Modeling Carbon Dynamics in the Twin Newberry Volcanic Lakes, Oregon

by

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# Table of Contents

Acknowledgements .................................................................................. 5  
Abstract ........................................................................................................ 6  

1. Introduction .......................................................................................... 8  
1.1 Purpose of Research ........................................................................ 8  
1.2 Limnological Processes ..................................................................... 8  
1.3 Volcanic Lakes .................................................................................. 14  
1.4 Carbon Dynamics in Volcanic Lakes .............................................. 16  

2. Geological and Hydrological Setting .................................................. 20  
2.1 Geologic Setting: Newberry Volcano ............................................. 20  
2.2 Hydrological Setting: Newberry Caldera ........................................ 22  
2.3 East Lake and Paulina Lake .............................................................. 24  
2.4 Previous Work .................................................................................. 28  

3. Methods .............................................................................................. 29  
3.1 Field Methods .................................................................................. 29  
3.1.1 Water Samples .......................................................................... 29  
3.1.2 CO₂ Evasion Flux Measurements .............................................. 30  
3.1.3 Draw-Down, Build-Up Flux Measurements ................................ 33  
3.1.4 Gas Samples: Chamber, Ambient, Hot Springs ......................... 35  
3.1.5 Sediment Cores .......................................................................... 35  
3.2 Sample Analysis ............................................................................... 37  
3.2.1 pH, Alkalinity, and DIC .............................................................. 37  
3.2.2 Cations and Anions .................................................................... 37  
3.2.3 Water Stable Isotopes .............................................................. 38  
3.2.4 DIC Stable Isotopes ................................................................. 38  
3.2.5 Methane Stable Isotopes .......................................................... 39  
3.2.6 Carbon and Nitrogen Analysis of Organic Matter ..................... 39  
3.3 Lab Experiments ............................................................................... 40  
3.3.1 Kiddie Pool .............................................................................. 40  
3.3.2 Lab Lake ................................................................................... 42  
3.4 Calculations ...................................................................................... 45  
3.4.1 Web-PHREEQ .......................................................................... 45  
3.4.2 Flux Rate .................................................................................. 47  
3.4.3 Sequential Gaussian Simulations .............................................. 48  

4. Results ............................................................................................... 48  
4.1 East Lake Water Chemistry ............................................................. 48  
4.1.1 Temperature ............................................................................ 48  
4.1.2 Alkalinity .................................................................................. 49  
4.1.3 pH ............................................................................................ 52  
4.1.4 Dissolved Oxygen .................................................................... 54  
4.1.5 Conductivity ............................................................................ 55
4.1.6 PCO₂ ................................................................. 56  
4.1.7 Major Cations .................................................. 58  
4.1.8 Major Anions ................................................... 63  
4.1.9 Phosphorus ..................................................... 65  
4.2 Stable Isotopes ...................................................... 66  
4.2.1 Water: δD and δ¹⁸O ............................................. 66  
4.2.2 DIC: δ¹³C .......................................................... 69  
4.3 CO₂ Gas ............................................................ 71  
4.3.1 Flux Data ......................................................... 71  
4.3.2 δ¹³C and δ¹⁸O chamber and ambient gas ............... 75  
4.4 Biota ................................................................. 78  
4.4.1 δ¹³C and δ¹⁵N, C:N Pine Needles and Nostoc balls ... 78  
4.5 Kiddie Pool Experiment ........................................... 80  
4.5.1 Flux Data ......................................................... 80  
4.6 Lab Lake Experiment ............................................. 83  
4.6.1 Flux Data ......................................................... 84  
4.6.2 Gas and Water Isotopes ...................................... 85  
5. Discussion ........................................................... 86  
5.1 Water Chemistry .................................................. 86  
5.1.1 General ............................................................ 86  
5.1.2 Water Stable Isotopes ........................................ 90  
5.1.3 DIC ............................................................... 92  
5.2 Organic Matter ................................................... 100  
5.3 CO₂ Flux .......................................................... 107  
5.3.1 Field Flux ....................................................... 107  
5.3.2 SGS Analysis .................................................. 110  
5.3.3 Theoretical Flux ............................................... 117  
5.3.4 Boundary Layer Model ..................................... 122  
5.3.5 Lab Lake ......................................................... 127  
5.3.6 Steady-State Model ......................................... 129  
5.4 CO₂ Gas Isotopic Composition and Fractionation ...... 138  
5.4.1 East Lake δ¹³C and δ¹⁸O CO₂ gas ......................... 138  
5.4.2 Ambient CO₂ .................................................. 143  
5.4.3 Lab Lake ......................................................... 146  
5.4.3.1 δ¹³C CO₂ ...................................................... 148  
5.4.3.2 δ¹⁸O CO₂ ...................................................... 154  
5.5 Bubble Transport of CO₂ in East Lake .................... 159  
5.5.1 Theory ............................................................ 159  
5.5.2 Application to East Lake ................................. 164  
5.6 Seasonal Carbon Dynamics ................................. 169  
5.6.1 Carbon Cycle .................................................. 169  
5.6.2 One-Box Model ............................................... 172
5.6.3 Two-Box Model ......................................................... 174

6. Methane ....................................................................... 183
   6.1 Background .............................................................. 183
   6.2 Results ..................................................................... 184
   6.3 Discussion ................................................................. 188
      6.3.1 Statistical Justification ......................................... 188
      6.3.2 Aerobic Methanogenesis ..................................... 191

7. Conclusions ................................................................. 198

References ..................................................................... 203
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Happy reading!
Abstract

East Lake and Paulina Lake are twin crater lakes in the Newberry caldera, near Bend, Oregon. Despite their proximity, the lakes are chemically different: CO$_2$ and H$_2$S inputs in East Lake, and hot carbonate-rich fluids in Paulina Lake. Paulina Lake has four times the concentration of dissolved species as East Lake. Dissolved carbon in East Lake is isotopically much heavier (up to +5.5‰) than in Paulina Lake (0‰). Both lakes have internal P$_{CO_2} > P_{CO_2}$ (atm), leading to diffusive CO$_2$ loss from the lake surfaces. The carbon budgets are different for the two lakes, and this study focuses on the carbon cycling in East Lake, which involves geothermal CO$_2$ input, diffusive CO$_2$ losses from the lake surface, no CO$_2$ uptake from the atmosphere, photosynthesis, respiration, and organic carbon burial. The isotopic composition and C:N of East Lake sediment indicates that buried organic matter is ~45% phytoplankton, 35% subaqueous vegetation, 15% cyanobacteria, and 5% pine needles. East Lake has a strong vertical $\delta^{13}C$ (DIC) gradient (up to 5‰), because volcanic and biological sources and sinks of carbon in East Lake cause identical trends in DIC concentration and isotopic composition with depth. Isotopically light geothermal CO$_2$ enters the bottom water and evades from the surface waters (-10.5‰ $\delta^{13}C$), while isotopically light organic carbon is removed from surface waters and falls to bottom waters through the photosynthetic-respiration loop. Field flux measurements, sequential Gaussian simulations, and models indicate that both Newberry lakes evade CO$_2$ at comparable rates for volcanic lakes with similar surface areas and that CO$_2$ flux rates are highest in the early summer. East Lake evaded an average of ~71 tonnes of CO$_2$ per day in early June 2016, compared to ~45 tonnes of
CO₂ per day in July 2015. Novel field and lab draw-down build-up experiments were completed to determine the isotopic composition of the evading CO₂ gas, and trends in δ¹³C and δ¹⁸O CO₂(aq)-(gas) offsets of up to 7‰ δ¹³C past equilibrium fractionation factors indicate a non-equilibrium fractionation component to lake degassing. Additionally, the well-oxygenated surface waters of both East Lake and Paulina Lake have 20-50 times higher CH₄ concentrations with much more negative δ¹³C and δD isotopic signatures. These profiles suggest aerobic methanogenesis by fermentation in the surface waters, whereas the deeper waters have thermogenic methane. All new field and experimental data for this study were collected in May-December of 2016.
1. Introduction

1.1 Purpose of Research

This research project was conducted to better understand the water chemistry and hydrothermal and limnological processes in East Lake and Paulina Lake, the two crater lakes associated with Newberry Volcano. This thesis contributes to the ongoing comprehensive dataset about the lakes, and takes the study deeper by adding field and laboratory experiments and new analyses. The data and analysis were used to develop conceptual models of the limnogeological system, incorporating geological, chemical, hydrological, physical, and biological data and experiments. The numerical simulations and experiments allow us to explore and predict the characteristics of East Lake and Paulina Lake’s limnological and hydrothermal systems. All aspects of the lakes’ carbon cycles were considered and modeled, including geothermal CO$_2$ input, photosynthesis and respiration, organic carbon burial, bubble transport, diffusive CO$_2$ losses from the lake surface, and isotopic fractionation. Rates of CO$_2$ loss and $\delta^{13}$C shifts during degassing are not well documented, and this study worked to determine the kinetic component of CO$_2$ degassing in terms of the difference in the partial pressure of CO$_2$ in between the lake water and the atmosphere. Ultimately, this study looked at the contribution of the Newberry lakes in the global carbon (CO$_2$ and CH$_4$) budget.

1.2 Limnological Processes
Lakes only comprise 0.01% of Earth’s surface, but both are extremely important resources to humans for everything from drinking water to recreation to runoff collection and are very susceptible to human alteration (Baker, 1994). Because both animals and over Earth processes are so dependent on lakes, it is necessary to understand the chemical, physical, and biological aspects and processes of lakes. Lake processes mirror ocean processes in many ways, but on a much smaller scale. Both lakes and oceans display vertical stratification, undergo biological cycling and sedimentation, and gain and lose water through precipitation and evaporation. Many lakes have additional inputs and outputs, such as rivers, streams, waterfalls, man-made irrigation channels, and groundwater seepage through the floor (Baker, 1994). When inputs and outputs of lake components, such as water or carbon, are equal, the lake maintains a constant level of the component, and the lake is at steady state. Residence time is the average amount of time water or a dissolved constituent spends in a lake that is at steady state before being removed. The residence time, or replacement time, of water in a lake is

\[ \tau_w = \frac{V}{F_i} \]  

(Baker, 1994)  

Equation 1.1

where \( \tau_w \) is the residence time of water, \( V \) is the volume of water in the lake, and \( F_i \) is the rate of water input (or output). The same equation can be used to calculate the residence time of other elements and molecules in lakes.

Freshwater lake chemistry is highly dependent on water temperature-driven circulation based on the distribution of heat. Water density and thus convection
patterns are highly dependent on temperature. Dilute fresh water is unusual in that it is most dense at 4°C and decreases density with increasing temperature (Figure 1.1). Ice is less dense than cold water and thus floats. Seasonal temperature changes dictate water density and thus lake circulation and classification. Holomixis the temperature-based wind-driven mixing of surface and bottom waters. Dimictic lakes have two mixing periods per year: vernal and autumn overturn (Baker, 1994).

![Figure 1.1: Density of fresh water in relation to temperature. Note that the maximum density is at 4°C (Baker, 1994).](image)

During the late summer, ambient air temperatures are the warmest and so are surface waters. Wind and waves determine the depth of water heating. Warm, wind-stirred surface waters are called the epilimnion of a lake (Figure 1.2). Below the epilimnion the temperature drops abruptly at the thermocline. The rest of lake waters below the thermocline constitutes the hypolimnion, which receives no warmth from
the atmosphere and thus has a homogeneous cold temperature. The coldest, most dense waters sink to the bottom, resulting in stable density stratification. Hypolimnion temperatures and the depth of thermocline after stratification are dependent on the length of the previous circulation period (Baker, 1994).

![Temperature profile diagram](image)

**Figure 1.2:** Profile of water temperature versus depth for a typical temperature freshwater lake in the summer. Exact depth of the thermocline and temperature trends is depending on the system (Baker, 1994).

In early fall, the air and surface cool, and epilimnion temperatures reach that of the hypolimnion. The thermocline disappears, and the lake has constant temperature with depth (Figure 1.3). By late fall, ambient and surface waters have cooled further, and surface waters become denser than bottom waters. This thermal instability, with the assistance of strong autumn winds, causes the mixing of surface and bottom waters, or annual fall turnover. As winter approaches, air and surface water temperatures cool below 4°C, while bottom waters remain at the denser 4°C.
This results in stable density stratification, with a colder epilimnion and hypolimnion around 4°C. By wintertime, surface waters have reached 0°C and a layer of ice covers the lake. The ice cap and less dense surface water prevent wind mixing of the lake and enhance winter stratification. As winter turns to spring, the ice begins to melt and surface waters warm, eventually reaching 4°C, while bottom waters remain around 3°C. The resulting density imbalance causes spring turnover and mixing of all lake waters. During spring heating, surface waters warm and become less dense, and the lake once again stratifies with a clear epilimnion, thermocline, and hypolimnion. These seasonal processes occur in all dimictic lakes, which comprise most temperate lakes. Temperatures and thermocline depths vary among lakes (Baker, 1994).

Figure 1.3: Evolution of lake water temperature with depth over the seasons for a typical temperate dimictic lake. Maximum water density is at 4°C and is represented by the vertical dashed line (Baker, 1994).

In addition to differing in temperature, the epilimnion and hypolimnion have distinct chemical compositions, mostly due to differences in biological processes.
During photosynthesis, plants use sunlight to convert CO₂ and water to organic matter and oxygen. Plants synthesize organic compounds that are mainly comprised of carbon, oxygen, and hydrogen, and have other essential nutrient elements, including phosphorus and nitrogen. Photosynthesis consequently involves the uptake of CO₂, phosphate, nitrate, and the production of O₂ (Physical Processes in Lakes book).

When lakes are rich in nutrients and photosynthesis occurs at high levels, lakes are net sinks for atmospheric carbon (Schindler et. al, 1997). Conversely, aerobic respiration occurs in plants, animals, and bacteria, and is the reverse chemical process of photosynthesis. Respiration causes the breakdown of organic matter, while photosynthesis involves the formation. The location and rate of these processes forms the biological pump common in aquatic ecosystems. The rates of photosynthesis and respiration are nearly identical in natural waters, but there is always slightly more photosynthesis. Photosynthesis only occurs in waters shallow enough for light to penetrate and drive the chemical reaction. Dead organic matter from the surface waters fall to the bottom waters as sediment, where it is broken down through respiration. In stratified lakes, there is net photosynthesis in the epilimnion and net respiration in the hypolimnion, causing changes in water composition (Physical Processes in Lakes book). Differences in water chemistry between the epilimnion and hypolimnion can also be the result of the epilimnitic exchange of heat and gases with the atmosphere (Christenson et al., 2015).

The carbon cycle in lakes extends beyond the biological pump. Major carbon inputs include dissolved inorganic carbon, dissolved organic carbon, particulate inorganic carbon, and particulate organic carbon (Tranvik et. al, 2009). Net removal
of carbon from lakes occurs through diffusion at the surface, making lakes sources of atmospheric carbon (Schindler et al., 1997). Another major outflow of carbon happens through burial and sedimentation, and the 820 Pg of carbon sequestered in lake sediments worldwide are important in the global carbon cycle. Earth’s lakes bury three times the amount of organic carbon annually than the oceans. Sedimentation rates are highest in small, eutrophic lakes. Lake sediments reflect the lake’s environment at the time of deposition, so sediment cores can be analyzed as indicated of past geological and environmental conditions. Carbon inflows, outflows, and pathways are affected by global and regional climate change, so sediment cores and water chemistry can be used to monitor the effects of climate change on limnological systems (Tranvik et al., 2009).

