, E. (2014) Consistently dated records from the Greenland GRIP, GISP2 and NGRIP ice cores for the past 104 ka reveal regional millennial-scale $\delta^{18}\text{O}$ gradients with possible Heinrich event imprint. *Quaternary Science Reviews* 106, 29-46.

Serreze, M., Barrett, A., Stroeve, J., Kindig, D. and Holland, M. (2009) The emergence of surface-based Arctic amplification. *The Cryosphere* 3, 11-19.

Serreze, M.C., Holland, M.M. and Stroeve, J. (2007) Perspectives on the Arctic's shrinking sea-ice cover. *science* 315, 1533-1536.

Severinghaus, J.P. and Brook, E.J. (1999) Abrupt climate change at the end of the last glacial period inferred from trapped air in polar ice. *Science* 286, 930-934.

Shakun, J.D. and Carlson, A.E. (2010) A global perspective on Last Glacial Maximum to Holocene climate change. *Quaternary Science Reviews* 29, 1801-1816.

Stroeve, J.C., Kattsov, V., Barrett, A., Serreze, M., Pavlova, T., Holland, M. and Meier, W.N. (2012) Trends in Arctic sea ice extent from CMIP5, CMIP3 and observations. *Geophys. Res. Lett.* 39.

Sturm, M., Racine, C. and Tape, K. (2001) Climate change: increasing shrub abundance in the Arctic. *Nature* 411, 546-547.

Thomas, E.K., McGrane, S., Briner, J.P. and Huang, Y. (2012) Leaf wax $\delta^2\text{H}$ and varve-thickness climate proxies from proglacial lake sediments, Baffin Island, Arctic Canada. *J. Paleolimnol.*, 1-15.

4.6 Tables and Figures

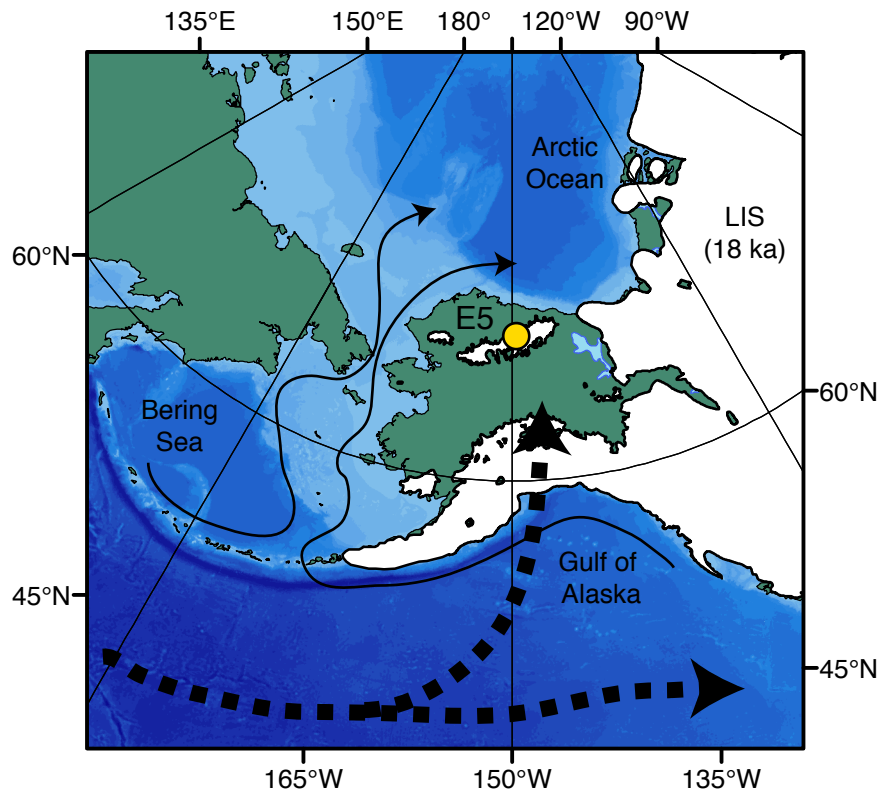


Figure 4.1 Map of study site (yellow dot) depicting the Laurentide Ice Sheet extent at 18 ka. Bold dashed arrows represent the LIS-orography forced northward advection of subpolar air into Alaska as simulated in CCSM3 (Otto-Bliesner et al., 2006). Solid arrows are modern surface currents through the Bering Strait

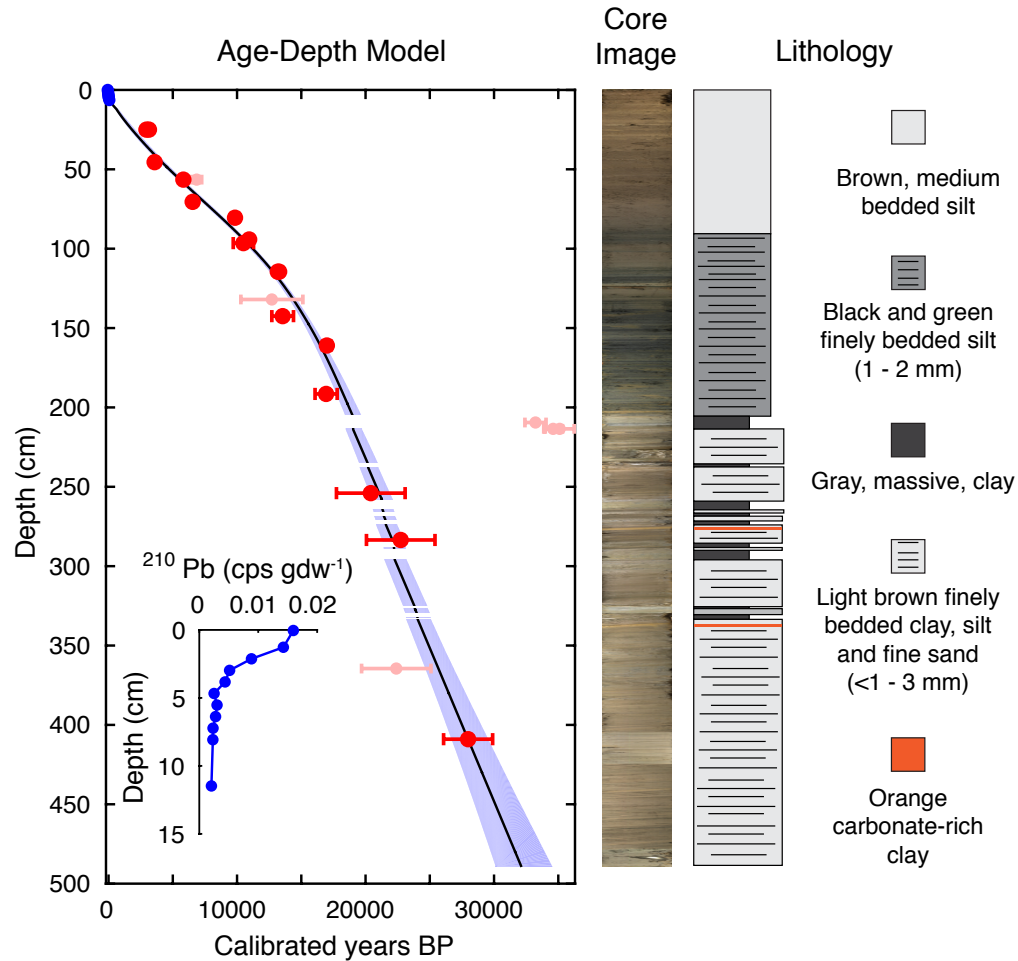


Figure 4.2 Age model for Lake E5 sediment core. Radiocarbon ages are calibrated using the Intcal13 calibration curve. Pink points are outliers and not included in the CLAM model (Blaauw, 2010). The blue inset curve shows ^{210}Pb concentration measured using gamma spectroscopy. The spline and 95% error envelope were modeled in clam.R software. Instantaneous deposition events are shown as gaps. The core image was generated with a GeoTek MSCL.

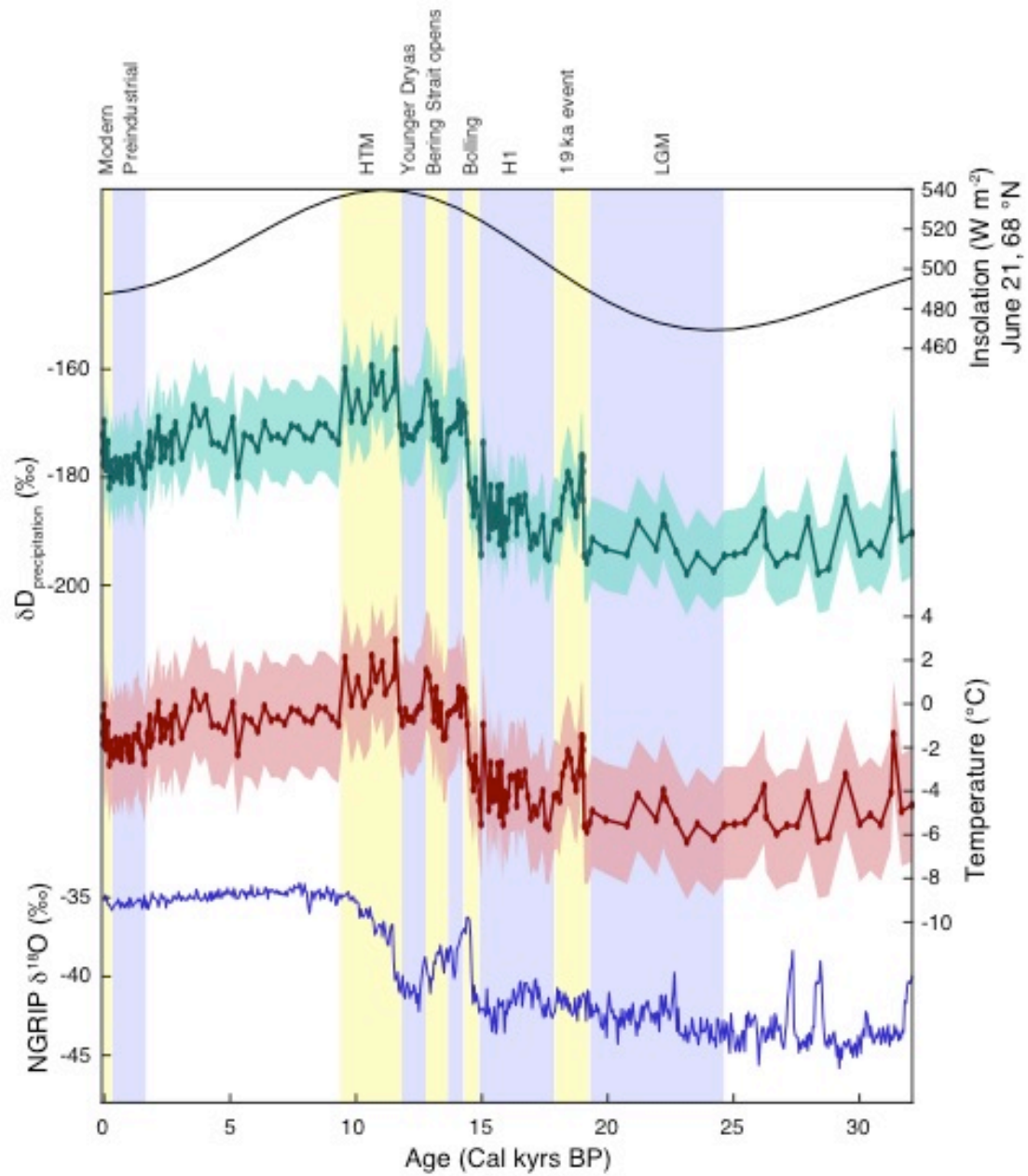


Figure 4.3 A comparison between the Lake E5 δD_{wax} -based climate record, insolation, and Greenland ice core oxygen isotopes. A) Summer solstice insolation at the latitude of Lake E5; B) $\delta D_{\text{precipitation}}$, after accounting for ice-volume effects and vegetation-based estimates of ϵ_{app} , with 75% and 25% confidence bounds; C) Temperature inferred from $\delta D_{\text{precipitation}}$, with 75% and 25% confidence bounds; D) NGRIP $\delta^{18}O$ (Andersen et al., 2004).

Bering Strait Experiments

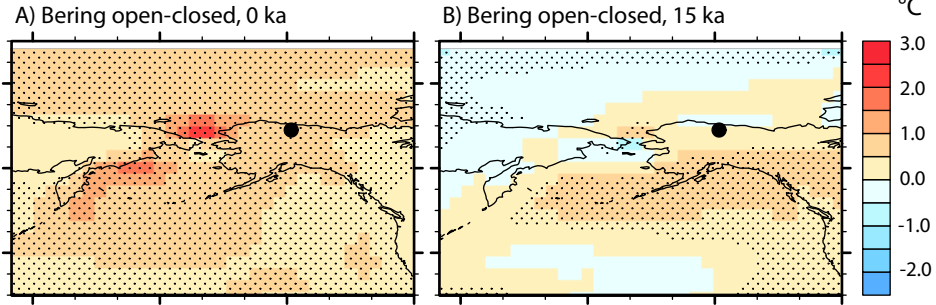


Figure 4.4 Surface temperature anomalies in Beringia in CCSM3 experiments. Stippling represents anomalies that are statistically significant at the $p = 0.05$ level. A and B) Mean annual temperature anomalies between simulations with open and closed Bering Strait under present-day (1990 A.D.) and 15 ka boundary conditions, respectively; C and D) Mean annual temperature anomaly between hosing experiments and control simulations under closed Bering Strait conditions for 0 ka and 15 ka; E and F) Same as C and D but with an open Bering Strait.

Time Slice	N	$\delta D_{\text{wax-raw}}$ (‰)	$\delta D_{\text{wax-IV}}$ (‰)	f(monocot)	f(dicot)	ϵ_{app} (‰)	δD_{precip} (‰)	Temp (°C)
LGM		-271	-279	0.38	0.62	-109	-191	-4.7
24-20 ka	16	(5)	(6)	(0.03)	(0.03)	(13)	(12)	(3.8)
Holocene		-258	-259	0.21	0.79	-103	-174	-1
11.6 - -0.064 ka	85	(5)	(4)	(0.06)	(0.06)	(14)	(13)	(3.9)
HTM		-251	-254	0.31	0.69	-106	-164	1.1
11.6-9.5 ka	11	(4)	(5)	(0.13)	(0.13)	(13)	(12)	(3.7)
PI		-262	-263	0.19	0.81	-102	-179	-2.1
1- 0.09 ka	16	(3)	(2)	(0.05)	(0.05)	(14)	(13)	(3.9)
Modern		-257	-257	0.19	0.81	-102	-173	-0.7
-0.064	1	(1)	(2)	(0.05)	(0.05)	(14)	(13)	(3.9)

Table 4.1 Summary of δD_{wax} (raw and ice-volume corrected), the relative abundance of monocots and dicot plants represented in Lake E5 pollen spectra, the fractionation factor based on pollen assemblages (ϵ_{app}), $\delta D_{\text{precipitation}}$, and air temperature for five time slices from the Lake E5 paleoclimate record. For reference modern mean annual weight $\delta D_{\text{precipitation}}$ is -166 ‰. 1 σ uncertainty is shown in parentheses.

4.7 Supplementary Text

This supplemental includes information for “*Amplification of climate change in the Western Arctic depends on the mean climate state*”. We present information on the radiocarbon dates used in sediment core chronology (Table 4.S1) and analytical precision of compound specific D/H measurements (Table 4.S2). It also includes an expanded explanation of the interpretation of δD_{wax} , including the corrections for ice volume and vegetation (Figure 4.S1), the temperature- $\delta D_{\text{precipitation}}$ relationship (Figures 4.S2-4.S3), and text on competing influences other than temperature as controls on $\delta D_{\text{precipitation}}$.

δD_{wax} interpretation

Previous quantitative reconstructions of $\delta D_{\text{precipitation}}$ from measurements of δD_{wax} have demonstrated a requirement to account for glacial-interglacial changes in oceanic D/H ratios (Konecky et al., 2016). We correct for this effect across the last glacial termination by subtracting the δD_{ocean} anomaly from measurements of δD_{wax} . The δD_{ocean} anomaly is determined by assuming LGM ocean was 1 ‰ enriched in $\delta^{18}\text{O}$ relative to today (Schrag et al., 1996), scaling the 1 ‰ glacial-interglacial change to the foraminifera-inferred changes in $\delta^{18}\text{O}$ (Lisiecki and Raymo, 2005), then converting to δD by multiplying by 8.

The C_{28} *n*-acid is commonly produced by terrestrial plants (Chikaraishi and Naraoka, 2007b) and is geochemically stable in sediments (Yang and Huang, 2003). While long chain ($>\text{C}_{24}$) *n*-acids can also be produced by aquatic plants, the extremely oligotrophic status of Lake E5 suggests that long-chain terrestrial waxes dominate. Determination of $\delta D_{\text{precipitation}}$ further requires accounting for changes in terrestrial plant

composition (Feakins, 2013; Konecky et al., 2016), as the D/H fractionation between water and lipids (ϵ_{app}) varies among plant types (Gao et al., 2014a). Generally, monocotyledonous plants fractionate more strongly than dicotyledonous plants. As the ratio of these plant types has fluctuated in the Lake E5 region between the LGM and today, so too has the ecosystem scale value of ϵ_{app} . In general, the Holocene is characterized by greater abundance of dicot shrubs, particularly of the genera *Betula*, *Salix*, and *Alnus*, whereas during the LGM, the graminoid *Poaceae* was relatively abundant (Livingstone, 1955; Eisner and Colinvaux, 1992; Abbott et al., 2010). During the glacial termination, transient peaks in *Artemisia* and sedges of the *Cyperaceae* family are evident around 16 and 11-15 ka, respectively (Eisner and Colinvaux, 1992; Abbott et al., 2010).

To account for these changes, we performed a vegetation correction based on pollen stratigraphy from a sediment core recovered from Lake E5 (Eisner and Colinvaux, 1992). Such corrections are likely imperfect because of uncertainty in the pollen-wax production ratios among different plants. Nonetheless, this approach has been used previously with success (Feakins, 2013) and improved estimates of the effect of vegetation on ϵ_{app} are available from the Arctic (Wilkie et al., 2012, Daniels et al. under review). The core was depth-correlated to our stratigraphy based on organic carbon profiles and a distinct marker bed dating to the beginning of the deglaciation. Based on a 24-lake training set in the Alaskan tundra (Daniels et al. in review), we determined that lakes in watersheds with a predominance of wet sedge tundra or grasses exhibit ϵ_{app} of $-135 \pm 20\text{‰}$, whereas forb/shrub dominated tundra have ϵ_{app} of $-96 \pm 16\text{‰}$. We used these two endmembers to generate a mixing model based on the pollen stratigraphy to calculate

ϵ_{app} for each time point in the data series. From this, we calculated $\delta D_{\text{precipitation}}$ (Figure 4.S2).

Due to the strong relationship between air temperature and $\delta D_{\text{precipitation}}$ in the Arctic (Dansgaard, 1964) and our site (Figure 4.S3), $\delta D_{\text{precipitation}}$ is a useful proxy for reconstructing past air temperature (Pautler et al., 2014). Therefore, we interpret changes in δD_{wax} as changes in air temperature using an appropriate transfer function (Klein et al., 2016; Porter et al., 2016). Here we use the Temperature- $\delta D_{\text{precipitation}}$ relationship determined from 20 years of precipitation monitoring at Toolik Field Station, approximately 5 km west of and at a similar elevation to Lake E5 (Figure 4.S3). The slope 2.6 ‰ per degree celsius, and agrees well with the slope determined across 12 sites across Alaska and Canada (Porter et al., 2016).

The temperature inferred from coretop δD_{wax} is -0.7 ± 3.9 °C. This compares favorably with May temperatures observed at the nearby Toolik Field Station, which average -1.0 ± 3.4 °C (Cherry et al., 2014). Alternatively, $\delta D_{\text{precipitation}}$ in May is virtually identical to the mean annual $\delta D_{\text{precipitation}}$ (Daniels et al. in review). As such, it appears that the δD_{wax} proxy is a viable proxy for early growing season or mean annual temperature at Lake E5.

Changes in moisture source are linked to air temperature, and are unlikely to be the main driver of $\delta D_{\text{precipitation}}$ at Lake E5 for two reasons. First, the Arctic Ocean and the North Pacific are the two dominant sources of moisture to the North Slope (Klein et al., 2015), with Arctic Ocean water being 15‰ depleted in deuterium relative to the North Pacific (Schmidt et al., 1999). Thus, reductions in Arctic sea ice from the LGM to Holocene should have the effect of lowering $\delta D_{\text{precipitation}}$ (Klein et al., 2015), opposite of

observations (Figure 4.3). Furthermore, we used an isotope-enabled version of the Community Atmosphere Model (IsoCAM) to examine changes in the slope of the $\delta D_{\text{precipitation}}-T$ relationship over the past 21 kyr in Alaska, as the slope might be expected to change with major moisture source changes (Figure 4.S2) (Tharammal et al., 2013).

4.8 Supplemental Figures and Tables

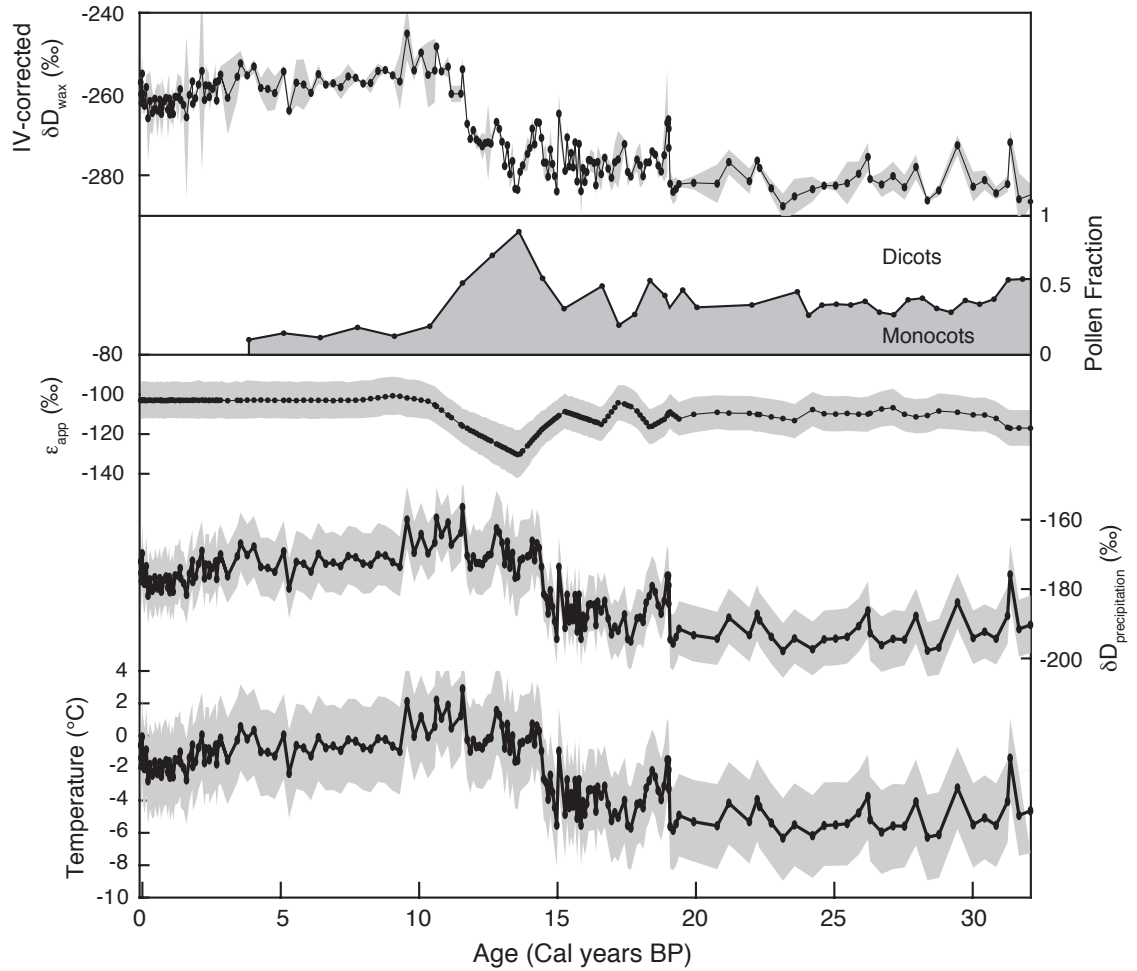


Figure 4.S1 Vegetation correction and temperature conversion of Lake E5 δD_{wax} . A) Ice volume-corrected δD_{wax} measurements (with 1s error of measurements). B) Relative abundance of monocot and dicot pollen in Lake E5 (Eisner and Colinvaux, 1992). The depth scale was aligned with our sediment core using total organic carbon profiles and marker beds (not shown). C) Estimates of ϵ_{app} based on the pollen assemblages and field estimates of ϵ_{app} representing these assemblages (Daniels et al. in review). End member values were $-135 \pm 20\text{‰}$ for the moist tundra dominated by sedges (monocots) and $-95 \pm 16\text{‰}$ for the drier tundra dominated by forbs and shrubs (dicots). Error bounds are 75% and 25% confidence intervals of 1000 iterations. D) $\delta D_{precipitation}$. Error bounds are 75% and 25% confidence intervals of 1000 iterations. E) Air temperature based on the modern $\delta D_{precipitation}$ -temperature relationship. Error bounds are 75% and 25% confidence intervals of 1000 iterations.

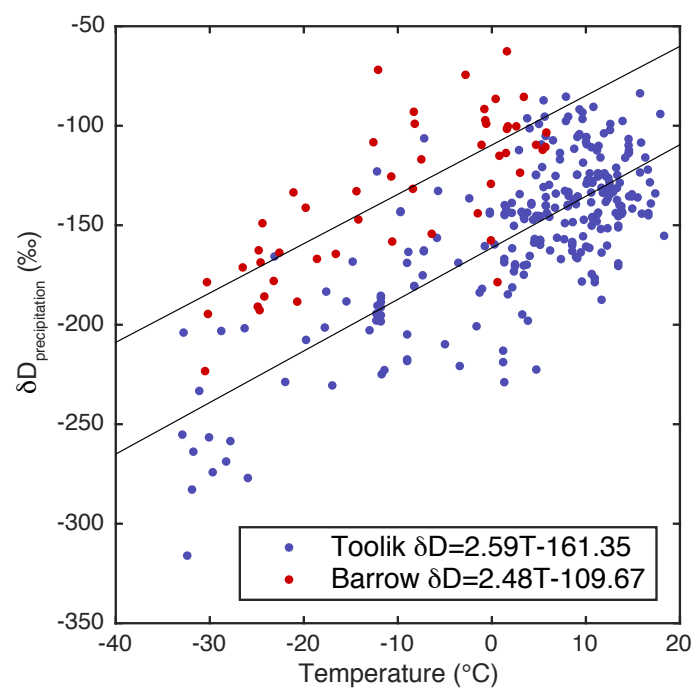


Figure 4.S2 Modern relationship between $\delta D_{\text{precipitation}}$ and air temperature at Toolik Lake, AK and Barrow, AK. Analysis of covariance shows that the slopes are indistinguishable ($dF=1$, $F=0.11$, $p=0.74$).

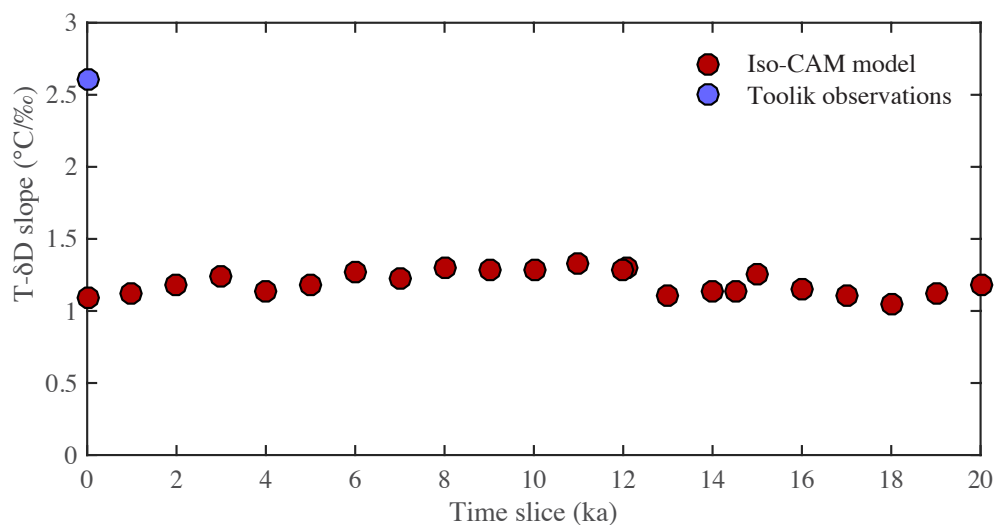


Figure 4.S3 Modeled relationship between temperature and $\delta D_{\text{precipitation}}$ over the last 20,000 years. The figure shows the linear slope between T and $\delta D_{\text{precipitation}}$ at 1000 year intervals, as modeled in IsoCAM. For each time slice, slopes are derived from 40 years of monthly $\delta D_{\text{precipitation}}$ and air temperature, averaging the six grid cells covering northern Alaska.

Depth (cm)	¹⁴ C Date (¹⁴ C yr B.P.)	Calibrated Age BP (1σ range and midpoint)	Description	Laboratory #
0		-64	Surface	
1.275		-45 (-43) -42	²¹⁰ Pb	
2.125		-28 (-26) -23	²¹⁰ Pb	
2.975		-18 (-14) -10	²¹⁰ Pb	
3.825		-5 (2) 9	²¹⁰ Pb	
4.675		5 (14) 22	²¹⁰ Pb	
5.1		14 (26) 38	²¹⁰ Pb	
6.375		30 (60) 89	²¹⁰ Pb	
24.5-25.5	2760 ± 100	2758 (2862) 2965	Plant fragments	OS-118632
24.5-25.5	2960 ± 55	3061 (3140) 3218	Insect eggs	OS-118642
44.5-46.5	3360 ± 50	3556 (3600) 3644	Plant and insect fragments	OS-123775
55.5-57.5	5090 ± 65	5749 (5790) 5830	Insect eggs	OS-123776
69.5-71.5	5740 ± 120	6408 (6536) 6664	Plant and insect fragments	OS-118631
79.5-81.5	8760 ± 70	9652 (9777) 9902	Plant and insect fragments	OS-123771
94.2	9600 ± 100	10782 (10911) 11040	Plant fragments	OS-112452
95-98	9320 ± 290	10221 (10549) 10877	Leaf	OS-118634
113.5-115.5	11300 ± 85	13117 (13195) 13272	Insect eggs	OS-123768
113.5-115.5	11400 ± 150	13127 (13264) 13400	Daphnia ephippia	OS-123779
142-143	11550 ± 370	13071 (13453) 13834	Plant fragments	OS-113019
161	14000 ± 90	16902 (17036) 17169	Plant fragments	OS-115775
191-192	13950 ± 330	16755 (17133) 17511	Insect fragments	OS-123780
253-255	16550 ± 1200	18613 (19945) 21277	Plant fragments	OS-118250
283-284	18550 ± 1200	20802 (22147) 23492	Plant fragments	OS-115834
408.5-409.5	23600 ± 980	27486 (28488) 29489	Plant fragments	OS-118653

Table 4.S1: Radiocarbon and ²¹⁰Pb age control points used in the CLAM.R age model for the Lake E5 sediment core. 0 ybp = 1950 AD.

	N	Mean (Reported)	Pooled Standard Deviation
Standards			
C ₂₆	172	-145.02 (-145.2)	1.60
C ₂₈	172	-162.73 (-163.8)	1.39
Samples			
C ₂₆	332	-259.53	1.16
C ₂₈	336	-256.82	1.28

Table 4.S2 Analytical statistics of fatty acid methyl ester (FAME) D/H analyses. Shown in parentheses are the manufacturer-reported δD values.

4.9 Supplementary References

Abbott, M.B., Edwards, M.E. and Finney, B.P. (2010) A 40,000-yr record of environmental change from Burial Lake in Northwest Alaska. *Quatern. Res.* 74, 156-165.

Cherry, J.E., Déry, S.J., Stieglitz, M. and Pan, F.-f. (2014) Meteorology and climate of Toolik Lake and the north slope of Alaska: Past, present and future. *Alaska's changing Arctic: Ecological consequences for tundra, streams, and lakes.* Oxford Univ. Press.