1.3 Volcanic Lakes

While there are approximately 304 million lakes worldwide, 769 are volcanic lakes, and about 12% of Holocene-age volcanoes have volcanic lakes (Tranvik et al., 2009; Pérez et al., 2011; Varekamp and Pasternack, 1996). Volcanic lakes are similar to regular lakes with one key difference: volcanic input. They have been dubbed “blue windows”, because they reflect the volcanic, hydrological, and degassing inner workers of their adjacent volcanos and magma source regions (Christenson et al., 2015). Volcanic lakes have unique formation mechanisms and relationships volcanic lakes can have with adjacent volcanos. Crater lakes are formed by explosive evacuation, caldera lakes are formed through collapse of the caldera, and some volcanic lakes are formed through the blockage of rivers and streams by mudflows,
lava flows or ash (Pérez et. al, 2011). The life span of a volcanic lake depends on the magnitude of volcanic hydrothermal heat input and the lake’s ability to dissipate the heat (Varekamp and Pasternack, 1996).

No two volcanic lakes are identical, with different formation processes, relationships with volcanos, geomorphology, colors, water chemistries, meteoric waters, and biological productivities. Christenson et al. (2015) delineated various methods to classify volcanic lakes. The most conceptual classification system is based on the formation mechanisms of volcanic lakes and uses a four-variable code. The volcanic system can be geotectonically assessed (G) as either monogenetic (0) or polygenetic (1). The relationship between the volcanism and the lake formation is expressed as either weak (0) or strong (1). Timing of lake formation relative to the last volcanic eruption (T) is either long (0) or short (1). In relationship to the volcanic center, the location of the lake (L) can be expressed as off (0) or over (1) the main vent. This genetic coding mechanism can be used in conjunction with other classification schemes to determine the biogeochemistry of the volcanic lake (Christenson et al., 2015).

Like a regular lake, the residence time of a volcanic lake is a function of its volume and input rate, some of which is volcanic input. Volcanic lakes with shorter times are more sensitive to potential changes and thus need to be monitored more frequently. Volcanic lakes are often stratified at the thermocline with a warm epilimnion and constantly cool hypolimnion. Lakes affected by volcanic fluid input generally have hotter bottom waters, and waters near hot springs are also usually warmer. Volcanic lakes are not just useful tools for monitoring volcanic activity; they
have their own dangers, including CO$_2$ and phreatic explosions, lahars, and toxic fluid leakage. One of the most notable attributes of volcanic lakes is their stunning colors, which are dependent on the lake’s chemical composition, biological productivity, and ecosystem. Biologically unproductive lakes appear deep blue, eutrophic lakes are greenish-blue, lakes with high concentrations of dissolved organic matter are brown, and extreme lakes with red algae appear deep red (Christenson et al., 2015).

The ionic concentrations of lake waters reflect volcanic gas compositions and meteoric water, with ratios between these endmembers dependent on the lake’s relationship with the volcanic system and whether the lake is at hydraulic steady state (Varekamp, 2015; Christenson et al., 2015). Geothermal gas enters hydrothermal system, delivering anions into the lake, including SO$_2$, HCl, HF, H$_2$S, and CO$_2$ (Christenson and Tassi, 2015). Common minerals in volcanic lakes include anhydrite, sulfur, gypsum, and jarosite, and often deplete waters of sulfur. Volcanic lakes that receive highly processed hydrothermal fluids (the Wonder bread of geothermal input) tend to be strongly mineralized and less rich in volcanic elements. Most cations found in volcanic lakes are the result of reactions between local volcanic rocks and volcanic fluids. Volcanic lake pH values tend to have a bimodal distribution, due to SO$_4^{2-}$, HSO$_4^-$ and H$_2$CO$_3$-HCO$_3^-$ buffers. Elements emitted from volcanos include potent contaminants that are extremely dangerous for humans and other animals. Volcanic lakes are often rich in these contaminants, especially As, Li, F, and Fe, making the waters not safe to drink or to use for irrigation (Varekamp, 2015).

1.4 Carbon Dynamics in Volcanic Lakes
Carbon dioxide emissions from volcanoes have been well studied and documented for decades, with estimations ranging from 300-448,000 Mt/year and beyond (Pérez et. al, 2011; Gerlach, 1992). However, recent estimates for global volcanic CO\textsubscript{2} emissions rates are smaller than global consumption of CO\textsubscript{2} subaerial silicate weathering. In order to balance the global carbon cycle, there must be additional sources of carbon into the atmosphere. Significant amounts of magmatic CO\textsubscript{2} are dissolved in volcanic lake water, but the CO\textsubscript{2} emitted from volcanic lake degassing had never been considered in the global carbon cycle until Pérez et. al (2011). They estimated that 117 Mt of CO\textsubscript{2} are degassed from volcanic lakes worldwide annually, with most emissions from acidic and neutral volcanic lakes, indicating that current estimates of total CO\textsubscript{2} emissions from subaerial volcanism are conservative. Total subaerial volcanic emissions are likely closer to 540 Mt/year, when all processes and structures are considered (Burton et. al, 2013).

In many volcanic lakes, carbon dioxide enters the system both from the atmosphere and from geothermal or hydrothermal sources below the lake. While sub-lacustrine gas inputs provide most dissolved CO\textsubscript{2} in volcanic lakes, biological processes regulate the transport and concentration of the DIC throughout the water column. Similar to regular lakes, algae, cyanobacteria, and plants take up CO\textsubscript{2} through photosynthesis in the aerobic epilimnion of volcanic lakes. Microbial reduction and respiration alter CO\textsubscript{2} concentrations in the anoxic or hypoxic hypolimnion (Christenson and Tassi, 2015). Much of the volcanic carbon is buried with organic matter in the bottom lake sediment or evaded through diffusion at the lake’s surface.
Most volcanic lake waters have different $\delta^{13}C$ compositions than the atmosphere or groundwater due to the input of volcanic CO$_2$. The isotopic composition of dissolved carbonate in the lake water reflects the $\delta^{13}C$ of inputs, dominantly subaqueous CO$_2$ gas inputs, plus fractionations due to phase changes and photosynthesis (Varekamp, 2015). The isotopic compositions of volcanic CO$_2$ are dependent on mantle signatures, which are present in rift margin and hot spot centers, and on organic material and carbonate signatures, found in subduction zone derived magmatic CO$_2$ (Christenson and Tassi, 2015). Most mantle CO$_2$ ($\delta^{13}C$ -6 to -3.5‰) has a similar isotopic composition as the modern atmosphere ($\delta^{13}C$ -8.5 to -7.5‰) (Varekamp, 2015). Isotopic signatures are also affected by melt-vapor equilibrium fractionation, causing volcanic gases to trend toward lighter $\delta^{13}C$ values and dissolved organic carbon to trend toward heavier $\delta^{13}C$ values (Varekamp, 2015; Christenson and Tassi, 2015). Additionally, carbonate species fractionate during phase changes, making H$_2$CO$_3$ and CO$_2$ lighter than the dominant HCO$_3^-$ at the pH of most volcanic lakes (Varekamp, 2015). Although fractionation may result in different gas compositions than the source magma, effects of fractionation and general trends in carbon isotopic composition can shed light on batch degassing processes and help predict new pulses of magmatic degassing (Christenson and Tassi, 2015).

It is important to monitor the CO$_2$ contents and degassing rates in volcanic lakes to predict and mitigate disasters, such as the catastrophic CO$_2$ explosions of Lake Monoun and Lake Nyos in Cameroon. Lake Monoun exploded in 1984, killing 37 people. Lake Nyos exploded just two years late in the same remote area of Cameroon, killing 1800 people. At the time, the causes and mechanisms behind these
odd tragedies were mysteries, though it is now understood that “limnic eruptions” had occurred. Lake Monoun and Lake Nyos lie within the crater of a supposedly inactive volcano in the volcanic chain of Cameroon, which includes the still active Mount Cameroon. Scientists believe that the gas bursts were caused by the release of large amounts of pressured carbon dioxide that had previously been dissolved in the bottoms of the stratified, meromictic lake (Halbwachs et. al, 2004). Although the CO2-rich water is denser than pure water, as the partial pressure of CO2 in the water increased, the hydrostatically stable water at the bottom of the lake became more dynamically unstable. Thus, an exogenic disturbance or intrinsic instability likely allowed the water to move up and to reach saturation (PCO2=Ptotal). Lethal CO2 bubbles formed, grew, and rose because they were less dense than water, and prompting the lakes to overturn and release the suffocating CO2 (Zhang, 1996). Lake Nyos (210 meters) had double the depth as Lake Monoun (95 meters), so the gas burst was significantly larger (Halbwachs et. al, 2004).

In the years following the explosions, scientists determined that disastrous amounts of dissolved CO2 remained in the lakes, and the gas is recharged quickly enough to substantially increase the risk of another catastrophe. As a result, pipes were installed to remove the CO2 from the bottom of the lakes in a controlled and safe manner, by bringing bottom water to the surface and allowing CO2 to diffuse out to the atmosphere. No suffocating bursts have since occurred. Since the deadline eruptions of Lake Monoun and Lake Nyos, monitoring of CO2 levels in volcanic lakes has increased to prevent similar eruptions in the future (Kling et. al, 2015).
Through this process, scientists have learned a lot about the effects on degassing on lakes’ physics, chemistry, ecology, and human impact (Halbwachs et. al, 2004).

2. Geological and Hydrological Setting

2.1 Geological Setting: Newberry Volcano

Newberry Volcano is located in central Oregon, 30 kilometers southeast of Bend (Morgan et. al, 1997). It stands 60 kilometers east of the main north-south crest of the Cascade Range Provence and on the western edge of the High Lava Plains. As one of the largest Quaternary volcanoes in the continental United States, Newberry is not a typical volcano for this region (Morgan et. al, 1997; Fitterman, 1988). The volcano is the site of convergence of three major fault zones: Sisters fault zone from the north, Brothers fault zone at the northeast, and Walker Rim fault zone from the southwest. Lower crustal rocks under the volcano are thinner than the surrounding area. While other volcanoes in the Cascade Range are stratocones, Newberry has a broad shieldlike shape, due to large quantities of very liquid lava (Fitterman, 1988). Its highest point, Paulina Peak, stands 7,984 feet high on the rim of the caldera (Donnelly-Nolen et. al, 2014). Newberry’s summit boasts a central caldera that expands four by five miles and rises to altitudes over 7,000 feet (Figure 2.1; Phillips, 1968; Morgan et. al, 1997; Donnelly-Nolen et. al, 2014). It has collapsed twice in the period of 0.3-0.5 Ma due to two large ash flow tuff eruptions and now is comprised of an outer ring of faults and an inner set of fractures. Pleistocene and Holocene flows and breccia fill the caldera to a depth of about 500 meters (Sammel et. al, 1988;
The caldera is home to scenic East Lake and Paulina Lake and a dense conifer forest, which is mostly comprised of lodgepole pines, with some yellow pines, alders, hemlocks, and firs (Phillips, 1968).

Figure 2.1: Map of Newberry Volcano caldera, including East Lake, Paulina Lake, Pumice Cone, Big Obsidian Flow, Paulina Peak, Paulina Creek, and hot springs (Sammel, 1983).

While the High Cascades region has been active for nine million years or more, Newberry Volcano has only been active for 500,000-700,000 years, erupting thousands of times over this period. The last eruptive period started 10,000 years ago and included at least 25 eruptions, most recently 1,300 years ago (Morgan et al., 1997; Sammel et al., 1988; Fitterman, 1988). Rocks from the most recent eruptive cycle indicate basaltic andesite lava flows on the flanks and rhyolite flows and domes in the caldera and southeast flank. Rhyolite composition indicates that they erupted
from a single magmatic chamber at near-solid temperatures and that basaltic underplating prevented crystallization of silicic magma. Silicic magma fragments were incorporated by mafic lava flows. A shallow, centrally-located silicic chamber likely shadowed mafic rocks from entering the same area as the rhyolites during the Holocene (MacLeod and Sherrod, 1988). The crater lakes were likely formed at least 8,000 years ago, when the ice holding the ash and lapilli from late phases of volcanic activity melted and these fine materials formed deposits that sealed the lake bed (Phillips, 1968; Lefkowitz et. al, 2016). Thus, the East Lake and Paulina Lake can be classified as crater lakes, with a genetic code of G1, R1, T1, L1 based on Christenson et al. (2015).

The United States Geological Survey still actively monitors the Newberry Volcano because it is considered a very high threat volcano. An eruption could drastically impact the nearby towns of Bend, La Pine, and Sunriver and destroy infrastructure such as highways, powerlines, and railways. Newberry National Volcanic Monument (NNVM) is a popular tourist attraction and maintained by the U.S. Forest Service as part of Deschutes National Forest. It encompasses 90 square miles of the 1,200-square-mile Newberry volcano, including the central caldera and Big Obsidian Flow (Donnelly-Nolen et. al, 2014).

2.2 Limnological Setting: Newberry Caldera Hydrology
It is important to understand Newberry Volcano’s hydrothermal system in order to predict future geothermal activity. East Lake and Paulina Lake dominate the hydrologic system of Newberry Volcano’s caldera. The two small, deep crater lakes are which are separated by a two-kilometer-wide ridge of subsidiary Holocene volcanic cones and lava flows that the divides the caldera in the middle along a north-south line (Figure 2.2; Phillips, 1968). No perennial streams are tributary to either lake, so precipitation, hot springs discharge, groundwater flow, and surface runoff due to heavy snowmelt comprise all aqueous inflow. Outflow in both lakes is due to evaporation and groundwater seepage. While East Lake is terminal, Paulina Lake surface waters outflow at ~0.51 m$^3$/sec into Paulina Creek, which flows west more than 13 miles into the Little Deschutes River. A concrete spillway and fish-screen
structure at southwest shore of Paulina Lake regulates Paulina Creek. The control structure raised the lake level, and increased storage relative to natural conditions, and prevents fish from leaving the lake. Stored water is used for irrigation downstream (Morgan et. al, 1997; Sammel and Craig, 1983).

Newberry’s caldera has a unique microclimate, with relatively high humidity, cool summers, and low evaporation rates (Phillips, 1968). It stands 1,500-2,000 feet above the adjacent La Pine and Fort Rock Valleys, resulting in a mean annual precipitation of approximately 30 cm per year in the caldera, as opposed to 12-15 in/year in the valleys. Other areas in the Cascade Range with similar elevations have more than twice the mean annual precipitation as Newberry, indicating that the caldera experiences an orographic rain shadow effect (data from 1995; Morgan et. al, 1997). Average annual evaporation from East Lake and Paulina Lake is ~71 cm and ~48 cm, respectively (Sammel and Craig, 1983).

Air temperatures are lowest between November and January, getting down to -20ºC. The caldera is warmest in May through September, though maximum temperatures are reached in July, getting as high as 27ºC. Surface water temperatures affect aquatic life and are controlled by energy-transfer processes from the geothermally heated water, radiative heat exchange with ambient air, and mixing. Highest median water temperatures were in East Lake Hot Springs, at 63.1ºC (Morgan et. al, 1997). Temperatures in the hydrothermal system have likely remained constant for a prolonged time (Fitterman, 1988).

2.3 East Lake and Paulina Lake
Figure 2.3: Bathymetry of East Lake. Altitude is in meters, and distance is in kilometers.

East Lake is higher, shallower, and smaller than Paulina Lake. East Lake has a surface elevation of 1,945 meters and surface area of 4.2 square kilometers (Johnson, 1985). It has a maximum depth of 55 meters, with most of the north and northwestern side more than 100 feet deep and the southern and western portions are less than 40 feet deep (Morgan et. al, 1997) (Figure 1.6). Total lake volume is $8.6 \times 10^7$ m$^3$, and more than half of the volume is shallower than 12 meters (Table 2.1; Johnson, 1985; Lefkowitz et al, 2016). The thermocline is at 15 meters, with warm epilimnion waters totaling around $4.9 \times 10^7$ m$^3$ and cold hypolimnionic waters comprising about $3.7 \times 10^7$ m$^3$, based on integrating cumulative percent surface area data. Paulina Lake has an elevation of 1,930 meters, which would need to be increased to 1,980 meters to connect its lake basin in East Lake’s (Foster and Stone, 2016). It has a surface area of 6.2 square kilometers, volume of $31 \times 10^7$ m$^3$, maximum depth of 76 meters, and average depth of 50 meters (Johnson, 1985; Lefkowitz et. al, 2016). Both lakes freeze
over from November to late May and are dimictic, with seasonal turnover in the spring and fall (Morgan et. al, 1997).

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Cumulative SA</th>
<th>% SA</th>
<th>SA (m³)</th>
<th>volume block (m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>100</td>
<td>4200000</td>
<td></td>
</tr>
<tr>
<td>12.2</td>
<td>50</td>
<td>50</td>
<td>2100000</td>
<td>0-12.2 m: 4.7 x10⁷</td>
</tr>
<tr>
<td>24.4</td>
<td>63</td>
<td>13</td>
<td>546000</td>
<td>12.2-24.4 m: 2.0 x10⁷</td>
</tr>
<tr>
<td>36.6</td>
<td>75</td>
<td>12</td>
<td>504000</td>
<td>24.4-36.6 m: 7.8 x10⁷</td>
</tr>
<tr>
<td>48.8</td>
<td>87</td>
<td>12</td>
<td>504000</td>
<td>36.6-48.8 m: 7.5 x10⁷</td>
</tr>
<tr>
<td>54.9</td>
<td>100</td>
<td>13</td>
<td>546000</td>
<td>48.8-54.9 m: 3.9 x10⁷</td>
</tr>
</tbody>
</table>

Table 2.1: Surface area and volume of East Lake by depth. Volume of each depth calculated through trapezoid integration with surface area and depth data from Lefkowitz et al., 2012.

Paulina Lake’s water levels are relatively stable, while East Lake’s stage has been shown to fluctuate about two feet annually (Phillips, 1968). East Lake is higher in elevation than Paulina Lake, creating a hydraulic gradient of about 40 feet per mile. Thus, there may be groundwater flow from East Lake into Paulina Lake through the relatively permeable ash and pumice deposits between the lakes. East Lake has been calculated to lose as much as 2.3 ft³/sec through seepage, and most of this water likely flows into Paulina Lake (Morgan et. al, 1997). However, studies and geochemical analyses suggest that the lakes are entirely separate hydraulically (Phillips, 1968; Lefkowitz et al., 2016). In general, the lakes are considered to be at hydrological steady state (Sammel and Craig, 1983).

Although they are associated with the same volcanic system, East Lake and Paulina Lake have very different chemical compositions. This difference can be attributed to unique forms of geothermal inputs into each lake: gas in East Lake and liquid in Paulina Lake. East Lake waters are close to neutral (pH ~6.5) while Paulina
Lake is slightly alkaline (pH ~8.0), so most dissolved carbon is present as bicarbonate. Paulina Lake generally is more concentrated in most elements except for sulfur. Geothermal input into East Lake is mostly CO$_2$ and hydrogen sulfide, which oxidizes into sulfate. Hot carbonate-rich fluids enter Paulina Lake, enriching the waters in calcium and magnesium (Lefkowitz et al., 2016). Geothermal waters had substantially higher alkalinities, specific conductance, and concentrations of major ions and dissolved solids than ground water in both lakes. Nutrient concentrations in the caldera are generally low. East Lake sediment is rich in organic carbon, mercury, and silica, while Paulina Lake has higher arsenic and Fe$_2$O$_3$ concentrations. Both lakes have internal PCO$_2$ higher than atmospheric PCO$_2$, leading to diffusive CO$_2$ loss from their respective lake surfaces. East Lake, Paulina Lake, and Paulina Creek waters are enriched in heavy oxygen and deuterium due to surface evaporation. The two lakes also have different mixing patterns as a result of their different morphologies (Morgan et. al, 1997; Lefkowitz et. al, 2016).

Biotic matter in the two lakes include fish, benthic and planktonic diatoms, cyanobacteria, unicellular chrysophytes, and chlorophytes (Johnson, 1985). Both lakes have been consistently stocked with fish since 1912, and East Lake fish have high mercury concentrations. Dominant fish species include Brown Trout, Kokanee, Atlantic Salmon, and Rainbow Trout (East Lake Resort). Because large part of East Lake is shallow enough for some sunlight to reach the bottom, it has large and diverse benthic diatoms. Diatom species present in the lakes indicate its water pH and nutrient levels, includin *Stephanodiscus excentricus, Aulacoseira ambigua, Asterionella Formosa, Cocconeis, Rhoicosphenia abbreviata*, and *Karyevia*
laterostrata (Foster and Stone, 2016). Nostoc cyanobacteria—small, colorful gelatinous spheroids—thrive around the perimeter of both lakes. East Lake has large floating islands of subaqueous metaphytes, possibly from submerged aquatic vegetation (Lefkowitz et. al, 2016).

2.4 Previous Work

Varekamp and his team of Wesleyan students have collected samples and data from East Lake and Paulina Lake in the summers of 2009-2012 and 2014-2016 as part of an ongoing studying on the geochemistry and limnogeology of the Newberry caldera. McKay and her students from the Oregon State University also surveyed in the lakes in spring and fall of 2015 and 2016 and sent samples to Wesleyan. During the 1980’s and 1990’s, Reynolds from Central Oregon Community College collected water column data for many years. Lefkowitz ’12 and Capece ’16 wrote Wesleyan honors theses on water and sediment samples collected in 2012 and 2016, respectively.
3. Methods

3.1 Field Methods

Fieldwork was conducted in the Newberry Caldera. June 11-15, 2016 was spent at East Lake, and on June 16, we sampled at Paulina Lake. The location of each sampling site on the lake was determined with a handheld GPS device. Weather in the Newberry caldera during June 11-14 was cloudy and 2-10°C during the day and around or below freezing at night. On June 15 and 16, temperatures were closer to 0-5°C during the day with occasional snow flurries. Most days, sampling and measurements could only be taken for a few hours, because the lake water was so rough.

Dissolved oxygen, temperature and conductivity were measured in vertical water profiles in East Lake. A YSI Model 52 Dissolved Oxygen Meter measured temperature and dissolved oxygen (DO) down to 30 meters and a 3000 T-L-C YSI Meter measured temperature and conductivity down to 45 meters.

3.1.1 Water Samples

Surface water samples were taken at Paulina Lake on June 16 and at East Lake on May 28, June 15, November 12, and November 14, 2016. Surface water from East Lake Resort’s docks was collected all four sampling days, while samples from the East Lake hot springs boat ramp and campground were only collected in May and November.
<table>
<thead>
<tr>
<th>Site ID</th>
<th>Location</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Dates Sampled</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELA</td>
<td>East Lake Resort Dock</td>
<td>43.72504</td>
<td>-121.19559</td>
<td>5/28/16 6/15/16 11/12/16 11/14/16</td>
</tr>
<tr>
<td>ELB</td>
<td>Hot Springs Boat Ramp</td>
<td>43.71987</td>
<td>-121.19796</td>
<td>5/28/16 11/12/16 11/14/16</td>
</tr>
<tr>
<td>ELC</td>
<td>East Lake Campground</td>
<td>43.72376</td>
<td>-121.19607</td>
<td>5/28/16 11/12/16</td>
</tr>
</tbody>
</table>

Table 3.1: Locations of surface water samples that were collected from East Lake Resort dock, East Lake hot springs boat ramp, and East Lake Campground in May, June, and November of 2016.

A Teflon van Dorne water sampler was used to collect water samples at 10-meter depth intervals from the surface to the bottom of each lake. Two profiles were taken in East Lake, HPEL1 and HPEL2, from 0 to 42 and 0 to 50 meters deep. One profile was taken in Paulina Lake, HPPL, from 0 to 60 meters. Water from the East Lake hot springs and water that accumulated in the pores of the Paulina Lake cores were also collected. All samples were filtered through 0.2µm and 0.45µm filters. Each 2016 water sample was then subsampled into a 30mL glass crimpcap vial for alkalinity measurements, a 50mL glass crimpcap vial for methane analysis, a five-mL glass exetainer for stable water isotopes, and a pre-evacuated 12 mL glass exetainer for δ¹³C DIC. The rest of each bulk water sample was stored in plastic 175 mL HDPE bottles, and subsampled later for major anion and cation analysis.

3.1.2 CO₂ Evasion Flux Measurements

CO₂ flux surveys were conducted at approximately 100 locations in East Lake over a period of two years. During the summer of 2015, 40 measurements were taken
over a seven-day period (June 26 to July 2; Capece, 2016). During the summer of 2016, 60 measurements were taken on June 11, 12, and 15. Eleven flux measurements were taken over Paulina Lake on June 16. The location of each site was determined with a handheld GPS device. At each site, a floating accumulation chamber (West Instruments, Pisa, Italy) was deployed. Anhydron (magnesium perchlorate) was used to absorb moisture from the gas, which was then pumped into a LICOR (LI-6252) CO₂ Analyzer. Every two seconds, the LICOR measured and a laptop computer recorded the CO₂ concentrations of the gas inside the chamber (Figure 3.1). Most initial CO₂ concentrations were close to local atmospheric values (~400 ppm), but then increased over a one to five-minute interval when lake CO₂ gas gradually filled the chamber. A hand-held digital thermometer measured the temperature of the surface water and air at each site.

![Diagram](image)

**Figure 3.1**: Field and experimental design for CO₂ build-up measurements. Gas was collected in the accumulation chamber, and then pumped through a water trap, into the LICOR for measurement, and then back into the chamber.

After select build-up runs, the gas inside the accumulation chamber was sampled for isotopic analysis. Twenty-six chamber gas samples were taken at East
Lake and three were taken at Paulina Lake. A 26-gauge needle attached to a 30mL plastic syringe was inserted into a septum on the top of the accumulation chamber, and a ~15 mL sample was collected, which was then injected into a pre-evacuated 12 mL exetainer for δ¹³C-CO₂ measurement. Exetainers were pressure-equilibrated at the ambient pressure of ~0.82 atmosphere at almost two kilometers of altitude; some vials were slightly overpressurized. The CO₂ concentration and temperature inside the chamber were recorded at the time of gas extraction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lake</th>
<th>Date Collected</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPELC1</td>
<td>East Lake</td>
<td>6/12/16</td>
<td>43.72498</td>
<td>-121.1977</td>
</tr>
<tr>
<td>HPELC2</td>
<td>East Lake</td>
<td>6/12/16</td>
<td>43.7263</td>
<td>-121.2053</td>
</tr>
<tr>
<td>HPELC3</td>
<td>East Lake</td>
<td>6/12/16</td>
<td>43.7273</td>
<td>-121.20909</td>
</tr>
<tr>
<td>HPELC4</td>
<td>East Lake</td>
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</tr>
<tr>
<td>HPELC5</td>
<td>East Lake</td>
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<tr>
<td>HPELC6</td>
<td>East Lake</td>
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<td>-121.22162</td>
</tr>
<tr>
<td>HPELC7</td>
<td>East Lake</td>
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<td>-121.22431</td>
</tr>
<tr>
<td>HPELC8</td>
<td>East Lake</td>
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<td>-121.22583</td>
</tr>
<tr>
<td>HPELC9</td>
<td>East Lake</td>
<td>6/12/16</td>
<td>43.73321</td>
<td>-121.22576</td>
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<tr>
<td>HPELC10</td>
<td>East Lake</td>
<td>6/12/16</td>
<td>43.7325</td>
<td>-121.2247</td>
</tr>
<tr>
<td>HPELC11</td>
<td>East Lake</td>
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<td>43.73132</td>
<td>-121.22246</td>
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<tr>
<td>HPELC12</td>
<td>East Lake</td>
<td>6/12/16</td>
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<td>-121.22168</td>
</tr>
<tr>
<td>HPELC13</td>
<td>East Lake</td>
<td>6/12/16</td>
<td>43.72732</td>
<td>-121.2202</td>
</tr>
<tr>
<td>HPELC14</td>
<td>East Lake</td>
<td>6/12/16</td>
<td>43.72471</td>
<td>-121.22124</td>
</tr>
<tr>
<td>HPELC15</td>
<td>East Lake</td>
<td>6/12/16</td>
<td>43.72263</td>
<td>-121.22015</td>
</tr>
<tr>
<td>HPELC16</td>
<td>East Lake</td>
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<td>-121.2185</td>
</tr>
<tr>
<td>HPELC17</td>
<td>East Lake</td>
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<tr>
<td>HPELC18</td>
<td>East Lake</td>
<td>6/12/16</td>
<td>43.72042</td>
<td>-121.2114</td>
</tr>
<tr>
<td>HPELC19</td>
<td>East Lake</td>
<td>6/12/16</td>
<td>43.72087</td>
<td>-121.20715</td>
</tr>
<tr>
<td>HPELC20</td>
<td>East Lake</td>
<td>6/12/16</td>
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<td>-121.20101</td>
</tr>
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<td>HPELC21</td>
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<td>6/12/16</td>
<td>43.72239</td>
<td>-121.1991</td>
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<tr>
<td>Code</td>
<td>Location</td>
<td>Date</td>
<td>GPS Latitude</td>
<td>GPS Longitude</td>
</tr>
<tr>
<td>---------</td>
<td>--------------</td>
<td>----------</td>
<td>--------------</td>
<td>---------------</td>
</tr>
<tr>
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<td>HPELC24</td>
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<td>43.72008</td>
<td>-121.2018</td>
</tr>
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<td>HPELC26</td>
<td>East Lake</td>
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<td>43.72154</td>
<td>-121.20307</td>
</tr>
<tr>
<td>HPPLC1</td>
<td>Paulina Lake</td>
<td>6/16/16</td>
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<td>-121.26295</td>
</tr>
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<td>HPPLC2</td>
<td>Paulina Lake</td>
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<td>43.72154</td>
<td>-121.26994</td>
</tr>
<tr>
<td>HPPLC3</td>
<td>Paulina Lake</td>
<td>6/16/16</td>
<td>43.71846</td>
<td>-121.27256</td>
</tr>
</tbody>
</table>

Table 3.2: Dates of collection and GPS coordinates of gas chamber samples for build-up monitoring. Twenty-six samples were collected at East Lake and three at Paulina Lake in 2016.

### 3.1.3 Drawdown, build-up experiments

In addition to the conventional gas accumulation chamber measurements, three draw-down, build-up field experiments were performed. The conventional method provides mixtures of ambient air with ~404 ppm CO₂ and accumulated lake gas. The draw-down, build-up method removes the ambient CO₂ prior to a build-up experiment to obtain samples with a larger fraction of lake gas. The accumulation chamber was deployed at a given site, and chamber gas (ambient air and incoming lake CO₂) was pumped through the moisture trap, then through a trap that removed CO₂, and then through the LICOR, with the remainder of the gas returned to the chamber (Figure 3.2). After about XX minutes, the system reached steady state and the CO₂ concentration in the chamber became constant at 101-194 ppm, depending on the run. Subsequently, the CO₂ trap was removed, and the chamber built up CO₂, which was monitored in the traditional way of establishing the lake CO₂ flux rate. The LICOR recorded the CO₂ concentration from ~150 to ~500 ppm in the chamber while the lake degassed. For each of the three draw-down build-up experiment runs,
chamber gas was collected in 12-mL pre-evacuated exetainers at the low steady state 
CO$_2$ concentration and after the build-up period to ~500 ppm CO$_2$ for $\delta^{13}$C 
determinations of the lake CO$_2$. GPS coordinates of the location where the initial 
draw-down began were taken, though the boat drifted significantly during the whole 
experiment (Table XX).