Chikaraishi, Y. and Naraoka, H. (2007) $\delta^{13}\text{C}$ and δD relationships among three n-alkyl compound classes (n-alkanoic acid, n-alkane and n-alkanol) of terrestrial higher plants. *Org. Geochem.* 38, 198-215.

Dansgaard, W. (1964) Stable isotopes in precipitation. *Tellus* 16, 436-468.

Eisner, W.R. and Colinvaux, P.A. (1992) Late Quaternary Pollen Records from Oil Lake and Feniak Lake, Alaska, U.S.A. *Arct. Alp. Res.* 24, 56-63.

Feakins, S.J. (2013) Pollen-corrected leaf wax D/H reconstructions of northeast African hydrological changes during the late Miocene. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 374, 62-71.

Gao, L., Edwards, E.J., Zeng, Y. and Huang, Y. (2014) Major Evolutionary Trends in Hydrogen Isotope Fractionation of Vascular Plant Leaf Waxes. *PLoS ONE* 9, e112610.

Klein, E., Nolan, M., McConnell, J., Sigl, M., Cherry, J., Young, J. and Welker, J. (2016) McCall Glacier record of Arctic climate change: Interpreting a northern Alaska ice core with regional water isotopes. *Quaternary Science Reviews* 131, 274-284.

Klein, E.S., Cherry, J.E., Young, J., Noone, D., Leffler, A.J. and Welker, J.M. (2015) Arctic cyclone water vapor isotopes support past sea ice retreat recorded in Greenland ice. *Scientific Reports* 5, 10295.

Konecky, B., Russell, J. and Bijaksana, S. (2016) Glacial aridity in central Indonesia coeval with intensified monsoon circulation. *Earth. Planet. Sci. Lett.* 437, 15-24.

Lisiecki, L.E. and Raymo, M.E. (2005) A Pliocene-Pleistocene stack of 57 globally distributed benthic $\delta^{18}\text{O}$ records. *Paleoceanography* 20.

Livingstone, D. (1955) Some pollen profiles from arctic Alaska. *Ecology*, 587-600.

Pautler, B.G., Reichart, G.-J., Sanborn, P.T., Simpson, M.J. and Weijers, J.W. (2014) Comparison of soil derived tetraether membrane lipid distributions and plant-wax δD compositions for reconstruction of Canadian Arctic temperatures. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 404, 78-88.

Porter, T.J., Froese, D.G., Feakins, S.J., Bindeman, I.N., Mahony, M.E., Pautler, B.G., Reichart, G.-J., Sanborn, P.T., Simpson, M.J. and Weijers, J.W.H. (2016) Multiple water isotope proxy reconstruction of extremely low last glacial temperatures in Eastern Beringia (Western Arctic). *Quaternary Science Reviews* 137, 113-125.

Schmidt, G.A., Bigg, G.R. and Rohling, E.J. (1999) Global Seawater Oxygen-18 Database - v1.21.

Schrag, D.P., Hampt, G. and Murray, D.W. (1996) Pore Fluid Constraints on the Temperature and Oxygen Isotopic Composition of the Glacial Ocean. *Science* 272, 1930.

Tharammal, T., Paul, A., Merkel, U. and Noone, D. (2013) Influence of Last Glacial Maximum boundary conditions on the global water isotope distribution in an atmospheric general circulation model. *Climate of the Past* 9, 789.

Wilkie, K., Chaplignin, B., Meyer, H., Burns, S., Petsch, S. and Brigham-Grette, J. (2012) Modern isotope hydrology and controls on δD of plant leaf waxes at Lake El'gygytyn, NE Russia. *Climate of the Past Discussions* 8, 3719-3764.

Yang, H. and Huang, Y. (2003) Preservation of lipid hydrogen isotope ratios in Miocene lacustrine sediments and plant fossils at Clarkia, northern Idaho, USA. *Org. Geochem.* 34, 413-423.

CHAPTER FIVE

A 32,000 year record of Arctic paleohydrology from Lake E5 in North-central Alaska

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5.1 Abstract

Future changes in Arctic precipitation are sensitive not only changes in mean temperature, but also to perturbations in moisture availability and transport which can vary dynamically in response to global climate change. As these factors vary spatially, reconstructions of paleohydrology are important for understanding regional sensitivity of the hydrologic cycle. Here we analyze sediments from Lake E5 in the Arctic foothills of northern Alaska for their lithologic and geochemical properties and the hydrogen isotopic composition of terrestrial and aquatic compounds to reconstruct hydrologic change over the past 32,000 years. We demonstrate that Lake E5 has fluctuated between open- and closed-basin status over this time, marked by varying authigenic mineral inputs to the sediment and varying degrees of evaporative enrichment of lake water isotopes, captured by the hydrogen isotope offset between aquatic and terrestrial waxes ($\Delta\delta D$). $\Delta\delta D$ values of +47‰ during the LGM relative to modern point to extreme aridity during that time. A transition to values as low as -30‰ marks the beginning of a shift toward more positive moisture balance beginning at 19 ka and maximum moisture at 14 ka. Fluctuations in $\Delta\delta D$ during the deglaciation suggest that the transition to a wetter Holocene was uneven, possibly being driven by fluctuations in sea ice cover, an important control on regional moisture availability.

The $\Delta\delta D$ inferred paleohydrology is supported by lithologic and geochemical evidence for changing environmental conditions at 19 ka. Organic-poor, carbonate-bearing sands and glacial loess deposited during the LGM provide evidence for low lake levels, elevated lake salinity, and regional aridity at that time. More reducing conditions, an increase in the chemical index of alteration of detrital sediment, and decreasing clastic

sediment fluxes point to soil stabilization, organic matter accumulation, and generally wetter conditions by 19 ka . These lithologic and isotopic data illustrate a complex precipitation history in which moisture balance is partially decoupled from temperature change, owing to interacting effects of atmospheric jet position and oceanic moisture source availability, and resulting in distinct climate regimes characterized as cool/dry, cool/wet, and warm/wet.

Keywords Paleohydrology, Arctic Alaska, biomarker hydrogen isotopes, loess, weathering, primary productivity

5.2 Introduction

In the future, the Arctic is predicted to warm more dramatically than anywhere else on Earth, due to well-know feedback processes that result in “Arctic amplification” (Serreze and Francis, 2006). Many paleoclimate records confirm this behavior in the past, with much larger temperature changes at high relative to low latitudes (Miller et al., 2010; Shakun and Carlson, 2010). Climate models predict large increases in Arctic precipitation in the future as well (Kattsov et al., 2007; Stewart et al., 2013; Bintanja and Selten, 2014), yet there are relatively few reconstructions of Arctic paleohydrology. That said, some records indicate that the Arctic experienced large hydrologic changes in the past. For instance, pollen records from Lake El’Gygytgyn in Western Beringia (Siberia) illustrate precipitation changes of $\sim 400 \text{ mm year}^{-1}$ over the past several hundred thousand years (Melles et al., 2012), a nearly 200% increase relative to the present.

In Alaska, steep gradients in modern precipitation across the state (Figure 5.1) suggest that climatologic controls on precipitation vary regionally (Stafford et al., 2000). Generally, fluctuations in the prevailing atmospheric circulation patterns govern large-scale precipitation patterns (Edwards et al., 2001). For example, the size and strength of the Aleutian Low is a robust influence on the hydrology of Southern Alaska (Anderson et al., 2005), but its influence diminishes northwards. Variations in moisture availability, which varies with sea ice extent at seasonal and longer timescales, is a second important control on Alaska precipitation. Characterizing how these two factors (circulation and sea ice) interact with mean climate state is aided by geologic reconstructions of past precipitation regimes. The large amplitude changes associated with the last glacial termination provide an excellent case for assessing precipitation sensitivity to global climate change.

Continuous glacial-interglacial records of moisture are rare in Northern Alaska due to a rarity in suitable geologic archives. Thus, while several lines of evidence point to an extremely arid environment during the LGM relative to today, the timing, rate, and possible reversals in moisture change during the last glacial termination and the Holocene are largely uncharacterized. It remains a critical question if precipitation fluctuated in Northern Alaska, and if so, how precipitation fluctuations relate to changes in global climate.

The importance of moisture change is evident in its role as a key driver of post-glacial landscape evolution in Northern Alaska (Mann et al., 2002; Viau et al., 2008). Nearly all available evidence, including lake low stands (Finkenbinder et al., 2015), activation of aeolian sand dunes (Carter, 1981), and appearance of xeric plant taxa

(Livingstone, 1955; Eisner and Colinvaux, 1992), indicate the North Slope was more arid during the Last Glacial Maximum (LGM). At that time, the vegetation community is thought to consist of a mosaic of forbs and grasses with well-drained soils and surprisingly high biomass across trophic levels, an assemblage referred to as both Mammoth steppe-tundra and moist non-acidic tundra (MNT) (Walker et al., 2001). Post-glacial contraction of MNT and other dryland biomes has previously been pointed to as a critical factor in the demise of ice age megafauna (Mann et al., 2013), and was probably driven by paludification and leaching of soil calcium, both of which would be strongly tied to the region's changing hydroclimate. A recent lake level record from Burial Lake shows that moisture balance became more positive around 19 ka (Finkenbinder et al., 2015), approximately synchronous with initial post-LGM glacier retreat in the Brooks Range (Pendleton et al., 2015), but several thousand years earlier than pollen-inferred changes in precipitation suggest (Viau et al., 2008). Together, these data suggest that hydrologic conditions began changing early during the last deglaciation, but the precise timing remains uncertain, and even less is known about hydrologic fluctuations within the deglacial period. Discontinuous geomorphic evidence indicates that the Younger Dryas was particularly dry (Mann et al., 2002). Additional paleohydrology records are necessary to document the timing and patterns of LGM-to-present hydrologic change in Arctic Alaska, and its relationship to regional temperatures and climate forcings.

Lake sediments provide the best archives of past continental climate change in Alaska's North Slope, a vast region (207,000 km²) of tundra between the Brooks Range and the Arctic Ocean. While most lakes in the region formed at the start of the Holocene, a small set of lakes, mostly situated in the Arctic foothills, contain sediments extending

through the Last Glacial Maximum (LGM). Lake E5 is one such lake. Palynological analysis of a sediment core from Lake E5 (previously called Oil Lake) in 1992 revealed a transition from xeric, grass-dominated ecosystem during the LGM to the moist acidic shrub tundra observed today, although because of radiocarbon limitations, the precise timing of this transition is poorly constrained (Eisner and Colinvaux, 1992). We have re-cored lake E5 and performed a more detailed and higher-resolution geochemical and lithostratigraphic analysis of the sediment profile. This study utilizes lithologic observations, geochemical observations of elemental composition (scanning X-ray fluorescence, or XRF), organic and inorganic carbon abundances, as well as compound specific hydrogen isotopic analyses of terrestrial and aquatic biomarkers (leaf waxes). Our chronology is based on AMS ^{14}C dates of macrofossils, allowing better constraints of the timing of climatic and ecological changes.

5.3 Study site

Lake E5 (68.643°N, -149.458°E) is located in the Arctic foothills of the Brooks Range (Figure 5.1). Meteorological monitoring at the nearby Toolik field Station (TFS) from 1989 to 2010 (Cherry et al., 2014) show that annual 5m air temperature averages -8.5 °C, and ranges from -24 °C in January to 11 °C in July. Precipitation averages 312 mm annually, with 60% falling in summer (JJA). Moisture sources include the Arctic Ocean and the North Pacific/Bering Sea (Klein et al., 2015), and there is a significant negative correlation between sea ice extent and precipitation at the TFS (Figure 5.S1).

Regional vegetation generally consists of moist acidic and shrub tundra, although in the foothills of the Brooks range, there is considerable variability in plant assemblages (Figure 5.1) related to the spatially heterogeneous glacial geology and edaphic histories.

Lake E5 is situated on glacial till deposited during the Sagavanirktok glaciation (280-125 ka) (Hamilton, 2003). Modern vegetation within the E5 watershed falls predominantly into two classes (Walker and Maier, 2008) - tussock-sedge/dwarf-shrub/moss tundra and hemi-prostrate dwarf shrub/fruticose-lichen tundra.

Lake E5 has a surface area of 10.8 ha, a maximum depth of 12 m, and an average depth of 6.3 m. It is a seasonally-open lake, with a small stream outlet flowing after the spring thaw and following rain events, but otherwise the water level is approximately equal to sill depth. The lake is extremely dilute with conductivity averaging $10.2 \pm 4.8 \mu\text{S cm}^{-1}$ (<http://arc-lter.ecosystems.mbl.edu/lakes-data>).

5.4 Methods

5.4.1 Core retrieval

We recovered overlapping sediment cores from two holes from the lake depocenter in May, 2014. The surface drive was recovered using a bolivia piston corer, while deeper sediments were recovered with a livingstone corer. In total, 5.53 m were recovered from hole 1 (E5-1A) and 3.95 m were recovered from hole 2 (E5-1B). Coring was interrupted at 5.5 m below lake floor by an impenetrable layer thought to be permafrost. Two additional surface cores were recovered in 2011 and 2012 (E5-11 and E5-12b) using a gravity corer.

5.4.2 Chronology

The four cores were used to develop a composite stratigraphy using magnetic susceptibility, TOC, and visual alignment of marker beds. A chronology for the

composite stratigraphy was generated using a combination of ^{210}Pb and radiocarbon. ^{210}Pb measurements were performed on core E5-12b using gamma spectroscopy at the Marine Biological Laboratory in Woods Hole, MA. We applied the constant rate of supply model to determine ages based on ^{210}Pb measurements (Binford, 1990). Material for radiocarbon dating came from E5-1A-1. 1 cm- or 2 cm-thick intervals were sieved for macrofossils. Material was treated acid-base-acid protocol (Olsson, 1991), and analyzed using accelerator mass spectrometry at the NOSAMS facility in Woods Hole, MA. Several samples were analyzed using the small-sample treatment at NOSAMS. An age-depth chronology was generated using both ^{210}Pb and ^{14}C ages using the Clam.R software (Blaauw, 2010) with the IntCal4.0 radiocarbon calibration curve (Reimer et al., 2013). All dates are presented as years before 1950.

5.4.3 Lithology, elemental composition

Cores were returned to Brown University where they were split, described, sampled for smear slide analysis, and the sediments were classified according to Schnurrenberger et al. (2003). Cores were scanned for their red, green, and blue color intensity (RGB), magnetic susceptibility, and elemental composition using a GeoTek™ multi-sensor core logger (MSCL) equipped with an Olympus Delta XRF scanner configured for 60 second scans each for major and minor elements. Volumetric samples were taken immediately after scanning for analysis of water content and dry bulk density.

The scanning-XRF results were calibrated to true elemental concentrations using a comparison of XRF data with chemical analyses of sediments measured via inductively coupled plasma optical emission spectroscopy (ICP-OES). For this calibration, we subsampled 40 1-cm intervals for chemical analysis. Approximately 0.04 g of dried

sediment was mixed with 0.16 g of lithium borate flux in a graphite crucible, heated to 1050°C for 10 minutes, then immediately dissolved in 10% nitric acid. Solutions were diluted to appropriate concentrations and analyzed for 12 major elements on ICP-OES in the Brown Environmental Chemistry Facility. For each element, the ratio of ICP:XRF was regressed against sediment water content, providing a basis for correcting the entire XRF data set (Russell et al., 2014).

Total inorganic carbon concentration (TIC) was measured at approximately 2 cm resolution throughout the E5-1A core using a UICinc coulometer. Samples were heated to 70 °C during coulometric analysis to ensure complete dissolution of the Fe- Mn- rich carbonates. Total organic carbon content (TOC) and total organic nitrogen content (TON) were measured at 1 cm resolution to 100 cm, 2 cm resolution to 225 cm, and approximately 4 cm for the remainder of the core composite using an elemental analyzer-isotope ratio mass spectrometer (EA-IRMS). Samples were soaked in 5 % HCl overnight and rinsed three times in DI water to remove carbonates prior to analysis on a Thermo-Finnigan Delta-X IRMS. A subset of samples (n=124) were also analyzed on a ThermoQuest NC2100 soil elemental analyzer. The difference between the two methods averaged 0.13 weight percent for carbon and 0.02 weight percent for nitrogen, indicating the TOC and TON measured on EA-IRMS are robust.

Principle component analysis was performed on the sediment geochemical data including the concentrations of eleven elements from ICP-corrected XRF data (Mn, Fe, Sr, S, Ca, Zn, Al, P, Mg, Ni, and Cu), as well as %TIC, TOC, and TON concentrations. Titanium was not included because XRF scanning returned a large number of null data. Because TIC, TOC, and TON were sampled at different resolution than the XRF-based

elemental data, all data were resampled at 150-year spacing (the average %TOC sampling resolution). All concentration data were normalized to z-scores prior to PCA.

The chemical index of alteration (CIA) was calculated based on elemental concentrations measured by ICP-OES. Because carbonate mineralogy and content changes throughout the composite stratigraphy, we did not attempt to perform a correction for the calcium content that was incorporated in carbonates rather than silicate minerals. Rather, we exclude calcium in the CIA calculation (Eq. 1), modifying the method originally proposed by Nesbitt and Young (1982).

$$\text{Eq. 1) } CIA = \frac{Al_2O_3}{Al_2O_3 + K_2O + Na_2O} * 100$$

5.4.4 Compound-specific Stable Isotopes

The isotopic composition of hydrogen in specific organic compounds was measured at Brown University. Dried sediments were extracted using a Dionex Accelerated Solvent Extraction device using dichloromethane:methanol (9:1). Lipid extracts were separated into neutral and acid fractions using aminopropyl silica gel chromatography using dichloromethane:isopropanol and 4% glacial acetic in ether. Acids were methylated at 60°C overnight using acidified methanol with a known isotopic composition. Fatty acid methyl esters (FAMES) were further purified using silica gel chromatography with dichloromethane and hexane as eluents. Hydrogen isotope ratios of FAMES were analyzed on a Thermo Finnegan Delta XL gas chromatograph-isotope ratio mass spectrometer (GC-IRMS). Because of differences in concentration between the short chain (C₁₆ and C₁₈) and long chain (>C₂₄) FAMES, not all homologues could be

analyzed in a single injection. As such, the isotopic composition of the long chain *n*-acids was measured separately from that of the short-chain acids. Each sample was analyzed at least twice for each set of chain lengths. A standard mixture containing C₁₆, C₁₈, C₂₂, C₂₆, and C₂₈ FAMES was analyzed every 6 injections throughout the analysis and the H₃⁺ factor was determined every other day. δD_{wax} values are mathematically corrected for instrument drift on a daily basis, for the added methyl groups from methylation and for the global ice-volume effect on D/H ratios (Konecky et al., 2016).

Uncertainty was calculated using the pooled standard deviation ($\sigma = \sqrt{\frac{\sum(n_i-1)*s^2}{\sum(n_i-1)}}$, where *i*=day for standards and *i*=sample for samples). The 2 σ error for standards was 1.4‰ for C₂₈ *n*-acid and 6.8‰ for C₁₆ *n*-acid and for samples was 1.3 ‰ for C₂₈ *n*-acid and 4.0‰ for C₁₆ *n*-acid.

Terrestrial plant leaf waxes primarily record the D/H ratios of spring and summer rainfall because much of the winter precipitation is lost as snowmelt runoff (Daniels et al. in review). Based on the strong correlation between $\delta D_{\text{precipitation}}$ and air temperature at our site and at the nearby GNIP station in Barrow, $\delta D_{\text{C}_{28}}$ is interpreted here as a growing-season temperature proxy (Chapter 3). In cases where the source water pools for aquatic and terrestrial organisms are differentially susceptible to evaporative enrichment, the offset between D/H ratios between aquatic and terrestrial biomarkers has potential utility as a proxy for aridity (Sachse et al., 2004; Mügler et al., 2008; Polissar and Freeman, 2010). Evaporation of the light isotopologues proceeds faster than the heavy isotopologues, leaving residual lake water isotopically enriched. In hydrologically open lakes with short water residence times, including small open lakes like E5, the lake water

isotopic composition (δD_{Lake}) is roughly equal to that of the mean annual precipitation, and we expect that variations in the δD of terrestrial leaf waxes and the δD_{Lake} will be controlled by changes in the δD of precipitation ($\delta D_{\text{Precipitation}}$). In closed-basin lakes with long residence time, however, δD_{Lake} evolves to more positive values (Mügler et al., 2008). In the case of a transiently closed lake in the cool environment of Northern Alaska, aquatic waxes should be more sensitive to the precipitation-evaporation balance than are the terrestrial waxes (Mügler et al., 2008; Balascio et al., 2016).

Currently, Lake E5 is considered an open lake, although the outflow is intermittent. Water column samples collected from the Arctic LTER show that water isotopes of Lake E5 fall on the meteoric waterline regardless of time of year (Figure 5.2), thus precluding a strong evaporation signal. The δD_{Lake} is similar to the mean annual $\delta D_{\text{precipitation}}$ and seasonal changes in δD_{Lake} and $\delta^{18}\text{O}_{\text{Lake}}$ are driven by shifts between summer and winter water sources. However, Vachula et al. (2017) show that the surface water isotopic composition of many lakes in Alaska differ from the meteoric water line, and define a distinct local evaporation line. Although information on the closed/open status or watershed characteristics of these lakes is unavailable, given this evaporative signal in other regional lakes, we expect that Lake E5 potentially experiences evaporative effects under different atmospheric or lake basin conditions.

We assess this effect through study of the isotopic difference between fatty acids derived primarily from aquatic versus terrestrial sources. Palmitic acid (C_{16} *n*-acid) is ubiquitous among photosynthetic organisms (Chikaraishi and Naraoka, 2007a), but is found in particularly high concentrations among algae. As such, it is generally regarded as an aquatic biomarker and has been shown to faithfully record δD_{lake} , with a D/H

fractionation (ϵ_{app}) between lake water and lipids of $-170 \pm 28 \text{ ‰}$ (Huang et al., 2002).

The C_{28} *n*-acid homologue is produced primarily by terrestrial plants and records growing-season precipitation isotopes in the tundra (Daniels et al. in review). With knowledge that plant assemblages, and therefore ϵ_{app} for the terrestrial waxes, have changed since the LGM, we apply a pollen-based vegetation correction factor, based on pollen stratigraphy from Lake E5 (Eisner and Colinvaux, 1992), to the $\delta\text{D}_{\text{C}_{28}}$ (Chapter 3) prior to comparing with the aquatic waxes.

Thus, using $\delta\text{D}_{\text{C}_{28}}$ as an indicator of $\delta\text{D}_{\text{precipitation}}$ and $\delta\text{D}_{\text{C}_{16}}$ as an indicator of $\delta\text{D}_{\text{Lake}}$, we can use the offset between the two ($\delta\text{D}_{\text{Lake}} - \delta\text{D}_{\text{Precipitation}} = \Delta\text{-}\delta\text{D}$) to qualitatively assess the extent of evaporative enrichment that occurred within the Lake E5 basin through time. We use a monte-carlo simulation technique to account for uncertainty in ϵ_{app} when calculating $\delta\text{D}_{\text{Lake}}$ and $\delta\text{D}_{\text{Precipitation}}$. Uncertainty is compounded when comparing two homologues. Here, the standard deviation of $\Delta\text{-}\delta\text{D}$ over 1000 iterations averages 20.3 ‰ throughout the core.

5.5 Results and Interpretation

5.5.1 Sediment Chronology

The composite section has a length of 500.5 cm and appears continuous. Of 20 radiocarbon ages measured (Chapter 3), six were determined to be outliers, likely due to reworking of macrofossils, and in some cases measurement errors related to very small sample size. There are a series of 0.5-3 cm thick normal-graded silt to sand packages,

with unconformably old radiocarbon ages, which we modeled as slump events in the Clam.R software.

We modeled the age-depth relationship using the smooth-spline setting in Clam.R. However, we found that the Clam.R software generated either drastic fluctuations in sedimentation rate between the ^{210}Pb and ^{14}C -dated portions of the composite with a low smoothing factor (0.6), or inaccurate modeling of the coretop age using stronger smoothing (0.8). To circumvent this, we used two smoothing factors: 0.6 for the top 11 cm, dated by ^{210}Pb , and 0.83 for the remainder of the composite. The two age models were spliced together at 11 cm, where they naturally intersect.

The modeled chronology is shown in Figure 5.3. The lowermost radiocarbon age is 28.5 ± 1 ka at 409 cm, and extrapolating to the bottom of the core yields a basal age of 32.7 ± 2.6 ka. Sedimentation rate averages $0.15 \text{ mm year}^{-1}$, and $172 \text{ g m}^{-2} \text{ year}^{-1}$, and is highly variable throughout the core as described below.

5.5.2 Sediment lithology

The sediment stratigraphy is divided into three lithologic units based on physical characteristics of the composite stratigraphy (Figures 5.3 and 5.4). Unit I (205-500.5 cm) spans the base of the core to the end of the LGM, Unit II (91-205 cm) spans the deglacial period and start of the Holocene, and Unit III (0-91 cm) spans the remainder of the Holocene. These units are further distinguished based on sediment chemistry (Figure 5.5), and a variety of other properties discussed below.

Unit I The Last Glacial Maximum

Unit I begins at the base of the section (500.5 cm) and extends to 205 cm, which represents the period from 32.7 ± 2.6 ka to 19.0 ± 0.6 ka (Figure 5.2), thus encompassing sediments deposited during the end of Marine Isotope Stage 3 (MIS3) and the last glacial maximum (LGM). The unit is composed primarily of medium to thinly bedded light reddish brown to gray clayey silts and fine sands, with a low Green/Red ratio indicating oxidized sediments (Figure 5.3). Magnetic susceptibility is high in this unit, averaging 25 SI units. Water content is low (20-40%), dry bulk density is high ($1-1.8 \text{ g cm}^{-3}$), and the mass accumulation rate is substantially higher than overlying units, averaging $275 \text{ g m}^{-2} \text{ year}^{-1}$ (Figure 5.2). Total organic carbon is low, averaging $1.0 \pm 0.3\%$.

Unit I contains coarse-grained lithologies suggesting that the lake shoreline was nearer our coring site. The persistence of thin parallel bedding, homogenous density and water content, and lack of obvious erosive surfaces, however, suggests that the lake never reached total dryness. In contrast, several other lakes from northern Alaska show sedimentary hiatuses associated with desiccation during the LGM (Oswald et al., 1999; Abbott et al., 2010). Currently, winter lake ice can become bedfast in lakes shallower than 2.2 m (Arp et al., 2012), and sediments from those lakes are susceptible to ice scouring. The thin bedding and relatively constant sediment deposition rates of this unit indicates little sediment disturbance and ice scouring. We interpret that the lake was never shallower than 2 m deep.

Calcium carbonate, primarily calcite, is intermittently present in low abundance throughout the unit in the form of silt-sized rhombohedral grains. Two 1-cm thick orange clay beds contain abundant fine silt-sized Fe-Mn-Ca-carbonate, at 277 cm (21.7 ± 0.9 ka) and 338 cm (24.3 ± 1.0 ka). Based on microscopic inspection of the carbonates we

conclude they are predominantly authigenic in origin. Today, Lake E5 is extremely dilute, with specific conductivity averaging 10.2 ms cm^{-1} ; calcite-forming organisms are absent and chemical precipitation does not occur. Precipitation of carbonate minerals therefore required a substantial increase in salinity during the LGM relative to today, which could have been driven by enhanced salt inputs or more likely, evaporative salt concentration. Carbonate minerals would have been further stabilized by high pH, possibly in relation to the weathering of fresh glacial till, as has been suggested for paraglacial lakes in Denmark (Postma, 1977). However, as other lines of evidence point to extreme cold and aridity, concentrating process was a key factor in promoting carbonate formation. The presence of these carbonates therefore confirms low lake levels throughout Unit I. Precipitation of discrete Fe-Mn- CaCO_3 beds would have further required reducing lake water conditions (Dean, 2002) permitting the presence of Fe^{2+} and Mn^{2+} . Low lake levels alone should lead to improved oxygenation of the water column, as inferred from the reddish-gray to brown color of the unit. This is at odds with the presence of reduced iron and manganese carbonate. We postulate that anoxic conditions may have been driven by perennial ice cover, which is supported by the fact that the occurrence of these beds at 24.3 ka and 21.7 ka align with the coldest periods of the last 30 thousand years, namely Heinrich event II and the LGM.

Lower lake levels may have also given rise to the high clastic sediment fluxes during the LGM. Without details of basin-wide accumulation patterns, it is difficult to assess how sediment focusing may have changed as a function of water levels.

Furthermore, as there is no evidence that Brooks Range glaciers extended into the Lake E5 watershed (Manley and Kaufman, 2002; Hamilton, 2003), even at the maximum

glacier extent, basin-scale sediment supply likely did not cause the increase in detrital accumulation. We speculate that as Lake E5 is a fairly small basin, changes in sediment focusing were minor compared to changes in the flux of detrital inputs entering the lake. Given evidence for regionally dry conditions, the potential for loess production by Brook Range glaciers, and aeolian dunes elsewhere in the region (Carter, 1981), aeolian transport of freshly eroded clastic material was likely an important mechanism promoting sediment deposition in Lake E5. A loess source would describe the clay- and fine-sand fraction found in Unit I.

Concentrations of Sr, Ti, K, and Si are highest in this unit, while Mn, Fe, and S are generally low. A principle component analysis (PCA) of the elemental abundance data cleanly separates the three major lithologic units (Figure 5.5), and helps to identify the major processes controlling sediment composition in the lake. Loading scores indicate that the first axis of the PCA, which controls 40.7% of the variance in the data, is primarily driven by the ratio of organic matter content (%TOC and TN) versus clastic indicators (Si, Sr), while the second axis is controlled by redox-sensitive elements such as sulfur, iron, and manganese (Table 5.2, Figure 5.5). Positive values on PC 1, and low values on PC 2, indicate high clastic sediment content and relatively oxidizing conditions during the deposition of Unit I. The chemical index of alteration averages 84 (Figure 5.5), the lowest observed in the composite stratigraphy. Based on regional glacial till weathering patterns (Keller et al., 2007), it is reasonable to conclude that this material was derived from freshly produced loess related to glacier activity in the nearby Brooks Range (Walker and Everett, 1991).

Overall, the $\delta D_{C_{28}}$ exhibits strong glacial-interglacial structure. During the LGM, values are fairly stable about -290‰ and are $\sim 20\text{‰}$ lower than Holocene values reflecting a temperature depression of approximately $4.1 \pm 3.6\text{ °C}$ relative to present day (Chapter 3), with the range depending largely on how vegetation change during the LGM may have impacted the D/H fractionation in the course of leaf wax production. In contrast, $\delta D_{C_{16}}$ is relatively D-enriched, resulting in positive values of $\Delta\text{-}\delta D$. The $\Delta\text{-}\delta D_{\text{wax}}$ reaches values as high as $+47\text{‰}$ at the base of the unit, and averages $+26\text{‰}$ through the unit. The high values of $\Delta\text{-}\delta D$ strongly indicate that Lake E5 was a closed basin during the LGM and was susceptible to sustained evaporative enrichment of lake water isotopes.

Unit II: The Last Deglaciation

Lithologic Unit II spans from 205 cm to 103 cm (19.0 ± 0.1 to 11.6 ± 0.2 ka) and encompasses the deglacial period and start of the Holocene. The transition from Unit I to Unit II is delineated on the basis of sediment color transitioning from light brown to black, the $\Delta\text{-}\delta D$ shifting from positive to negative values, and both the first and second components of the geochemical PCA changing abruptly.

Sediments from Unit II are comprised of thinly bedded black/green and dark brown silt and clays (Figure 5.2). The average accumulation rate is $72\text{ g m}^{-2}\text{ year}^{-1}$, approximately one-fourth that of Unit I. Magnetic susceptibility generally declines upwards, but is highly variable. In the top of the unit, oscillations in color correspond with oscillations in magnetic susceptibility, with the darker beds having higher MS (Figure 5.3).

The darker color of the sediment, and an increase in the Green/Red ratio, both indicate more reducing conditions in the sediment. This is confirmed by high sulfur, iron, and TOC concentrations (Figure 5.5), as well as much higher PC2 scores than Units I and III. The stratigraphic increase in Fe and S and shift to greater reducing capacity in sediments usually originates from increases in lake productivity (Engstrom and Wright Jr, 1984) and we previously showed that small increases in productivity can drive anoxia in Lake E5 hypolimnion (Daniels et al., 2015). Reduced mixing may have contributed to reducing conditions. As the δD_{wax} indicated temperatures were still cold during this interval, reduced mixing would most likely have been caused by extensive lake ice. However, higher lake productivity, reflected by the dramatic rise in %TOC and calcite precipitation, supports productivity as the driver of lake anoxia.