![Diagram of CO$_2$ draw-down monitoring](image)

Figure 3.2: Drawdown experimental design, incorporating a CO$_2$ trap.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPELD1-1</td>
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<td>43.72697</td>
<td>-121.1974</td>
</tr>
<tr>
<td>HPELD1-2</td>
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<td>43.72697</td>
<td>-121.1974</td>
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<td>6/15/16</td>
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<td>-121.1974</td>
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<td>HPELD3-2</td>
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<td>43.72467</td>
<td>-121.19721</td>
</tr>
</tbody>
</table>

Table 3.3: Dates of collection and GPS coordinates of gas chamber samples from 
draw-down, build-up runs. For each of the three runs, one gas sample was taken after 
the draw-down portion of the experiment and a second one after the CO$_2$ had built-up 
again in the chamber.
3.1.4 Gas Samples: Chamber, Ambient, Hot Springs

In addition to the gas samples collected from the accumulation chamber during the build-up measurements, gas samples were collected from the East Lake hot springs and from ambient air over and near East Lake. To collect gas from the East Lake hot spring gas bubbles, a plastic funnel was attached to tubing that fed into a lake-water filled plastic HDPE bottle. The funnel was inverted and held below the water surface directly above the underwater hot springs. The gases traveled into the plastic bottle and displaced the water, providing gas samples free of air contamination. An hour later, after the bottles had cooled to ambient temperature, the hot spring gases were transferred via a plastic syringe into eight pre-evacuated 12 mL exetainers for CO₂ and CH₄ concentration measurements and isotopic analysis.

Ambient air samples were collected at sites around and over East Lake on May 28, June 15, and November 14, 2016 (Table 3.4).

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Location</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Dates Sampled</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELA</td>
<td>East Lake Resort</td>
<td>43.72504</td>
<td>-121.19559</td>
<td>5/28/16 6/12/16 11/14/16</td>
</tr>
<tr>
<td>ELB</td>
<td>Hot Springs Boat Ramp</td>
<td>43.71987</td>
<td>-121.19796</td>
<td>5/28/16 11/14/16</td>
</tr>
<tr>
<td>ELC</td>
<td>East Lake Campground</td>
<td>43.72376</td>
<td>-121.19607</td>
<td>11/14/16</td>
</tr>
</tbody>
</table>

Table 3.4: Locations and dates of ambient air samples that were collected from East Lake Resort, East Lake host springs boat ramp, and East Lake Campground.

3.1.5 Sediment Cores

Two sediment cores were extracted from East Lake and Paulina Lake using a percussion corer. In each lake, one short core (shorter than 100 cm) and one long core
(longer than 100 cm) were collected. One core from each lake was extruded in the rock room at Wesleyan. They were each sliced into two-cm intervals and spread out on Styrofoam plates to dry. The wet and dry weight was recorded for later calculations of the bulk dry density of each core slice. Subsequently, the samples were put into plastic containers for further sediment analysis.

<table>
<thead>
<tr>
<th>Name</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Lake</th>
</tr>
</thead>
<tbody>
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<td>East Lake</td>
</tr>
<tr>
<td>EL2016-2</td>
<td>43.72278</td>
<td>-121.20176</td>
<td>East Lake</td>
</tr>
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<td>PL2016-1</td>
<td>43.71726</td>
<td>-121.26344</td>
<td>Paulina Lake</td>
</tr>
<tr>
<td>PL2016-2</td>
<td>43.71846</td>
<td>-121.27256</td>
<td>Paulina Lake</td>
</tr>
</tbody>
</table>

Table 3.5: Name, GPS coordinates and core length of the sediment cores collected in June 2016.

Figure 3.3: Locations of all sediment cores collected in 2015 and 2016, including two 2016 Paulina Lake cores, two 2016 East Lake cores, and seven 2015 East Lake cores (KCEL1 through KCEL7) (Google Earth).
3.2. Sample Analysis

A series of laboratory analyses was conducted on the 2016 bulk water samples to determine their physical and chemical properties. In total, 29 water samples were analyzed: six from each of the two East Lake vertical water profiles, seven from the Paulina Lake vertical water profile, three East Lake surface samples collected in May, five East Lake surface samples collected in October, East Lake hot spring water, and pore water from a Paulina Lake core.

3.2.1 pH, Alkalinity, and DIC

Alkalinity and pH of all water samples were measured using a Mettler DL12 auto-titrator at Wesleyan. The titrator was calibrated using NBS standard liquids at pH of 4, 7 and 10. Each sample was titrated with 0.1 N HCl until a final pH of 4.3 was reached. Water samples from Long Island Sound, samples from previous years, and a standard ocean water sample and synthetic standard with known pH and alkalinity were measured repeatedly to check for the precision and accuracy of the titration procedure. The pH values were determined at lab temperature, ~22°C, which is significantly warmer than the field temperature.

3.2.2 Cations and Anions

All East Lake and Paulina Lake, water samples were analyzed using an Ion Chromatograph Dionex 600 to determine the concentration of chloride (Cl⁻), sulfate (SO₄²⁻), and nitrate (NO₃⁻). Sets of five standard solutions were used to create
calibration curves, and additional standards and blanks were run as hidden samples to check the calibration.

To determine the concentrations of the major cations Ca, Mg, Na, K, Si, and P, Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was carried out at Smith College (Teledyne Leeman Labs Instrument). A stock solution of 2500 ppm of each Ca, Mg, Na, K and Si was diluted with DI water to create standards of 1 ppm, 2 ppm, 5 ppm, 10 ppm, 25 ppm, 50 ppm, and 125 ppm. Four P standards between 9 and 985 ppb were created by diluting a 10,008 ppm P stock solution with DI water. The DI water used to dilute the cation standard was from Wesleyan University, while the DI water used to dilute the P standard was from Smith College.

3.2.3 Water Stable Isotope

All water samples from both lakes were analyzed for $\delta^{18}O$ and $\delta D$ in water and for $\delta^{13}C$(DIC). The isotopes in water were measured at the UC-Davis Stable Isotope Facility (SIF) using a Picarro Laser Analyzer V2. Each sample was injected at least six times, and the average of the last four injections was used to calculate isotopic compositions. Reference waters that were calibrated against IAEA reference waters were used for standardization. Instrument precision is <0.3 per mil for $^{18}O$ and <2 per mil for $\delta D$. The isotopic ratios were reported relative to international standard VSMOW (Vienna-Standard Mean Ocean Water).

3.2.4 DIC Stable Isotopes
In preparation for $\delta^{13}$C DIC analysis, one mL of pure phosphoric acid was injected into a 12mL glass exetainer, which was then evacuated and flushed with He for 30 seconds. About four mL of each water sample was added to each exetainer, and the total mass of the sample was recorded. The $\delta^{13}$C values of the evolved CO$_2$ were then measured at the UC-Davis SIF on their GasBench II system interfaced to a Delta V Plus IR-MS (Thermo Scientific, Bremen, Germany). Lithium carbonate dissolved in degassed deionized water and deep seawater were run as reference materials every 10 samples. Results were expressed relative to the V-PDB (Vienna PeeDee Belemnite) standard.

3.2.5 Methane stable isotopes

Water samples (30 ml glass crimp cap bottles) for the determination of $\delta^{13}$C, $\delta$D, and concentration of methane were sent to the UC Davis SIF. They were analyzed using a ThermoScientific GasBench-Prescon-IRMS concentration unit interfaced to a ThermoScientific Delta V Plus isotope ratio mass spectrometer. All methane $\delta$-values are expressed relative to the international standards V-PDB for $\delta^{13}$C and V-SMOW for $\delta$D.

3.2.6 Carbon and Nitrogen Analysis of Organic Matter

Pine needles were collected around East Lake, at the East Lake Resort and East Lake Hot Springs Boat Ramp (Tables 1&2 for coordinates) and then finely ground using a mortar and pestle. Three nostoc ball samples, one from East Lake and two from Paulina Lake, that were collected in 2012 were freeze-dried in vacuum for
one week and then finely ground. Duplicates of each sample, in three to seven mg portions, were wrapped in tin cups and shaped into spheres. Four standards of l-cystine and three of l-aspartic acid between 0.2 and 10 mg were included for calibration. The organic matter samples and standards were placed into a circular tray, which was mounted onto the sample holder of Wesleyan’s Elemental analyzer (EA). The EA analyzed each sample for ~320 seconds.

Duplicates of each pine needle sample and nostoc ball sample were also measured into two two-mg or one-mg portions, respectively, and wrapped into tin cups. These samples were brought to the Yale Analytical and Stable Isotope Center for isotopic analysis using a zero-blank auto sampler with a Costech EA attached to an isotope ratio mass spectrometer. Reference materials calibrated with IAEA standards were used, with a precision of ±0.17‰ for each δ¹⁵N and δ¹³C.

3.3 Lab Experiments

3.3.1 Kiddie Pool Experiment

To test the methodology of the field draw-down, build-up experiments and confirm the flux models, similar draw-down, build-up experiments were completed in the laboratory on July 25 and 26, 2016. A simulated lake was created by filling a 20-gallon blue hard plastic kiddie pool halfway up with tap water, so it was approximately six inches deep. The experimental setup was nearly identical to the field draw-down, build-up experiments (Figure 3.2). Our floating accumulation chamber was deployed on the kiddie pool. The gas from the chamber was pumped
through PVC tubing that connected to an anhydronic cartridge to absorb moisture from the gas. Every two seconds, the LICOR measured and a laptop computer recorded the CO₂ concentrations of the gas inside the chamber.

The experiment had three stages, and each was repeated up to five times. The first component was draw-down by pumping CO₂ out of the chamber. In an identical fashion to the field draw-down experiment, when the accumulation chamber, it was naturally initially filled with ambient room CO₂ (~500 ppm). This ambient gas was pumped out of the chamber at one to four L per minute and through a trap that removed the CO₂, and the remainder of the gas was returned to the chamber. This continued for about 45 minutes per run until a near-steady state of 23-43 ppm (depending on the run) was reached in the chamber. At this point, no ambient air CO₂ remained in the chamber. The rate of decrease of CO₂ concentration in the chamber over time was recorded, graphed, and modeled. The second component was a measurement of the natural kiddie-pool degassing. When the draw-down component of the experiment was completed, it was anticipated that the chamber CO₂ concentration would get down to ~0 ppm, because CO₂ was pumped out of the chamber and none was pumped in. However, an apparent steady state was reached at 23-43 ppm, so there must be some source of CO₂ in the pool (leakage or dissolved CO₂ in water). At this stage, CO₂ was pumped out of the chamber, the CO₂ trap was removed, and the chamber gas was monitored by the LICOR. The final stage of the experiment was a controlled build-up of CO₂. For this component, as much CO₂ was sucked out of the chamber air as possible, and the CO₂ trap was removed from the setup. A PVC tube connected to an air pump was placed inside the kiddie pool below
the accumulation chamber. Ambient room air with ~ 500 ppm CO₂ was pumped into the kiddie pool below the chamber at one to four liters per minute depending on the run, and that CO₂ carrying air in the bubbles collected in the chamber and mixed with the resident almost CO₂ free gas. The chamber gas was then pumped through the LICOR setup for concentration measurements over time and then returned to the chamber. The known influx was then compared with the calculated evasion rate into the chamber.

3.3.2 Lab Lake Experiment

During the CO₂ evasion measurements at the Newberry lakes, all variations common to natural systems (wind, currents, boat drift, temperature fluctuations, etc.) were additional uncontrolled variables. To assess the impacts of these various fluctuations, we decided to simulate lake degassing under fully controlled conditions in the lab. Our main goal was to determine the δ¹³C and δ¹⁸O (CO₂) that evolves from the synthetic lake water with known alkalinity, pH, δ¹³C (DIC) and δ¹⁸O H₂O, and compare those data with our field data.

To create Lab Lake, a 13-liter clear plastic cell was sealed, and holes for water inflow, gas inflow, gas outflow, and an electric metal stirrer with two fan blades were drilled in the top (Figure 3.4, of lab lake set up). Inlets and outlets where affixed with quick connects and vinyl tubing. The tubing for gas evading leaving the cell attached to glass vessel of a desiccant, then a three-way valve with a septum covering one prong, then a pump, a flow meter, and the LICOR.
The overall experiment consisted of the creation of an acidified carbonate solution and the monitoring of the concentration and $\delta^{13}$C of the CO$_2$ degassing into a headspace. The goal was to create a solution with a similar pH and alkalinity of East Lake, so prior to the experiment, many solutions with different amounts of NaHCO$_3$ in DI water were created. Two-endpoint titrations were completed to pH 6.5 (pH of East Lake) and then pH 4.3, to identify the amount of HCl necessary to bring the solution to East Lake pH and alkalinity.

On the day of the experiment, December 12, 2016, the Lab Lake cell was flushed with He to remove all CO$_2$ (gas). Eight liters of DI water were mixed with three grams of NaHCO$_3$, and then poured into the cell through a funnel attached to the water input port. The port was sealed with a septum, and the pump was turned on, so the headspace gas traveled through the water trap and into the LICOR, which was set to record the concentration of CO$_2$ in the gas every 30 seconds. The temperature of the water and the air in the cell was recorded throughout the experiment. After the LICOR came a CO$_2$ trap, and then the gas is directed back into the chamber (Figure 3.4). The CO$_2$-free air was then pumped back into the cell, and this continued until the cell headspace reached a steady state of 45 ppm due to leakage or lake degassing at high pH.

Then the CO$_2$ trap was removed, 33.5 mL of 0.5 N HCl was injected into the cell with a syringe through the septum cap, and the stirrer was flipped on (Figure 3.5). As the NaHCO$_3$ and HCl reacted in the water and degassed CO$_2$ (gas) into the headspace, the pump continuously carried the air through the desiccant and the LICOR recorded the CO$_2$ concentration. For every few hundred ppm CO$_2$ added to the headspace, 12
mL of gas were removed from the gas sampling port septum and injected into a pre-evacuated 12 mL exetainer using a syringe and a needle for carbon and oxygen isotopic analysis in CO₂. Gas samples were taken at 300, 700, 900, 1200, 1400, 1600, 1800, 1900, 2100, 2250, 2450, 2700, and 3100 ppm, until LICOR saturation. Samples of original Lab Lake water (just DI water and NaHCO₃) and final Lab Lake water (after degassing) were saved for alkalinity and pH determination and carbon and oxygen isotopic analysis.

**CO₂ Draw Down Monitoring Lab Lake**

![Diagram](image)

Figure 3.4: Lab Lake experimental design, with CO₂ trap inserted for the initial draw down stage.
The gas samples from the headspace during the buildup and the initial and final water samples from Lab Lake were sent to the University of Wyoming’s Stable Isotope Facility for carbon and oxygen isotopic analysis, along with a few remaining East Lake gas and water field samples from June and November. Gas samples were analyzed using a Thermo Gasbench coupled to a Thermo Delta Plus XP IRMS, and $\delta^{13}C$ and $\delta^{18}O$ values are reported relative to VPDB. Water samples were analyzed for $\delta^{13}C$ and $\delta^{18}O$ with Cavity Ring Down Spectroscopy using a Picarro L2130-I liquid water analyzer, and $\delta^{18}O$ values were reported relative to VSMOW.

3.4 Calculations

3.4.1 Web-PHREEQ
Lab pH measurements were amended using Web-PHREEQ and Geochemist’s Workbench (GWB), which are programs used for geochemical analyses, to determine the pH and aqueous speciation at the field temperature. In the first run of Web-PHREEQ or GWB, the measured alkalinity, level of $O_2$ saturation expressed as $pe$, total cation and anion concentrations, lab temperature, and pH as fixed were used and total dissolved carbon (DIC) was calculated. In order to obtain a perfect charge balance, chloride was manually subtracted or added in the input until an error of less than 0.1% was achieved. In the second round of modeling, the calculated DIC value was entered instead of alkalinity, pH was set as “floating”, field temperature was used, and all other analytes remained the same. The pH and the aqueous speciation of carbonate at the field temperature was calculated for each sample, and the molality (moles/kg) of each species was recorded. This procedure was completed in both Web-PHREEQ and GWB for both East Lake water depth profiles and the Paulina Lake water depth profile, yielding similar results.

Water samples were collected at field temperatures (4.8-15°C) and chemical analysis was later completed at warmer laboratory temperatures (22°C). However, water has different compositions and densities at different temperatures, so properties measured in the laboratory might not exactly reflect field compositions. In an attempt to correct for the difference in temperature, each of the 19 water profile samples was run five times at correct for five temperatures: lab (22°C), June actual (temperature measured in depth profile in the field), winter (5°C), early summer surface (15°C), and late summer surface (19°C). Output files from Web-PHREEQ calculations for all East Lake, Paulina Lake, and Lab Lake water samples can be accessed:
3.4.2 CO₂ Flux Rates

The flux data was analyzed using similar statistical techniques as Capece (2016), with modifications and corrections. The flux rate for each of the 58 East Lake sites and 11 Paulina Lake sites was determined by graphing the change in CO₂ concentration over time and creating a best fit line to determine the slope. The increase in CO₂ ppm per second was scaled by a factor K, which is based on the geometry of the float chamber and the ideal gas law:

\[ K = \frac{(86400 \times V/A \times P)}{(10^6 \times R \times T)} \]  
Equation 3.1

where \( P \) represents the barometric pressure in the accumulation chamber in hPa, \( R \) is the gas constant 0.0831451 hPa L K⁻¹ mol⁻¹, \( T \) is the gas temperature in Kelvin, and \( 0.167702 \) L is the volume of the chamber over the surface area of the base of the chamber (chamber height). Multiplying the linear increase in CO₂ over time with the \( K \) factor yields, the CO₂ evasion rate in moles of CO₂ m⁻² day⁻¹.

The flux rates for all measured points over each lake were averaged to determine the mean lake flux, and then this value was multiplied by the surface area of each lake (4220000 m² for East Lake and 6196000 m² for Paulina Lake) to get a first rough estimate of the total daily CO₂ evasion rate for each lake at that time. This value was then multiplied by the molar mass of CO₂, 44.01 g/mol, to convert the
daily CO\textsubscript{2} evasion from moles to metric tonnes of CO\textsubscript{2} evaded from the surface of each lake per day.

**3.4.3 Sequential Gaussian Simulations**

Sequential Gaussian Simulation (SGS) is a geostatistical technique used to interpolate the flux data, to estimate the total amount of CO\textsubscript{2} evading from the entire surface of the lake, and assess the uncertainty of these estimations. The SGS program involves a normal score transformation of the data, experimental variogram computation, variogram model assignation, sequential Gaussian simulation of equiprobable realizations, and generating simulated values through back-transforming normal score data (Padrón et. al, 2008). Four full SGS’s were completed using the statistical program R: 2015 East Lake fluxes, 2016 East Lake fluxes, combined 2015 and 2016 East Lake fluxes, and 2016 Paulina Lake fluxes. Because latitude and longitude does not directly correlate to meters and SGS depends on absolute distance, each flux point was graphed on a grid representing the lake and scaled by meters in each direction before interpolated. This step was not completed in 2015, which is why the results presented here are not identical to those in Capece (2016). For each of the four SGS, 1,000 interpolation simulations were generated and averaged.

**4. Results**

**4.1 East Lake Water Chemistry**

**4.1.1 Temperature**
East Lake surface waters in June 2016 were ~14°C, waters at 10 meters depth were ~8°C, and all deeper water was ~4.5-5.5°C. Thus, East Lake’s thermocline is at ~15 meters. The 2016 vertical depth profiles were taken in especially cold days for this early summer. East Lake epilimnion reaches temperatures of 19°C in the late summer months, while the hypolimnion remains ~5°C year-round.

4.1.2 Alkalinity
Figure 4.2: Bicarbonate concentrations with depth in Paulina Lake and East Lake in 2016.

Figure 4.3: Depth versus concentration bicarbonate based on alkalinity in East Lake waters. Depth profiles from the summers of 2011, 2012, 2014, 2015, and 2016, and surface water samples from May and November of 2016.
Figure 4.4: Molar concentrations of HCO$_3^-$ and dissolved CO$_2$ (or H$_2$CO$_3$) as the temperature increases from the coldest recorded field temperature to the lab temperature. Dissolved CO$_2$ (or H$_2$CO$_3$) decreases and the HCO$_3^-$ slightly increases with the decrease from lab to field temperatures. Speciation completed in Geochemist’s Workbench. Example is a water sample at 50m in East Lake.

Total alkalinity is largely carbonate alkalinity, with HCO$_3^-$ the main species at the close to neutral pH (Figure 4.2-4.4). The alkalinites determined by the titrator were converted into HCO$_3^-$ concentrations and plotted against depth (Figure 4.3). East Lake waters have ~124-135 ppm HCO$_3^-$ at all depths depending on the year, with no clear trend over the years (Figure 4.3). Paulina Lake has a high alkalinity, with ~400 ppm HCO$_3^-$ at all depths. The 2016 surface waters had significantly lower alkalinity whereas 10m deep waters had a significantly higher alkalinity than the mean at Paulina Lake. Water samples were taken in August 2011, August 2012, mid-June 2014, early July 2015, and early June 2016, so season effects should be considered, because carbonate speciation varies with temperature (Figure 4.4).
4.1.3 pH

Figure 4.5: Vertical pH profiles of East Lake waters sampled in 2016. The “lab” values were determined in the lab at 22°C through titration. The “field” values have been corrected to measured field water temperatures for each depth, which are significantly cooler than the lab temperature, using Web-PHREEQ. The pH values at all depths were also corrected to 5°C, as demonstrated by the “5C” values.

Figure 4.6: Vertical pH profile of Paulina Lake waters sampled in 2016. The “lab” values were determined in the lab at 22°C through titration. The “field” values have been corrected to the measured field water temperatures for each depth with Web-PHREEQ. The pH values at all depths were also corrected to 5°C, as demonstrated by the “5C” values.
Figure 4.7: Cooling of the fluid under closed system conditions leads to increased pH values through the shifting carbonate speciation with temperature. Example is a water sample at 50m in East Lake.

Paulina Lake had significantly higher pH than East Lake, 7-8.5 at all depths (Figures 4.5 and 4.6). Waters below the thermocline had pH consistently around 8.2, while surface waters had an elevated pH 8.5. The pH of water is highly affected by the temperature due to the shifting of carbonate speciation (Figure 4.7). Because pH values of all water samples were determined in the lab at 22°C, these values are underestimations of the pH of the actual water in the field. To more directly compare the pHs and other properties at different depths, water samples from both lakes at all depths were corrected to the actual field temperatures using Web-PHREEQ, as measured in temperature profiles in 2015 and 2016, as well as to 5°C, 15°C and 19°C.

As expected, the temperature corrected pH in both lakes almost always was approximately 0.2 higher than the warmer lab measurements. The pH values corrected to 5°C were slightly higher than the measured field water temperatures, and
this correction only changed values for the upper 20 meters of water, because the bottom waters are ~5°C year-round. At the measured field temperature, East Lake waters in both profiles had pH 6.8 at the surface, and then the pH decreased slightly at 10 meters, increased slightly at 20 meters, decreased at 30 meters, and then increased again at 40 meters. In the bottom water sample, EL1 showed similar pH values to the rest of the profile, while EL2 spiked to pH 7.9. Compared to the June depth profiles, May surface samples had low pH, and June hot springs and November surface samples had high pH. When corrected to field temperatures, Paulina Lake waters at 10 meters had a neutral pH, significantly less than the rest of the lake.

4.1.4 Dissolved Oxygen

![Dissolved Oxygen Graph](image)

Figure 4.8: Dissolved oxygen concentration in East Lake in 2016.

East Lake displays moderate dissolved oxygen concentrations above the thermocline at 0-15 meters of depth (8-8.5 mg/L). The decrease in DOX along the
water column is not very strong, but the percent oxygen saturation change is stronger because bottom waters get colder. Due to the limited cable length, no DO measurements were taken below 30 meters. Similar trends in DO with depth are recorded in Lefkowitz et. al (2016).

### 4.1.5 Conductivity

![Temperature Corrected Conductivity](chart)

Figure 4.9: Depth profile of conductivity (m\(\mu\)/cm) in East Lake from 2016.

The electrical conductivity of natural waters helps estimate the concentration of electrolytes in the water (Smith, 1962). Measured conductivities were corrected to 25°C, because water conductivity increases with temperature and the steep temperature gradient make the raw data not comparable. East Lake surface water has a conductivity of 0.349 m\(\mu\)/cm and steadily increases with depth to 0.365 m\(\mu\)/cm in the bottom waters. At 40 meters, the conductivity decreases slightly, but this may be
well in the analytical noise (+/- 0.001). Still, the conductivity increases with depth about 4% which is under isochemical conditions a change in speciation or there is a concentration gradient with depth.

4.1.6 PCO₂

Figure 4.10: Vertical PCO₂ profiles of East Lake waters sampled in 2016. The “field” values have been corrected to measured field water temperatures for each depth, which are significantly cooler than the lab temperature, using Web-PHREEQ. The PCO₂ values at all depths were also corrected to 5°C, as demonstrated by the “5C” values.
At the field temperature, East Lake has higher PCO₂ than Paulina Lake (Figures 4.10 and 4.11). East Lake PCO₂ is around 0.01 to 0.03 atm, with a sharp decrease to 0.001 atm in at 45 meters in EL1. Paulina Lake surface waters have a PCO₂ of 0.0006 atm and increase with depth to 0.003 atm in the bottom waters. At 10 meters, the pCO₂ in Paulina Lake water increases dramatically to 0.029 atm when corrected to 5°C and to 0.037 atm when corrected to the field temperature in June (12°C). The PCO₂ under field conditions was calculated based on carbonate speciation from Web-PHREEQ. The temperature of the water and thus the season directly affects the PCO₂ in water, because PCO₂ increases with temperature at constant total carbonate (Figure 4.12).
Figure 4.12: Temperature decrease leads to a much lower FCO\(_2\) and PCO\(_2\) in the solution at constant carbonate. FCO\(_2\) and PCO\(_2\) are nearly identical at these low pressures. Example is a water sample at 50m in East Lake.

4.1.7 Major Cations

Figure 4.13: Sodium and potassium concentrations in East Lake and Paulina Lake profiles from 2016.
Figure 4.14: Calcium and magnesium concentrations in East Lake and Paulina Lake profiles from 2016.

Figure 4.15: Silica concentrations in East Lake and Paulina Lake profiles from 2016.
Figure 4.16: Sodium concentrations in East Lake and Paulina Lake in 2011, 2012, 2014, 2015, and 2016.


Figure 4.19: Calcium concentrations in East Lake and Paulina Lake in 2011, 2012, 2014, 2015, and 2016. East Lake waters trends are shown in warm colors, and Paulina Lake waters are shown in cool colors.
Water samples from all depths of East Lake and Paulina Lake in 2011, 2012, 2014, 2015, and 2016 were compared for major cation concentrations. In general, the two lakes had concentrations on the same order of magnitude, though Paulina Lake tended to have higher cation concentrations for every element. East Lake and Paulina Lake had sodium concentrations around 25 ppm and 50 ppm, respectively, with little variation with depth. In both lakes, the concentrations of sodium increases over time, with an increase of ~0.5-1.5 ppm per year (Figures 4.13 and 4.16). For all years and depths, East Lake had around 4 ppm potassium, and Paulina Lake had around 5-5.5 ppm (Figures 4.13 and 4.17). Magnesium concentrations were the most different in each lake, with ~12-13 in East Lake and ~42-43 in Paulina Lake at all depths (Figures 4.14 and 4.18). East Lake waters have 5-7 ppm silica in all years, trending toward
higher values in bottom waters (Figures 4.15 and 4.20). Paulina Lake waters have ~20 ppm silica in every year but 2016, which had a concentration of ~18 ppm. The two lakes have extremely similar calcium concentrations, ~24-29 ppm, with slightly lower concentrations in the epilimnion than the hypolimnion (Figures 4.14 and 4.19).

4.1.8 Major Anions

Figure 4.21: The Cl⁻ concentrations in water samples from the Paulina Lake 2016 depth profile and East Lake 2016 two depth profiles, hot springs, and May and November surface waters.
Figure 4.22: The $\text{SO}_4^{2-}$ concentrations in water samples from the Paulina Lake 2016 depth profile and East Lake 2016 two depth profiles, hot springs, and May and November surface waters.

Figure 4.23: The $\text{SO}_4^{2-}$ versus $\text{Cl}^-$ concentrations in water samples from the Paulina Lake 2016 depth profile and East Lake 2016 two depth profiles, hot springs, and May and November surface waters. The chemical composition of the waters from each of these five groups is very distinct.
East Lake and Paulina Lake waters have very different concentrations of major anions. Paulina Lake has more chloride, while East Lake has significantly more sulfate. East Lake waters consistently have ~0.7 ppm chloride, with a peak to two ppm at 30 meters. Slightly higher concentrations of chloride were found in East Lake surface waters near the hot springs and in May 2016. Paulina Lake surface waters had 11 ppm chloride, while the bulk of the lake’s water had about 4 ppm. All depths of East Lake waters have ~63 ppm sulfate in the summer and fall of 2016, through the hot springs had significantly less (~39 ppm) and the surface waters in May were enriched (~76 ppm). Paulina Lake waters uniformly had about four ppm of sulfate at all depths. Because the two lakes, their hot springs and different temporalities have such distinct chemical compositions, they all plot in clear clusters on a graph of sulfate versus chloride concentration. Nitrate peaks were also monitored in IC analysis, but Paulina core pore water was the only sample with significant nitrate concentrations, with 5.4 ppm.

4.1.9 Phosphorus
Figure 4.24: Phosphorus concentrations in water samples from the Paulina Lake 2016 depth profile and East Lake 2016 two depth profiles, hot springs, and May and November surface waters.

Phosphorus concentrations in the two lakes are similar and vary with depth between ~5-17 ppb, with Paulina Lake slightly more depleted than East Lake. East Lake surface samples from the early summer and late fall also have phosphorus concentrations on that scale. Hot springs waters at significantly higher concentrations, ~39 ppb. Concentrations fell on the low end of the range of ICP standards and although the values will be low, the accuracy may not be very good (+/- 10%).

4.2 Stable Isotopes

4.2.1 Water: δD and δ^{18}O
Figure 4.25: Stable oxygen isotopic composition ($\delta^{18}$O‰) of East Lake waters from two water depth profiles collected in 2016.

Figure 4.26: Stable oxygen isotopic composition ($\delta^{18}$O‰) of East Lake, Paulina Lake and East Lake Hot Springs waters from 2016.
The $\delta^{18}O$ in the two East Lake water profiles have values of -8.6 to -8.0‰, with a slight depletion in the surface water sample at -8.6‰ (Figure 4.25). East Lake hot springs have waters that are significantly lighter, with $\delta^{18}O = -12‰$. The Paulina Lake waters have a narrow range of $\delta^{18}O$ values with depth, around -11.3‰ (Figure 4.26). The East Lake trend with depth suggest a weak trend of heavier water towards the surface.