Pyrite is evident in smear slides; however, between Units I and II, Fe increases by an average of 40 ppt by weight, while S increased by 10 ppt by weight implying a considerable excess of Fe. Typically, Fe is mobilized out of sediment under anoxic conditions and so its elevated concentrations are surprising given the indications of anoxia. We therefore interpret the excess Fe as an indication of enhanced mobilization of Fe from land to the lake during this interval. Reduced concentrations of Si, Ti, and K, a sharp reduction in PC1 scores relative to Unit I, and lower sedimentation rates suggest that particulate deposition was not likely the main cause, and so we speculate that soil OM accumulation and waterlogging promoted reduction and mobilization of soil Fe in the dissolved form. In the lake this Fe, together with Mn, precipitated as sulfides, magnetite, and other reduced or partially-reduced species. Corresponding fluctuations in color, magnetic susceptibility, and Fe and S concentrations during the late deglacial

derived from redox-sensitive chemical speciation, and point to variable degrees of anoxia in Lake E5.

The chemical index of alteration increases monotonically through Unit II, reflecting the long-term leaching of base cations from loess deposited during the LGM. Today, geochemical profiles from soils on the Sagavanirktok glacial surface illustrate that intense weathering has occurred in the soil active layer, leaving surficial soils depleted in calcium, barium, strontium, and other cations relative to deeper permafrost soils (Keller et al., 2007). While these soils were generally ancient (>100 ka) even prior to the LGM (Hamilton, 2003), accumulated glacial loess during MIS2 may have helped reset the soil CIA value, with these low values then reflected in the detrital component of the Lake E5 composite. Weathering of this material likely progressed rapidly upon intensification of the hydrologic cycle at 19 ka, and would have been further enhanced by soil water acidification which accompanied the development of organic-rich soils. We speculate that the aquatic productivity may have been stimulated by phosphorus release (Keller et al., 2010) during this period of most active weathering.

Increased inflow/evaporation beginning at 19 ka is supported by lithologic evidence of lake infilling. As water levels rose and the shoreline retreated from the coring site, clastic sediment flux and sediment grain size decreased. Reduction in clastic accumulation was probably also driven by stabilization of soils in a wetter environment. The lower portion of the unit (200-160 cm, 19-16 ka) has elevated TIC, and smear slide analysis reveals abundant round 30-50 μm calcite grains of authigenic origin. Little to no calcite is observed above 160 cm. Increasing organic carbon at 19 ka suggests that enhanced in-lake productivity may have driven the sharp increase in calcite deposition

from 19-16 ka, as photosynthesis can increase pH sufficiently to allow carbonate precipitation (Kelts and Hsü, 1978). The cessation of carbonate deposition despite continued increase in TOC implies that the ionic strength of Lake E5 declined at 16 ka to levels too low to support calcite precipitation, reflecting a rapid change in lake salinity.

The hydrogen isotope ratios are indicative of a moist environment with variable temperature. The $\delta D_{\text{precipitation}}$ shows a short-lived positive excursion of $\sim 4^\circ\text{C}$ lasting from 19 ka to 17.5 ka. Following this, there is a persistent D-enrichment trend which is punctuated by several oscillations which may be linked to global climate oscillations or the flooding of the Bering Strait at ~ 13 ka (Chapter 3). Near the top of this unit, there is a rapid increase in $\delta D_{\text{precipitation}}$ marking the termination of the Younger Dryas chronozone (11.6 ka), after which time $\delta D_{\text{C}_{28}}$ indicates much warmer conditions. In contrast, the $\delta D_{\text{C}_{16}}$ becomes more depleted before showing minor fluctuations through Unit II. Overall, the $\Delta\text{-}\delta D$ shifts from $+26\text{‰}$ in Unit I to -16‰ in Unit II (Figure 5.4).

In agreement with lithologic indicators, $\Delta\text{-}\delta D$ begins to shift toward more negative values at 19 ka, signifying the beginning of increased effective moisture. A shift to a more positive moisture balance lowered the residence time of water in the lake and limited evaporative effects on δD_{Lake} . $\Delta\text{-}\delta D$ began to stabilize at ~ 16 ka, the same time that %TIC declined rapidly. We interpret this to indicate that Lake E5 achieved its present level at this time, and began to overflow, resulting in a dramatic decline in salinity.

Upon reaching the sill depth, the rapid decline in water residence time likely reduced the sensitivity of the $\Delta\text{-}\delta D$ proxy to evaporative enrichment. Nonetheless, possible millennial scale fluctuations occur. Notable are shifts toward lower $\Delta\text{-}\delta D$ (wet)

from 13.8-13 ka and toward higher $\Delta\delta D$ (dry) from 16-15 ka and 13 to 11 ka. While these shifts are for the most part within the $\pm 20\text{‰}$ (1σ) uncertainty, they roughly align with global climate oscillations. We previously attribute an abrupt warming at 13.5 ka to the opening of the Bering Strait (Chapter 3). This same occurrence likely drove the increased moisture convergence over Alaska at 13.5 ka, although we cannot determine if it was decreased continentality alone or changes in ocean heat transport that drove the moisture change. Of the dry periods, the latter roughly aligns with the Younger Dryas chronozone, which has previously been associated with floodplain incision and drying across the North Slope (Mann et al., 2002). The earlier transient dry period is represented by an equally large positive excursions in $\Delta\delta D$ as that of the YD, and we postulate that Lake E5 water levels were below sill depth during at that time. Drying from 16-15 ka has not been previously reported from the region, although Brooks Range mountain glaciers receded from 16-15 ka (Pendleton et al., 2015). The drying event observed here may be linked to this glacier recession, and more broadly with Heinrich Stadial I (Seierstad et al., 2014).

The transient hydrologic fluctuations between 16 and 11.6 are apparent in both $\Delta\delta D$ and the first component of the XRF-based PCA analysis. Thus the shorter-lived precipitation oscillations may have had significant impacts on the deglacial ecology and paleolimnology of Lake E5, possibly through its impact on weathering of glacial till as described above.

Unit III: The Holocene

The uppermost lithologic unit (III, 91-0 cm; $\sim 10,130 \pm 100$ to -64 ybp) spans most of the Holocene. The Unit III/II boundary marks the point at which magnetic susceptibility, Green/Red ratio, and TOC begin to decline. Unit III consists of thin and medium beds of brown silts (Figure 5.2). The unit has low magnetic susceptibility, consistent with decreasing clastic sediment accumulation rate and relatively high organic content, low Green/Red ratio, low dry bulk density, and high water content. Sediment accumulation rate is $25 \text{ g m}^{-2} \text{ year}^{-1}$, which is nearly identical to that of current accumulation rates estimated in nearby Toolik Lake (Cornwell and Kipphut, 1992), and extremely slow compared to lakes worldwide, thus highlighting the overall stability of tundra soils, low lake productivity, and relative lack of aeolian transport occurring on the North Slope relative to the LGM.

The elemental composition of Unit III differs from both Unit I and II. Detrital indicators are low, and the abundant Fe, Mn, and S seen in Unit II also decrease to the lowest values observed (Figure 5.4), indicating that mobile elements were largely depleted from soils by this time. Soil cation depletion is further substantiated by relatively stable CIA values throughout the Holocene, and agrees well with modern soil geochemistry which demonstrate that soils of the Saganavirktok glacial deposits are depleted in easily-leachable cations (Keller et al., 2007). The absence of carbonate precipitation implies that, in addition to salt inputs being low due to soil cation depletion, any period of lake level lowering were too short-lived for the lake to accumulate substantial salinity through evaporative concentration.

PC2 declines to values similar to those of Unit I. TOC averages $8.2 \pm 1.5\%$, and decreases in a stepwise fashion with a 5% decline occurring from 91 to 75 cm (10.1 ± 0.2 to $9.6 \pm 0.2\%$).

to 8.0 ± 0.2 ka) and another 4% decline from 32 to 13 cm (2.6 ± 0.3 to 0.7 ± 0.2 ka). In combination with the Green/Red ratio, these data suggesting increasing lake floor oxygenation and decreasing primary production through this interval.

δD_{C28} gradually becomes more D-depleted indicating a cooling trend through the Holocene (Chapter 3). A local minimum is reached near the core top (685 ± 175 to 69 ± 36 years bp), followed by a 5‰ enrichment in the uppermost 133 years (Figure 5.4), likely recording the post-industrial warming observed in the instrumental record (Chapter 3). The $\Delta\delta D$ is less negative in Unit III compared to Unit II, indicating that the Holocene is relatively drier compared to the deglacial period. Fluctuations during the Holocene may have resulted from temporary lake level depressions below the sill depth. Which again, were too short of intervals for the lake to acquire high salinity, but long enough to drive isotopic evolution of the lake water. Maximum Holocene aridity occurred from 6-8 ka, and the late-Holocene was generally wetter with brief periods of possible extreme aridity.

5.6 Discussion

Taken together, the sedimentary and geochemical stratigraphy of Lake E5 document large changes in moisture balance and landscape evolution in Arctic Alaska. We infer a much drier and colder climate than the present from ~33 to 19 ka BP. Lake E5 was a substantially smaller, saltier, evaporatively concentrated lake, with occasional periods of perennial ice cover. Sedimentation was dominated by poorly weathered aeolian silt and sand. The climate became wetter beginning at 19 ka, resulting in several environmental changes, including enhanced chemical weathering of soils, high lake

productivity and lake anoxia, and organic accumulation in the watershed. As soils became stabilized, accumulation of clastic material slowed. Peak moisture and temperature occurred following the termination of the Younger Dryas, after which gradual cooling and drying are observed over the Holocene. With decreasing temperatures, precipitation, and cation/nutrient inputs, the lake became less productive and better oxygenated over the Holocene.

5.6.1 Climatic interpretation

The combined lithologic, geochemical, and isotopic results from Lake E5 reflect large-scale changes in moisture balance that impact catchment-scale sedimentology. Generally, Arctic precipitation scales positively with temperature due to enhanced evaporation from Arctic Ocean and enhanced moisture flux from low latitudes (Bintanja and Selten, 2014). Overall, this theory holds true in the Lake E5 record presented here, which exhibits a cool and dry LGM compared to a warm and moist Holocene. However, the hydrogen isotope data indicate four distinct climatic modes: cold/dry conditions from 32 to 19 ka, cold/wet, and warm/wet conditions from 19 to 11.6 ka, and warm/wet (and possibly warm/dry) conditions from 11.6 ka to present. This is generally supported by lithologic data, although the second transition, identified by the peak carbon content last signs of anoxia, does not occur until 10.1 ka.

The general picture of a cool, dry, and windswept LGM agrees with most available lines of evidence from northern Alaska, particularly the activation of aeolian dune fields on the Alaskan Coastal Plain, 150 km northwest of our site (Carter, 1981). Cool and dry conditions prevail when the arctic jet shifts southward and Arctic air mass dominates over northern Alaska (Edwards et al., 2001). During the LGM, expansion of

sea ice in both the Arctic and North Pacific would have diminished both sources of moisture, and in the case of the Arctic Ocean, probably to the point of irrelevance (Bradley and England, 2008).

The timing of moisture intensification at 19 ka precedes pollen-based estimates across the region by several millennia (Viau et al., 2008; Abbott et al., 2010) but is consistent with lake level increases at Burial Lake around 19 ka (Finkenbinder et al., 2015). Northern Brooks Range mountain glaciers were largely receding from 21-15 ka with the exception of a standstill or slight advance at 18 ka (Pendleton et al., 2015). The glacial retreat may have been interrupted due to enhanced moisture convergence in the area as our record would suggest. Yet, since moisture continued to increase, subsequent glacial retreat was probably driven by warming beginning around 19 ka. Alternatively, if the increase in precipitation reported here fell in the form of summer rainfall, it may have contributed to glacial retreat rather than expansion.

At present, three moisture sources contribute to precipitation at the Toolik Lake area – the Arctic Ocean, the North Pacific/Bering Sea, and recycling of continental moisture (Klein et al., 2015). Enhanced recycling of inland waters cannot explain the secular change in moisture balance that occurred at 19 ka, as aridity was widespread across the region. New fluxes of moisture were required to increase moisture balance. Eustatic sea level rise decreased the continentality of interior Alaska beginning around 19 ka, and likely influenced moisture balance in the newly-maritime regions. The sea level effect may have contributed some moisture to our site, but the combined evidence for dry periods during the Holocene when sea level is highest and the fact that precipitation

increased prior to substantial sea level rise (Figure 5.6) suggests it is not the main driver of post-glacial hydrologic change.

Variations in moisture source proximity, as determined by continentality (Finkenbinder et al., 2015) and sea ice extent (Hebbeln et al., 1994; Klein et al., 2015), are important controls on Arctic precipitation and can vary independently of temperature (McKay et al., 2008). Sea ice cover is a particularly important control on atmospheric moisture in the Arctic (Bintanja and Selten, 2014). Indeed, precipitation at Toolik Field Station is strongly associated with sea ice cover in the adjacent Chukchi Sea. LGM and deglacial sea ice records from the western Arctic Ocean are unavailable, but ice extent likely increased given the much colder climate that existed at this time. Over the Holocene, temporary contraction of sea ice away from the Chukchi coast from 6-5 ka and from 4-2 ka (de Vernal et al., 2005; McKay et al., 2008) co-occur with $\Delta\delta D$ -inferred moist periods observed in the Lake E5 record. Based on the correlation between precipitation and ice cover and the correspondence between our hydrogen-isotope based paleohydrology record and Arctic sea ice extent and we posit that over the course of the deglaciation, moisture availability as regulated by sea ice extent heavily influenced precipitation over northern Alaska. This link is strengthened by the knowledge that Arctic cyclones are presently an important source of moisture to Arctic Alaska (Klein et al., 2015), and that strong temperature gradients at the ice edge contribute to the formation of mesoscale storms at high-latitudes (Tsukernik et al., 2007).

At 19 ka, sea ice contracted in the Ohkstk Sea (Sakamoto et al., 2005), and contracted slightly in the Bering Sea, although here a more pronounced retreat occurred at ~17 ka (Caissie et al., 2010). The behavior of sea ice in the Western Arctic Ocean

during the early deglacial is unknown at this time. Sea ice retreat in the North Atlantic sector of the Arctic ocean at ~19.5 ka provided a new moisture source which partially aided the growth of the Barents Ice Sheet locally (Hebbeln et al., 1994) and may have provided a source of moisture to our site. Although this is distant from Arctic Alaska, the agreement in timing suggests a moisture connection between the two locations. A northward shift in the jet from 19 to 17.5 ka cannot be entirely ruled out as an important driver of warm and wet temperatures at that time. A return to cool temperatures in association with increasing moisture, however, implies a growing moisture source after 17.5 ka.

Hydrologic conditions appear highly variable during the deglaciation. A dry YD is in agreement with floodplain incision on the North Slope and lake level declines in interior Alaska (Abbott et al., 2000; Mann et al., 2002). Our data indicate that the Bølling was also marked by high moisture availability. In contrast, the climate of the Holocene is relatively stable. There is a long term cooling evident in the $\delta D_{\text{precipitation}}$ data (Chapter 3), driven by the declining insolation over this time (Figure 5.6, Chapter 3). The paleohydrology data show generally declining moisture balance through the Holocene, with particularly dry conditions prevailing from approximately 8 to 6 ka. A dry early Holocene is also reported by Anderson et al. (2001), from cellulose $\delta^{18}\text{O}$ measurements from nearby Meli Lake. Thus, despite warm temperatures, the early Holocene was quite dry. Intriguingly, charcoal analysis from several cores on the North Slope identified fire activity about 7 ka (Chipman et al., 2015), coincident with the driest time in the Holocene observed here.

Overall, precipitation and temperature are positively correlated through the record. Excursions from this relationship must emanate from surface and atmospheric dynamics. The periods from 8-6 ka and 19-14 ka offer two contrasting excursions from this basic relationship. The first case illustrates the importance of sea ice as a control on moisture over Alaska – at this time, Chukchi Sea ice extent was the highest in the Holocene, thereby cutting off an important moisture source (McKay et al., 2008), resulting in dry conditions over the continent. In the latter case, rapid changes in temperature coupled with continually increasing moisture probably resulted from the dual influences of shifting atmospheric jet location (Edwards et al., 2001) and reduced sea ice in the Bering Sea (Caissie et al., 2010).

5.6.2 The role for moisture balance in deglacial environmental change

Arctic ecosystems are highly sensitive to temperature fluctuations, and temperature is often considered the primary control on Arctic ecology at glacial-interglacial timescales. However, our record indicates dramatic ecological changes beginning at 19 ka in association with large changes in hydrology. We infer that hydrologic variations played a major role in ecological changes during the last deglaciation.

The establishment of moss carpets and soil cation depletion are two principle controls on modern tundra ecosystems that would have been strongly affected by precipitation. Widespread calcium-rich tundra (also referred to as moist non-acidic tundra, MNT) was extremely important to the high abundance of megafauna during the last ice age (Walker et al., 2001). MNT was widespread during and after the LGM, but today occurs sparsely, either on relatively young glacial surfaces in the Arctic foothills, in

locations where the glacial till is mostly derived from limestone and dolomite formations in the Brooks Range, and in regions with low rainfall (Figure 5.1).

Can increased moisture induce the transition from MNT to moist acidic tundra (MAT)? The glacial-aged soils were poorly weathered, dry, and nutrient and calcium rich, as indicated by the high CIA values in our record. With characteristically small grain size and carbonate rich mineralogy, loess would have been highly susceptible to weathering, particularly under moist conditions. Vertical profiles of soils from the Sagavanirktok glacial surface demonstrate that soil carbonates are highly depleted in the soil active layer today (Keller et al., 2007). We postulate that these weathering profiles were reset at the time of greatest loess deposition (during the LGM in our sediment core), and then developed over the following tens of millennia after post-glacial precipitation increased.

The chemical composition of E5 sediment stratigraphy shows that a major pulse in precipitation at 19 ka lead to both soil stabilization, indicated by reduced sediment accumulation rates, and to accelerated chemical weathering of soils (Figure 5.5). Changes in Fe, redox state, and lake productivity that occurred at 19 ka can be linked to increasingly waterlogged/anaerobic soils. Data on basal peat ages suggest that most peat initiation on the North Slope began around 11.6 ka (Jones and Yu, 2010), coinciding with the abrupt warming reported here. It is possible that peat initiation occurred early within confined locations of the North Slope, such as the E5 catchment. Alternatively, peat initiation may have been preceded by a phase characterized by intermediate levels of soil organic matter, soil moisture, and cation content and was neither typical of MNT nor

MAT. Overall, the evidence points to an earlier onset of paludification relative to other North Slope sites, driven largely by enhanced moisture availability.

The transition to a wetter climate also affected aquatic ecosystems. The combination of high rates of chemical weathering of soils, increasing lake levels, and cool temperatures appear to be conducive to high lake productivity and water column anoxia during the last glacial termination. The positive inflow-evaporation balance after 19 ka led to increasing lake levels, shifting Lake E5 from a shallow pond to a lake capable of thermal stratification, a condition necessary for the apparently anoxic conditions that prevailed during the deglaciation. At present, the water column oxygenation of Lake E5 is extremely sensitive to even small increases in nutrient loading (Daniels et al., 2015). The strong correlation between phosphorus and calcium carbonate in regional soils (Keller et al., 2007) suggests that the period of intense soil weathering beginning at 19 ka may have resulted in sufficient P delivery to promote productivity to the point of driving bottom waters anoxic. High in-lake productivity is evident based on the presence of calcium carbonate and increased organic carbon content. Upon breaching its sill, Lake E5's salinity dropped precipitously, but high productivity was sustained through the deglacial period, possibly through continued P-loading. Notably, CIA values continue to rise well after the lake achieved overflow, suggestion continued soil leaching into the Holocene. However, over the Holocene, as soils continued to become leached of exchangeable cations and moist acidic tundra became a sink for nutrients, the lake was driven towards oligotrophication and acidification.

5.7 Conclusions

A continuous sediment core from Lake E5 provides a record of hydroclimatological and limnological change from ~30 ka to present. Lithological and geochemical observations indicate that cool and dry conditions during the LGM gave way to wetter, but still cool, conditions beginning at 19 ka, and were followed by a transition to warm and wet conditions at 11.6 ka, synchronous with the termination of the Younger Dryas. Reorganization of the atmospheric circulation patterns at 19 and again at 11.6 ka may have contributed to development of three observed climate modes, including cold/dry, cold/moist, and warm/wet conditions, but reductions in sea ice were also an important factor governing precipitation over the North Slope. Our multi-proxy assessment also reveals several climate oscillations during the last deglaciation. Curiously, drying is evident during both the Younger Dryas and the Bølling-Allerød, and a climatic and ecological shift occurred between these two events, which is likely related to local climate forces such as the Bering Strait flooding or the retreat of the LIS. During the Holocene, cooling was most likely driven by the strong decline in summer insolation, and resulted in gradual drying.

We infer that hydrologic intensification was critical to, if not the main factor driving ecological changes during the early deglacial. The increase in effective moisture promoted stabilization of soils and chemical weathering of recently deposited glacial loess. These changes were intimately linked to the gradual transition from moist non-acidic tundra to the moist acidic tundra observed today at Lake E5. Primary productivity in Lake E5 peaked during the deglaciation, and the lake was commonly anoxic from 19 to 10 ka. Climatically, this period was wet (lake filling and at overflow) but still cold.

Primary productivity was high in the lake due to enhanced weathering-driven nutrient loading. Land cover gradually transitioned from well-drained and poorly weathered soils to the moist acidic tundra observed today. Soil moistening initially mobilized nutrients through mineral weathering, but eventually paludification became a major nutrient sink driving oligotrophication and acidification of Lake E5.

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5.9 References

- Abbott, M.B., Edwards, M.E. and Finney, B.P. (2010) A 40,000-yr record of environmental change from Burial Lake in Northwest Alaska. *Quatern. Res.* 74, 156-165.
- Abbott, M.B., Finney, B.P., Edwards, M.E. and Kelts, K.R. (2000) Lake-level reconstruction and paleohydrology of Birch Lake, central Alaska, based on seismic reflection profiles and core transects. *Quatern. Res.* 53, 154-166.
- Anderson, L., Abbott, M.B. and Finney, B.P. (2001) Holocene climate inferred from oxygen isotope ratios in lake sediments, central Brooks Range, Alaska. *Quatern. Res.* 55, 313-321.
- Anderson, L., Abbott, M.B., Finney, B.P. and Burns, S.J. (2005) Regional atmospheric circulation change in the North Pacific during the Holocene inferred from lacustrine carbonate oxygen isotopes, Yukon Territory, Canada. *Quatern. Res.* 64, 21-35.

- Arp, C.D., Jones, B.M., Lu, Z. and Whitman, M.S. (2012) Shifting balance of thermokarst lake ice regimes across the Arctic Coastal Plain of northern Alaska. *Geophys. Res. Lett.* 39.
- Badding, M.E., Briner, J.P. and Kaufman, D.S. (2013) ^{10}Be ages of late Pleistocene deglaciation and Neoglaciation in the north - central Brooks Range, Arctic Alaska. *Journal of Quaternary Science* 28, 95-102.
- Balascio, N.L., D'Andrea, W.J., Gjerde, M. and Bakke, J. (2016) Hydroclimate variability of High Arctic Svalbard during the Holocene inferred from hydrogen isotopes of leaf waxes. *Quaternary Science Reviews*.
- Binford, M.W. (1990) Calculation and uncertainty analysis of ^{210}Pb dates for PIRLA project lake sediment cores. *J. Paleolimnol.* 3, 253-267.
- Bintanja, R. and Selten, F.M. (2014) Future increases in Arctic precipitation linked to local evaporation and sea-ice retreat. *Nature* 509, 479-482.
- Blaauw, M. (2010) Methods and code for 'classical' age-modelling of radiocarbon sequences. *quaternary geochronology* 5, 512-518.
- Bradley, R.S. and England, J.H. (2008) The Younger Dryas and the sea of ancient ice. *Quatern. Res.* 70, 1-10.
- Caissie, B.E., Brigham-Grette, J., Lawrence, K.T., Herbert, T.D. and Cook, M.S. (2010) Last Glacial Maximum to Holocene sea surface conditions at Umnak Plateau, Bering Sea, as inferred from diatom, alkenone, and stable isotope records. *Paleoceanography* 25, PA1206.
- Carter, L.D. (1981) A Pleistocene sand sea on the Alaskan Arctic coastal plain. *Science* 211, 381-383.
- Cherry, J.E., Déry, S.J., Stieglitz, M. and Pan, F.-f. (2014) Meteorology and climate of Toolik Lake and the north slope of Alaska: Past, present and future. *Alaska's changing Arctic: Ecological consequences for tundra, streams, and lakes*. Oxford Univ. Press.
- Chikaraishi, Y. and Naraoka, H. (2007a) $\delta^{13}\text{C}$ and δD relationships among three n-alkyl compound classes (n-alkanoic acid, n-alkane and n-alkanol) of terrestrial higher plants. *Org. Geochem.* 38, 198-215.

Chipman, M., Hudspeth, V., Higuera, P., Duffy, P., Kelly, R., Oswald, W. and Hu, F. (2015) Spatiotemporal patterns of tundra fires: late-Quaternary charcoal records from Alaska. *Biogeosciences* 12, 4017-4027.

Cornwell, J. and Kipphut, G. (1992) Biogeochemistry of manganese- and iron-rich sediments in Toolik Lake, Alaska. *Hydrobiologia* 240, 45-59.

Daniels, W.C., Kling, G.W. and Giblin, A.E. (2015) Benthic community metabolism in deep and shallow Arctic lakes during 13 years of whole-lake fertilization. *Limnol. Oceanogr.*, n/a-n/a.

de Vernal, A., Hillaire-Marcel, C. and Darby, D.A. (2005) Variability of sea ice cover in the Chukchi Sea (western Arctic Ocean) during the Holocene. *Paleoceanography* 20, PA4018.

Dean, W. (2002) A 1500-year record of climatic and environmental change in Elk Lake, Clearwater County, Minnesota II: geochemistry, mineralogy, and stable isotopes. *J. Paleolimnol.* 27, 301-319.

Edwards, M.E., Mock, C.J., Finney, B.P., Barber, V.A. and Bartlein, P.J. (2001) Potential analogues for paleoclimatic variations in eastern interior Alaska during the past 14,000 yr: atmospheric-circulation controls of regional temperature and moisture responses. *Quaternary Science Reviews* 20, 189-202.

Eisner, W.R. and Colinvaux, P.A. (1992) Late Quaternary Pollen Records from Oil Lake and Feniak Lake, Alaska, U.S.A. *Arct. Alp. Res.* 24, 56-63.

Engstrom, D.R. and Wright Jr, H. (1984) Chemical stratigraphy of lake sediments as a record of environmental change. *Lake sediments and environmental history: studies in palaeolimnology and palaeoecology in honour of Winifred Tutin*/edited by EY Haworth and JWG Lund.

Finkenbinder, M., Abbott, M., Finney, B., Stoner, J. and Dorfman, J. (2015) A multi-proxy reconstruction of environmental change spanning the last 37,000 years from Burial Lake, Arctic Alaska. *Quaternary Science Reviews* 126, 227-241.

Gibson, W. (2009) Mean Precipitation for Alaska 1971-2000. National Park Service Alaska Regional Office GIS Team.

Hamilton, T.D. (2003) Surficial geology of the Dalton Highway (Itkillik-Sagavanirktok rivers) area, southern Arctic foothills, Alaska.

Hebbeln, D., Dokken, T., Andersen, E.S., Hald, M. and Elverhøi, A. (1994) Moisture supply for northern ice-sheet growth during the Last Glacial Maximum.

Hu, F.S., Higuera, P.E., Walsh, J.E., Chapman, W.L., Duffy, P.A., Brubaker, L.B. and Chipman, M.L. (2010) Tundra burning in Alaska: Linkages to climatic change and sea ice retreat. *Journal of Geophysical Research* 115.

Huang, Y., Shuman, B., Wang, Y. and Webb, T. (2002) Hydrogen isotope ratios of palmitic acid in lacustrine sediments record late Quaternary climate variations. *Geology* 30, 1103-1106.

Jasechko, S., Lechler, A., Pausata, F., Fawcett, P., Gleeson, T., Cendón, D., Galewsky, J., LeGrande, A., Risi, C. and Sharp, Z. (2015) Glacial-interglacial shifts in global and regional precipitation δ 18O. *Clim. Past Discuss* 11, 831-872.

Jones, M.C. and Yu, Z. (2010) Rapid deglacial and early Holocene expansion of peatlands in Alaska. *Proceedings of the National Academy of Sciences* 107, 7347-7352.

Kattsov, V.M., Walsh, J.E., Chapman, W.L., Govorkova, V.A., Pavlova, T.V. and Zhang, X. (2007) Simulation and projection of Arctic freshwater budget components by the IPCC AR4 global climate models. *Journal of Hydrometeorology* 8, 571-589.

Keller, K., Blum, J. and Kling, G. (2007) Geochemistry of Soils and Streams on Surfaces of Varying Ages in Arctic Alaska. *Arct. Antarct. Alp. Res.* 39, 84-98.

Keller, K., Blum, J.D. and Kling, G.W. (2010) Stream geochemistry as an indicator of increasing permafrost thaw depth in an arctic watershed. *Chem. Geol.* 273, 76-81.

Kelts, K. and Hsü, K. (1978) Freshwater carbonate sedimentation, Lakes. Springer, pp. 295-323.

Klein, E.S., Cherry, J.E., Young, J., Noone, D., Leffler, A.J. and Welker, J.M. (2015) Arctic cyclone water vapor isotopes support past sea ice retreat recorded in Greenland ice. *Scientific Reports* 5, 10295.

- Konecky, B., Russell, J. and Bijaksana, S. (2016) Glacial aridity in central Indonesia coeval with intensified monsoon circulation. *Earth. Planet. Sci. Lett.* 437, 15-24.
- MacDonald, G.M. and Case, R.A. (2005) Variations in the Pacific Decadal Oscillation over the past millennium. *Geophys. Res. Lett.* 32, n/a-n/a.
- Majoube, M. (1971) Oxygen-18 and deuterium fractionation between water and steam. *J. Chim. Phys. Phys.-Chim. Biol.* 68, 1423-+.
- Manabe, S. and Stouffer, R.J. (1980) Sensitivity of a global climate model to an increase of CO₂ concentration in the atmosphere. *Journal of Geophysical Research: Oceans* 85, 5529-5554.
- Manguin, E. (1961) Contribution à la flore diatomique de l'Alaska: Lac Karluk, espèces critiques ou nouvelles. *Revue Algologique, Nouvelle Série* 5, 266-288.
- Manley, W.F. and Kaufman, D. (2002) Alaska paleoglacier atlas. Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Boulder, CO.
- Mann, D.H., Groves, P., Kunz, M.L., Reanier, R.E. and Gaglioti, B.V. (2013) Ice-age megafauna in Arctic Alaska: extinction, invasion, survival. *Quaternary Science Reviews* 70, 91-108.
- Mann, D.H., Groves, P., Reanier, R.E., Gaglioti, B.V., Kunz, M.L. and Shapiro, B. (2015) Life and extinction of megafauna in the ice-age Arctic. *Proceedings of the National Academy of Sciences* 112, 14301-14306.
- Mann, D.H., Groves, P., Reanier, R.E. and Kunz, M.L. (2010) Floodplains, permafrost, cottonwood trees, and peat: What happened the last time climate warmed suddenly in arctic Alaska? *Quaternary Science Reviews* 29, 3812-3830.
- Mann, D.H., Peteet, D.M., Reanier, R.E. and Kunz, M.L. (2002) Responses of an arctic landscape to Lateglacial and early Holocene climatic changes: the importance of moisture. *Quaternary Science Reviews* 21, 997-1021.
- McKay, J., de Vernal, A., Hillaire-Marcel, C., Not, C., Polyak, L. and Darby, D. (2008) Holocene fluctuations in Arctic sea-ice cover: dinocyst-based reconstructions for the eastern Chukchi Sea. *Canadian Journal of Earth Sciences* 45, 1377-1397.

McMinn, A. (1995) Comparison of diatom preservation between oxic and anoxic basins in Ellis Fjord, Antarctica. *Diatom Research* 10, 145-151.

Melles, M., Brigham-Grette, J., Minyuk, P.S., Nowaczyk, N.R., Wennrich, V., DeConto, R.M., Anderson, P.M., Andreev, A.A., Coletti, A., Cook, T.L., Haltia-Hovi, E., Kukkonen, M., Lozhkin, A.V., Rosén, P., Tarasov, P., Vogel, H. and Wagner, B. (2012) 2.8 Million Years of Arctic Climate Change from Lake El'gygytyn, NE Russia. *Science* 337, 315-320.

Meyer, H., Schirrmeister, L., Yoshikawa, K., Opel, T., Wetterich, S., Hubberten, H.W. and Brown, J. (2010) Permafrost evidence for severe winter cooling during the Younger Dryas in northern Alaska. *Geophys. Res. Lett.* 37.