**Stable Isotopes of Hydrogen in East Lake, Paulina Lake and East Lake Hot Springs Waters**

![Graph](image_url)

Figure 4.27: Stable hydrogen isotopic composition ($\delta^{D}‰$) of East Lake, Paulina Lake and East Lake Hot Springs waters from 2016. Use same symbols and colors for $\delta^{18}O$

The two East Lake profiles display different trends in $\delta^{D}$ with depth. EL1 has $-77.2‰$ in the surface water and trends heavier until -75.1‰ at 20 meters, and steadily becomes heavier with depth until reaching -75.7‰ at 50 meters. EL2, on the
other hand, is extremely enriched in the surface waters with δD -58.5‰ and trending lighter until 75.1‰ at 20 meters, and then becomes more enriched throughout the bottom waters until -72.2 at 42 meters. East Lake hot springs waters have more depleted δD (-94.4‰). The Paulina Lake waters have δD values of -91 to -89‰ with the lighter values toward greater depths.

4.2.3 DIC: δ¹³C

![Figure 4.28: Profiles of δ¹³C (DIC) in 2016 East Lake and Paulina Lake waters.](image)
Figure 4.29: Variations in the $\delta^{13}$C (DIC) gradient in East Lake with water depth over the past four field seasons. Profiles were taken during different months in each year.

Figure 4.30: Trend in the $\delta^{13}$C (DIC) with Paulina Lake water depth over the past four field seasons. Profiles were taken during different months in each year.
East Lake’s surface waters in 2016 had δ¹³C ~4.5‰, and bottom waters had δ¹³C ~2‰, depending on the year. Paulina Lake DIC was constant with depth at δ¹³C ~0‰. Profiles were taken in different months each year, so it is difficult to conclusively determine any compositional trends between years, though it seems the waters are getting slightly heavier over the years.

The three East Lake surface water samples taken in May 2016 have δ¹³C ~1.9‰, and the five surface water samples obtained in November had δ¹³C ~1‰. These values, compared to the ~4.4‰ in the surface water samples from June 2016, suggest a trend of enrichment of surface water throughout the season. East Lake hot springs water from 2016 was relatively light, with δ¹³C ~2.6.

4.3 CO₂ GAS

4.3.1 Flux Data

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Table 4.1: Fifty-seven flux measurements collected over East Lake in the summer of 2016.
Fluxes are calculated by scaling the observed linear rise in CO$_2$ concentration over time with a temperature-dependent factor that contains also the sampling...
geometry (K, equation XX). The CO$_2$ flux rate from East Lake ranged between 0.03 and 0.9 moles CO$_2$ m$^{-2}$ day$^{-1}$ in 2015 and 2016 (Figure 6). The average East Lake flux rate in 2015 was ~0.2 moles CO$_2$ m$^{-2}$ day$^{-1}$, providing a lake-wide CO$_2$ emission rate of ~45 tonnes per day (Capece, 2016). The East Lake CO$_2$ flux rates were slightly higher in 2016, with an average flux of 0.3 moles CO$_2$ m$^{-2}$ day$^{-1}$ and a total surface loss of ~72.5 tonnes CO$_2$ per day. Different values are at different locations. The three draw-down build-up experiments had flux rates of 0.19, 0.49, and 0.35 moles CO$_2$ m$^{-2}$ day$^{-1}$, slightly higher than regular East Lake fluxes.

The Paulina Lake CO$_2$ flux rates ranged from 0.04 to 0.35 moles CO$_2$ m$^{-2}$ day$^{-1}$ in 2016, slightly lower than at East Lake, with an average of ~0.17 moles CO$_2$ m$^{-2}$ day$^{-1}$ (although there were much fewer data points with less spread through the lake). Based on these limited data, Paulina Lake’s surface still evades a similar amount of CO$_2$ as East Lake (~46 tonnes per day), because it has 50 percent more surface area than East Lake.
Image 4.3: Screenshot of ArcGIS Online map of CO₂ flux rates over East Lake from 2015 and 2016 and over Paulina Lake from 2016. The interactive webmap can be seen here: https://arcg.is/1yn5v8. By clicking on any point, one can see the exact GPS coordinates and the flux measurement. Round symbols are from 2016, and square symbols are from 2015.

4.3.2 δ¹³C and δ¹⁸O Chamber and Ambient Gas

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<td>-10.7</td>
<td>-16.9</td>
<td>Wyoming</td>
<td>ELA</td>
<td>June</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HPEL air5</td>
<td>-10.1</td>
<td>-18.5</td>
<td>Wyoming</td>
<td>ELA</td>
<td>June</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HPEL air6</td>
<td>-10.0</td>
<td>-18.0</td>
<td>Wyoming</td>
<td>ELA</td>
<td>June</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HPEL air7</td>
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<td></td>
<td>UC Davis</td>
<td>ELB</td>
<td>June</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HPEL air8</td>
<td>-10.2</td>
<td>-20.4</td>
<td>Wyoming</td>
<td>ELB</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>EL 5-28-1-A</td>
<td>-10.9</td>
<td>-20.4</td>
<td>Wyoming</td>
<td>ELA</td>
<td>May</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EL 5-28-1-B</td>
<td>-10.7</td>
<td>-20.5</td>
<td>Wyoming</td>
<td>ELA</td>
<td>May</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EL 5-28-2-B</td>
<td>-11.1</td>
<td>-20.4</td>
<td>Wyoming</td>
<td>ELB</td>
<td>May</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EL 5-28-3-A</td>
<td>-12.6</td>
<td>-19.8</td>
<td>Wyoming</td>
<td>ELA</td>
<td>May</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EL 5-28-3-B</td>
<td>-10.5</td>
<td>-21.7</td>
<td>Wyoming</td>
<td>ELB</td>
<td>May</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EL 1A Nov16</td>
<td>-10.8</td>
<td>-19.9</td>
<td>Wyoming</td>
<td>ELA</td>
<td>November</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EL 2A Nov16</td>
<td>-10.6</td>
<td>-20.0</td>
<td>Wyoming</td>
<td>ELA</td>
<td>November</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EL 1B Nov16</td>
<td>-10.8</td>
<td>-20.1</td>
<td>Wyoming</td>
<td>ELB</td>
<td>November</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EL 2B Nov16</td>
<td>-11.0</td>
<td>-19.6</td>
<td>Wyoming</td>
<td>ELB</td>
<td>November</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EL 3A Nov16</td>
<td>-10.5</td>
<td>-20.0</td>
<td>Wyoming</td>
<td>ELC</td>
<td>November</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EL 3B Nov16</td>
<td>-10.1</td>
<td>-19.6</td>
<td>Wyoming</td>
<td>ELC</td>
<td>November</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4: Carbon and oxygen isotopic composition of ambient air samples collected above and near East Lake in May, June, and November 2016. Coordinates of sampling sites in Table XX (in methods, locations of ambient air sampling sites).

Isotopic analysis of some gas samples was completed at UC Davis and some at UWyoming. Samples analyzed at UWyoming where analyzed for $\delta^{13}$C and $\delta^{18}$O,
while samples run at UC Davis were just analyzed for δ13C. There is the potential of inter-instrument variability or a difference in standards and calibration. Most of the 2016 samples with δ13C ~ -9‰ were measured at UWyoming, while the rest of the chamber samples with δ13C ~ -11 to -10‰ were analyzed at UC Davis. It is possible that the UWyoming instrument preferentially gave higher δ18O signatures with higher CO₂ concentrations. However, because δ18O and δ13C were run together, there would also be visible errors in δ13C CO₂ (gas).

Based on the temperature-dependent equilibrium fractionation factor for the exchange of oxygen between CO₂ and water is

$$\varepsilon_{eq}(T) = \frac{17604}{T} - 17.93 \text{ (Affek and Yakir, 2003)}$$  \hspace{1cm} \text{Equation 4.1}

where T is degrees Kelvin and dε_{eq}/dT = -0.20‰°C. At 25°C, equilibrium fractionation between CO₂ and water is 41.11‰ ± 0.07‰. This fractionation factor is almost exactly compensated by the difference between the V-PDB-CO2 and V-SMOW scales (Affek and Yakir, 2003). Thus it is convenient to compare δ18O CO2 on the V-PDB scale with δ18O H2O on the V-SMOW scale.

4.4 Biota

4.4.1 δ¹³C, and δ¹⁵N, C:N Pine Needles and Nostoc Balls
### Table 4.5: Weight percent of carbon and nitrogen and C:N ratio of pine needles and nostoc balls collected at various locations in and around East Lake and Paulina Lake in 2012 and 2016. Each sample was run on the EA twice to account for sample heterogeneity, and the two C:N values for each sample were averaged.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample type</th>
<th>Site</th>
<th>Date collected</th>
<th>weight % N</th>
<th>weight % C</th>
<th>C:N</th>
<th>C:N Mean (duplicates)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EL1A-1</td>
<td>pine needles</td>
<td>East Lake Resort</td>
<td>11/14/16</td>
<td>1.18</td>
<td>47.92</td>
<td>40.56</td>
<td></td>
</tr>
<tr>
<td>EL1A-2</td>
<td>pine needles</td>
<td>East Lake Resort</td>
<td>11/14/16</td>
<td>1.27</td>
<td>47.89</td>
<td>37.73</td>
<td>39.14</td>
</tr>
<tr>
<td>EL1B-1</td>
<td>pine needles</td>
<td>East Lake HS Boat Ramp</td>
<td>11/14/16</td>
<td>1.54</td>
<td>46.80</td>
<td>30.42</td>
<td></td>
</tr>
<tr>
<td>EL1B-2</td>
<td>pine needles</td>
<td>East Lake HS Boat Ramp</td>
<td>11/14/16</td>
<td>1.49</td>
<td>47.5544</td>
<td>32.00</td>
<td>31.21</td>
</tr>
<tr>
<td>ELCO-1</td>
<td>nostoc balls</td>
<td>East Lake</td>
<td>8/17/12</td>
<td>11.87</td>
<td>41.3864</td>
<td>3.49</td>
<td></td>
</tr>
<tr>
<td>ELCO-2</td>
<td>nostoc balls</td>
<td>East Lake</td>
<td>8/17/12</td>
<td>12.20</td>
<td>41.2606</td>
<td>3.38</td>
<td>3.43</td>
</tr>
<tr>
<td>LPAWS1-1</td>
<td>nostoc balls</td>
<td>Paulina Lake</td>
<td>8/18/12</td>
<td>6.19</td>
<td>21.4590</td>
<td>3.47</td>
<td></td>
</tr>
<tr>
<td>LPAWS1-2</td>
<td>nostoc balls</td>
<td>Paulina Lake</td>
<td>8/18/12</td>
<td>6.76</td>
<td>24.2091</td>
<td>3.58</td>
<td>3.54</td>
</tr>
<tr>
<td>LPA-1</td>
<td>nostoc balls</td>
<td>Paulina Lake</td>
<td>8/18/12</td>
<td>5.72</td>
<td>29.7458</td>
<td>5.20</td>
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</tr>
<tr>
<td>LPA-2</td>
<td>nostoc balls</td>
<td>Paulina Lake</td>
<td>8/18/12</td>
<td>8.56</td>
<td>39.4275</td>
<td>4.61</td>
<td>4.90</td>
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</tbody>
</table>
Table 4.6: Carbon and nitrogen isotopic composition of pine needles and nostoc balls collected at various locations in and around East Lake and Paulina Lake in 2012 and 2016. Each sample was run on the mass spectrometer twice to account for sample heterogeneity, and the two $\delta^{13}$C and $\delta^{15}$N values for each sample were averaged.

<table>
<thead>
<tr>
<th></th>
<th>Paulina Lake</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LPAWS1-1 nostoc</td>
<td>Paulina Lake</td>
<td>4.09</td>
<td>-10.23</td>
</tr>
<tr>
<td>balls</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>LPAWS1-2 nostoc</td>
<td>Paulina Lake</td>
<td>3.82</td>
<td>-12.74</td>
</tr>
<tr>
<td>balls</td>
<td></td>
<td>3.95</td>
<td>-11.48</td>
</tr>
<tr>
<td>LPA-1 nostoc</td>
<td>Paulina Lake</td>
<td>-0.15</td>
<td>-13.84</td>
</tr>
<tr>
<td>balls</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPA-2 nostoc</td>
<td>Paulina Lake</td>
<td>-0.20</td>
<td>-14.96</td>
</tr>
<tr>
<td>balls</td>
<td></td>
<td>-0.18</td>
<td>-14.40</td>
</tr>
</tbody>
</table>

East Lake pine needles are lighter in $\delta^{13}$C and have higher C:N than East Lake nostoc balls (Table 4.6). East Lake nostoc ball have similar isotopic compositions as East Lake samples from previous years, while Paulina Lake nostoc balls have compositions closer to East Lake nostoc balls rather than Paulina Lake nostoc ballss from previous years (Capece, 2016).

4.5 Kiddie Pool Experiment

4.5.1 Flux Data

Lab experiments were completed to test the flux models and methodology for field build-up and draw-down build-up experiments. Ten total kiddie pool experiments were completed, including draw-down, build-up, and ambient. The trends in CO$_2$ flux rates were similar for duplicates of each of the three types of kiddie pool experiments, so a few typical graphs are displayed below.
In both of these draw-down experiments and in the two other draw-down experiments run, CO$_2$ initially decreased rapidly and eventually leveled out at a steady state concentration. In the first run of the draw-down experiment (Figure 4.33), CO$_2$ was pumped out of the chamber at 1.88 liters per minute, and the CO$_2$ in the chamber decreased from 560 ppm to a steady state of 33 ppm. During the second run, the pump was set to 3.995 liters per minute, and the CO$_2$ in the chamber decreased from 81 ppm to 4 ppm. Despite the faster pump out rate, the second run had a smaller, less negative slope due to the lower initial CO$_2$ concentration than the first draw-down experiment. The second run reached a lower equilibrium concentration of CO$_2$ (4 ppm versus 33) due to the higher pump rate.
During the third of five kiddie pool runs (Figure XX), ambient room CO$_2$ was pumped into the chamber, and the CO$_2$ in the chamber increased from 43 ppm to 470 ppm. The CO$_2$ concentration in the chamber at first increased rapidly and eventually leveled out at approximately the lab air concentration. At the time of the experiment, ambient lab air was approximately 470-500 ppm, depending on how many people where in the room and time of day (Figure 4.35).
When the CO₂ absorber was removing the CO₂ from the chamber, the chamber air never reached a steady state of 0 ppm. Thus it was hypothesized that there must be an additional source of carbon in the kiddie pool, such as ambient carbon absorbed by the tap water and degassed once the PCO₂ in the kiddie pool water was equivalent to or greater than the PCO₂ in the chamber. To determine the rate of carbon leakage, the chamber air was first pumped down as low as possible, to a steady state 41 ppm. When the pool and chamber air was not manipulated (no CO₂ pumped into or out of the water or chamber), and 0.00162 ppm of CO₂ per second entered the chamber through leakage.

4.6 Lab Lake Experiment
To create the Lab Lake water, NaHCO$_3$ and HCl were mixed into DI water. Stoichiometric calculations and titrations on test mixtures were performed in advanced in the hopes of creating similar pH, alkalinity, and PCO$_2$ in Lab Lake water as East Lake. The initial Lab Lake water with just the bicarbonate and DI water had pH 6.5 and alkalinity 0.00206. The final Lab Lake water with all components after the experiment ran had pH 6.08 and alkalinity 0.00206 mol/L. This was close to East Lake water, which has a pH ~6.5 and an alkalinity ~0.00220 mol/L. Both the initial and final solution had 0.004464 mol/L Na and 0.0021 mol/L Cl. The initial solution had 0.00446 mol/L DIC, and the final solution had approximately 0.00438 mol/L DIC.

4.6.1 Flux data

Figure 4.36: Concentration of CO$_2$ in the headspace of Lab Lake over the course of the experiment.
A linear increase of 4.5 ppm CO$_2$ per second was measured in the headspace of Lab Lake that had degassed from the water. Over East Lake, a linear rise of 0.7 ppm CO$_2$ per second was determined during degassing into the chamber. A flux value was calculated by scaling the linear rise in concentration per second by the temperature-dependent K-factor (Equation 3.1). Lab Lake and East Lake had similar K factors, though slightly higher for East Lake. In East Lake, the calculated flux was 0.4 moles/m$^2$/day, while in Lab Lake, the calculated flux was 1.95 moles/m$^2$/day. Thus, if Lab Lake were East Lake, it would diffuse 329 tonnes CO$_2$ per day.