Michelutti, N., Blais, J.M., Cumming, B.F., Paterson, A.M., Rühland, K., Wolfe, A.P. and Smol, J.P. (2009) Do spectrally inferred determinations of chlorophyll a reflect trends in lake trophic status? *J. Paleolimnol.* 43, 205-217.

Mügler, I., Sachse, D., Werner, M., Xu, B., Wu, G., Yao, T. and Gleixner, G. (2008) Effect of lake evaporation on δD values of lacustrine n-alkanes: a comparison of Nam Co (Tibetan Plateau) and Holzmaar (Germany). *Org. Geochem.* 39, 711-729.

Nesbitt, H. and Young, G. (1982) Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature* 299, 715-717.

Olsson, I.U. (1991) Accuracy and precision in sediment chronology. *Hydrobiologia* 214, 25-34.

Oswald, W.W., Brubaker, L.B. and Anderson, P.M. (1999) Late Quaternary vegetational history of the Howard Pass area, northwestern Alaska. *Canadian Journal of Botany* 77, 570-581.

Pendleton, S.L., Ceperley, E.G., Briner, J.P., Kaufman, D.S. and Zimmerman, S. (2015) Rapid and early deglaciation in the central Brooks Range, Arctic Alaska. *Geology* 43, 419-422.

Polissar, P.J. and Freeman, K.H. (2010) Effects of aridity and vegetation on plant-wax δD in modern lake sediments. *Geochim. Cosmochim. Acta* 74, 5785-5797.

Postma, D. (1977) The occurrence and chemical composition of recent Fe-rich mixed carbonates in a river bog. *Journal of Sedimentary Research* 47.

Reimer, P.J., Bard, E., Bayliss, A., Beck, J.W., Blackwell, P.G., Bronk Ramsey, C., Buck, C.E., Cheng, H., Edwards, R.L. and Friedrich, M. (2013) IntCal13 and Marine13 radiocarbon age calibration curves 0-50,000 years cal BP.

Russell, J.M., Vogel, H., Konecky, B.L., Bijaksana, S., Huang, Y., Melles, M., Wattrus, N., Costa, K. and King, J.W. (2014) Glacial forcing of central Indonesian hydroclimate since 60,000 y BP. *Proceedings of the National Academy of Sciences* 111, 5100-5105.

Sachse, D., Radke, J. and Gleixner, G. (2004) Hydrogen isotope ratios of recent lacustrine sedimentary n-alkanes record modern climate variability. *Geochim. Cosmochim. Acta* 68, 4877-4889.

Sakamoto, T., Ikehara, M., Aoki, K., Iijima, K., Kimura, N., Nakatsuka, T. and Wakatsuchi, M. (2005) Ice-rafted debris (IRD)-based sea-ice expansion events during the past 100 kyrs in the Okhotsk Sea. *Deep Sea Research Part II: Topical Studies in Oceanography* 52, 2275-2301.

Schnurrenberger, D., Russell, J. and Kelts, K. (2003) Classification of lacustrine sediments based on sedimentary components. *J. Paleolimnol.* 29, 141-154.

Serreze, M.C. and Francis, J.A. (2006) The Arctic Amplification Debate. *Clim. Change* 76, 241-264.

Stafford, J., Wendler, G. and Curtis, J. (2000) Temperature and precipitation of Alaska: 50 year trend analysis. *Theoretical and Applied Climatology* 67, 33-44.

Stewart, B.C., Kunkel, K.E., Stevens, L.E., Sun, L. and Walsh, J.E. (2013) Part 7. Climate of Alaska, Regional Climate Trends and Scenarios for the U.S. National Climate Assessment. Department of Commerce

Tsukernik, M., Kindig, D.N. and Serreze, M.C. (2007) Characteristics of winter cyclone activity in the northern North Atlantic: Insights from observations and regional modeling. *Journal of Geophysical Research: Atmospheres* 112.

Vachon, R., Welker, J., White, J. and Vaughn, B. (2010) Monthly precipitation isoscapes ($\delta^{18}\text{O}$) of the United States: Connections with surface temperatures, moisture source conditions, and air mass trajectories. *Journal of Geophysical Research: Atmospheres* 115.

Vachula, R.S., Chipman, M.L. and Hu, F.S. (2017) Holocene climatic change in the Alaskan Arctic as inferred from oxygen-isotope and lake-sediment analyses at Wahoo Lake. *The Holocene*.

Viau, A., Gajewski, K., Sawada, M. and Bunbury, J. (2008) Low-and high-frequency climate variability in eastern Beringia during the past 25 000 years. *Canadian Journal of Earth Sciences* 45, 1435-1453.

Walker, D., Bockheim, J., Chapin Iii, F., Eugster, W., Nelson, F. and Ping, C. (2001) Calcium-rich tundra, wildlife, and the “Mammoth Steppe”. *Quaternary Science Reviews* 20, 149-163.

Walker, D. and Everett, K. (1991) Loess ecosystems of northern Alaska: regional gradient and toposequence at Prudhoe Bay. *Ecol. Monogr.* 61, 437-464.

Walker, D.A. and Maier, H.A. (2008) Vegetation in the vicinity of the Toolik Field Station, Alaska. University of Alaska. Institute of Arctic Biology.

Walsh, J.E., Chapman, W.L. and Fetterer, F. (2015) Gridded monthly Sea Ice Extent and Concentration, 1950 Onward, V. 1, in: Center, N.S.a.I.D. (Ed.), 1 ed.

5.10 Figures and Tables

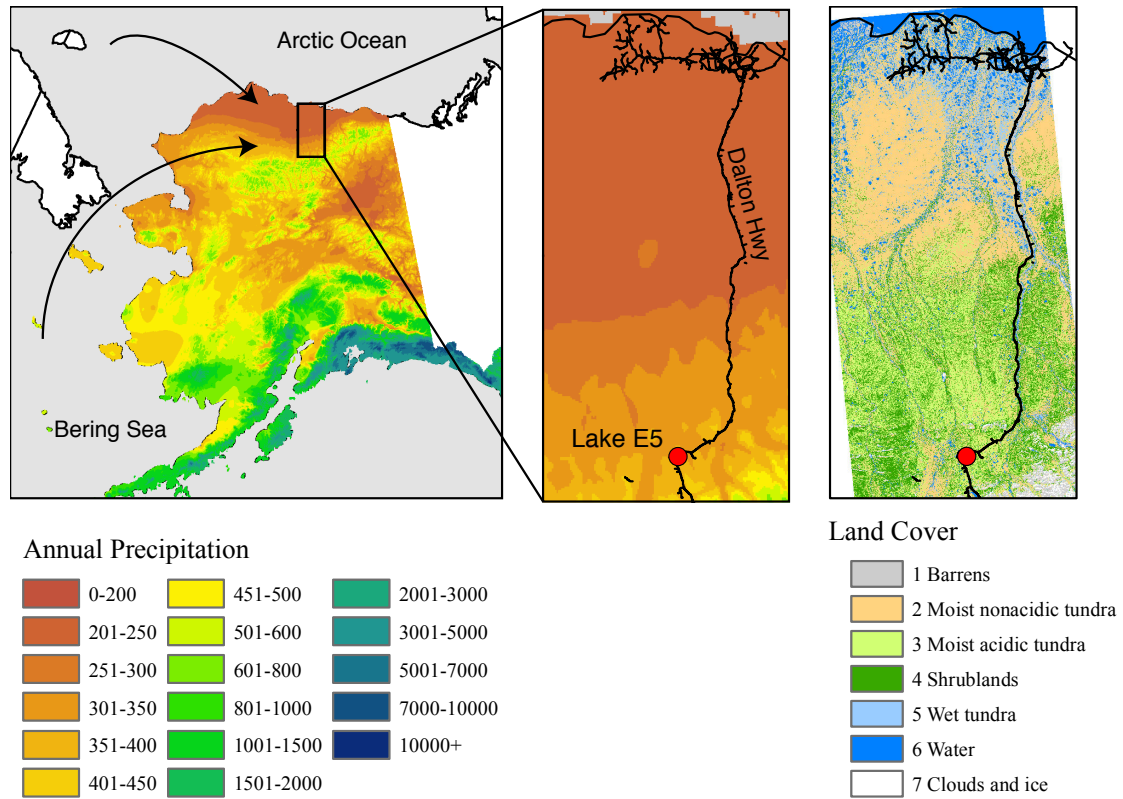


Figure 5.1 Map of study site and mean annual precipitation amounts across Alaska. Precipitation data from Gibson (2009). Arrows indicate major moisture sources for the North Slope of Alaska as described by Klein et al. (2016).

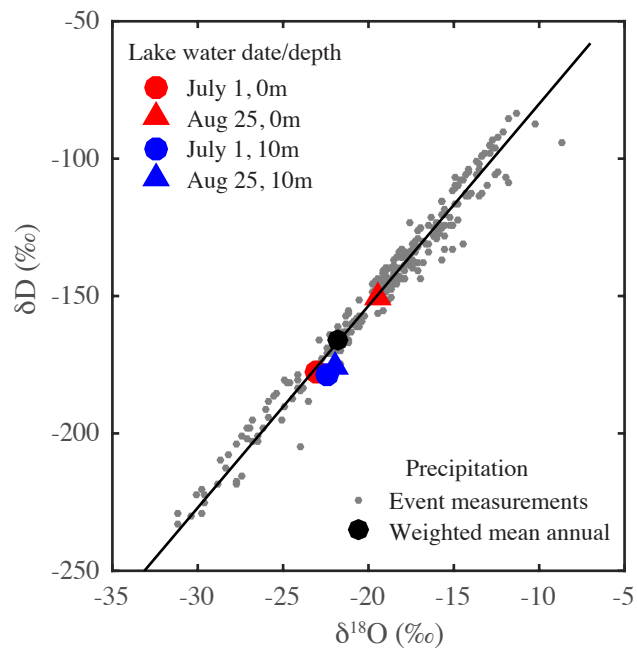


Figure 5.2 Hydrogen and oxygen isotope data from rainfall at Toolik Field Station (Chapter 3) and from Lake E5 water on different dates in 2014.

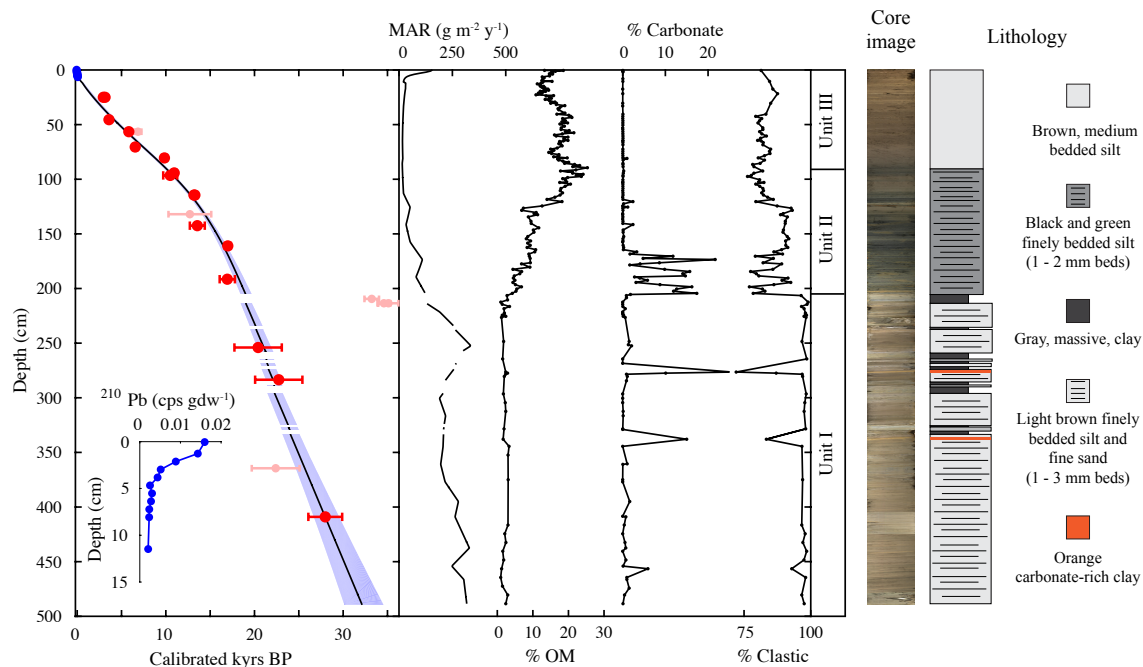


Figure 5.3 Lake E5 core chronology, sediment accumulation rate and bulk physical properties, core image, and lithostratigraphy. In the core chronology, red points are calibrated radiocarbon with 2σ error bars, pink points are outliers and not included in the age model, and the black line with blue envelope is the Clam.R modeled mean ages and 95% error ranges. The inset ^{210}Pb profile spans the surface 12 cm. Unit divisions are described in the text.

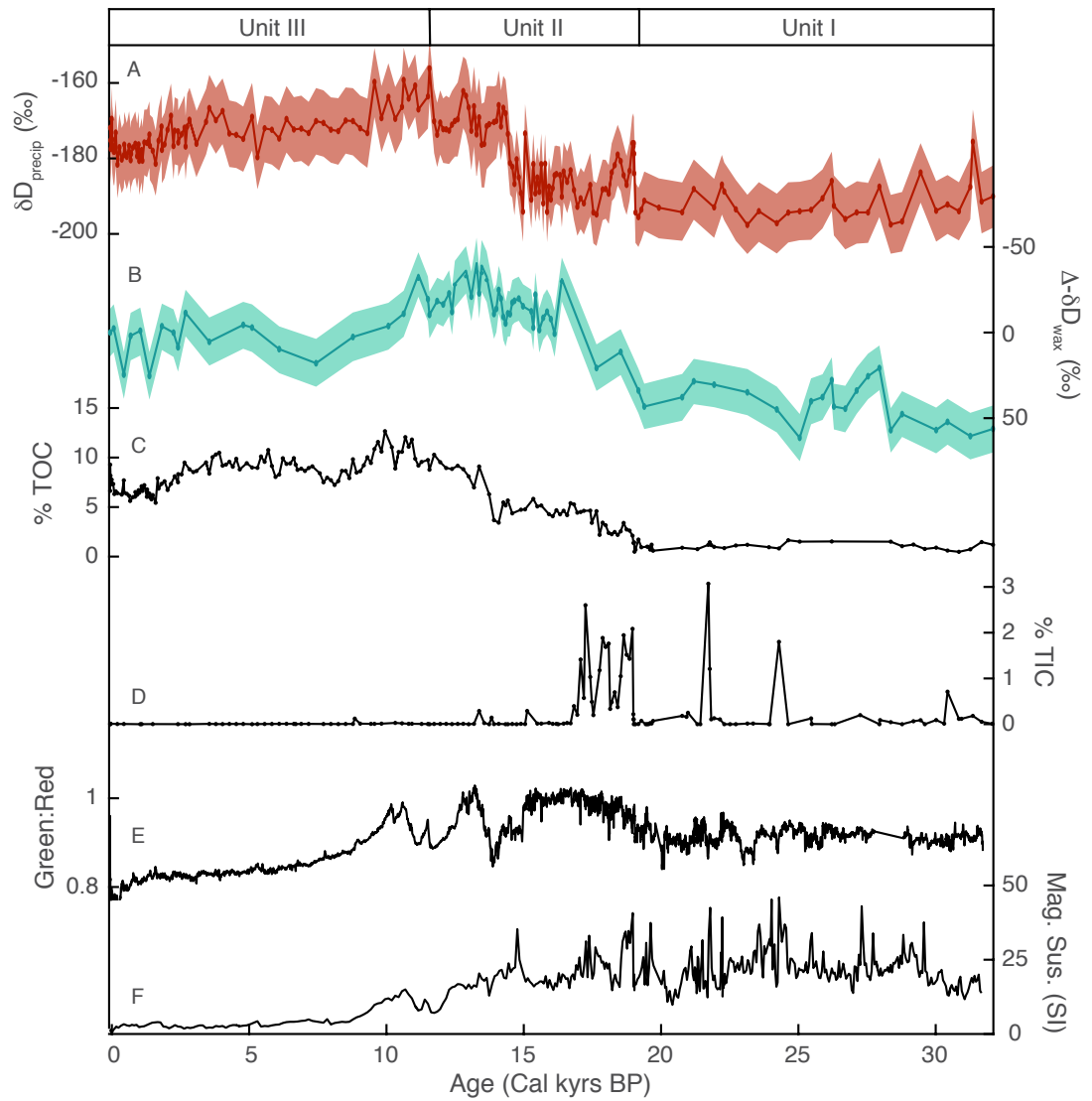


Figure 5.4 Hydrogen isotope, and bulk physical and compositional parameters for the Lake E5 composite stratigraphy. A) $\delta D_{\text{precipitation}}$, a proxy for summer temperature; B) The aquatic-terrestrial δD_{wax} offset ($\Delta\delta D$), an indicator of moisture balance; C) Total organic carbon; D) Total inorganic carbon; E) Sediment color (green:red ratio); F) Magnetic susceptibility.

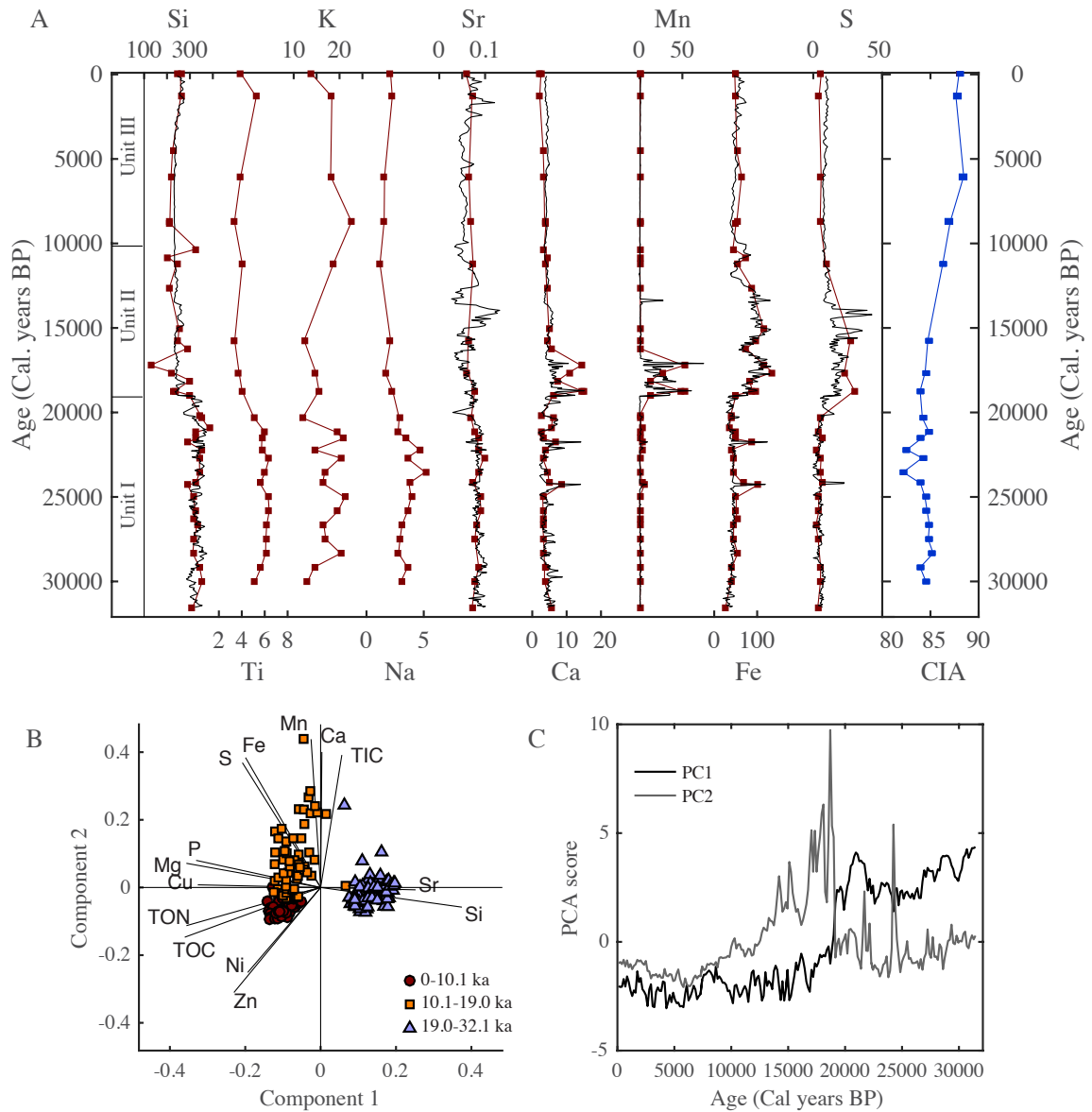


Figure 5.5 Geochemical composition of Lake E5 sediments. A) The FF-ICP-AES data (red) and corrected XRF data (black) are corrected for water content effects (See Methods). Units are parts per thousand (relative to dry weight). In blue is the chemical index of alteration, calculated as: $CIA = \frac{Al_2O_3}{Al_2O_3 + K_2O + Na_2O} * 100$. B) The first and second components of the PCA analysis of elemental data. Colored points relate to the three sediment units described in the text. C) Time series of the first two principle components, which explain 41% and 21% of the variance, respectively.

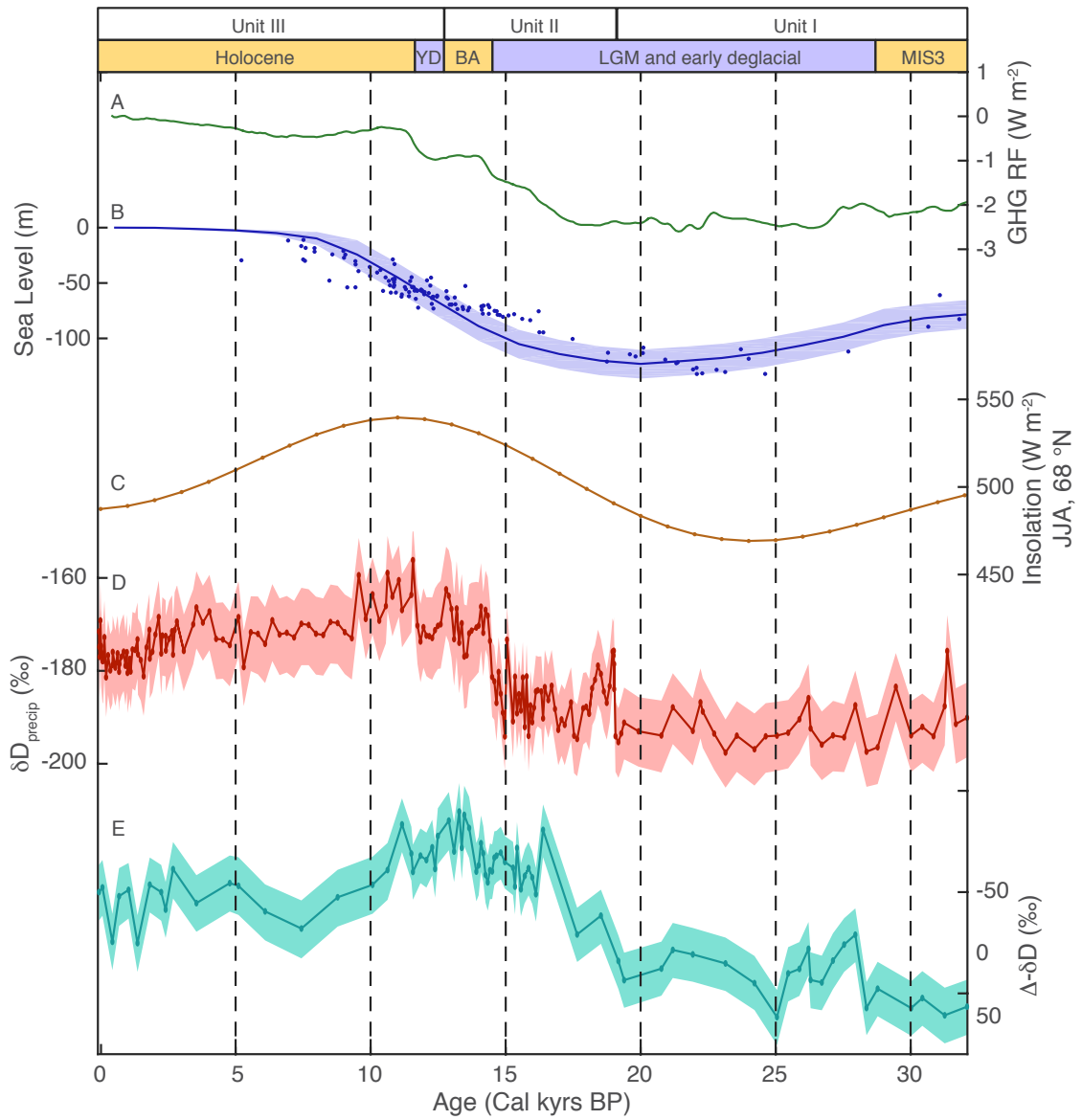


Figure 5.6 A comparison of hydrogen isotope proxy data to global climate forcings. A) Greenhouse gas radiative forcing (Schilt et al., 2010); B) Global sea level inferred from benthic oxygen isotopes (Thompson and Goldstein, 2006) and corals (Waelbroeck et al., 2002); C) Summer insolation at the latitude of lake E5; D) The δD of n -acid from Lake E5, a proxy for growing-season temperature; E) The $\Delta\text{-}\delta D$ from Lake E5, a proxy for moisture balance. The axis for $\Delta\text{-}\delta D$ is reversed such that up implies wetter conditions. Lake E5 lithologic units are shown for reference.

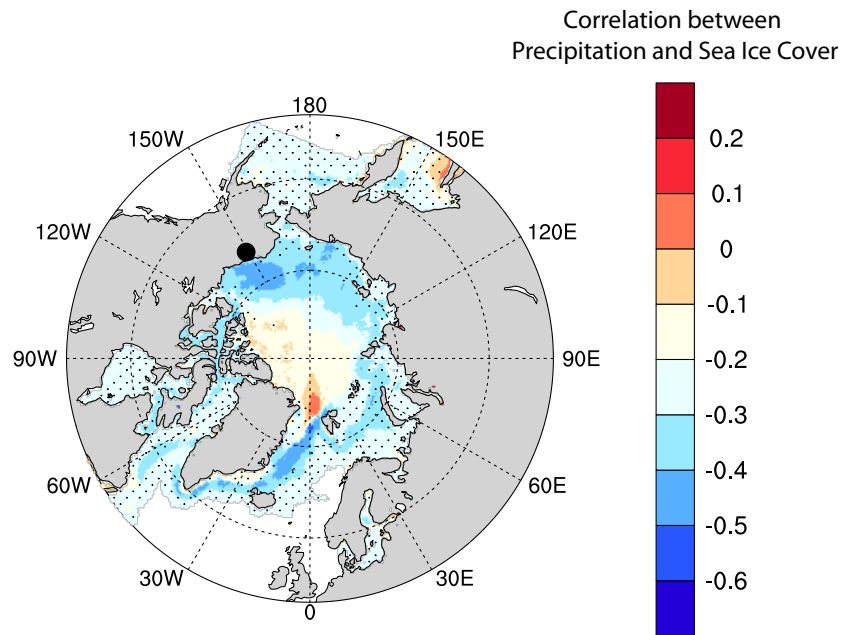


Figure 5.S1 Correlation between the monthly precipitation at Toolik Field Station (black dot) (Toolik Environmental Data Center Team, 2016a) and monthly sea ice extent, derived from satellite and shipboard observations between 1985 and 2014 (Walsh et al., 2015). Areas with stippling are significant at the 95% confidence level. Negative correlation implies that months with less sea ice are associated with more rainfall at TFS.

Surface area (ha)	11.3
Max depth (m)	12.7
Mean depth (m)	6.2
Summer T max (°C)	15.7 ± 1.5
Mixed layer depth (m)	7.6 ± 3.5
Light extinction coefficient (k)	0.9 ± 0.3
Secchi depth (m)	3.5 ± 0.7
pH	6.3 ± 0.5
Chlorophyll a (µg L ⁻¹)	3.1 ± 1.8
Total phosphorus (µM)	0.34 ± 0.17
Total nitrogen (µM)	17.6 ± 3.4
DOC (µM)	492.6 ± 117.2
Specific conductivity (µS cm ⁻¹)	10.2 ± 4.8
Chloride (µM)	7.8 ± 10.3
Sulfate (µM)	2.7 ± 0.4

Table 5.1 Lake E5 physical and chemical properties. Data represent repeated samplings from 2000 to 2014.

	Component 1	Component 2
Variance explained (%)	40.7	21.4
Element		
Si	0.375	-0.058
TOC	-0.361	-0.147
TON	-0.356	-0.113
Mg	-0.356	0.072
P	-0.330	0.080
Cu	-0.326	0.008
Sr	0.252	-0.007
Zn	-0.230	-0.310
S	-0.208	0.369
Fe	-0.199	0.384
Ni	-0.194	-0.251
Al	-0.141	-0.041
TIC	0.056	0.392
Mn	-0.025	0.438
Ca	0.003	0.400

Table 5.2 Component loading table of the PCA performed on elemental concentrations.

CHAPTER SIX

Partitioning aquatic and terrestrial organic carbon accumulation in an Arctic lake

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6.1 Abstract

Temperature, light, dissolved organic carbon, and nutrient concentrations interact to control rates of aquatic primary productivity and organic carbon accumulation (OCAR) in lakes. Predicting future changes in carbon cycling and burial in Arctic lake ecosystems requires an understanding of how these interactions vary under different climatic conditions. We use independent paleoecological and paleoclimatic datasets from a 32,000 year sedimentary record of from Lake E5 in northern Alaska to assess if and how climate change and carbon cycling co-vary in Arctic lakes. Total OCAR averages $2.4 \text{ g C m}^{-2} \text{ yr}^{-1}$, and correlates negatively with lipid D/H-inferred air temperature. Several mechanisms link OCAR with temperature at our site. During the Last Glacial Maximum (LGM; 30-19 ka), high sedimentation rates and lower temperatures facilitated high carbon burial efficiency. During the deglaciation (19 to 11.6 ka), low oxygen exposure time and variable rates of primary production and terrigenous organic carbon (OC) inputs occurred in response to landscape changes that resulted in higher but variable rates of OCAR. During the Holocene (11.6 ka to present), temperature and OCAR are not correlated despite a relatively large temperature decline ($3.2 \text{ }^{\circ}\text{C}$). Tradeoffs between terrigenous OC loading and aquatic productivity may have worked in concert to stabilize OCAR. These results suggest that, while temperature is an important predictor of carbon burial in high latitude lakes, the mechanisms governing this relationship are complex and involve coupled changes in aquatic primary production and landscape evolution.

Keywords: Arctic, Paleolimnology, Carbon burial, Diatoms, Chrysophytes, compound-specific stable isotopes

6.2 Introduction

Small high-latitude lakes play an important role in global carbon (C) cycling. They sequester organic carbon (OC) in sediments and simultaneously serve as reaction sites for the breakdown of terrestrial OC, often releasing carbon to the atmosphere during this process. On an areal basis, Arctic and boreal lakes sequester about 20 to 40 Tg C in their sediment annually (Heathcote et al., 2015), although OC accumulation rates from undisturbed polar sites vary widely, from 0.2 to 15 g C m⁻² yr⁻¹ (Kortelainen et al., 2004; Anderson et al., 2009; Sobek et al., 2009). Explaining the determinants of OCAR variations among lakes and through time can improve predictions of future C sequestration in lakes globally. To this end, there are several fundamental and outstanding questions about what limits primary productivity and carbon sequestration in Arctic and boreal lakes, and, how these controls may be impacted by climatic influences.

At a broad scale, the influence of temperature on OC accumulation rates (OCAR) in high latitude lakes remains unclear. Theory predicts that because bacterial respiration is more sensitive to temperature than is photosynthesis, OCAR should decrease as temperature rises (Gudas et al., 2010; Yvon-Durocher et al., 2010). Field measurements, however, do not always support this model. Across spatial climatic gradients, there is no relationship between temperature and OCAR in large lakes (Alin and Johnson, 2007), while small lakes, exhibit a positive relationship between air temperature and OCAR (Heathcote et al., 2015). From a temporal perspective, OCAR is insensitive to temperature changes over the Holocene in a suite of Greenland lakes (Anderson et al., 2009), but positively correlated with air temperature over the past 700 years in a Finnish lake (Rantala et al., 2016). The paradox between predicted effects of

warming and field observations likely arises from the myriad influences of climate on organic matter source, composition, and burial efficiency.