4.6.2 Gas and Water Isotopes

Figure 4.37: Isotopic composition of CO$_2$ gas in the headspace of Lab Lake, which evaded from the Lab Lake water, in relation to the concentration of gas in the headspace.
With an increase in concentration of CO₂ in the cell from 300 to 3100 ppm, the δ¹³C of headspace CO₂ decreased steadily from ~ -9 to -11‰. The δ¹⁸O headspace CO₂ increased significantly from 300-1400 ppm, at which point it started increasing less per amount of CO₂ added. Periodically, the δ¹⁸O would decrease slightly, but in the following measurement, the δ¹⁸O would increase significantly.

Initial water samples of just DI water and bicarbonate and final water samples of all three components after degassing where analyzed for δ¹⁸O, δD, and δ¹³C. The initial water had δD -57‰, the final water had δD -56‰, which is not a statistical valid difference, because values are within 2‰ analytically. Both water samples had δ¹⁸O -8.9‰. Lab Lake δ¹³C DIC started at -7‰ and ended at -4.8‰ after the degassing experiment.

5. Discussion

5.1 Water Chemistry

5.1.1 General Water Chemistry

Although East Lake and Paulina Lake are both associated with Newberry Volcano, their waters exhibit very different chemical compositions. The difference in their water chemistries can be attributed to differences in geothermal sources, because East Lake has gaseous input, while Paulina Lake has hot aqueous input (Lefkowitz et al, 2016). East Lake waters are neutral (pH ~6.8) and Paulina Lake waters tend toward alkaline (pH ~8) (Figures 4.5 and 4.6), while most volcanic lakes are highly acidic (Mazot and Bernard, 2015). Samples from 2016 show that Paulina Lake waters
are more concentrated in major cation and anion species than East Lake. Paulina Lake has approximately double the concentration of sodium, 1.5 times the concentration of potassium, four times the concentration of magnesium, three times the concentration of silica, and four times the concentration of chloride as East Lake. The overall concentrations of silica in both lakes are high for a freshwater lake, despite the silica removal by diatoms (Lefkowitz et. al, 2016). The two lakes are also relatively rich in magnesium, which is common for CO₂-rich volcanic lakes, because their geothermal inputs interchange with magnesium rich-basalt (Varekamp, 2015). The two lakes have identical concentrations of calcium, and East Lake has significantly more sulfate (~63 ppm in East Lake and ~4 ppm in Paulina Lake), likely due to oxidation of geothermal H₂S (Figure 4.22; Lefkowitz, 2012).

The significantly greater concentration of dissolved ions in Paulina Lake than East Lake suggests that Paulina Lake’s hydrothermal input is more concentrated in dissolved species than East Lake’s, because both lakes have similar meteoric inputs. Paulina Lake gets true fluid input with dissolved species, while East Lake’s geothermal input is largely gaseous. The little bit of moisture in the gaseous input brings fewer dissolved ions into East Lake. Cation and anion concentrations in both lakes are constant with depth, indicating that the lakes do not have a chemocline. This is surprising, because most of the dissolved species enter the lakes subaqueously, so ionic concentrations are expected to increase in the hypolimnion and as the waters stratify through the summer. However, over the six years studied, with samples taken in all summer months, ionic concentrations in the lakes have remained constant with depth, indicating that no significant extractions or additions occur after the winter
mixing events. This is important, because it suggests that models based on 2016 field measurements can be extrapolated to the lakes in all years under typical conditions.

While the two lakes have unique properties due to their volcanic inputs, East Lake and Paulina Lake are in many ways typical oligotrophic, dimictic lakes (Wetzel, 2001). Vertical temperature profiles from June 2016 demonstrate clear summer stratification in East Lake and Paulina Lake waters into a warmer epilimnion (0-15m) and cold hypolimnion (15 m-bottom) (Figure 4.1). East Lake and Paulina Lake bottom waters tend to have higher alkalinities and conductivities and more bicarbonate and phosphorus than surface waters (Figures 4.2, 4.3, 4.9, 4.24). Contrastingly, surface waters have significantly higher dissolved oxygen concentrations than bottom waters (Figure 4.8). As the summer progresses, surface waters gain higher pH values and bottom waters pH lowers (Figure 5.1). These trends can at least partially be attributed to the processes of photosynthesis and respiration. During the summer months, in a stratified lake where photosynthesis is limited to the epilimnion, surface waters become depleted in carbon, nitrogen, and phosphorus, because photosynthesis uptakes all of these elements (Baker, 1994). Much of the organic matter gets respired in situ or eaten by other organisms, while some of it falls to the hypolimnion, increasing concentrations of dissolved solids and thus water conductivity. Some of the organic matter is buried in bottom sediment, as seen in sediment cores. Bacteria decomposes some of the organic matter, liberating carbon, nitrogen, and phosphorus into the bottom waters. The hypolimnion becomes enriched in these elements because the water is too deep and dark for them to be taken up during photosynthesis (Baker, 1994). Well-oxygenated surface waters can be
attributed to oxygen production by zooplankton, phytoplankton, and other photosynthesizers, and hypoxic bottom waters due to respiration. The rise in surface water pH and alkalinity as the summer progresses can also be attributed to increased photosynthesis, which diminishes the aqueous CO$_2$ pool (4.29; Kling et. al, 1992).

![East Lake Water pH Shift Over Summer](image)

Figure 5.1: Trend in pH of East Lake surface waters during part of year that the lake is not frozen over. Data from 2011-2016 collected in different months every year.

The concentration and isotopic composition of other elements are also affected by biological processes. Dissolved oxygen levels in upper 15 meters are higher than the bottom waters (Figure 4.8, Results DO). Surface DO is supplied through photosynthesis and levels remain constant in the surface waters throughout the summer because O$_2$ is constantly exchanging with the atmosphere through diffusion. In the hypolimnion, however, there is no photosynthesis or atmospheric regulation, so any oxygen lost during bacterial respiration is not immediately replaced (Baker, 1994). New anoxic, bacteria-mediated reactions can occur in the oxygen-free
bottom waters, including the reduction of $\text{SO}_4^{2-}$ to $\text{H}_2\text{S}$. East Lake bottom waters are depleted in $\text{SO}_4$ relative to surface waters (Figure 4.22), likely due to the bacterial reduction (Baker, 1994).

Water composition is also affected by the photosynthetic organisms themselves. Opaline silica diatoms fall into the hypolimnion and dissolve. As a result, bottom waters become slightly enriched in silica (Figures 4.15 and 4.22; Capece, 2016). Bottom waters tend to be more acidic, due to the production of carbonic acid from respiratory CO$_2$ and the massive CO$_2$ input from below. Paulina Lake waters demonstrate this trend, while the trend in pH with depth in East Lake is less clear (Figures XXs, from Results).

Paulina Lake has ~3% carbon in its sediment, while East Lake has ~8% (Lefkowitz, et. al, 2016). This disparity in sediment organic carbon suggests that Paulina Lake has lower primary productivity than East Lake. Deeper lakes tend to have lower rates of primary productivity than shallow lakes, because they receive less sunlight (Wetzel, 2001).

5.1.2 Water Stable Isotopes

The effects of evaporation, precipitation and water mixing on East Lake and Paulina Lake’s hydrological cycles can be understood by looking at the stable isotope composition of water in the lakes and local meteoric waters. The local meteoric water line (LMWL) for Oregon was determined based on the stable isotopic composition of Oregon rivers (Kendall and Coplen, 2001; Lefkowitz et. al, 2016). All of the Newberry lake data from 2012, 2014, 2015, and 2016 plots on a single evaporation
line (dotted line in Figure 5.2). Both East Lake (light and dark blue squares) and Paulina Lake (pink and red triangles) water and hot springs samples from 2011 are more isotopically evolved, and plot on an evaporation line with a slightly less steep slope (dashed line in Figure 5.2). Local meteoric water has $\delta^{18}O \approx -15\%$ and $\delta D \approx -114\%$, which is close to the intersection of the LMWL and the lake evaporation lines. In both lakes over all the years, surface water samples have the highest $\delta D$ and $\delta^{18}O$, due to the combined effects of evaporation (farther up evaporation line) and precipitation (closer to LMWL). One 2016 East Lake surface water sample plots on the local meteoric water line, because of the rain and snowfall during the week of sampling. Hot spring waters from both lakes plots close to the local meteoric water endmember. Due to the isotopic similarity between the local meteoric water and the hot spring waters, it is not possible to determine the exact composition and amount of geothermal water input from an isotope mass balance.

There are a few reasons why East Lake and Paulina Lake waters were more evolved in 2011 than in more recent years. Precipitation rates were lower than usual in 2011, so lake levels were lower (Lefkowitz, 2012). The meteoric water endmember was less abundant and the effects of evaporation were more pronounced. Another reason the 2011 samples are more evolved is that they were taken mid-August, after a full summer of evaporation had occurred. Samples from 2014 and 2015 were taken in July, and 2016 samples were taken in June. The 2016 water samples plot the closest to the local meteoric water line, because they were taken relatively shortly after a large amount of meteoric water was being added to the lakes from melting snow running off the mountains. Employees of the East Lake Resort noted that lake water
levels were lower in 2016 than usual due to less precipitation (Weather Underground). However, the stable isotope composition of 2016 lake water is much less evolved than the 2011 lake water and very similar to the composition of waters in 2012, 2014, and 2015, when the lakes experienced normal precipitation rates. Thus, the slight decrease in precipitation and potentially lake level in 2016 likely did not affect the water composition in a significant way.

Figure 5.2: Water stable isotopes in samples from 2011, 2012, 2014, 2015, and 2016, with meteoric water samples and literature signatures (Kendall and Coplen, 2001; Lefkowtiz et. al, 2016). East Lake samples are filled squares, and Paulina Lake samples are filled triangles. Water samples from both lakes from 2012 and 2014-2016 are plotted on an evaporation line (dotted line). Water samples from 2011 are more isotopically evolved in both lakes, so they plot on a less steep evaporation line (dashed line).

5.1.3 DIC
The dominant inputs of carbon into East Lake and Paulina Lake are geothermal input (gas in East Lake and fluid in Paulina Lake) and respiration of biotic matter. Major sinks of carbon are surface degassing into the atmosphere, photosynthesis, and organic matter burial. The sources and sinks of carbon in the lakes have different isotopic values and can thus be used as endmembers in isotopic mixing models, to trace lake DIC, and to understand the limnological processes and fractionation that determines the observed $\delta^{13}$C CO2 values. The $\delta^{13}$C (DIC) values are extremely high in East Lake surface waters, and the gradient in $\delta^{13}$C (DIC) with depth can be up to 4‰. This gradient seems to build up over the summer season and is likely caused by degassing and photosynthetic fractionation in surface waters and the addition of light CO$_2$ in the bottom waters. Due to the strong gradient, it is unlikely that East Lake waters fully mix throughout the summer. The gradient is erased during holomixis in the fall (Figure 5.50). The $\delta^{13}$C (DIC) gradient in PL is much weaker (~0.5‰) and surface values are close to 0‰. The $\delta^{13}$C (DIC) gradients for the years 2011, 2014, 2015 and 2016 (Figure 4.29) represent both seasonal and secular influences in East Lake. Because of the unique trends in carbon composition in East Lake, the amounts and isotopic compositions of sources, sinks, and fractionation processes within East Lake are explored here.
Both East Lake and Paulina Lake had relatively constant DIC concentrations with depth in June 2016 (Figure 5.3). East Lake waters tended to have around 0.003 mol/L at all depths, with slightly lower values in the surface waters, while Paulina Lake waters generally had over double the concentration, at around 0.0067 mol/L. Paulina Lake surface waters had less carbon than the rest of the profile, 0.00505 mol/L, and waters at 10 meters showed a significant spike in carbon, 0.00897 mol/L. The slight depletion in carbon in the surface waters of both lakes was also noted in East Lake in 2015, and could be due to the withdrawal of carbon through degassing and photosynthetic processes (Capece 2016).

East Lake surface waters displayed decreasing quantities of carbon as the season progressed from May to November 2016. This could be due to the increased photosynthetic uptake of carbon as the summer progresses and the weather warms.
With increasing temperature, the solubility of CO$_2$ in water decreases (Henry’s Law constant $K_H$ increases), so more degassing might occur in the warmer late summer months. Additionally, the May and June water samples were taken shortly after the lake thawed and turned over, and perhaps some residual carbon that had built up during the winter had not yet been released.

![Figure 5.4: Total dissolved carbon in East Lake over the years sampled.](image)

A comparison of total lake wide DIC in East Lake over the years sampled based on Web-PHREEQ calculations shows slight variations over the years (Figure 5.4). In 2011, East Lake had about 3000 tonnes of carbon, which decreased to about 2500 in 2012 and 2014. Carbon content in 2015 and 2016 increased to almost 4000 tonnes. Water samples were taken at different times in all years (August 2011, August 2012, mid-June 2014, July 2015, early June 2016). Seasonal cycles could also explain
the difference in total DIC over the years, because the lake tends to lose carbon to
degassing and to photosynthates as the season progresses (Figure 5.3). In the early
summer, some residual DIC built up over the winter could remain in the water
column, accounting for elevated DIC concentrations in 2015 and 2016 samples.

Additionally, this comparison assumes constant lake volume over all the
years, because the total quantity was calculated by scaling that year’s DIC
concentration by the average lake volume. Bend saw significantly less precipitation
than average in 2011 and slightly less in than average in 2015 and 2016. Lake levels
might have been lower in those years, making the total lake DIC shown here an
overestimation (U.S. Climate Data). Based on the volume and total DIC reservoir of
the lake, if lake water levels were two meters lower during dry years, the total DIC
would be 372 tonnes less than in Figure 5.4. Then, total DIC in 2011 would be nearly
identical to 2012 and 2014, while 2015 and 2016 would still have higher
concentrations. Thus, East Lake probably has relatively constant DIC concentrations
over the years, and variations in measured values are due to seasonal effects and
precipitation patterns.
Figure 5.5a: Calculated $\delta^{13}$C CO$_2$ (aq) in East Lake as a function of water temperature, which is dependent on depth. Based on carbon speciation completed using Geochemist’s Workbench, Web-PHREEQ, interspecies fractionation factors, $\delta^{13}$C of total DIC, and mixing model. The “field” values have been corrected to measured field water temperatures for each depth, and the “5C”, “15C”, and “19C” samples were corrected to water conditions at 5°C, 15°C, and 19°C, respectively.

Figure 5.5b: Calculated $\delta^{13}$C CO$_2$ (aq) in Paulina Lake as a function of water temperature, which is dependent on depth. Based on carbon speciation completed using Web-PHREEQ, interspecies fractionation factors, $\delta^{13}$C of total DIC, and mixing model. The “field” values have been corrected to measured field water temperatures for each depth, and the “5C” samples were corrected to water conditions at 5°C.
Theoretical $\delta^{13}C$ CO$_2$ can be calculated from the measured $\delta^{13}C_{\text{DIC}}$, concentrations of each carbon species calculated with Web-PHREEQ, temperature-dependent inter-species carbonate species equilibrium fractionation factors (Mook, 2001), and the molar isotope mass balance equation (Wanninkhof, 1985):

$$\delta^{13}C_{\text{DIC}} = m_1 \cdot \delta^{13}C_{\text{CO}_2(aq)} + m_2 \cdot \delta^{13}C_{\text{HCO}_3^-} + m_3 \cdot \delta^{13}C_{\text{CO}_3^{--}}$$  \hspace{1cm} \text{Equation 5.1}

where $m_1$, $m_2$, and $m_3$ are the mole fractions of their corresponding carbonate species.