Climate warming has been linked to an increased flux of dissolved and particulate material to Arctic lakes via permafrost thaw and increased soil decomposition (Bowden et al., 2008; Keller et al., 2010). However, it is uncertain how changing fluxes of terrigenous materials will affect carbon sequestration in Arctic lakes because of potential tradeoffs between autochthonous and allochthonous carbon inputs to sediments, and between benthic and pelagic primary production (Karlsson et al., 2015). There is debate about whether nutrients (nitrogen and phosphorus), the flux of which is enhanced by permafrost melting, or light, which is reduced by permafrost melting, are the dominant control on rates of whole-lake primary production. Instantaneous rates of pelagic production respond positively to N or P addition (ex. Schindler, 1978; Levine and Whalen, 2001), signifying nutrient limitation of phytoplankton productivity. Indeed, water quality parameters are strongly correlated with nutrient loading (ex. Dillon and Rigler, 1974). However, enhanced phytoplankton abundance inhibits benthic algal productivity because of increased light interception in the water column (Vadeboncoeur et al., 2001; Vadeboncoeur et al., 2008; Genkai-Kato et al., 2012; Jäger and Diehl, 2014). In effect, imbalanced resource supply (light from above, nutrients from below) results in competition between adjacent niches (pelagic vs. benthic) and buffers the effect of nutrient stimulation on whole-lake production. Moreover, dissolved organic carbon (DOC) can further limit primary biomass production by suppressing light available for both pelagic and benthic algae, a process known as lake “brownification” (Karlsson et al., 2009; Karlsson et al., 2015) (Kritzberg et al., 2014). Pelagic production (i.e. nutrient

loading) positively influences OCAR (Anderson et al., 2013), while the effect of brownification on OCAR is unknown.

Independent estimates of temperature, primary productivity, DOC concentrations, and OCAR in paleolimnologic archives can provide insight into the interaction of these variables in response to climatic change. Here, we reconstruct the ecology and carbon cycling of Lake E5 in Arctic Alaska over the past 32,000 years, an interval that encompasses dramatic changes in temperature and terrestrial ecology (Eisner and Colinvaux, 1992, Chapters 3 and 4). In contrast to previous studies, which have generally lacked estimates of temperature independent from the lacustrine paleoecological data, our reconstructions of OCAR and limnologic parameters are compared directly with isotopic estimates of past air temperature from the Lake E5 core.

6.3 Methods

Sites, cores and chronologies

Lake E5 is regularly monitored by the Arctic Long-term Ecological Research program at Toolik Lake Field Station. The lake is generally ice-free from early June to mid-September. Water column profiling shows thermal stratification occurs at an average depth of 7.6 m. The lake is ultra-oligotrophic, low in dissolved phosphorus and nitrogen, but rich in DOC. Secchi depths average 3.5 m during summer.

Sediment cores were retrieved from Lake E5 in 2011, 2012, and 2014. The composite stratigraphy and age-depth model was presented in Chapter 3. The chronology is based on Clam.R modeling of the ^{210}Pb profile and 15 radiocarbon dates (average every ~1,500 years over the Holocene and ~every 2,500 years over the last glacial period). The

composite stratigraphy has a basal age of 32,100 years and lithology varies dramatically from the LGM to the Holocene. The core was previously characterized in three units (Chapter 4) and those units are maintained here.

Assessing OC burial, OC sources, and controls on primary production

We previously report lipid hydrogen isotope ratios as proxies for past temperature at this site. These temperature estimates are incorporated here to assess the influence of climate on lake ecology. We assess total OC burial rates, and examine the drivers of temporal changes in OC burial. In this case, straight chain *n*-acids, in conjunction with primary productivity indicators, serve as a qualitative tracer of organic matter source. While *n*-acids are produced by a mixture of species, the shortest chain length homologues (C_{16} , C_{18} *n*-acids) are predominantly produced by aquatic algae, whereas long-chain ($>C_{24}$) are predominantly produced by land plants (ex. Wang and Liu, 2012). While only one component of buried organic matter, the fluxes and relative ratios of *n*-acids can provide insights on the causes of C burial fluctuations through time. Sedimentary records of diatom assemblages provide a qualitative record of lake DOC, pH, the distribution between planktonic and benthic production, and overall controls on autochthonous production.

Bulk sediment properties and OCAR

Total organic carbon and nitrogen was measured at 1-4 cm intervals in conjunction with nitrogen isotope ratios using elemental analyzer-isotope ratio mass spectrometry (EA-IRMS). Samples were soaked in 5% HCl overnight and rinsed three

times in DI water to remove carbonates prior to analysis. Samples were analyzed on a Thermo-Finnigan Delta-X IRMS with an elemental analyzer for sample introduction. Pine, cyclohexane, peach, Montana Soil, or USGS-40 standards were analyzed every 10 samples to provide a calibration for C and N content, and to ensure quality control of isotope measurements. Isotopic ratios are reported in standard delta-notation. A subset of samples (n=124) was also analyzed on a ThermoQuest NC2100 soil elemental analyzer. The difference between the two methods averaged 0.13 weight % for carbon and 0.02 weight % for nitrogen, indicating the TOC and TON measured on EA-IRMS are robust.

Dry bulk density (DBD) was measured every 8 cm along the core. 1 cm³ samples were weighed, dried at 105 °C overnight, and weighed again. Mass accumulation rates were calculated at 1 cm intervals by interpolating DBD to 1 cm resolution and multiplying by the linear sedimentation rate of the smoothed age-depth model (Figure 1). OCAR were calculated by multiplying the TOC, at the resolution of TOC measurements, by the mass accumulation rate.

Chlorophyll spectrometry

Chlorophyll content was measured qualitatively using reflectance spectroscopy. This method has been tested and validated by Wolfe et al. (2006) and Michelutti et al. (2009) and has the advantage of being non-destructive with regards to sample material. Dried sediments were sieved at 100 µm, and analyses was performed on the <100 µm portion using a 3-channel ASD FieldSpec3 FR spectrometer with a constant light source held at approximately 45°. Absorption spectra were collected from 350 nm to 2500 nm,

the channels were spliced and transformed to units of reflectance using RS3 software. We calculated the 650-700 nm spectral trough area using the method outlined by Wolfe et al. (2006). No effort was made to calibrate spectrally-inferred concentration to actual concentration. Rather, we report concentrations (trough area) relative to the maximum value observed in the sediment core.

Diatoms

Diatoms are present in the Holocene section of Lake E5 stratigraphy, and species assemblages were determined at 2 cm intervals. For diatom preparation, 0.1-0.2 g of dry sediment was heated to 85°C with 30% hydrogen peroxide for two hours to remove organic matter. After two hours, 1 mL of concentrated nitric acid was added for further diatom cleaning. Samples were rinsed three times with DI water, and mounted on microscope slides using Hyrax mounting medium. Relative abundance was determined for each sample by identifying and enumerating at least 300 valves using a Leica microscope with an oil immersion lens at 1000x. Identifications follow the guides of Patrick and Freese (1960), Manguin (1961), Krammer and Lange-Bertalot (2008), and Spaulding et al. (2010). Chrysophyte cysts were also tallied and their abundance calculated relative to the total number of diatom valves.

Organic geochemistry

We analyzed the concentration of short and long chain *n*-acids and *n*-alkanes in an attempt to partition the relative contribution of aquatic and terrestrial carbon sequestered. Dried sediments were extracted using Accelerated Solvent Extraction. Lipids were then

separated using amino-propyl chromatography with dichloromethane:isopropynol (2:1) and acetic acid:ether (5:95) as eluents. Acid fractions were spiked with an internal standard of *cis*-eicosenoic acid. Acids were methylated overnight at 60°C in acidified methanol, then further purified with silica gel chromatography and hexane and dichloromethane as eluents. Both fractions were analyzed on GC-FID using an HP-1 chromatography column, with an injector temperature of 320 °C, and a temperature program beginning at 60 °C, ramping by 20 °C min⁻¹ for 5 minutes, then 6 °C min⁻¹ for 20 minutes. Peak areas were determined using PeakArea software developed at Brown University, and concentrations were calculated based on the internal standard peaks. We calculated the ratio of C₁₆/C₂₈ *n*-acids as an indicator of the relative contribution of aquatic and terrestrial organisms.

6.4 Temperature control on OCAR

Temperature is inferred from the hydrogen isotope ratios of terrestrial leaf waxes. Over the past 32,000 years, temperature exhibits a distinct glacial-interglacial structure with ~5.5 °C of warming during the last glacial termination and ~3.2 °C of cooling over the Holocene (Chapter 3). The OCAR in Lake E5 varied from 0.9 to 14.1 g m⁻² yr⁻¹ and averaged 2.5 g m⁻² yr⁻¹ over the past 32,000 (Figure 1). These values fall within the range reported from other high latitude lakes (Kortelainen et al., 2004; Anderson et al., 2009; Sobek et al., 2009). The OCAR shows a distinct glacial-interglacial structure, with values decreasing from the Last Glacial Maximum to the Holocene. We also observe an increase in OCAR in the most recently deposited sediments, which we attribute to the combined effects of an ongoing whole-lake fertilization experiment (Daniels et al., 2015)

and the incomplete OC respiration, rather than to the effects of climate or other natural variations. We do not interpret these surface (0-6 cm, 49 to -64 years b. 1950) estimates further, and after their removal, OCAR varies from 0.9 to 4.9 g m⁻² yr⁻¹.

There is a positive relationship between reconstructed air temperature and %TOC ($p < 0.001$) and a negative correlation between temperature and OCAR ($p < 0.001$) (Figure 2). This finding agrees with theoretical predictions of a temperature effect on OCAR (Yvon-Durocher et al., 2010), and lends support to predictions that the ability for lake sediments to absorb carbon could diminish in a warming climate (Gudasz et al., 2010; Yvon-Durocher et al., 2010). However, the majority of this correlation is driven by OCAR and temperature changes happening during the deglaciation, during which time Arctic Alaskan landscapes experienced dramatic changes in soil and vegetation structure very different from the changes likely to occur in the coming centuries. When the Holocene section is analyzed alone, the OCAR-temperature relationship disappears ($p = 0.21$), despite large temperature-driven changes in aquatic ecosystem structure over that time (Figure 3, see discussion below).

6.5 OCAR during the LGM and glacial termination

At the glacial-interglacial scale, an inverse relationship between temperature and OCAR implies that the cooler conditions of the LGM were favorable to either carbon deposition, carbon burial efficiency, or both. High C/N ratios and low C₁₆:C₂₈ ratios indicate that autochthonous productivity was low during the LGM and therefore cannot account for high OC accumulation. Likewise, flux of terrestrial OC during the LGM is not expected to increase substantially considering the more sparsely vegetated landscape.

We do note, however, very fine (<100 μm) plant fragments in the LGM sediments that could indicate plant fragmentation and aeolian deposition. We propose that the high rates of carbon burial during the LGM (sediment Unit I, 32-19 ka) were principally sustained by low rates of remineralization and by the high sedimentation rate that promoted increased carbon burial efficiency by decreasing the oxygen exposure time of organic matter (Alin and Johnson, 2007; Sobek et al., 2009). In this case, the effect of cooler temperature is expressed through its indirect controls on sediment supply. The LGM climate included extreme aridity in Arctic Alaska (Carter, 1981, Chapter 4), which promoted high aeolian flux of soil particles and glacial loess to Lake E5. Although aridity-induced lower lake levels sustained water column mixing and sediment oxygenation, these effects appear not to have overcome the impacts of more rapid sedimentation on OCAR.

High carbon burial efficiency may have also been maintained by particularly recalcitrant OC. C/N ratios above 12 and low $\text{C}_{16}/\text{C}_{28}$ *n*-acid ratios indicate that the OC being deposited during the LGM was predominantly terrigenous (Figure 1). Longo (Dissertation, 2017) showed that the terrestrial lignin contained in these glacial sediments was upwards of 10,000 years old at the time of deposition. Pre-aged OC is typically resistant to remineralization in the tundra (Vonk et al., 2010). With dry soils and an absence of sphagnum/sedge peat, which is prevalent today, dissolved inputs of highly labile OC were likely low. Preservation of a labile OC pool would have been particularly poor in light of the well-oxygenated water column that characterized Lake E5 during the LGM.

During the deglacial period (sediment Unit II, 19-11.6 ka), OCAR varies from 1.6 to 4.9 g m⁻² yr⁻¹. Considerable scatter between temperature and OCAR during this interval (Figure 2) indicates that multiple factors, probably related to soil weathering (Engstrom et al., 2000) and paludification (Mann et al., 2015), controlled OCAR. Redox-sensitive elemental data indicate that the lake was poorly oxygenated during the deglacial (Chapter 4), implying that oxygen exposure time was short and conditions were conducive to OC preservation. Small increases in phosphorus loading that likely accompanied post-glacial weathering of loess soils (Keller et al., 2007) would have promoted algal productivity (Daniels et al., 2015), and indeed, increasing chlorophyll and %TOC at 19 ka suggest increased inputs of algal OC to the sediment. Sedimentation rate was slowing, so these increases may result from less dilution by clastic material, but ratios of C/N, C₁₆/C₂₈ *n*-acids, and ¹⁵N/¹⁴N also suggest a shift to algal OC inputs at 19 ka (Figure 1, supplemental text).

Today, pelagic production in our study area is co-limited by nitrogen and phosphorus (ex. Whalen and Cornwell, 1985). The increase in δ¹⁵N_{org} at a time of high aquatic productivity could have resulted from a shift towards greater nitrogen limitation such that ¹⁴N/¹⁵N discrimination was reduced (Jones et al., 2004). Such a shift could have occurred in response to accelerated P-loading, which would have resulted from weathering of freshly-produced glacial loess soils. P is positively correlated with the carbonate fraction of soils around Lake E5, which is the fraction is the most susceptible to weathering (Keller et al., 2007). Increasingly anoxic conditions may have led to further δ¹⁵N_{org} enrichment through denitrification. Denitrification is rare in Arctic Alaska lakes today because of extreme nitrogen limitation, but the alignment between high

$\delta^{15}\text{N}_{\text{org}}$ and calcite deposition suggests that it may have occurred from 19 to 16 ka.

Alternatively, high $\delta^{15}\text{N}_{\text{org}}$ values could have originated from incorporation of ^{15}N -enriched animal feces from the watershed as the lake level rose. As Lake E5 is one of few North Slope lakes deep enough to remain partially filled during the arid LGM, it would have been an important water source for Ice Age megafauna, and fecal matter may have accumulated around the lake. Nitrogen addition via this mechanism would have further promoted lake productivity.

These lines of evidence indicate that the period from 19 to 15 ka was characterized by the highest rates of primary production in the 32,000-year history of Lake E5. A second pulse of high OCAR occurred between 14 and 13.3 ka. In contrast to the early deglacial, this event is marked by a decline in aquatic OC indicators (chlorophyll, $\text{C}_{16}/\text{C}_{28}$ *n*-acids, etc.) and indications of a rise in terrestrial OC (Figure 1) flux. We interpret that this marks the onset of peat development in the Lake E5 watershed. Thus, over the deglaciation, we cannot attribute OCAR fluctuations strictly to a temperature influence on remineralization of organic matter. Post-glacial soil weathering and vegetation development is known to impact lake ecosystems (Engstrom et al., 2000), but the combined effects of climate change and lake succession on OCAR have not been examined. We postulate that the immediate response to deglacial warming and moistening was an increase in lake productivity, the peak of which lasted until rates of P input from soils began to decline and inputs of terrestrial DOC began to rise, limiting light availability in the lake.

6.6 Carbon cycling during the Holocene

Over the Holocene (sediment Unit III, 11.6 ka to present), the Lake E5 watershed was relatively stable. Temperature declined by ~ 3.2 °C from the Early- to Late-Holocene, and evidence from diatom assemblages, C/N ratios, and nitrogen isotopes indicate significant changes in the ecology of Lake E5. Despite these changes, OCAR is remarkably stable, averaging $1.7 \text{ g m}^{-2} \text{ yr}^{-1}$, suggesting that ecological changes induced by Holocene cooling were well-balanced with regards to the lake carbon cycle.

Based on relatively high C/N ratios and low C_{16}/C_{28} *n*-acid ratios, most of the carbon preserved during the Holocene is terrestrial in origin. TOC and C/N ratios are anti-correlated over the Holocene (Figure 1), suggesting greater relative terrestrial, or at least degraded, OC input when there is less TOC. In the present, allochthonous inputs of DOC are an important factor limiting light (Daniels et al., 2015), and thereby primary production, and the relationships between TOC and C/N suggest this process extended over the course of the Holocene. Light limitation is more pronounced in low-nutrient systems (Karlsson et al., 2009). An increase in $\delta^{15}\text{N}_{\text{org}}$ over the Holocene indicates that N availability decreased as temperatures cooled, and so it appears that changes in light and nutrients worked in tandem to decrease *in-situ* production of OC.

Diatom subfossils are present in the Holocene section of the core and provide some insights on how climate-driven changes in terrestrial and OC burial balanced one another over the Holocene. Specifically, a shift from planktonic to benthic diatoms, and an increase in the relative abundance of chyrophytes point to greater nutrient limitation and higher lake DOC (Figure 3) during the Late-Holocene. A taphonomic bias is evident in the nearly monotonic increase with depth in the relative abundance of particularly recalcitrant *Aulocoseira* valves (Verschuren et al., 2002). We account for this by

removing *Aulocoseira* in calculations of the planktonic: benthic ratios and chrysophyte cysts: diatom ratios discussed below.

Besides *Aulocoseira* spp., *Cyclotella rossii* dominates the assemblages in the Early Holocene, but a transition occurs from 2 to 0.15 ka, wherein the abundance of *C. rossii* gives way to a rise in acidophilous benthic taxa including *Eunotia* spp., *Pinnularia* spp., and *Brachysira* spp. (Spaulding et al., 2010). This time period has been identified as the Alaska Neoglacial period (Badding et al., 2013), and is marked by temperatures approximately 1.5 °C cooler than modern (Chapter 3). The ratio of planktonic to benthic diatoms (P:B) decreased from 3 to 0.3 during the Neoglacial, and P:B is positively correlated with temperature over the entire Holocene ($p < 0.05$). *Cyclotella* spp. (planktonic) prefer a stratified and relatively nutrient-rich water column, which may occur under relatively warm conditions (Saros et al., 2013; Saros and Anderson, 2015). Their relative decrease during the Neoglacial is indicative of pelagic habitat degradation associated with increasing ice cover and reduced nutrient inputs.

The cooler climate of the Neoglacial was favorable to acidophilous benthic diatoms, relative to planktonic diatoms, for multiple reasons. First, prolonged ice cover under a cooler climate may limit pelagic habitat space while still allowing littoral diatoms along the lake margin to thrive, because lake ice thaws from the lake shore toward the center (Smol, 1983; Smol et al., 2005). Secondly, greater ice cover can promote the winter accumulation of CO₂ in the lake, and thereby decrease lake pH (Karlsson et al., 2008; Karlsson et al., 2013). Lastly, cooling could promote low pH and high DOC by limiting decomposition rates of terrigenous OC. This final explanation is supported by the nearly ten-fold increase in the ratio of chrysophyte cysts to diatom valves, as high

DOC would promote the growth of mixotrophic chrysophytes relative to the obligate photoautotrophic diatoms (Smol, 1983). An abundance of allochthonous C, is also supported by high carbon-normalized lignin concentrations during the Neoglacial period (Longo 2017).

Despite the apparent changes in nutrient availability, pelagic productivity, and DOC concentrations during the Holocene, there is little change in OCAR (Figure 4). The stability of OCAR likely resulted from tradeoffs wherein climatic cooling decreased pelagic OC production but increased the preservation of allochthonous OC and possibly the production of benthic algae. At present, benthic algae in Lake E5 and many other lakes in northern Alaska perform a substantial portion of the whole-lake productivity (Whalen et al., 2008; Daniels et al., 2015). While benthic productivity could have increased in response to less light interception by phytoplankton during the cool Neoglacial (Vadeboncoeur et al., 2001), greater DOC concentrations would have decreased light available to benthic producers and so any increase in benthic productivity was likely small. Thus, assuming that some portion of the DOC eventually is deposited on the lake floor, the principle tradeoff that occurred in Lake E5 was between terrestrial and aquatic OC, rather than between pelagic and benthic algae.

6.7 Conclusions

The lake E5 geochemical and biotic stratigraphy illustrate several important linkages between temperature and lake carbon cycling. The most significant linkage is the theory-confirming negative correlation between temperature and OCAR across the last glacial-interglacial transition. At shorter timescales, however, there is little

correlation between OCAR and temperature, a finding which agrees with reports from Greenland (Anderson et al., 2009), but at odds with a study demonstrating a positive correlation between temperature and OCAR in boreal lakes of North America (Heathcote et al., 2015). The stability of OCAR is surprising in light of the relatively large-amplitude temperature and aquatic ecosystem changes that occurred at our site over the Holocene. The different responses among high-latitude sites highlights the role of watershed characteristics and non-climatic drivers as important controls on OCAR. As such, replacing space for time may not be ideal for in assessing the response of lake OCAR to climate change. Over the Holocene, OCAR is remarkably stable due to tradeoffs between autochthonous and allochthonous OC inputs and to a lesser extent, between benthic and pelagic primary production. This stability suggests that OCAR in deep Arctic lakes will remain fairly constant with future temperature change.

6.8 Acknowledgements

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6.9 References

Alin S. R., and Johnson T. C. (2007) Carbon cycling in large lakes of the world: A synthesis of production, burial, and lake - atmosphere exchange estimates. *Global Biogeochem. Cycles* 21 (3).

Anderson N., D'andrea W., and Fritz S. C. (2009) Holocene carbon burial by lakes in SW Greenland. *Global Change Biol.* 15 (11), 2590-2598.

Anderson N. J., Dietz R. D., and Engstrom D. R. (2013) Land-use change, not climate, controls organic carbon burial in lakes. *Proceedings of the Royal Society B: Biological Sciences* 280 (1769).

Badding M. E., Briner J. P., and Kaufman D. S. (2013) ^{10}Be ages of late Pleistocene deglaciation and Neoglaciation in the north - central Brooks Range, Arctic Alaska. *Journal of Quaternary Science* 28 (1), 95-102.

Bowden W. B., Gooseff M. N., Balser A., Green A., Peterson B. J., and Bradford J. (2008) Sediment and nutrient delivery from thermokarst features in the foothills of the North Slope, Alaska: Potential impacts on headwater stream ecosystems. *J. Geophys. Res.* 113 (G2), G02026.

Carter L. D. (1981) A Pleistocene sand sea on the Alaskan Arctic coastal plain. *Science* 211 (4480), 381-383.

Daniels W. C., Kling G. W., and Giblin A. E. (2015) Benthic community metabolism in deep and shallow Arctic lakes during 13 years of whole-lake fertilization. *Limnol. Oceanogr.*, n/a-n/a.

Dillon P., and Rigler F. (1974) The phosphorus-chlorophyll relationship in lakes. *Limnol. Oceanogr.* 19 (5), 767-773.

Eisner W. R., and Colinvaux P. A. (1992) Late Quaternary Pollen Records from Oil Lake and Feniak Lake, Alaska, U.S.A. *Arct. Alp. Res.* 24 (1), 56-63.

Engstrom D. R., Fritz S. C., Almendinger J. E., and Juggins S. (2000) Chemical and biological trends during lake evolution in recently deglaciated terrain. *Nature* 408 (6809), 161-166.

Genkai-Kato M., Vadeboncoeur Y., Liboriussen L., and Jeppesen E. (2012) Benthic-planktonic coupling, regime shifts, and whole-lake primary production in shallow lakes. *Ecology* 93 (3), 619-631.

Gudas C., Bastviken D., Steger K., Premke K., Sobek S., and Tranvik L. J. (2010) Temperature-controlled organic carbon mineralization in lake sediments. *Nature* 466 (7305), 478-481.

Heathcote A. J., Anderson N. J., Prairie Y. T., Engstrom D. R., and del Giorgio P. A. (2015) Large increases in carbon burial in northern lakes during the Anthropocene. *Nature Communications* 6, 10016.

Jäger C. G., and Diehl S. (2014) Resource competition across habitat boundaries: asymmetric interactions between benthic and pelagic producers. *Ecol. Monogr.* 84 (2), 287-302.

- Jones R. I., King L., Dent M. M., Maberly S. C., and Gibson C. E. (2004) Nitrogen stable isotope ratios in surface sediments, epilithon and macrophytes from upland lakes with differing nutrient status. *Freshwat. Biol.* 49 (4), 382-391.
- Karlsson J., Ask J., and Jansson M. (2008) Winter respiration of allochthonous and autochthonous organic carbon in a subarctic clear - water lake. *Limnol. Oceanogr.* 53 (3), 948-954.
- Karlsson J., Bergström A.-K., Byström P., Gudas C., Rodríguez P., and Hein C. L. (2015) Terrestrial organic matter input suppresses biomass production in lake ecosystems. *Ecology*.
- Karlsson J., Byström P., Ask J., Ask P., Persson L., and Jansson M. (2009) Light limitation of nutrient-poor lake ecosystems. *Nature* 460 (7254), 506-509.
- Karlsson J., Giesler R., Persson J., and Lundin E. (2013) High emission of carbon dioxide and methane during ice thaw in high latitude lakes. *Geophys. Res. Lett.* 40 (6), 1123-1127.
- Keller K., Blum J., and Kling G. (2007) Geochemistry of Soils and Streams on Surfaces of Varying Ages in Arctic Alaska. *Arct. Antarct. Alp. Res.* 39 (1), 84-98.
- Keller K., Blum J. D., and Kling G. W. (2010) Stream geochemistry as an indicator of increasing permafrost thaw depth in an arctic watershed. *Chem. Geol.* 273 (1-2), 76-81.
- Kortelainen P., Pajunen H., Rantakari M., and Saarnisto M. (2004) A large carbon pool and small sink in boreal Holocene lake sediments. *Global Change Biol.* 10 (10), 1648-1653.
- Krammer K., and Lange-Bertalot H., 2008, Freshwater flora of Central Europe, *in* Ettl, H., Gerloff, J., and Heynig, H., eds., *Bacillariophyceae Parts 1-4: Germany*, Springer.
- Kritzberg E. S., Granéli W., Björk J., Brönmark C., Hallgren P., Nicolle A., Persson A., and Hansson L.-A. (2014) Warming and browning of lakes: consequences for pelagic carbon metabolism and sediment delivery. *Freshwat. Biol.* 59 (2), 325-336.
- Levine M., and Whalen S. (2001) Nutrient limitation of phytoplankton production in Alaskan Arctic foothill lakes. *Hydrobiologia* 455 (1), 189-201.
- Manguin E. (1961) Contribution à la flore diatomique de l'Alaska: Lac Karluk, espèces critiques ou nouvelles. *Revue Algologique, Nouvelle Série* 5, 266-288.
- Mann D. H., Groves P., Reanier R. E., Gaglioti B. V., Kunz M. L., and Shapiro B. (2015) Life and extinction of megafauna in the ice-age Arctic. *Proceedings of the National Academy of Sciences* 112 (46), 14301-14306.

Michelutti N., Blais J. M., Cumming B. F., Paterson A. M., Rühland K., Wolfe A. P., and Smol J. P. (2009) Do spectrally inferred determinations of chlorophyll a reflect trends in lake trophic status? *J. Paleolimnol.* 43 (2), 205-217.

Patrick R., and Freese L. R. (1960) Diatoms (Bacillariophyceae) from Northern Alaska. *Proc. Acad. Nat. Sci. Phila.*), 129-293.

Rantala M. V., Luoto T. P., and Nevalainen L. (2016) Temperature controls organic carbon sequestration in a subarctic lake. *Scientific Reports* 6, 34780.

Saros J., and Anderson N. (2015) The ecology of the planktonic diatom *Cyclotella* and its implications for global environmental change studies. *Biological Reviews* 90 (2), 522-541.

Saros J. E., Strock K. E., Mccue J., Hogan E., and Anderson N. J. (2013) Response of *Cyclotella* species to nutrients and incubation depth in Arctic lakes. *J. Plankton Res.*), fbt126.

Schindler D. (1978) Factors regulating phytoplankton production and standing crop in the world's freshwaters. *Limnol. Oceanogr.*), 478-486.

Smol J. P. (1983) Paleophycology of a high arctic lake near Cape Herschel, Ellesmere Island. *Canadian Journal of Botany* 61 (8), 2195-2204.

Smol J. P., Wolfe A. P., Birks H. J., Douglas M. S., Jones V. J., Korhola A., Pienitz R., Rühland K., Sorvari S., Antoniades D., Brooks S. J., Fallu M. A., Hughes M., Keatley B. E., Laing T. E., Michelutti N., Nazarova L., Nyman M., Paterson A. M., Perren B., Quinlan R., Rautio M., Saulnier-Talbot E., Siitonen S., Solovieva N., and Weckstrom J. (2005) Climate-driven regime shifts in the biological communities of arctic lakes. *Proc Natl Acad Sci U S A* 102 (12), 4397-4402.

Sobek S., Durisch-Kaiser E., Zurbrügg R., Wongfun N., Wessels M., Pasche N., and Wehrli B. (2009) Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source. *Limnol. Oceanogr.* 54 (6), 2243.

Spaulding S., Lubinski D., and Potapova M. (2010) Diatoms of the United States. Available at: Westerndiatoms.colorado.edu.

Vadeboncoeur Y., Lodge D. M., and Carpenter S. R. (2001) Whole-Lake Fertilization Effects on Distribution of Primary Production between Benthic and Pelagic Habitats. *Ecology* 82 (4), 1065-1077.

Vadeboncoeur Y., Peterson G., Vander Zanden M. J., and Kalff J. (2008) Benthic algal production across lake size gradients: interactions among morphometry, nutrients, and light. *Ecology* 89 (9), 2542-2552.

Verschuren D., Johnson T. C., Kling H. J., Edgington D. N., Leavitt P. R., Brown E. T., Talbot M. R., and Hecky R. E. (2002) History and timing of human impact on Lake

Victoria, East Africa. *Proceedings of the Royal Society of London B: Biological Sciences* 269 (1488), 289-294.

Vonk J. E., van Dongen B. E., and Gustafsson Ö. (2010) Selective preservation of old organic carbon fluviually released from sub-Arctic soils. *Geophys. Res. Lett.* 37 (11), n/a-n/a.

Wang Z., and Liu W. (2012) Carbon chain length distribution in n-alkyl lipids: A process for evaluating source inputs to Lake Qinghai. *Org. Geochem.* 50, 36-43.

Whalen S., and Cornwell J. (1985) Nitrogen, phosphorus, and organic carbon cycling in an arctic lake. *Can. J. Fish. Aquat. Sci.* 42 (4), 797-808.

Whalen S. C., Chalfant B. A., and Fischer E. N. (2008) Epipelagic and pelagic primary production in Alaskan Arctic lakes of varying depth. *Hydrobiologia* 614 (1), 243-257.

Wolfe A., Vinebrooke R., Michelutti N., Rivard B., and Das B. (2006) Experimental calibration of lake-sediment spectral reflectance to chlorophyll &a concentrations: methodology and paleolimnological validation. *J. Paleolimnol.* 36 (1), 91-100.

Yvon-Durocher G., Jones J. I., Trimmer M., Woodward G., and Montoya J. M. (2010) Warming alters the metabolic balance of ecosystems. *Philosophical Transactions of the Royal Society B: Biological Sciences* 365 (1549), 2117-2126.

6.10 Figures

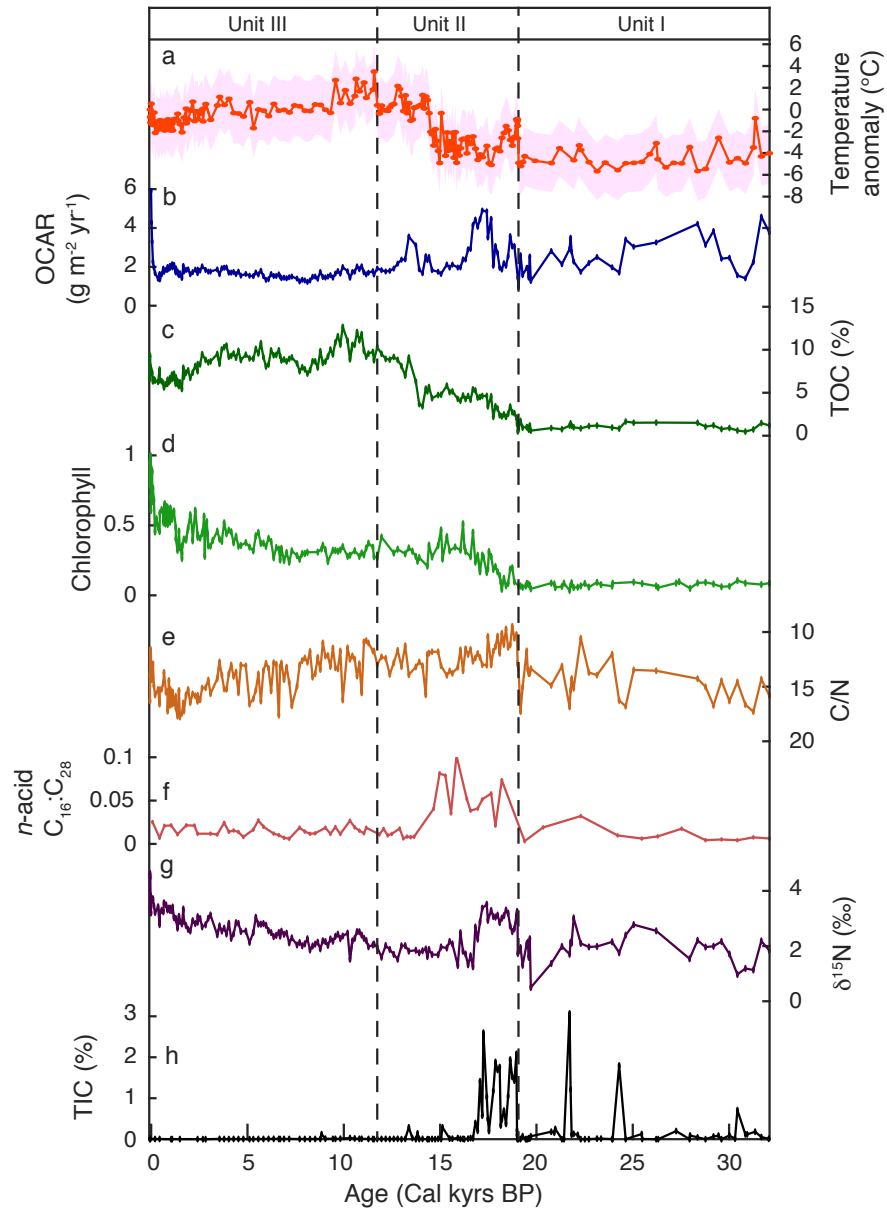


Figure 6.1 Geochemical and environmental variables of Lake E5. Unit divisions are described in the text. a) $\delta D_{\text{precipitation}}$ (Chapter 3), a proxy for summer air temperature, b) Organic carbon accumulation rate, c) Total organic carbon (TOC), d) Spectrally-inferred chlorophyll concentration, scaled to the maximum value in the core, e) C/N ratio (axis reversed), d) n -acid $C_{16}:C_{28}$ ratio, a proxy for relative contribution of aquatic and terrestrial OC; g) $\delta^{15}\text{N}$; h) Total inorganic carbon (TIC).

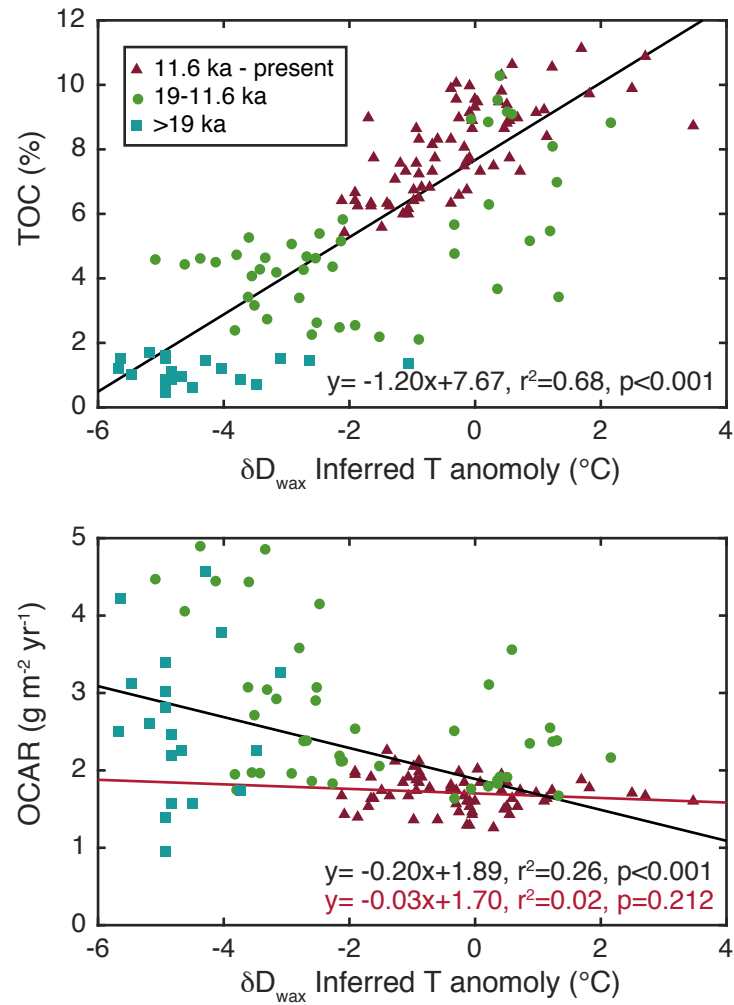


Figure 6.2 Total organic carbon (TOC) and organic carbon accumulation rate (OCAR) plotted against δD_{wax} -inferred temperature anomaly. Colors correspond to sedimentary units described in Chapter 4. For OCAR, the overall correlation is significant (black line), but the subset of Holocene samples (red) is not significantly correlated with temperature.

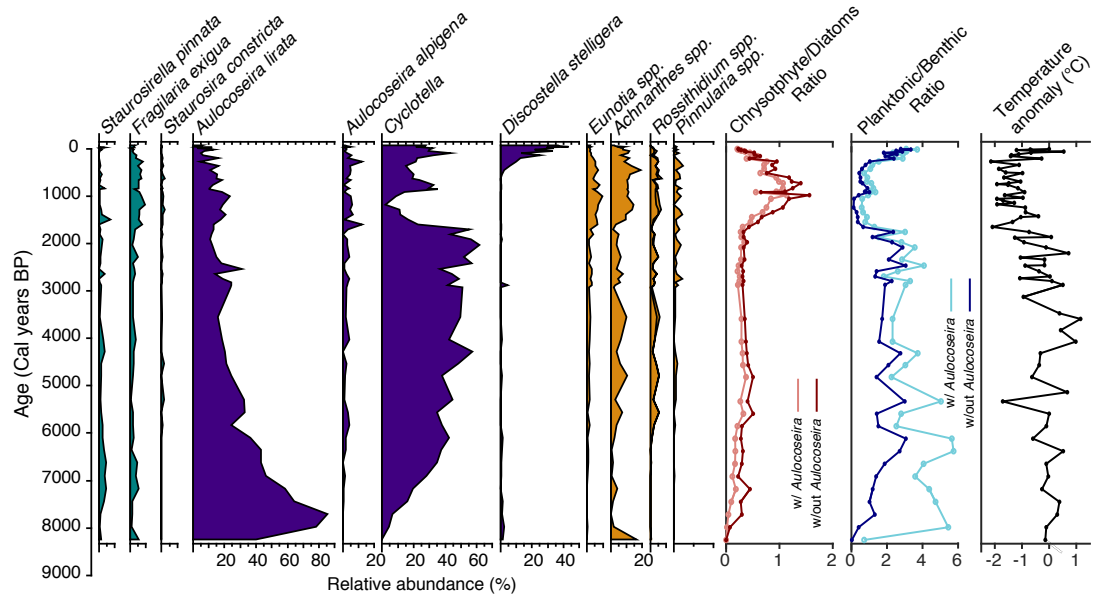


Figure 6.3 Diatom and chrysophyte relative abundances over the Holocene. Due to taphonomic bias favoring *Aulocoseira* spp. (Verschuren et al., 2002), the two ratios (chrysophyte:diatom and planktonic:benthic) are calculated with and without *Aulocoseira*. At the far right is the δD_{wax} -inferred temperature (Chapter 4).

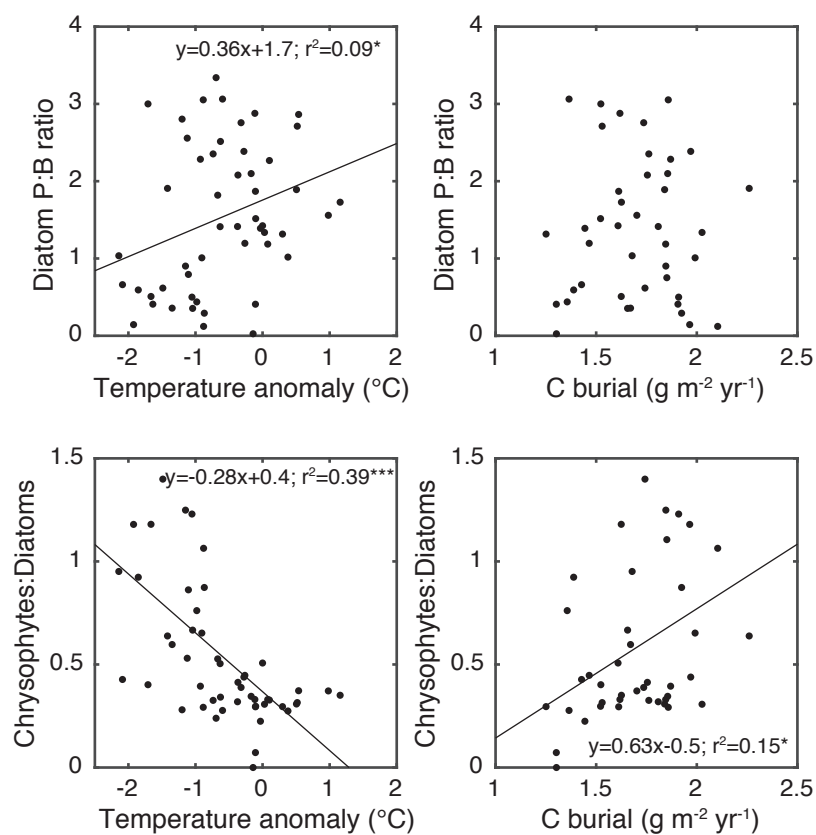


Figure 6.4 Top row: Diatom planktonic:benthic ratio plotted against δD_{wax} -inferred temperature and OC burial. Bottom row: The chrysophyte:diatom ratio plotted against δD_{wax} -inferred temperature and OC burial. *: $p < 0.05$, ***: $p < 0.001$.

CHAPTER SEVEN

Benthic community metabolism in deep and shallow arctic lakes during 13 years of whole-lake fertilization

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7.1 Abstract

Benthic primary production and oxygen consumption are important components of lake biogeochemical cycling. We performed whole-lake nutrient manipulations in arctic Alaska to assess the controls of lake morphometry, nutrients, and light on benthic community metabolism. One deep, stratified lake (Lake E5) and one shallow, well-mixed lake (Lake E6) in the Alaskan Arctic were fertilized with low levels of nitrogen ($56 \text{ mg N m}^{-3} \text{ y}^{-1}$) and phosphorus ($8 \text{ mg P m}^{-3} \text{ y}^{-1}$) from 2001-2013. Benthic primary production was not stimulated by fertilization in either lake. In the deep lake, decreased water clarity is consistent with an increase in phytoplankton biomass during fertilization. Benthic GPP decreased by $7 - 47 \text{ mg C m}^{-2} \text{ d}^{-1}$ (not statistically significant) and benthic respiration increased from 87 ± 20 to 167 ± 9 (SE) $\text{mg C m}^{-2} \text{ d}^{-1}$. The areal hypolimnetic oxygen deficit increased by $15 \text{ mg O}_2 \text{ m}^{-2} \text{ d}^{-1}$ each year during the 13 years of monitoring, apparently driven by lower (more negative) benthic NEP. In the shallow lake, phytoplankton concentration did not change with fertilization. As a result, the light environment did not change and benthic GPP did not decrease. Overall the data suggest that (1) benthic algae are not nutrient limited in either the deep or shallow lake, (2) lake morphometry modulated the overall nutrient impact on benthic metabolism by controlling the response of phytoplankton, and by extension, light and organic carbon supply to the benthos, (3) year-to-year variability in light attenuation explains considerable variability in benthic GPP between lakes and years, (4) correlations between both dissolved organic carbon concentrations and light attenuation coefficients (k_d) between lakes suggests a regional control on light attenuation, and (5) the dissolved oxygen concentrations in the deep experimental lake are highly sensitive to nutrient enrichment.

Keywords Lake carbon balance, Benthic photosynthesis, Benthic respiration, whole-lake fertilization, light limitation

7.2 Introduction

Quantifying the ecosystem level response to variations in nutrient loading has been the focus of many water quality and lake ecosystem studies (Schindler 1978, Howarth 1988, Morris and Lewis 1988). However, recent work on the importance of primary production by benthic algae, including epipelton, epilithon, and epiphyton, suggests that assessments of nutrient limitation based only on pelagic responses may not accurately reflect whole-lake nutrient limitation (Vadeboncoeur et al. 2001 and 2003, Karlsson et al. 2009). The reason is that there is a compensatory trade-off between benthic and pelagic GPP across trophic gradients because the concentration of phytoplankton affects the amount of light available to benthic habitats (Vadeboncoeur and Steinman 2002). In most cases epipellic algae are light limited, rather than nutrient limited, and, much of the epipelton nutrient demand is met by within-sediment remineralization (Jäger and Diehl 2014). As such, nutrient addition to the water column tends to benefit phytoplankton more than benthic algae. The resulting effect of decreased water clarity can suppress benthic primary production. Nutrient addition impacts on whole-lake primary production are therefore proportionately smaller if both benthic and pelagic processes are considered than if pelagic processes are considered alone.

In lakes where benthic substrates are well-lit, either because of low background light attenuation or because they are shallow, nutrient addition can potentially stimulate

benthic production while simultaneously increasing phytoplankton production and biomass (Hansson 1992, Stanley 1976, Jäger and Diehl 2014). Ultraoligotrophic lakes at high latitudes commonly fit this description. In these cases, model simulations show that the stimulation of benthic algae and benthic nutrient uptake can act to diminish the anticipated increase in phytoplankton growth (Genkai-Kato et al. 2012). Benthic algae are effective at trapping nutrients when water column P concentration is less than approximately 10 mg P m^{-3} , depending on background light attenuation. Below this level, increasing nutrients can either increase (Jäger and Diehl 2014) or have little effect (Genkai-Kato et al. 2012) on total lake production. At phosphorus concentrations on the order of $10\text{-}100 \text{ mg P m}^{-3}$ (Jäger and Diehl 2014) or P loading rates of $2\text{-}5 \text{ mg P m}^{-2} \text{ d}^{-1}$ (Genkai-Kato et al. 2012), phytoplankton shading overwhelms benthic productivity, benthic production decreases, and a positive feedback of sediment nutrient release further fuels planktonic production (Jäger and Diehl 2014). Above these levels, models indicate that benthic algae decline precipitously.

At the whole-lake scale, lake morphometry is an important control on the relative contribution of benthic production to total lake production (Whalen et al. 2008, Vadeboncoeur et al. 2008). The reason again relates to the light environment of the lake – benthic GPP may be relatively more important in shallow lakes because the ratio of sediments in the photic zone to the volume of the epilimnion is high. In deep lakes, especially those with steep slopes (Vadeboncoeur et al. 2008), phytoplankton may dominate the annual GPP on a whole-lake scale.

Morphometry can also influence the fate of nutrients entering a lake and the dynamic biological response to changing nutrient inputs (Fee 1979, Vadeboncoeur et al.

2008). Fee proposed that in deep and stratified lakes, phytoplankton are more likely to settle through the thermocline where the nutrients they contain are more effectively trapped in the hypolimnion. In such cases, additional nutrients may not benefit benthic algae especially considering the shading effects of increased phytoplankton biomass in surface waters. In shallow lakes with weak or no stratification, there is a balance between greater recycling of nutrients to the photic zone through physical mixing (Fee 1979, Nolen et al. 1985) and greater uptake of nutrients by benthic algae (Jäger and Diehl 2014).

In most arctic lakes, pelagic primary production is low because the growing season is short and nutrient concentrations are low. Benthic algae therefore tend to be relatively important to whole lake production – they can fix up to $18 \text{ g C m}^{-2} \text{ y}^{-1}$ (Welch and Kalff 1974) or contribute upwards of 98% of a lake's total annual production (Vadeboncoeur 2003, see also review by Quesada et al. 2008). Because of the extremely low nutrient levels in arctic lakes, there is potential for benthic algae to be nutrient limited rather than light limited (Hansson 1992, Stanley 1976). We tested this hypothesis by performing two whole-lake fertilization experiments in ultraoligotrophic arctic lakes. The study lakes and their un-manipulated reference lakes are located near Toolik Lake in the arctic tundra of northern Alaska. Because the nutrient impact may depend on lake shape, as described above, the two lakes in this experiment were chosen to represent two basic morphometries – one was shallow ($z_{\text{max}} = 3.2 \text{ m}$) and polymictic while the other was deeper ($z_{\text{max}} = 12.7 \text{ m}$) and dimictic. We hypothesized that benthic GPP would only be stimulated in the shallow lake where a greater proportion of lake floor lies above the 1% light level (100% of lake floor in the shallow lake vs. 35% of lake floor in the deep lake),

and that nutrients added to the deeper lake would be recycled within the water column or lost to the hypolimnion during the summer growing season resulting in no effect on benthic algae.

We assessed changes in the benthic communities during the fertilization time course in both experimental and both reference lakes by examining chlorophyll content, measured and modeled photosynthesis parameters, and respiration rates. We also calculated benthic GPP and NEP by combining the photosynthesis parameters with measured light availability, which is influenced by changes in water transparency and ambient incoming insolation.

While most arctic lakes are not exposed to point-source nutrient pollution because of their distance from population centers, it has been suggested that global climate change will increase the delivery of nutrients from land to water (Hobbie et al. 1999). Increased nutrient loading may result from enhanced precipitation and runoff events (MacIntyre et al. 2009) or from thermally-driven erosion and weathering of permafrost soils (Bowden et al. 2008, Rowland et al. 2010, Mesquita et al. 2010). Thermokarst failures exemplify one type of thermal erosion and are characterized by mass transport of soil (turbidity), vegetation, and dissolved constituents (nutrients) into surface waters.

7.3 Methods

7.3.1 Study Sites

The four study lakes lie within 25 km of the Toolik Lake Field Station on the North Slope of Alaska (68°37' N, 149°36' W, Figure 7.1). Mean annual air temperature for the region is -7 °C and mean July temperature is 12 °C (Cherry et al. 2014). The

study lakes are surrounded by permafrost soils with summer active layers less than 1 m thick. The lakes are ultraoligotrophic (Table 7.1; surface TP 3.8 - 17 mg m⁻³; surface chlorophyll a 0.4 - 9.3 mg m⁻³) and ice free from mid-June to late-September. Dissolved organic carbon (DOC) concentrations range from 200 - 895 µmol L⁻¹. The lakes represent two basic morphometries: Lake Fog 2 and E5 are classified as deep ($z_{\max} > 12$ m, $z_{\text{mean}} > 5$ m) and thermally stratify during summer. Lakes Fog 4 and E6 are shallow ($z_{\max} < 5$ m, $z_{\text{mean}} < 2.5$ m) and the water columns are frequently mixed. Two of the lakes underwent artificial N and P additions from 2001 until 2013. Fog 2 served as a reference lake for the deep, fertilized Lake E5. Fog 4 was intended to serve as a reference lake for the shallow, fertilized Lake E6. From 2002 to 2005, however, a small thermokarst failure occurred along its northern shoreline and a plume of sediment could be seen entering the lake. While we did not quantify the nutrient or sediment loading during this event, it is likely to have impacted the lake ecosystem rendering it unsuitable as a reference lake. Fog 4, however, did serve as an additional model system in which to examine the impact of nutrient and light disturbance on benthic production. The benthic substrate of the lakes is dominated by unconsolidated silt-sized clastic sediments. Unlike benthic communities of many polar freshwaters (Quesada et al. 2008), the benthic algae in our study lakes were not mat-forming, but instead exhibited a gradual transition from algae-rich to algae-poor moving down the sediment column. With the exception of Lake Fog 2, the sediment matrices are visibly greenish. Rocks are present along the lake margins to the depth of ice-scour (approximately 1.5 m) and sparse macrophytes were observed only in Lake Fog 2.

7.3.2 Fertilization regime

Benthic monitoring of the lakes began in 1999 in the experimental E lakes and in 2000 in the Fog lakes. Nutrient manipulations began in 2001. For the nutrient manipulation, N and P were added at the Redfield Ratio by slowly dripping a solution of ammonium nitrate and phosphoric acid into the lakes from a raft tethered near the lakes' centers. The target fertilization rates of $56 \text{ mg N m}^{-3} \text{ y}^{-1}$ and $8 \text{ mg P m}^{-3} \text{ y}^{-1}$ were approximately three times larger than the background loading rates of inorganic N and P to nearby Toolik Lake (Whalen and Cornwall 1985). The fertilization increased the annual loading by approximately four-fold. For Lake E5, the amount of added N and P was scaled to the epilimnion volume only, whereas for Lake E6 the fertilization was scaled for the entire volume. On an areal basis, this equates to $280 \text{ mg N m}^{-2} \text{ y}^{-1}$ and $40 \text{ mg P m}^{-2} \text{ y}^{-1}$ for the 5 m deep mixed layer in Lake E5, and $112 \text{ mg N m}^{-2} \text{ y}^{-1}$ and $16 \text{ mg P m}^{-2} \text{ y}^{-1}$ for the 2 m average depth of Lake E6. In comparison to other whole-lake fertilization experiments, the manipulation strength is quite moderate (Table 7.2; Bettez et al. 2002, Bjork-Ramberg and Anell 1985, Bergmann and Welch 1990, Vadeboncoeur 2001, O'Brien et al. 2005). The level of enrichment in this experiment represents a low-intensity press disturbance to the lakes.

7.3.3 Meteorological and water column data

Hourly incident photosynthetically active radiation (PAR, 400-700 nm) was obtained from the Arctic-LTER meteorological station (ARC LTER database). Mean summer values of incident PAR were calculated using hourly data over the time period of June 15 to August 31. Measurements of water column light attenuation were made every 10 days during the summer for the fertilized lakes. The same measurements were made

1-3 times each summer in Fog 2 and Fog 4. Light attenuation coefficients with depth (k_d) were calculated as the absolute value of the slope of the natural logarithm of PAR, measured at 1 m intervals, plotted against depth. A Hydrolab multisonde unit (DS4) was used to measure depth profiles of dissolved oxygen (DO), temperature, pH, and conductivity at the same time that light measurements were made.

7.3.4 Benthic metabolism

Because most of the benthic surface area in each lake is comprised of soft sediments, we focused on characterizing the epipelagic algal community rather than the marginal epilithic communities. We measured the oxygen flux across the sediment-water interface to estimate net ecosystem production (NEP), community respiration (R), and gross primary production ($GPP = NEP + R$) during the ice-free season from 1999-2005, 2007, and 2009-2013. No measurements were made in Lake Fog 4 from 2009-2012. Two O_2 flux methods were used. From 1999-2003, O_2 flux was measured in-situ using plexiglass chambers placed on the lake floor using SCUBA (see Gettel et al. 2013 for method details). From 2001-2013 we generated photosynthesis-irradiance (PI) curves by measuring O_2 flux in sediment cores incubated in laboratory facilities at the Toolik Field Station. We compared results from these two methods in years where both were employed. Estimates of GPP from the laboratory PI incubations were on average $40 \text{ mg C m}^{-2} \text{ d}^{-1}$ higher than from in-situ chamber measurements ($p = 0.072$). Respiration averaged $87 \text{ mg C m}^{-2} \text{ d}^{-1}$ higher with the laboratory incubations method ($p = 0.005$). As such, the two methods are reported independently for both GPP and respiration.

Between late-June and mid-July of each core-sampling year, oxygen flux measurements were performed on 6-8 sediment cores. Sampling sites and depths were

dictated in part by the substrate distribution in the lake and in part by the desire to sample sediments representative of the shallow littoral zone and the deep hypolimnetic zone. In the shallow lakes (E6 and Fog 4), epipelon were confined to depths between 1 m (shallower depths had rocks), and 3 m (maximum depth), and we sampled at approximately 1.5 and 2.5 m depth. In the deep lakes (E5 and Fog 2), rocks extend to about 3 meters depth and the lake basins are steep-sided. For these lakes, half the cores were taken from the epilimnetic sediments (3-4 m) and half were from the hypolimnetic sediments (5-7 m). The cores were 9.5 cm in diameter and 40 cm long. For each sample, we collected approximately 25 cm of sediment, leaving about 15 cm of water-filled headspace in each core. Cores were returned to the laboratory within 2 hours of sampling and placed in water baths at in situ lake temperatures for 8-12 hours prior to the start of incubation. The overlying water of each core was replaced with filtered lake water (0.45 μm) in order to minimize the influence of pelagic particulates on oxygen flux. Cores were sealed bubble-free and a DO probe (membrane probes 2001-2009, optical probes 2010-2012) was inserted into a port in each core top. Core headspaces were gently mixed by magnetic stirrers activated by an external rotating magnet. DO probes were programmed to record DO every 5 minutes. Cores were first incubated in the dark and then under multiple light intensities in order to generate photosynthesis-irradiance relationships. Community respiration (R) in the dark, and net ecosystem production (NEP) in the light, were calculated from the change in oxygen over time. Oxygen fluxes were converted to carbon flux assuming photosynthetic and respiratory quotients of 1.0. We assumed that R_{light} was equivalent to R_{dark} , although in some cases R_{light} exceeds R_{dark} because of photorespiration (Bender 1987).

Typically, 4-5 light levels, ranging from < 50 to $> 350 \mu\text{mol quanta } (\mu\text{Einstein}) \text{ m}^{-2} \text{ s}^{-1}$ were used to model GPP against PAR using Michaelis-Menten kinetics (Equation 1) for each core. We assumed GPP is a function of light-saturated GPP (P_{max}), the PAR half-saturation constant ($k_{1/2}$), and the incoming PAR (I). Optimized values of P_{max} and $k_{1/2}$ and associated error for each sampling effort were simultaneously solved using Graphpad PRISM software.

$$\text{Eq. 1} \quad GPP = \frac{(P_{\text{max}} \times I)}{(k_{1/2} + I)}$$

Average rates of GPP at the depth of sampling were estimated by combining parameters for the above relationship with the hourly incident PAR from June 15 to August 31, and lake-specific light attenuation coefficients linearly-interpolated between sampling times. Hourly PAR measurements were modified to account for reflectance off the water surface. Reflectance was calculated hourly using zenith angle of the sun (<http://www.nrel.gov/midc/solpos/solpos.html>, Vahatalo et al. 2000) and averaged 35.5% over the time period of interest. The resulting value agrees well with a suite of empirical values measured for lakes around the Toolik Field Station (average 30%; ARC LTER database). For the deep lakes, Fog 2 and E5, GPP was estimated at 3.5 m and 6 m depth. For the shallow lakes, Fog 4 and E6, GPP was estimated at 2 m depth. Error was estimated by Monte Carlo simulation with error attributed to the photosynthetic parameters. The average and standard deviation (SD) of 500 simulations was used to characterize the GPP of each year. In addition to simulating GPP at the sampling depths, we calculated GPP on a whole lake basis by applying the P-I curves to light calculated at 1 meter depth intervals, summing the calculated GPP, and dividing by the total surface area of each lake.

7.3.5 Benthic Chlorophyll a

Acetone-extractable chlorophyll a was measured from surface sediments to help characterize the benthic algal community. While benthic chlorophyll a is not a direct measure of algal biomass, it can serve as a useful proxy for benthic algal photosynthetic capacity. From 1999-2003, a 2.7 cm diameter core was used to collect sediment samples for chlorophyll analysis in association with the GPP chamber measurements (Gettel et al. 2013). After 2003, benthic algae biomass was assessed in sediments from the cores used for the incubations. In all cases, the surface 2 cm from each core was homogenized, and five mL of wet sediment were subsampled and frozen. We later added 35 mL of 100% acetone (which, with porewater, led to a 90% acetone solution) and extracted in the dark overnight with occasional shaking. All samples were kept frozen in the dark until analysis. Samples were analyzed spectrophotometrically, using the acidification protocol and equations of Lorenzen (1967) to correct for phaeopigments.

Statistical analysis—For each fertilized lake we compared pre- and post-fertilization values of benthic chlorophyll, GPP, and water column light extinction. Because it was not possible to transform all data to have normal distributions, the non-parametric Mann-Whitney rank test was used for all comparisons. For the thermokarst-impacted lake, we pooled years of active thermokarst slumping (2002-2005) and non-thermokarst years (1999-2001 and 2006-2013) for comparison. Standard errors are reported for light extinction coefficients and benthic and pelagic chlorophyll a. Standard deviations are reported for benthic GPP and respiration.

7.4 Results

Light environment

Photosynthetically active radiation (PAR) incident at the water surface averaged $354 \mu\text{mol quanta m}^{-2} \text{ s}^{-1}$ from June 15 to August 31 when all years and hours of the day were pooled. There was no temporal trend in incoming PAR during the 13 years, but there was large year-to-year variability with summer averages ranging from $306 \mu\text{mol quanta m}^{-2} \text{ s}^{-1}$ in 2006 to $473 \mu\text{mol quanta m}^{-2} \text{ s}^{-1}$ in 2007 (Figure 7.2a).

Light attenuation was lowest in the deep reference lake, Fog 2 ($k_d = 0.33 \pm 0.02 \text{ m}^{-1}$) and did not change over time (Figure 7.2b). In the deep fertilized lake, E5, k_d increased significantly from $0.71 \pm 0.01 \text{ m}^{-1}$ before fertilization to $0.96 \pm 0.03 \text{ m}^{-1}$ after fertilization ($p < 0.0009$). Water column chlorophyll a increased from 1.7 ± 0.06 to $2.65 \pm 0.06 \mu\text{g L}^{-1}$ ($p = 0.0002$, ARC LTER database). In the shallow fertilized lake, E6, k_d did not increase significantly (pre-fertilization: 1.12 ± 0.08 ; post-fertilization: 1.27 ± 0.04 ; $p = 0.153$). Water column chlorophyll a was also unchanged with fertilization (pre-fertilization: $2.1 \pm 0.06 \mu\text{g L}^{-1}$; post-fertilization: $2.2 \pm 1.1 \mu\text{g L}^{-1}$; $p = 0.23$, ARC LTER database). In the shallow, thermokarst-impacted lake Fog 4, non-thermokarst years had significantly lower k_d values of $1.02 \pm 0.05 \text{ m}^{-1}$ compared to $1.38 \pm 0.15 \text{ m}^{-1}$ during thermokarst years ($p = 0.04$). However, water column chlorophyll a concentrations were not statistically higher during thermokarst years ($p = 0.074$).

Deep reference Lake, Fog 2

In the deep reference lake, Fog 2, benthic chlorophyll a in the epilimnetic sampling sites ranged from 29 to 368 mg m^{-2} (average 141 mg m^{-2} to 2 cm depth; Figure

7.3). Concentrations were similar at the deeper (6 m) sampling sites. At our sampling depths, benthic respiration exceeded benthic GPP in most, but not all years (Figure 7.3). In this unmanipulated lake there was considerable interannual variability in PAR striking the sediment surface, as well as benthic chlorophyll a, $P_{\max}$, GPP, and respiration. The benthic variables increased from 2002 to a peak in 2007, then declined to a local minimum in 2011.

Shallow reference lake, Fog 4

Lake Fog 4 was intended as the shallow reference lake, but experienced a shoreline failure during our monitoring program. Sediment was observed slumping from a localized point along the northwest shore and mixing into the water column during four consecutive summers (2002-2005). Of our study lakes, Fog 4 had the highest concentration of benthic chlorophyll a and there was more chlorophyll a during the years of high sediment influx relative to the years with a stable shoreline - concentrations averaged $573 \pm 24 \text{ mg m}^{-2}$ during the years of active thermokarst failure and $361 \pm 40 \text{ mg m}^{-2}$ during the non-thermokarst years ($p = 0.0001$, Table 7.3). Years in which the shoreline failure was an active sediment source were also characterized by lower rates of benthic GPP ($105 \pm 59 \text{ mg C m}^{-2} \text{ d}^{-1}$ compared to $235 \pm 106 \text{ mg C m}^{-2} \text{ d}^{-1}$ for years with no thermokarst activity; $p < 0.0001$) (Table 7.3, Figure 7.3 and 7.5). Respiration was variable during the thermokarst disturbance, but on average was lower ($223 \pm 77 \text{ mg C m}^{-2} \text{ d}^{-1}$ compared to $347 \pm 88 \text{ mg C m}^{-2} \text{ d}^{-1}$ for years with no thermokarst activity; $p = 0.0024$).

Deep fertilized lake, E5

In the deep fertilized lake, E5, chlorophyll concentrations in the epilimnetic sediments were $139 \pm 7 \text{ mg m}^{-2}$ in 1999 and 2000, and $179 \pm 13 \text{ mg m}^{-2}$ after fertilization, which was not a statistically significant change ($p = 0.75$, Table 7.3). There was less year-to-year variation in chlorophyll a in this lake compared to the other lakes, but we note that, as in the deep reference lake, both chlorophyll a and P_{max} increased from 2002 to 2007, and declined in the following 3 years (Figure 7.4). Based on in-situ chamber measurements, the pre-fertilization GPP in the deep manipulated lake, E5, was $68 \pm 13 \text{ mg C m}^{-2} \text{ d}^{-1}$. The in-situ chamber measurements in the two years after the fertilization began were unchanged (Gettel et al. 2013). After incorporating the longer time series of simulated GPP, we found that GPP remained unchanged during the fertilization period ($p = 0.32$; Table 7.3) although considering the change in methodology, where lab incubation estimates of GPP averaged $40 \text{ mg C m}^{-2} \text{ d}^{-1}$ higher than the in-situ chamber measurements for the same time periods, it is possible that fertilization induced a reduction in benthic GPP. Respiration rates were $87 \pm 28 \text{ mg C m}^{-2} \text{ y}^{-1}$ in 1999 and 2000 and $167 \pm 80 \text{ mg C m}^{-2} \text{ d}^{-1}$ during the fertilization period ($p = 0.11$), which suggests that fertilization induced a positive change in benthic respiration. Benthic net ecosystem production was substantially lower during the fertilization period (Table 7.3). Hypolimnetic (6 m depth) GPP averaged $8 \text{ mg C m}^{-2} \text{ d}^{-1}$ and respiration averaged $185 \pm 94 \text{ mg C m}^{-2} \text{ d}^{-1}$ during the fertilization period. No pre-fertilization data is available from the hypolimnetic site of this lake.

Shallow fertilized lake, E6

In the shallow fertilized lake, E6, chlorophyll a increased from $126 \pm 13 \text{ mg m}^{-2}$ in pre-fertilization years to $212 \pm 12 \text{ mg m}^{-2}$ after the onset of fertilization ($p = 0.02$, Figure 7.4), although in the last three years of monitoring, chlorophyll a had returned to pre-fertilization levels. In-situ chamber data revealed no difference in GPP with fertilization for the shallow lake, E6 (Gettel et al. 2013). The longer-term GPP measurements made from core incubations also show no statistically significant change upon fertilization – GPP was $62 \pm 46 \text{ mg C m}^{-2} \text{ d}^{-1}$ prior to fertilization and $131 \pm 147 \text{ mg C m}^{-2} \text{ d}^{-1}$ ($p = 0.19$) after fertilization. Taking into account the change in methodology described above, GPP only increased by approximately $30 \text{ mg C m}^{-2} \text{ d}^{-1}$. Respiration rose from a pre-fertilization average of $111 \pm 35 \text{ mg C m}^{-2} \text{ d}^{-1}$ to a post-fertilization average of $297 \pm 157 \text{ mg C m}^{-2} \text{ d}^{-1}$ ($p = 0.0007$). However, considering the methods change, the respiration increased by approximately $107 \text{ mg C m}^{-2} \text{ d}^{-1}$ from pre- to post-fertilization and there was no clear temporal trend in respiration in either the chamber or core data alone.

Benthic photosynthesis parameters

From the photosynthesis vs. irradiance curves, the average P_{max} for all lakes and years was $495 \text{ mg C m}^{-2} \text{ d}^{-1}$ and the average $k_{1/2}$ was $163 \text{ } \mu\text{mol quanta m}^{-2} \text{ s}^{-1}$. From P_{max} and $k_{1/2}$ values, we calculated the quantum efficiency ($\text{mol C fixed mol quanta}^{-1}$) for the sub-saturating part of the P-I curves. The efficiency ranged from 0.0001 to 0.014 mol C per mol quanta (Figure 7.4) with an average for all lakes and sampling dates of $0.004 \text{ mol C mol quanta}^{-1}$. Quantum efficiency was significantly related to benthic chlorophyll a across all lakes in the post fertilization period (Figure 7.6). Unfortunately, estimates of P_{max} and $k_{1/2}$ are not available from the chamber measurements made before fertilization

started. The model parameters for each lake, year, and sampling depth can be found in the supplemental tables 7.1-7.3.

To test the fertilization impact on benthic GPP without the confounding factor of changing light, we looked for differences in quantum efficiency between lakes, expecting that the fertilized lakes would have greater efficiency. A one-way ANOVA showed no differences between lakes ($p = 0.273$). We also plotted average summer GPP vs average summer ambient light levels at the sediment surface (Figure 7.S1). There is considerable scatter ($R^2 = 0.37$) but the results show no clear impact of fertilization on average summer GPP, especially considering the pre-fertilization years may be somewhat underestimated. Core incubation temperature was not strongly or significantly correlated with either $P_{\max}$ ($p = 0.43$), $k_{1/2}$ ($p = 0.42$) or summer GPP ($p = 0.982$).

Community metabolism at the whole-lake scale

Integrating benthic GPP across all lake depths and area and normalizing to lake surface area reveals that benthic respiration exceeded benthic GPP (NEP was negative, sediments were net heterotrophic) in all lakes (Figure 7.7). At this scale, benthic GPP was highest in the shallow fertilized lake, E6 ($15 \text{ g C m}^{-2} \text{ summer}^{-1}$), and lowest in the deep fertilized lake, E5 ($4 \text{ g C m}^{-2} \text{ summer}^{-1}$). The reference lakes were intermediate at $11 \text{ g C m}^{-2} \text{ summer}^{-1}$ for the deep Lake Fog 2 and $9 \text{ g C m}^{-2} \text{ summer}^{-1}$ in the shallow Lake Fog 4. Whole lake benthic NEP ranged from -12 to $-15 \text{ g C m}^{-2} \text{ summer}^{-1}$.

The nutrient manipulation effect on the benthic NEP lead to increased oxygen depletion in the deep stratified lake, E5. Prior to fertilization, the lowest DO concentration in E5 at any water depth was 5.96 mg L^{-1} . As fertilization progressed, the

hypolimnion became increasingly depleted in DO at the time of late-summer stratification. Using 8 m water depth as an indicator, DO declined by $0.3 \text{ mg L}^{-1} \text{ y}^{-1}$ over the 13 years of measurement. The first incidences of hypoxia ($\text{DO} < 3 \text{ mg L}^{-1}$) and anoxia ($\text{DO} < 0.5 \text{ mg L}^{-1}$) in the bottom waters at 11 m depth occurred in 2008 and 2011, respectively. In contrast, there was no trend in DO concentrations over time in reference lake Fog 2 (Figure 7.8), suggesting that the oxygen depletion was a response to fertilization rather than to factors independent of the fertilization. No change in summertime dissolved oxygen levels was evident in the shallow fertilized lake (E6) because the lake did not stratify during our monitoring.

The areal hypolimnetic oxygen deficit (AHOD) in E5 was calculated from bathymetric maps and summertime oxygen profiles for periods when thermal stratification was stable. The AHOD was between 203 and $664 \text{ mg O}_2 \text{ m}^{-2} \text{ d}^{-1}$ and increased by $15 \text{ mg O}_2 \text{ m}^{-2} \text{ d}^{-1}$ per year during the 13 years of monitoring ($R^2 = 0.34$, $p = 0.042$; Figure 7.9a). The AHOD of Lake E5 is positively, but not statistically, correlated with the estimated NEP of the benthic community at 6 m depth ($R^2 = 0.26$, $p = 0.16$; Figure 7.9b). Water column sampling of the deep reference lake Fog 2 lacked the temporal resolution necessary to calculate AHOD with confidence.

7.5 Discussion

We performed whole-lake nutrient enrichment experiments to test the relative importance of nutrients and light as limiting factors to benthic primary production in arctic lakes. Our results support several previous studies which demonstrate that water clarity and lake morphometry are important regulators of benthic GPP at the whole-lake scale (Liboriussen and Jeppesen 2003, Vadeboncoeur et al. 2008, Whalen et al. 2008).

Our results also suggest that (1) slight nutrient enrichment did not stimulate benthic algae regardless of lake shape, (2) variation in PAR is an important control on benthic GPP in the study lakes and the effect of fertilization on water column light attenuation was greater in the deep lake than in the shallow lake, and (3) low-level nutrient enrichment can drive an increase in AHOD by increasing benthic respiration and decreasing benthic NEP.

7.5.1 Benthic algae response to nutrient addition

Previous experiments in arctic and sub-arctic lakes have tested the response of benthic microalgae to nutrient additions. From shallow ponds ($z_{\max} = 0.2$ m) near Barrow, AK, Stanley (1976) observed a doubling of benthic GPP from 540 to 1080 mg C $\text{m}^{-2} \text{d}^{-1}$ with the addition of phosphorus. Likewise, N and P addition stimulated benthic chlorophyll (but not GPP) in shallow Lake Hymenjaure ($z_{\max} = 3.4$ m) in Sweden (Bjork-Ramberg and Anell 1985). However, in the majority of whole-lake enrichment experiments, especially those in lakes that we would classify as deep enough to routinely stratify, there was no such response by benthic algae, and in many cases, benthic GPP was suppressed due to lower light conditions upon fertilization (Vadeboncoeur et al. 2001). As such, benthic microalgae are generally considered light, rather than nutrient limited.

Light seems to be the limiting resource for benthic algae in our study lakes, despite the low water column nutrient concentrations. This is exemplified at two scales in our study. First, the interactions of lake depth and water quality interact to affect available light, and by extension benthic GPP, at the whole-lake scale. Specifically, even though the clear and deep reference lake (Fog 2) had similar benthic $P_{\max}$ and $k_{1/2}$ values

as did the DOC-rich lake of similar morphometry (E5), it had ~250% higher summer benthic GPP on an areal basis because light penetrated to sediment deeper in the lake. Likewise, the shallow lakes, E6 and Fog 4, had 370% and 220% higher productivity on an areal basis than did Lake E5 at the whole-lake scale, despite similar water column light attenuation properties. Secondly, nutrient addition did not stimulate benthic GPP at the depth-specific scale. While the increase in benthic chlorophyll a in the first 3 years of fertilization in both Lake E5 and E6 suggested a positive response of benthic algae to fertilization (Gettel et al. 2013), during the 13-year fertilization period, benthic chlorophyll a returned to pre-fertilization levels. This, together with the observations that (1) there was no difference in quantum efficiency between the fertilized and reference lakes, (2) no obvious change in the relationship between GPP and ambient PAR from pre- to post-fertilization (Figure 7.S1), and (3) GPP did not increase significantly during the course of the experiment in either fertilized lake, indicates that the nutrient addition did not positively impact benthic algae.

The prevalence of light limitation is further supported by nutrient addition experiments performed on individual cores incubated under saturating light conditions by Gettel et al. (2013). They added N, P, or N plus P to the overlying water of cores from Lake Fog 2 and observed no response in terms of GPP or chlorophyll a over periods up to 9 days. A similar finding, in terms of benthic pigments, was found in Ward Hunt Lake in Canada by Bonilla et al. (2005). While the turnover time of benthic algae is on the order of 2 months to years in high-latitude lakes (Bjork-Ramberg and Anell 1985), longer than the 9-day incubations, our time series of 13 years should be sufficiently long to capture potential nutrient stimulation effects.

Our measured lack of benthic stimulation to nutrients may have been different in the epilithon of the rocky littoral area because epilithon do not have access to sediment porewater nutrients and because they receive more light (Vadeboncoeur et al. 2001). The rocky littoral zone, however, comprises a relatively small proportion of each lake study and thus is unlikely to impact the overall benthic GPP at the whole-lake scale.

The concentrations of benthic chlorophyll a we observed are quite high compared to benthic mats, epilithon, and epipelon measured in other polar freshwaters (Quesada et al. 2008, Bowden et al. 2014), but are not unprecedented. Whalen et al. (2008) measured benthic chlorophyll a concentrations of 258-699 mg m⁻² in the top 2 cm of sediment in Alaska tundra lakes, which were two orders of magnitude greater than the areal phytoplankton chlorophyll a. We also measured chlorophyll a in the surface two cm of sediment. The positive correlation between benthic chlorophyll a and quantum efficiency suggests that chlorophyll a over this sediment depth is a reasonable parameter for estimating community photosynthetic potential, although we expect the relationship in Figure 7.6 would have been stronger had we sampled a thinner layer of sediment because only algae residing in the sediment photic zone (1-4 mm) can actively photosynthesize at a given time (MacIntyre and Cullen 1995). Regardless, one would expect an increase in benthic chlorophyll a concentrations during the experiment if N and P from the overlying water column were limiting benthic algae growth. Because benthic chlorophyll a was not higher in a sustained way in either lake, we conclude that these benthic algae were not limited by N or P during the summers.

7.5.2 Regulation of light

Because light is commonly limiting for benthic algae production (Vadeboncoeur et al. 2001), understanding the fertilization impact on light attenuation is an important aspect of this study. High concentrations of DOC, and especially the fraction of colored dissolved organic matter (CDOM), and lake morphology can interact to modulate the impact of nutrient addition on light availability to benthic algae. To our knowledge, our study is the first to assess the dynamic, long-term response of benthic algae in high-DOC, low-chlorophyll lakes (Table 7.1) during low-level nutrient enrichment (Table 7.2). This scenario may typify the trajectory of boreal lakes and some arctic lakes (Tranvik et al. 2009, Rautio et al. 2011) in a warmer and more nitrogen-rich world (Hobbs et al. 2010, Prowse et al. 2006, Elser et al. 2009).

In this study, the fertilization experiments had a higher impact on light extinction coefficients in the deep lake (E5) than in the shallow lake (E6). This different response suggests a morphological control on the impact of low-level enrichment. The difference derives from lower stimulation of phytoplankton biomass, on a volumetric basis, observed in Lake E6. In the absence of a strong benthic algal response, we hypothesize that high abiotic nutrient sequestration by lake sediments contributes to the weak phytoplankton response in Lake E6. This explanation is plausible considering the affinity for phosphorus to complex with the iron-rich lake sediments (Cornwell and Kipphut 1992) and the potentially rapid transfer of phosphorus to the sediments in a shallow setting. Gekai-Kato et al. (2012) proposed that at nutrient loading rates above $2\text{--}5 \text{ mg P m}^{-2} \text{ d}^{-1}$, lakes could alternate from a clear to a turbid stable state. We did not observe such a transition in Lake E6 despite our experimental loading rates of $16 \text{ mg m}^{-2} \text{ d}^{-1}$. The

threshold for stable-state transition may therefore be somewhat higher in these experimental lakes due to the abiotic P absorption capacity of the sediments. In the deeper Lake E5, we suggest that added nutrients had less contact with the sediments, allowing for greater recycling within the water column, thereby having a stronger effect on phytoplankton biomass than in the shallow lake.

The similar temporal variation of light attenuation and benthic GPP in the non-thermokarst lakes suggests a regional influence on the light environment and benthic processes. The amount of light absorbed in these lakes by CDOM is related strongly to DOC concentrations (e.g., Cory et al. 2014; ARC LTER database), and because summer average DOC concentrations were correlated between lakes (ARC LTER database), a regional control on DOC inputs may explain the temporal patterns in light attenuation. The export of DOC from land to surface waters is dependent on water flow, and by extension, spring melting and precipitation events (Judd and Kling 2002), and thus it is not surprising that light attenuation would vary synchronously across nearby lakes. Factors that regulate DOC in arctic lakes on seasonal and interannual timescales no doubt play an important role on the annual benthic GPP. Our experiment was meant to mimic slight changes to nutrient loading that may result from warming climate. However, excess nutrients that stem from increased flushing of soils are likely to be accompanied by additional allochthonous DOC (Kling et al. 2014, Sobek et al. 2007, Prowse et al. 2006). Thus, stimulated phytoplankton biomass and greater DOC delivery can work in tandem to reduce the light available to benthic algae.

7.5.3 Benthic respiration and dissolved oxygen

Benthic respiration exceeded gross primary production in nearly all lakes, years, and sampling depths in our study. This is a common, but not universal (Ask et al. 2009), trait of lake benthos and contributes to the net heterotrophic nature of most lakes worldwide (Cole et al. 2000). In the arctic, benthic communities are important for oxygen consumption in lakes (Miller and Reed 1975, Lienesch et al. 2005, Jonsson et al. 2003), although the oligotrophic status of most arctic lakes usually prevents development of hypoxia or anoxia.

Dissolved oxygen depletion is a well-established sign and symptom of nutrient enrichment (Wetzel 2001 and references therein). In two enrichment experiments using high nutrient levels in lakes near Toolik Lake, anoxia was induced after just three years of fertilization (Lake N2; O'Brien et al. 2005) and two years of fertilization (Lake N1; Lienesch et al. 2005). In the second experiment, anoxia near the sediment-water interface lead to reduced survivorship of fish eggs and reduced recruitment of lake trout during the fertilization period (Lienesch et al. 2005). The AHOD of Lake E5 is comparable to other oligo- to mesotrophic lakes (e.g., Wetzel 2001) but less severe than the oxygen depletion from other nearby arctic experimental lakes (O'Brien et al. 2005). The difference in severity probably stems from the lower-level of nutrient addition employed in our study.

The strong oxygen depletion observed in Lake E5 was not observed in the reference lake and was accompanied by a decline in benthic NEP over time due to the steady increase in benthic respiration. It is extremely difficult to separate benthic respiration into autotrophic and heterotrophic components. Because autotrophic respiration is proportional to GPP, and GPP did not increase, we assume that

heterotrophic activity must be the cause of the increased respiration. It is probable that this increase in respiration in the deep fertilized lake, E5, was due to greater flux of phytoplankton to the sediments. In E5, pelagic NPP rates increased six-fold between the pre- and post-fertilization periods (pre-fertilization NPP $18 \pm 10 \text{ mg C m}^{-2} \text{ d}^{-1}$ versus post-fertilization average of $108 \pm 30 \text{ mg C m}^{-2} \text{ d}^{-1}$ for 2001-2009; M. Evans, G. Kling unpubl. data). This equates to an extra $\sim 90 \text{ mg C m}^{-2} \text{ d}^{-1}$, compared to an increase in benthic respiration of $80 \text{ mg C m}^{-2} \text{ d}^{-1}$. While some fraction of the extra pelagic production is respired in the water column, the similarity in these values suggests that increased phytoplankton deposition can account for the majority of the increase in benthic respiration in E5.

There is less potential for significant oxygen depletion in the bottom of Lake E6 compared to Lake E5 because bottom waters are more frequently equilibrated with the atmosphere through wind-driven mixing of the water column. The benthic data from Lake E6 hint at increases in both benthic GPP and respiration (Figure 7.5), resulting in little change in benthic NEP. In Lake E5 settling phytoplankton likely contributed to decreasing benthic NEP during the experiment. This effect was smaller in shallow Lake E6 where pelagic NPP only increased by $\sim 41 \text{ mg C m}^{-2} \text{ d}^{-1}$ (pre-fertilization NPP $38 \pm 24 \text{ mg C m}^{-2} \text{ d}^{-1}$ in 2000, versus post-fertilization average of $79 \pm 29 \text{ mg C m}^{-2} \text{ d}^{-1}$ for 2001-2009; M. Evans, G. Kling unpubl. data) and pelagic chlorophyll a was unchanged. This difference may result from the different area-based fertilization rates among the experimental lakes (E5 received higher N and P loading on an area-basis than E6, even though volumetric loading was the same), which could have produced a higher depth-

integrated phytoplankton response. Because pelagic chlorophyll a did not increase on a volumetric-basis in Lake E6, however, this explanation is less likely.

7.5.4 Thermokarst failure

The frequency of thermokarst failures is thought to be increasing in the Arctic (Rowland 2010). When active layer detachments or retrogressive thaw slumps occur adjacent to lakes, they have the potential to radically alter lake ecosystem processes. The lifespan of these disturbance events is generally on the order of 1-5 years of active release of nutrients and sediment into surface waters (Bowden et al. 2008), and the impact can vary in severity.

In terms of benthic processes, it is thought that clastic sediment released from thermokarst failures initially has a smothering effect on benthic algae, effectively burying the benthic community and suppressing photosynthesis (C. Johnson unpubl. data). Additionally, during the period of active sediment delivery from these features, water clarity is likely to be reduced because of greater suspended solids. This was observed in Lake Fog 4 as an increase in light attenuation coefficients from 2002-2005 that lowered light available at the sediments by 53% at 2 m depth, and lowered GPP by $120 \text{ mg C m}^{-2} \text{ d}^{-1}$, or ~55%. This decrease is considerably greater than the decrease driven by our low-level fertilization in Lake E5. Mesquita et al. (2010) reported that suspended clay particles delivered during a thermokarst failure are effective at adsorbing and removing CDOM from lakes, resulting in a clarifying effect upon settling, which would benefit the benthic algae. In Lake Fog 4 light attenuation recovered to, but not below, pre-thermokarst values, which we suggest is due to a combination of low initial DOC concentration (less potential for a clarifying effect) and active resuspension of sediments.

As such, one must consider initial lake properties when predicting shoreline disturbance impacts on lake light attenuation and benthic productivity response.

Benthic changes in the thermokarst-impacted Fog 4 differed from the experimental N and P manipulation lakes. GPP and respiration both decreased, while benthic chlorophyll increased to the highest values observed in any lake. The decrease in respiration is consistent with the smothering effect by clastic deposition. While we did not do textural analysis of the thermokarst-sourced material, we postulate that dilution of organic matter by clay and silt, and capping of the active surface sediments, would have lowered the rates of both autotrophic and heterotrophic respiration. It is difficult to ascertain whether this conclusion is consistent with the large increase in chlorophyll a concentration. An explanation for such high chlorophyll a concentrations could be that as sediment rapidly accumulated during the summers of thermokarst activity, the surface layer was constantly colonized by algae, resulting in a relatively deep layer of active chlorophyll-containing sediments. This scenario would explain why Lake Fog 4 sediments fall below the regression line in Figure 7.6 – only the surface-most sediment contribute to the observed $P_{\max}$ and quantum efficiency observed in the core incubations, because light is typically absent below millimeters of the sediment surface (Stanley 1976, MacIntyre and Cullen 1995); therefore, despite high chlorophyll a concentrations over 2 cm, the photosynthesis parameters were not especially high.

7.8 Conclusion

Our results indicate that rates of benthic GPP of our study lakes did not respond to low-level nutrient addition, despite the extremely oligotrophic nature of the lakes. Instead, light seems to limit benthic algae productivity, even for sediments in the shallow

littoral zone. Changes in light attenuation caused by variations in DOC appear correlated between lakes and can possibly be linked to meteorological controls. Changes in light attenuation due to fertilization were different in the two experimental lakes, with an effect on water column properties only evident in the deep, stratified lake. Likewise, benthic respiration was impacted by the addition of nutrients only in the deep, stratified lake. Lake morphology may therefore play an important role in the fate of nutrients and subsequent impact on benthic processes. If our low-level fertilization regime realistically simulates future changes in nutrient loading to deep arctic lakes, then hypoxia driven by benthic respiration could become a more common feature of those lakes. The importance of light is also illustrated by our observations in a shallow lake that experienced a shoreline thermokarst failure. In this case, elevated nutrients and sediment inputs and deposition worked in tandem to increase water-column light attenuation and substantially decrease benthic GPP during the period of active sediment delivery.

7.9 Acknowledgments

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7.10 References

Arctic LTER database. <http://ecosystems.mbl.edu/ARC/datacatalog.html>

Ask, J., J. Karlsson, L. Persson, P. Ask, P. Byström, and M. Jansson. 2009. Whole-lake estimates of carbon flux through algae and bacteria in benthic and pelagic habitats of clear-water lakes. *Ecology* 90: 1923-1932.

Bender, M., K. Grande, K. Johnson, and others. 1987. A comparison of four methods for determining planktonic community production. *Limnol. Oceanogr.* 32: 1085-1098.

Bergmann, M. A., and H.E. Welch. 1990. Nitrogen fixation by epilithic periphyton in small arctic lakes in response to experimental nitrogen and phosphorus fertilization. *Can. J. Fish. Aquat. Sci.* 47: 1545-1550.

Bettez, N. D., P. A. Rublee, J. O'Brien, and M. C. Miller. 2002. Changes in abundance, composition and controls within the plankton of a fertilised arctic lake. *Freshwater Biol.* 47: 303-311.

Björk-Ramberg, S. 1983. Production of epipelagic algae before and during lake fertilization in a subarctic lake. *Holarctic Ecol.* 6: 349-355.

Björk-Ramberg, S., and C. Ånell. 1985. Production and chlorophyll concentration of epipelagic and epilithic algae in fertilized and nonfertilized subarctic lakes. *Hydrobiologia* 126: 213-219.

Bonilla, S., V. Villeneuve, and W. F. Vincent. 2005. Benthic and planktonic algal communities in a high Arctic lake: Pigment structure and contrasting responses to nutrient enrichment. *J. Phycol.* 41: 1120-1130.

Bowden, W. B., M. N. Gooseff, A. Balser, A. Green, B. J. Peterson, and J. Bradford. 2008. Sediment and nutrient delivery from thermokarst features in the foothills of the North Slope, Alaska: Potential impacts on headwater stream ecosystems. *J. Geophys. Res.* 113: G02026

Bowden, W. B., B. J. Peterson, L. A. Deegan, and others. 2014. Ecology of Streams of the Toolik Region. Pg. 173-237. In J. E. Hobbie and G. W. Kling (editors), *Alaska's Changing Arctic: Ecological Consequences for Tundra, Streams, and Lakes*. Oxford University Press.

Cherry, J. E., S. J. Déry, M. Stieglitz, F. Pan. 2014. Meteorology and climate of Toolik Lake and the North Slope of Alaska: Past, present and future, p. 143-172. In J. E. Hobbie and G. W. Kling (eds.), *Alaska's changing Arctic: Ecological consequences for tundra, streams, and lakes*. Oxford University Press.

Cole, J. J., M. L. Pace, S. R. Carpenter, and J. F. Kitchell. 2000. Persistence of net

- heterotrophy in lakes during nutrient addition and food web manipulations. *Limnol. Oceanogr.* 45: 1718-1730.
- Cornwell, J., and G. Kipphut. 1992. Biogeochemistry of manganese- and iron-rich sediments in Toolik Lake, Alaska. *Hydrobiologia* 240: 45-59.
- Cory, R. M., C. P. Ward, B. C. Crump, and G. W. Kling. 2014. Sunlight controls water column processing of carbon in arctic fresh waters. *Science* 345:925-928.
- Elser, J. J., T. Anderson, J. S. Baron, and others. 2009. Shifts in lake N:P stoichiometry and nutrient limitation driven by atmospheric nitrogen deposition. *Science* 326: 835-837.
- Fee, E. J. 1979. A relation between lake morphometry and primary productivity and its use in interpreting whole-lake eutrophication experiments. *Limnol. Oceanogr.* 24: 401-416.
- Gettel, G. M., A. E. Giblin, and R. W. Howarth. 2013. Controls of benthic nitrogen fixation and primary production from nutrient enrichment of oligotrophic, Arctic lakes. *Ecosystems* 16: 1550-1564.
- Genkai-Kato, M., Y. Vadeboncoeur, L. Liboriussen, and E. Jeppesen. 2012. Benthic-planktonic coupling, regime shifts, and whole-lake primary production in shallow lakes. *Ecology* 93: 619-631.
- Hansson, L.-A. 1992. Factors regulating periphytic algal biomass. *Limnol. Oceanogr.* 37: 322-328.
- Hecky, R., and R. Hesslein. 1995. Contributions of benthic algae to lake food webs as revealed by stable isotope analysis. *J. N. Am. Benthol. Soc.* 14: 631-653.
- Hershey, A. E. 1992. Effects of experimental fertilization on the benthic macroinvertebrate community of an arctic lake. *J. N. Am. Benthol. Soc.* 11: 204-217.
- Hobbs, W. O., R. J. Telford, H. J. B. Birks, J. E. Saros, R. R. O. Hazewinkel, B. B. Perren, É. Saulnier-Talbot, and A. P. Wolfe. 2010. Quantifying recent ecological changes in remote lakes of North America and Greenland using sediment diatom assemblages. *PLoS ONE* 5: e10026.
- Hobbie, J. E., B. J. Peterson, N. Bettez, and others. 1999. Impact of global change on the biogeochemistry and ecology of an Arctic freshwater system: *Polar Res.* 18: 207-214.
- Hobson, K. A., and H. E. Welch. 1995. Cannibalism and trophic structure in a high Arctic lake: insights from stable-isotope analysis. *Can. J. Fish. Aquat. Sci.* 52: 1195-1201.
- Howarth, R. W. 1988. Nutrient limitation of net primary production in marine ecosystems. *Annu. Rev. Ecol. Syst.* 19: 89-110.

- Jonsson, A., J. Karlsson, and M. Jansson. 2003. Sources of carbon dioxide supersaturation in clearwater and humic lakes in northern Sweden. *Ecosystems* 6: 224-235.
- Judd, K. E., and G. W. Kling. 2002. Production and export of dissolved C in arctic tundra mesocosms: the roles of vegetation and water flow. *Biogeochemistry* 60: 213-234.
- Karlsson, J., P. Byström, J. Ask, P. Ask, L. Persson, and M. Jansson. 2009. Light limitation of nutrient-poor lake ecosystems. *Nature* 460: 506-509.
- Keller, K., J. D. Blum, and G. W. Kling. 2010. Stream geochemistry as an indicator of increasing permafrost thaw depth in an arctic watershed. *Chem. Geol.* 273: 76-81.
- Kling, G. W., H. E. Adams, N. D. Bettez, and others. 2014. Land-water interactions, p. 143-172. *In* J. E. Hobbie and G. W. Kling (eds.), *Alaska's changing Arctic: Ecological consequences for tundra, streams, and lakes*. Oxford University Press.
- Jäger, C. G. and S. Diehl. 2014. Resource competition across habitat boundaries: asymmetric interactions between benthic and pelagic producers. *Ecol. Monogr.* 84: 287-302.
- Judd, K. E., and G. W. Kling. 2002. Production and export of dissolved C in arctic tundra mesocosms: the roles of vegetation and water flow. *Biogeochemistry* 60: 213-234.
- Liboriussen, L., and E. Jeppesen. 2003. Temporal dynamics in epipelagic, pelagic and epiphytic algal production in a clear and a turbid shallow lake. *Freshwater Biol.* 48: 418-431.
- Lienesch, P. W., M. E. McDonald., A. E. Hershey, W. J. O'Brien, and N. D. Bettez, 2005. Effects of a whole-lake, experimental fertilization on lake trout in a small oligotrophic arctic lake. *Hydrobiologia* 548: 51-66.
- Lorenzen, C. J. 1967. Determination of chlorophyll and phaeo-pigments: Spectrophotometric equations. *Limnol. Oceanogr.* 12: 343-346.
- Luecke, C., A. E. Giblin, N. D. Bettez, and others. 2014. The response of lakes near the Arctic LTER to environmental change, p. 238-286. *In* J. E. Hobbie and G. W. Kling (eds.), *Alaska's changing Arctic: Ecological consequences for tundra, streams, and lakes*. Oxford University Press.
- MacIntyre, H. L. and J. J. Cullen. 1995. Fine-scale vertical resolution of chlorophyll and photosynthetic parameters in shallow-water benthos. *Mar. Ecol.: Prog. Ser.* 122: 227-237.
- MacIntyre, S., J. P. Fram, P. J. Kushner, N. D. Bettez, W. J. O'Brien, J. Hobbie, and G. W. Kling. 2009. Climate-related variations in mixing dynamics in an Alaskan arctic lake. *Limnol. Oceanogr.* 54: 2401-2417.
- Mesquita, P. S., F. J. Wrona, and T. D. Prowse. 2010. Effects of retrogressive permafrost

- thaw slumping on sediment chemistry and submerged macrophytes in Arctic tundra lakes. *Freshwater Biol.* 55: 2347-2358.
- Miller, M. and J. Reed. 1975. Benthic metabolism of arctic coastal ponds, Barrow, Alaska. *Verh. Intern. Verein. Limnol.* 19: 459-465.
- Morris, D. P., and W. M. Lewis, W. M. 1988. Phytoplankton nutrient limitation in Colorado mountain lakes. *Freshwater Biol.* 20: 315-327.
- Nolen, S. L., J. Wilhm, and G. Howick. 1985. Factors influencing inorganic turbidity in a great plains reservoir. *Hydrobiologia* 123: 109-117.
- O'Brien, W. J., M. Barfield, N. Bettez, A. E. Hershey, J. E. Hobbie, G. W. Kipphut, G. W. Kling, and M. C. Miller, 2005, Long-term response and recovery to nutrient addition of a partitioned arctic lake. *Freshwater Biol.* 50: 731-741.
- Prowse, T. D., F. J. Wrona, J. D. Reist, J. J. Gibson, J. E. Hobbie, L. M. J. Lévesque, and W. F. Vincent. 2006. Climate change effects on hydroecology of Arctic freshwater ecosystems. *AMBIO: A Journal of the Human Environment* 35: 347-358.
- Quesada, A., E. Fernandez-Valiente, I. Hawes, C. Howard-Williams, and W. F. Vincent. 2008. Benthic primary production in polar lakes and rivers. Oxford University Press, Oxford.
- Rautio, M., F. Dufresne, I. Laurion, S. Bonilla, W. F. Vincent, and K. S. Christoffersen. 2011. Shallow freshwater ecosystems of the circumpolar Arctic. *Ecoscience* 18: 204-222.
- Rowland, J., C. Jones, G. Altmann, and others, 2010. Arctic landscapes in transition: responses to thawing permafrost. *Trans., Am. Geophys. Union* 91: 229-230.
- Schindler, D. 1978. Factors regulating phytoplankton production and standing crop in the world's freshwaters. *Limnol. Oceanogr.* 23: 478-486.
- Sierszen, M. E., M. E. McDonald, and D. A. Jensen. 2003. Benthos as the basis for arctic lake food webs. *Aquat. Ecol.* 37: 437-445.
- Sobek, S., L. J. Tranvik, Y. T. Prairie, P. Kortelainen, and J. J. Cole. 2007. Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. *Limnol. Oceanogr.* 52: 1208-1219.
- Stanley, D. W. 1976. Productivity of epipelagic algae in tundra ponds and a lake near Barrow, Alaska. *Ecology* 57: 1015-1024.
- Tranvik, L. J. and others. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. *Limnol. Oceanogr.* 54: 2298-2314.
- Vadeboncoeur, Y., E. Jeppesen, M. J. Vander Zanden, H.-H. Schierup, K. Christoffersen, and D. M. Lodge. 2003. From Greenland to green lakes: cultural eutrophication and the

loss of benthic pathways in lakes. *Limnol. Oceanogr.* 48: 1408-1418.

Vadeboncoeur, Y., D. M. Lodge, and S. R. Carpenter. 2001. Whole-lake fertilization effects on distribution of primary production between benthic and pelagic habitats. *Ecology* 82: 1065-1077.

Vadeboncoeur, Y., and A. D. Steinman. 2002. Periphyton function in lake ecosystems. *Sci. World J.* 2: 1449-1468.

Vadeboncoeur, Y., G. Peterson, M. J. Vander Zanden, and J. Kalff. 2008. Benthic algal production across lake size gradients: interactions among morphometry, nutrients, and light. *Ecology* 89: 2542-2552.

Vähätalo, A. V., M. Salkinoja-Salonen, P. Taalas, and K. Salonen. 2000. Spectrum of the quantum yield for photochemical mineralization of dissolved organic carbon in a humic lake. *Limnol. Oceanogr.* 45: 664-676.

Vander Zanden, M. J., and Y. Vadeboncoeur. 2002. Fishes as integrators of benthic and pelagic food webs in lakes. *Ecology* 83: 2152-2161.

Welch, H., and J. Kalff. 1974. Benthic photosynthesis and respiration in Char Lake. *J. Fish. Res. Board Can.* 31: 609-620.

Wetzel, R. G. 1990. Land-water interfaces: metabolic and limnological regulators. *Verh. Intern. Verein. Limnol.* 25: 6-24.

Wetzel, R. G. 2001. *Limnology: lake and river ecosystems*. Academic press.

Whalen, S. and J. Cornwell. 1985. Nitrogen, phosphorus, and organic carbon cycling in an arctic lake. *Can. J. Fish. Aquat. Sci.* 42: 797-808.

Whalen, S. C., B. A. Chalfant, and E. N. Fischer. 2008. Epipelagic and pelagic primary production in Alaskan Arctic lakes of varying depth. *Hydrobiologia* 614: 243-257.

7.11 Figures and Tables

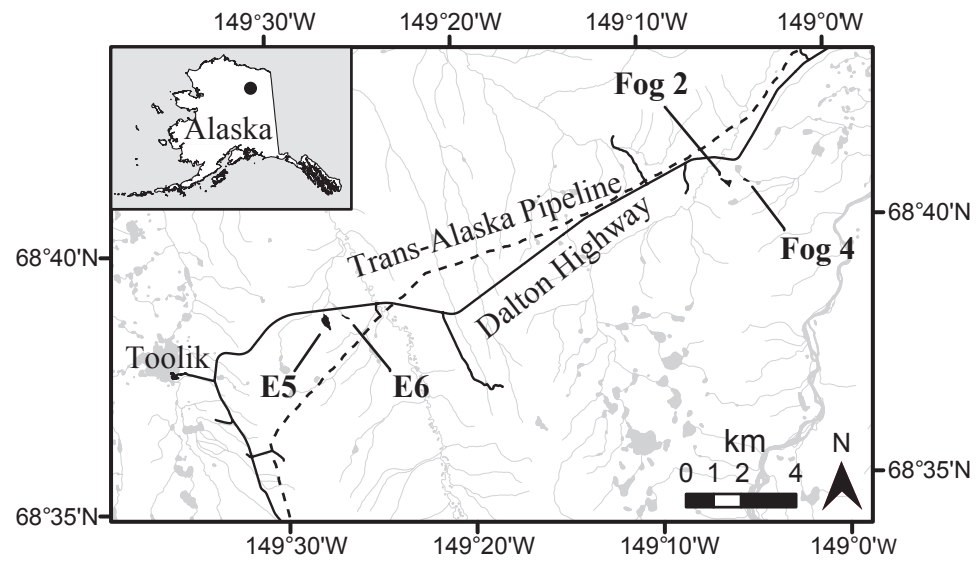


Figure 7.1 Map of the study region showing locations of the fertilized lakes (E5, E6) and reference lakes (Fog 2, Fog 4) and the proximity to Toolik Lake Field Station.

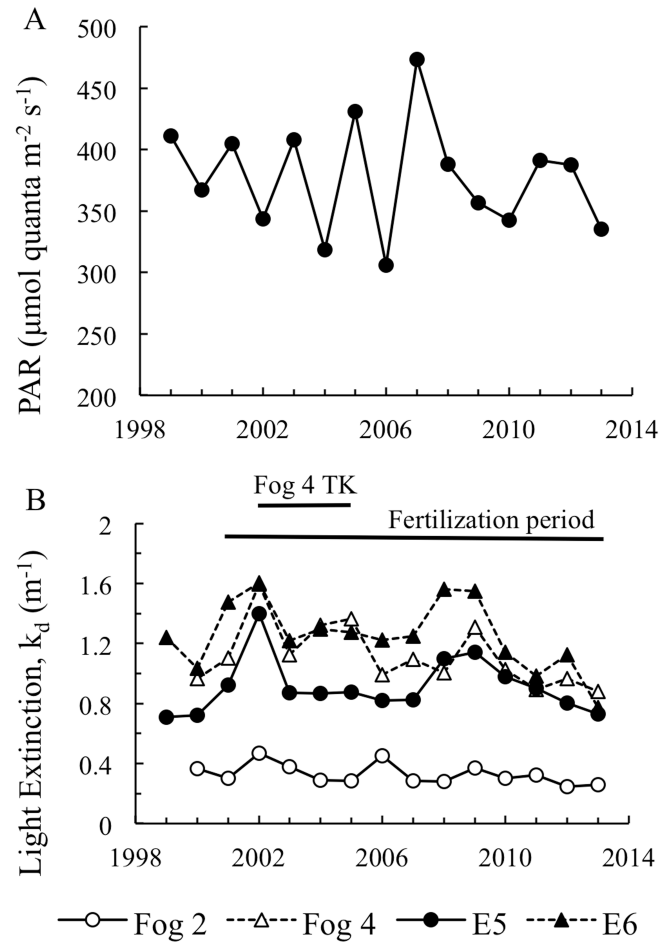


Figure 7.2 A) Average incoming PAR, measured at Toolik Field Station, from June 15 to August 31 during each year of the experiment. B) Time series of light extinction coefficients. Points are summer averages for each year. Standard deviation within years ranged from 0.02 to 0.5. Horizontal bars denote periods of fertilization and the thermokarst failure (TK) in Lake Fog 4.

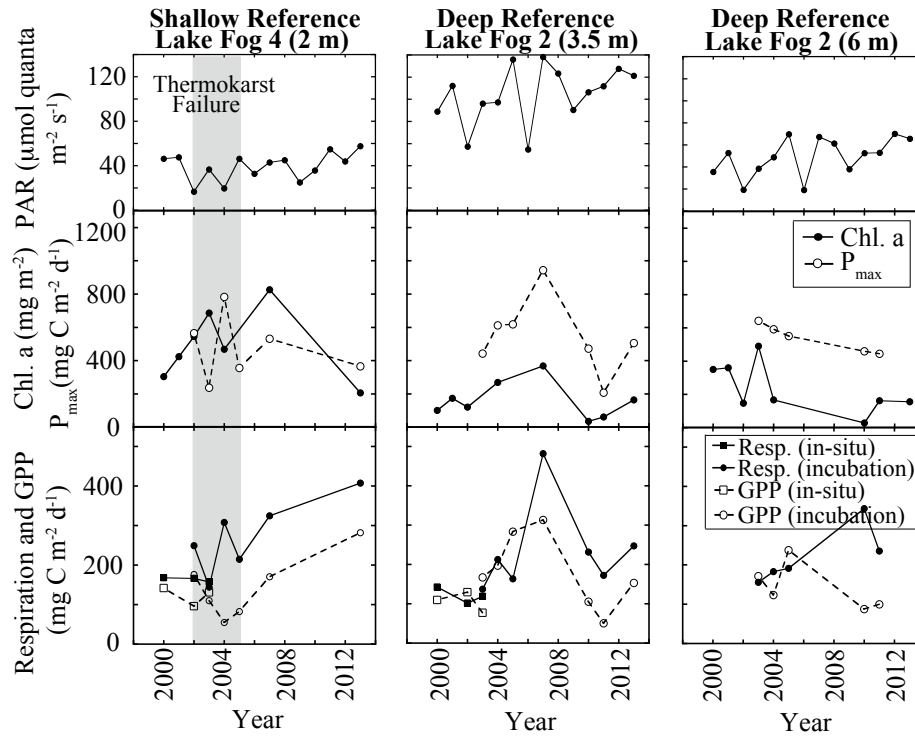


Figure 7.3 Benthic data from the shallow reference Lake Fog 4 and the two sampling sites in the deep, reference lake, Fog 2. Top panel: Average PAR from June 15-August 31 at the sampling depth (2 m for Fog 4, 3.5 and 6 m for Fog 2). Middle panel: Benthic chlorophyll a and modeled P_{max} from core incubations. Bottom panel: Benthic respiration and GPP. Vertical gray bar in Lake Fog 4 panels represents years with an observed sediment plume.

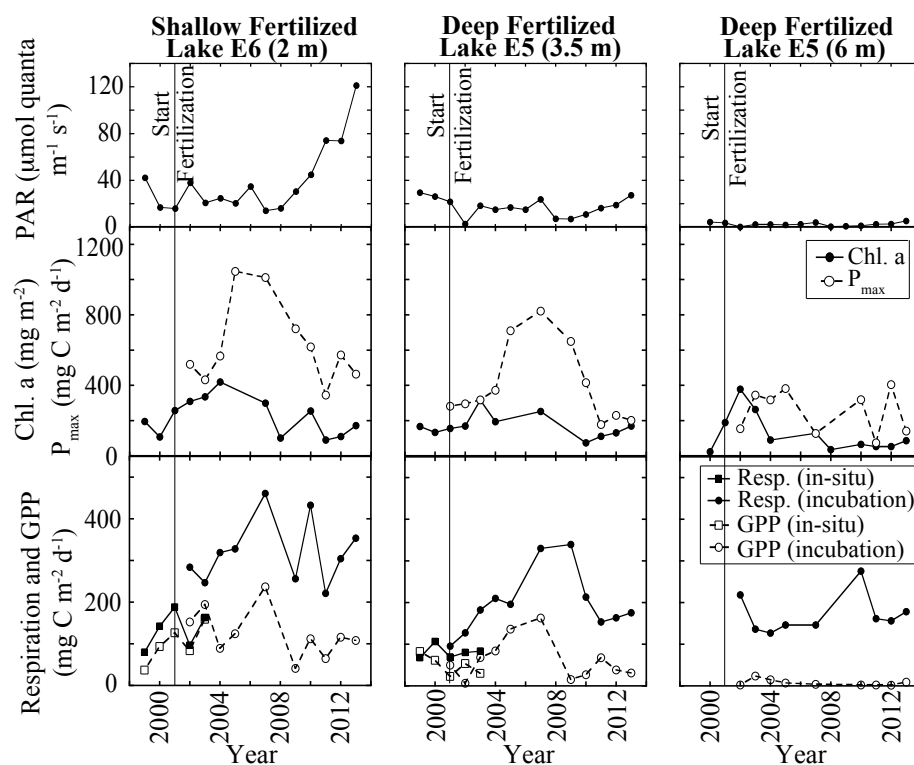


Figure 7.4 Same as in Figure 7.3, but for the fertilized E lakes. Measurements in the shallow lake, E6, were taken at 2 m depth and in the deep lake, E5, at 3.5 and 6 m depth. The vertical bar in 2001 represents the first year of fertilization.

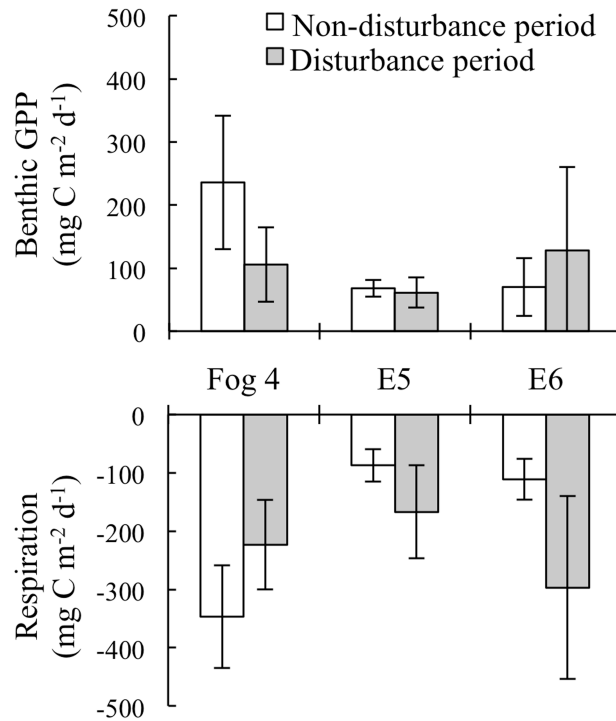


Figure 7.5 Summary of disturbance impacts on benthic GPP and respiration. This combines *in-situ* chamber measurements and core-incubation modeled GPP so does not account for the change in methodology. For thermokarst-impacted Lake Fog 4, disturbance years are 2002-2005, for the deep and shallow fertilized lakes (E5 and E6, respectively), disturbance years refers to the fertilization period 2001-2013. Only thermokarst-impacted Lake Fog 4 showed a statistically significant difference in benthic GPP ($p < 0.001$).

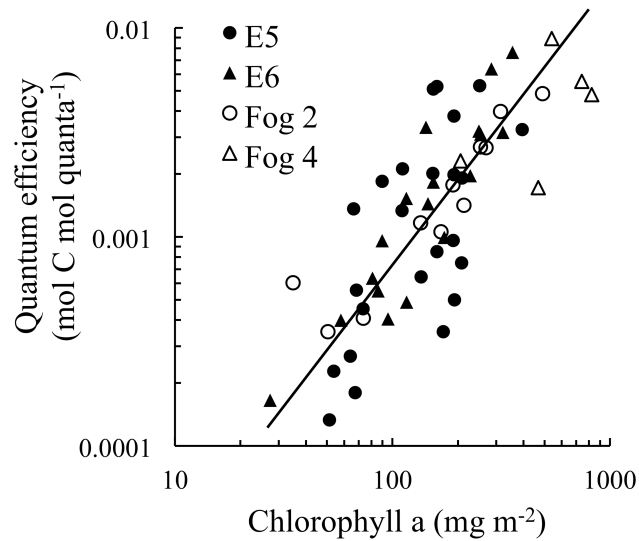


Figure 7.6 Quantum efficiency determined from laboratory core incubations plotted against areal benthic chlorophyll a concentration. Points represent each sampling date and depth. The line is the type II least squares regression fit for all lakes combined. The equation is $\log_{10}QE = 1.45 \times \log_{10}Chl - 6.04$, where QE is quantum efficiency (mol C mol photons⁻¹), Chl is chlorophyll a (mg m⁻²), and the standard deviations for the slope and y-intercept are 0.12 and 0.27, respectively. Lake treatments are: Fog 2 – deep, reference; Fog 4 – shallow, reference; E5 – deep, fertilized; E6 – shallow, fertilized.

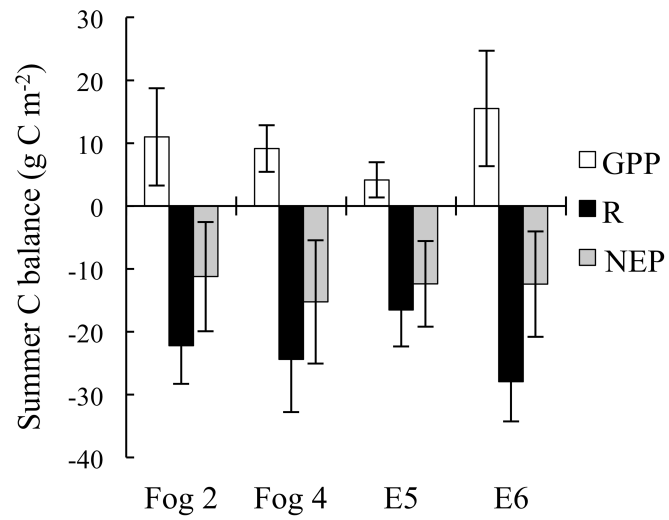


Figure 7.7 GPP, R, and NEP (g C m⁻² summer⁻¹) calculated at the whole-lake scale and summed from June 15 to August 31. Lake treatments are: Fog 2 – deep, reference; Fog 4 – shallow, reference; E5 – deep, fertilized; E6 – shallow, fertilized.

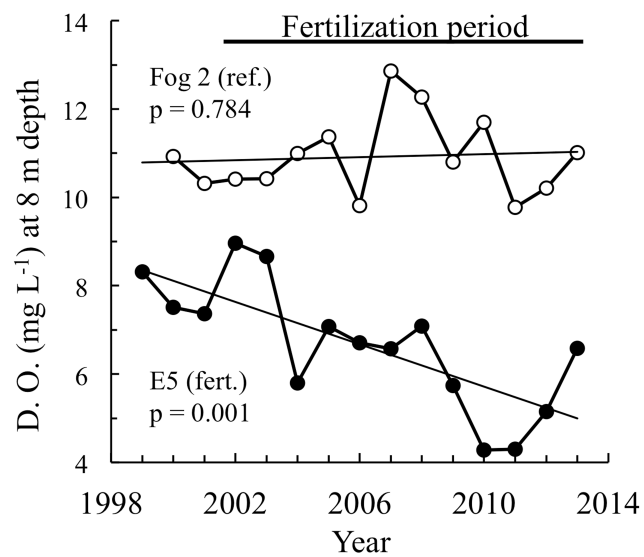


Figure 7.8 Summer (JJA) average dissolved oxygen concentrations measured at 8 m depth in the two deep stratified lakes. Horizontal bar as in previous figures.

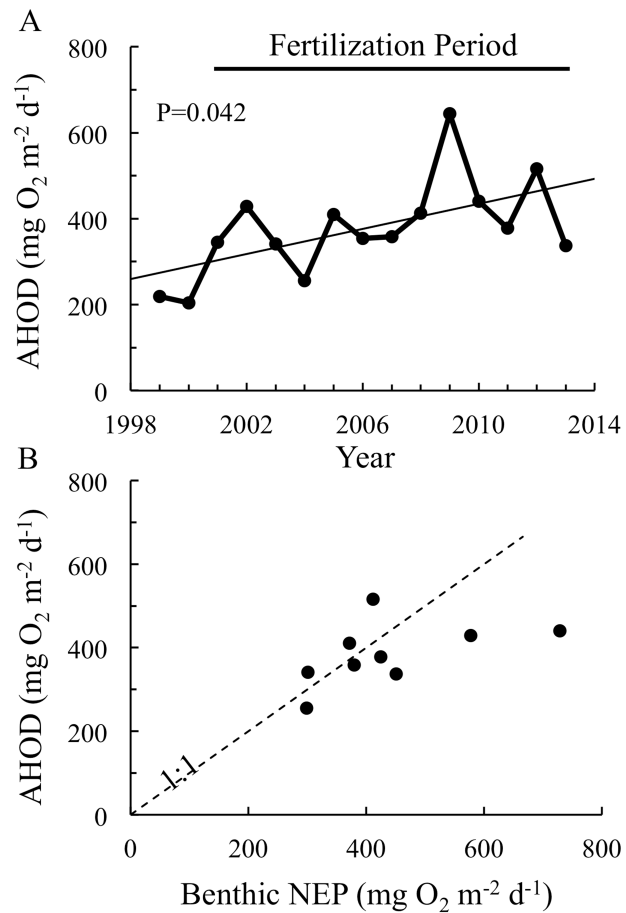


Figure 7.9 A) Summertime areal hypolimnetic oxygen deficit in Lake E5, with the fertilization period represented by the horizontal bar. B) Lake E5 AHOD versus benthic net ecosystem production determined from our hypolimnion sampling stations.

	Fog 2 (reference)	Fog 4 (reference)	E5 (fertilized)	E6 (fertilized)
Surface area (ha)	5.6	1.9	11.3	2.0
Maximum depth (m)	20.3	5.4	12.7	3.2
Mean depth (m)	8.3	2.3	5.2	2.0
A_e/V_e	0.07	0.44	0.1	0.63
Secchi depth (m)	6.8	2.0	3.5	2.3
Sp. conductivity ($\mu\text{S cm}^{-1}$)	143	85	13	12
DOC (mg L^{-1})	4.1	4.8	6.0	6.6
Epilimnion PP (mg m^{-3})	5	13	7	12
Epilimnion chl. a (mg m^{-3})	1.8	8.1	5.0	6.1
Fish	Present	Absent	Present	Absent

Table 7.1 Physical and chemical properties of the study lakes. Values are from pre-fertilization monitoring in 1999 and 2000 (ARC LTER Lakes database). Epilimnion values are averages from 0-3 m water depth. PP = particulate phosphorus.

Study	Lake	P ambient	P added	N Ambient	N added
This study	E5		8		56
	E6		8		56
Bettez et al. 2002	N1		44 - 65		250 - 368
O'Brien et al. 2005	N2		75 - 91		426 - 535
Vadeboncoeur et al. 2001	Peter	105	41-122		
	West Long	105	42-150		
	East Long	105	92-134		
Bjork-Ramberg and Anell 1985	Hymenjaure		75-258		3216
Bergmann and Welch 1990	Spring	88	0	175	0
	Far	108	25	145	0
	P&N	82	25	115	290

Table 7.2 Background and fertilized rates of annual P and N loading ($\text{mg m}^{-3} \text{y}^{-1}$) to the lake surface mixed layer (equivalent to the whole lake for shallow systems). Values from other whole-lake manipulations are either as reported or converted to a volumetric basis (m^{-3}) from an areal basis (m^{-2}) by dividing by the mean depth of the lake or mixed layer where appropriate and scaled to the annual addition rates.

	Benthic chlorophyll (mg m ⁻²)		Benthic GPP (mg C m ⁻² d ⁻¹)		Benthic R (mg C m ⁻² d ⁻¹)		Benthic NEP (mg C m ⁻² d ⁻¹)	
	Pre-fert	Post-fert	Pre-fert	Post-fert	Pre-fert	Post-fert	Pre-fert	Post-fert
Fog 2								
3.5m	100 (48)	150 (23)	110	175 (142)	-142	-220 (105)	-32	-45 (176)
6 m	351 (54)	303 (29)		197 (148)		-256 (206)		-59 (253)
E5								
3.5 m	139 (7)	179 (13)	68 (13)	61 (24)	-87 (28)	-167 (80)	-19 (35)	-106 (83)
6 m	66 (26)	121 (12)		8 (57)		-185 (94)		-177 (110)
E6								
2 m	126 (13)	210 (12)	62 (40)	128 (132)	-111 (35)	-297 (157)	-49 (21)	-169 (205)
	NTK	TK	NTK	TK	NTK	TK	NTK	TK
Fog 4								
2 m	372 (44)	573 (23)	235 (106)	105 (59)	-347 (88)	-223 (77)	-112 (138)	-118 (97)

Table 7.3 Pre-disturbance and post-disturbance estimates of the epipelagic community characteristics (average (SE) for chlorophyll; average (SD) for GPP and R; NEP calculated as sum of GPP and R with a combined SD). Pre-fertilization values are from chamber measurements while post-fertilization values are from a combination of chamber and core measurements. For lake Fog 4, TK and NTK refer to the periods with an observed thermokarst-related sediment plume, and periods with no sediment plume, respectively.

7.12 Supplementary Figures and Table

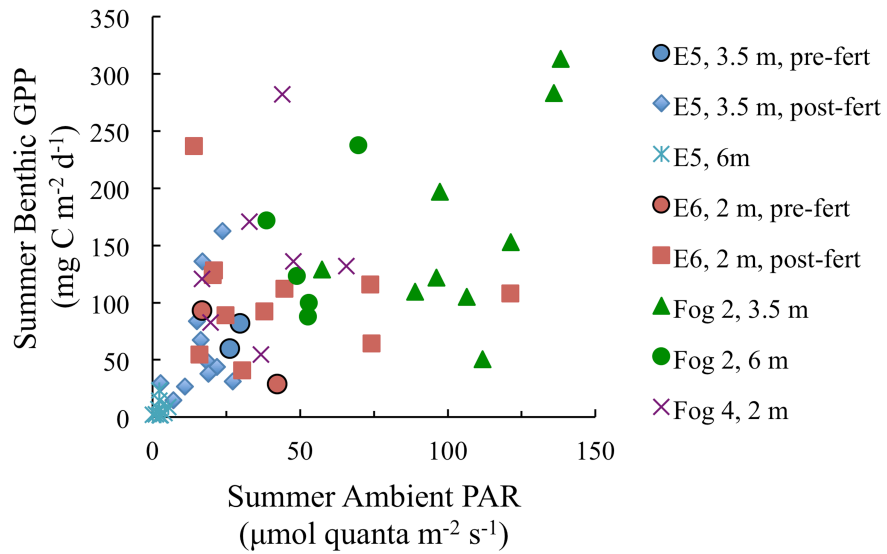


Figure 7.S1 Average summer benthic GPP vs. ambient PAR incident at the sediment surface from June 15 to Aug. 31. Each point represents one year of data for each lake and depth. For the experimental lakes, E5 (deep lake) and E6 (shallow lake), pre-fertilization points are outlined in black. Across all lakes, depths, and years, $r^2=0.37$.

Tables 7.1A, 7.1B, 7.1C: Model parameters with standard errors for estimating benthic GPP. $P_{\max}$ and $K_{1/2}$ are Michaelis-Menten parameters estimated from all benthic flux measurements for each sampling effort. These values were used, in combination with measured light intensity in the field, to estimate summer GPP of lake benthos. Quantum efficiency was determined as the slope of the P-I curves at low light intensities

Table 7.1A. $P_{\max}$ ($\text{mg C m}^{-2} \text{ d}^{-1}$)

	Fog2 3.5 m	Fog2 6 m	E5 3.5 m	E5 6 m	E6 2 m	Fog4 2 m
2001			281 ± 68			
2002			295 ± 150	154 ± 32	519 ± 37	564 ± 45
June, 2003			317 ± 22	468 ± 25	624 ± 113	
July, 2003	442 ± 39	642 ± 41				236 ± 53
2004	612 ± 302	592 ± 183	372 ± 85	317 ± 43	565 ± 81	783 ± 158
2005	618 ± 34	551 ± 34	709 ± 162	382 ± 204	1046 ± 199	356 ± 36
2007	944 ± 538	1915 ± 460	822 ± 192	126 ± 37	1012 ± 705	531 ± 353
2009			650 ± 173		721 ± 579	
June, 2010	492 ± 312	389 ± 76	577 ± 137	463 ± 120	688 ± 92	
July, 2010	415 ± 216	668 ± 290	366 ± 96	235 ± 54	492 ± 74	
Aug, 2010			168 ± 88	293 ± 149	707 ± 101	
June, 2011	208 ± 97	390 ± 143	48 ± 14	88 ± 37	164 ± 77	
July, 2011	205 ± 48	499 ± 145	278 ± 40		462 ± 128	
Aug, 2011			226 ± 26	92 ± 7	356 ± 77	
June, 2012			322 ± 128		353 ± 168	
July, 2012			234 ± 34		780 ± 271	
June, 2013			227 ± 42	144 ± 62	437 ± 131	
July, 2013			173 ± 115	133 ± 29	408 ± 167	
Aug, 2013	505 ± 203					365 ± 23
Average	493	706	367	237	575	473

Table 7.1B $K_{1/2}$ ($\mu\text{mol quanta m}^{-2} \text{s}^{-1}$)

Year	Fog2 3.5 m	Fog2 6 m	E5 3.5 m	E5 6 m	E6 2 m	Fog4 2 m
2001			71 ± 54			
2002			152 ± 146	16 ± 17	19 ± 7	20 ± 8
June, 2003			47 ± 12	42 ± 9	123 ± 54	
July, 2003	79 ± 20	67 ± 13				9 ± 13
2004	104 ± 120	133 ± 102	36 ± 40	60 ± 39	96 ± 44	292 ± 117
2005	64 ± 11	41 ± 10	64 ± 46	221 ± 210	164 ± 64	98 ± 27
2007	59 ± 81	164 ± 60	75 ± 35	35 ± 33	77 ± 105	53 ± 69
2009			358 ± 164		397 ± 511	
June, 2010	337 ± 370	161 ± 77	325 ± 134	180 ± 102	134 ± 45	
July, 2010	332 ± 291	291 ± 223	112 ± 85	266 ± 108	110 ± 40	
Aug, 2010			81 ± 131	477 ± 384	103 ± 53	
June, 2011	233 ± 238	161 ± 148	17 ± 43	238 ± 218	276 ± 269	
July, 2011	242 ± 121	136 ± 107	67 ± 35		310 ± 189	
Aug, 2011			51 ± 25	80 ± 21	120 ± 74	
June, 2012			441 ± 289		331 ± 286	
July, 2012			61 ± 33		210 ± 161	
June, 2013			146 ± 67	52 ± 96	108 ± 98	
July, 2013			167 ± 261	100 ± 65	198 ± 176	
Aug, 2013	172 ± 160					76 ± 17
Average	180	144	134	147	174	91

Table 7.1C Quantum efficiency (mol C mol quanta⁻¹)

Year	Fog2 3.5m 3.5 m	Fog2 6m 6 m	E5 3.5m 3.5 m	E5 6m 6 m	E6 1.5m 2 m	Fog4 1.5m 2 m
2001			0.0019			
2002			0.0009	0.0045	0.0132	0.0135
June, 2003			0.0033	0.0054	0.0024	
July, 2003	0.0027	0.0046				0.0121
2004	0.0028	0.0021	0.0050	0.0025	0.0028	0.0013
2005	0.0047	0.0064	0.0053	0.0008	0.0031	0.0017
2007	0.0077	0.0056	0.0053	0.0017	0.0064	0.0048
2009			0.0009		0.0009	
June, 2010	0.0007	0.0012	0.0009	0.0012	0.0025	
July, 2010	0.0006	0.0011	0.0016	0.0004	0.0022	
Aug, 2010			0.0010	0.0003	0.0033	
June, 2011	0.0004	0.0012	0.0014	0.0002	0.0003	
July, 2011	0.0004	0.0018	0.0020	0.0000	0.0007	
Aug, 2011			0.0021	0.0006	0.0014	
June, 2012			0.0004	0.0002	0.0005	
July, 2012			0.0018	0.0001	0.0018	
June, 2013			0.0008	0.0013	0.0020	
July, 2013			0.0005	0.0006	0.0010	
Aug, 2013	0.0014					0.0023
Average	0.0024	.0030	.0021	.0013	.0028	.0059