The molar isotope mass balance was used to predict the CO$_2$(aq) concentration in the epilimnion in both lakes to examine the effects of photosynthesis and degassing and to calculate PCO$_2$ (aq), which was used for theoretical flux calculations. Surface water temperatures vary from ~5-19ºC when the lake is not frozen over, so water compositions were calculated at the 2016 measured field temperatures, as well as 5 ºC, 15 ºC, and 19ºC. The mass balance predicts $\delta^{13}C$ CO$_2$(aq) around -5 to -1.8‰ in East Lake (Figure 5.5a) and -10 to -8‰ in Paulina Lake in June (Figure 5.5b), depending on the depth and water temperature. Dissolved CO$_2$ in water near East Lake’s hot springs is much lighter than the rest of the lake’s CO$_2$, with $\delta^{13}C$ -11.3 to -10.6‰. East Lake surface water dissolved CO$_2$ in May 2016 is generally slightly lighter ($\delta^{13}C$ -5.8 to -2‰) than June 2016 surface water ($\delta^{13}C$ -3 to -1.5‰), because the effects of photosynthetic fractionation become enhanced as the summer progresses.

Also, as the temperature of the water increases, the $\delta^{13}C$ CO$_2$ (aq) becomes enriched compared to cooler temperatures, due to the temperature-dependence of
fractionation factors. As the summer progresses, the epilimnion continues to warm and becomes heavier in $\delta^{13}$C CO$_2$ (aq) because evading CO$_2$ gas is lighter in $\delta^{13}$C and the hypolimnion remains around 5°C, enhancing the $\delta^{13}$C DIC gradient in the water column. Depending on equilibrium and kinetic fractionation factors between dissolved and gaseous CO$_2$, evading lake gas possibly becomes enriched in heavy carbon as the summer progresses and waters warm.

![East Lake $d^{13}$C Ctot](image)

Figure 5.6: Relationship between the total amount of carbon in East Lake water samples from 2015 and 2016 and the total amount of carbon scaled by the $\delta^{13}$C DIC. Samples with outlying pH and alkalinity were not included.

The slope of the regression line in Figure 5.6 (of $C_{tot} \times \delta^{13}$C) suggests that isotopic composition of the geothermal carbon input is $\sim$4.1‰. Other estimations using the same method from other years put the geothermal input at -10.5‰, -8.3‰, and -5.7‰ (Capece, 2016; Lefkowitz, 2012). Hot springs bubbles from 2016 had $\delta^{13}$C
~ -6.5 to -7‰. Assuming that these bubbles had not exchanged any or much carbon with the DIC in the few feet they traveled to the sampling site, they closely reflect the composition of the geothermal input. Thus for modeling and fractionation calculations, the δ¹³C of the geothermal input was estimated at -7‰. This estimate is in agreement with the range of carbon isotopic compositions of carbon dioxide from volcanic systems from around the world has δ¹³C -8 to -6‰, with variations dependent on subducted organic matter (Clark and Fritz, 1997; Craig, 1953; D’Alessandro et. al, 1997).

5.2 Organic Matter

Biotic matter plays a relatively small but important roll in East Lake and Paulina Lake’s carbon cycles: photosynthetic uptake, respiratory release, and possibly through mineralization of sedimentary carbon. The organic carbon in the sediment may reach 12% in EL and 4% in PL and consists of at least three aquatic organisms: cyanobacteria (Nostoc sp.) and phytoplankton (diatoms) in both lakes, and submerged aqueous vegetation (SAV or “phytobersgs”) in East Lake. (Capece, 2016; Lefkowitz, 2012). Mixing models for the sedimentary Corg were derived based on the C/N, δ¹³C, and δ¹⁵N of these aquatic producers (Capece, 2016). For East Lake, three mixing models were created: δ¹⁵N vs δ¹³C, N:C vs. δ¹³C, and δ¹⁵N vs. C/N. In each model, three mixing curves were created, comparing cyanobacteria-SAV, SAV-phytoplankton, and phytoplankton-cyanobacteria. For Paulina Lake, one model with one mixing curve was created between cyanobacteria and phytoplankton δ¹³C and δ¹⁵N. The models use the bulk weight percentage of organic matter, not the percent
carbon or nitrogen. The bulk weight percentage of organic matter based on $\delta^{13}C$ and C/N was calculated by scaling the composition of each endmember by the relative amount of carbon in that endmember. The bulk weight percentage based on $\delta^{15}N$ and N/C was determined by scaling the composition of each endmember by its relative amount of nitrogen.

The $\delta^{13}C$ and $\delta^{15}N$ values of organic matter from cores from Paulina Lake and East Lake were plotted on the mixing model. Because East Lake has three endmembers, isopleth lines can be used to approximate the fraction of each of the biotic endmembers in each core sample based on their isotopic compositions, C/N, and N/C. Samples that fall along any of the lines directly connecting two endmembers are a mixture of only those two types of organic matter. Samples that follow outside of the mixing model isoploeths indicate the presence of additional organic matter sources or diagenic alterations of the original signal. The applicability of the mixing model can be expanded by 10% based on the tolerance interval. Samples that fall outside the isospleths but within 10% of the plot area are considered binary mixtures of the two nearest endmembers (Gonneea et al, 2004).
Figure 5.7: Mixing curve for organic matter in Paulina Lake sediment.

Based on field data (Capece, 2016; Table XX Results of nostoc balls), East Lake cyanobacteria was approximated at $\delta^{15}N -0.32\%o$, $\delta^{13}C -11\%o$, and C:N 4.13; aqueous macrovegetation at $\delta^{15}N 2\%o$, $\delta^{13}C -16\%o$, and C:N 14.41; and phytoplankton at $\delta^{15}N 4\%o$, $\delta^{13}C -28\%o$, and C:N 8. Paulina Lake’s cyanobacteria was approximated at $\delta^{15}N -1\%o$ and $\delta^{13}C -13\%o$ and phytoplankton at $\delta^{15}N 4\%o$ and $\delta^{13}C -33\%o$. Paulina Lake’s biotic matter tend to have similar $\delta^{15}N$ and lighter in $\delta^{13}C$ as East Lake’s. This offset is likely because Paulina Lake’s $\delta^{13}C$ DIC is 2-5\%o lighter than East Lake DIC (Figure XX, $\delta^{13}C$ DIC results). The composition of Paulina Lake sediment falls neatly between the cyanobacteria and phytoplankton on the Paulina mixing curve, indicating that the two endmembers comprise most of the carbon deposited, with slightly more phytoplankton than cyanobacteria (Figure 5.7).
The composition of most East Lake sediment samples also fell directly between the three endmembers in all three models. Based on the isopleths of the tertiary mixture considering $\delta^{15}$N and $\delta^{13}$C, the sediment is approximately 45% diatoms (~25-60%), 25% cyanobacteria (~10-40%), and 30% SAV (0-65%), depending on the sample (Figure 5.8). Based on the mixing model comparing N:C to $\delta^{13}$C, all sediment organic matter is exactly half diatoms and half SAV (Figure 5.9). In the mixing model comparing $\delta^{15}$N to C:N, the two cores plot very differently, but both are dominantly diatoms and SAV (Figure 5.10). East Lake sediment is rich in biogenic silica, which comprises diatom frustules, confirming that diatoms are the dominant contributor to East Lake sediment (Capece, 2016).

Figure 5.8: Three endmember mixing model and isopleths for $\delta^{15}$N versus $\delta^{13}$C in cyanobacteria, aqueous macrovegetation, and diatoms in East Lake sediment. Pine needle composition is also shown as a potential fourth endmember. Blue are samples from East Lake core CLE12, and purple circles are samples from East Lake core KCEL5.
Figure 5.9: Three endmember mixing model and isopleths for N/C versus $\delta^{13}$C in cyanobacteria, aqueous macrovegetation, and diatoms in East Lake sediment. Pine needle composition is also shown as a potential fourth endmember.

Figure 5.10: Three endmember mixing model and isopleths for $\delta^{15}$N versus C/N in cyanobacteria, aqueous macrovegetation, and diatoms in East Lake sediment. Pine needle C/N is very high and goes off scale.
However, a few East Lake core samples had lighter $\delta^{13}$C, higher C/N, and lower N/C than the three endmembers and fell outside the mixing curves, indicating that a fourth endmember contributes to sedimented carbon. Pine needles collected from two sites around East Lake in fall 2016 showed average C/N 35, $\delta^{15}$N 2‰, and $\delta^{13}$C -29‰, which is a typical value for C$_3$ plants due to photosynthetic fractionation, making it the overall lightest organic carbon source (Kohn, 2010). The composition of all the core samples would fall within the bounds of a quaternary mixing model that includes the pine needles, because the outlying samples had lighter combined $\delta^{15}$N and $\delta^{13}$C and higher C:N than could be explained by any mixture of the other three endmembers. Ergo, debris from coniferous trees dotting the lake contribute to the organic matter buried in East Lake and thus the lake’s overall carbon cycle.

Pine needles have very high C/N by weight percent (C/N 30.4-40.6, Table 4.6), while East Lake sediment has C/N ~10-16 (Capece, 2016). The other sources of organic matter have much lower C/N (cyanobacteria ~4, diatoms ~8, phytoberg ~14). Thus pine needles make up a very small percentage of East Lake sediment. Paulina Lake’s sediment, on the other hand, is lighter than East Lake’s ($\delta^{15}$N 1‰ and $\delta^{13}$C -28‰) (Capece, 2016), and nearly has the same isotopic composition of pine needles. However, the sediment has a low C/N ratio, so the light isotopic signature is due to lighter carbon used by phytoplankton and cyanobacteria in photosynthesis (Table 4.6).

Most organic matter from East Lake sediment cores have $\delta^{13}$C -24 to -20‰, and in East Lake the $\delta^{13}$C CO$_2$ (aq) is around -3.5 to -1.5‰, depending on the water
temperature and depth (Figure 5.5a-b). Assuming that aquatic biotic matter use CO$_2$ (aq) for photosynthesis, the photosynthetic $\delta^{13}$C offset would be $\sim$20‰, which is the accepted value for C3 pathway photosynthesis (Smith et. al, 1980). Using on the sediment density, sedimentation rate, and organic carbon contents, it was determined that $\sim$138 tonnes of organic carbon are buried in East Lake each year (Capece, 2016). This represents the minimum drawdown rate of CO$_2$ from the epilimnion in the summer.

In addition to sedimentation, carbon is removed from the epilimnion through photosynthesis and then respired into the bottom waters. This oxidation regeneration-respiration component is not recorded in the sediment cores, though it does affect the total DIC and $\delta^{13}$C DIC in the epilimnion and hypolimnion. For every mole of organic matter, one mole of O$_2$ is added to the epilimnion through photosynthesis and one mole of O$_2$ removed from the hypolimnion through respiration, creating an offset of two moles of O$_2$ between surface and bottom waters. Assuming that the whole lake has identical concentrations of O$_2$ at the beginning of the summer due to spring turnover and the epilimnion O$_2$ concentration does not change due exchange with atmospheric air, the amount of oxidized respired Corg can be calculated from the dissolved oxygen balance. Based on the concentration of dissolved oxygen in the surface ($\sim$10 mg/L) and bottom ($\sim$3 mg/L) waters in mid-August (Lefkowtiz et. al, 2016) and the estimated volumes of the epilimnion and hypolimnion (Table 2.1), $\sim$71 tonnes of organic carbon removed from the epilimnion through photosynthesis and returned to the hypolimnion through respiration. Between the Corg buried in the sediment and Corg respired in the hypolimnion, $\sim$209 tonnes of carbon are
photosynthesized annually. The significant trend in $\delta^{13}$C(DIC) with depth can be explained by the true burial sink of Corg and the respiration loop.

5.3 CO$_2$ Flux

5.3.1 Field Flux

East Lake flux measurement from 2016 showed an average flux rate of 0.3 moles CO$_2$ m$^{-2}$ day$^{-1}$ (0.04-0.7), while 2015 measurements showed an average flux rate of 0.2 mol m$^{-2}$ day$^{-1}$ (0.04-0.5). Multiple factors could account of the higher flux rates in 2016 and 2015. The 2016 field measurements where taken in early June, soon after the melting of the ice cover, spring turnover, and may be part of the catastrophic release of built-up CO$_2$ from the winter. The 2015 field measurements were taken in late June, once the lake likely reached normal summer conditions. At this point, the lake was much warmer and photosynthesis was well underway, removing carbon from the surface waters.

Additionally, wind-induced waves increase flux rates, and floating accumulation chambers are less effective at wind speeds higher than 8-10 m/s (Mazot and Bernard, 2015). June 2016 weather data from the Bend Municipal Airport, which is 897 meters lower than East Lake elevation, gives mean wind speeds of around 1.9 m/s and maximum wind speeds around 8.9 m/s (Weather Underground). June 2015 wind speeds reached 6.2 m/s (Capece, 2016). Wind speeds above the twin lakes were likely significantly higher than those in Bend, because of the increase in altitude, though the lakes are somewhat sheltered by the caldera and forest. The higher flux
rates for 2016 than 2015 and the outliers in the dataset could be a result of the higher wind speeds and waves, which would cause more intense degassing because the boundary layers get disturbed by physical mixing.

Paulina Lake showed a wide range of flux rates in 2016, from 0.04 to 0.35 mol m\(^{-2}\) day\(^{-1}\), with an average of 0.17 mol m\(^{-2}\) day\(^{-1}\). Only 11 measurements were taken and they were close together, so this dataset is not a good representation of Paulina Lake flux rates, and more accumulation chamber measurements will be taken in the 2017 field season. Nevertheless, Paulina Lake clearly seems to have a lower CO\(_2\) evasion rate than her sister lake. Paulina Lake has a higher pH and nearly four times the quantity of bicarbonate as East Lake. East Lake surface waters have PCO\(_2\) is \(~0.02\) atm, and Paulina Lake’s surface waters have PCO\(_2\) \(~0.0006\) atm. Because Paulina Lake’s waters are more alkaline, more of the DIC is present as HCO\(_3^-\) and not dissolved CO\(_2\) ripe for gaseous evasion (Mazot and Bernard, 2015). Paulina Lake has a less dramatic \(^{\delta^{13}}C\) DIC gradient with depth than East Lake (Figures 4.28-4.30), which could be attributed to better mixing, less biological productivity, or less degassing-induced equilibrium and kinetic fractionation. It is important to note that the flux data from both lakes represents only a few sampling days each year and should not be considered an accurate depiction of CO\(_2\) fluxes year-round.
Figure 5.11: Comparison of CO$_2$ flux rates from different volcanos across the world based on surface area. Red circles are acidic lakes, blue circles are neutral lakes, and green circles are alkaline lakes (Mazot and Bernard, 2015; Pérez et. al, 2011). The orange circle indicates East Lake, and the purple circle indicates Paulina Lake.

Thus the Newberry twin crater lakes emit CO$_2$ at a comparable rate to other lakes of their size and pH (orange and purple circles in Figure 5.11). East Lake and Paulina Lake have surface areas of 4.22 km$^2$ and 6.20 km$^2$, respectively. Based on 2016 field measurements, East Lake emits ~72.5 tonnes CO$_2$ per day and Paulina Lake emits ~46 tonnes per day. Acidic lakes tend to have higher flux rates (614.2 tonnes/km2/day) than neutral (201.2 ton/km2/day) or alkaline lakes (5.5 ton/km2/day) (Pérez et. al, 2011). The Newberry lakes are the most similar in area, CO$_2$ emissions, and pH to Lake Nyos and Lake Laacher See (Pérez et. al, 2011). East Lake and Paulina Lake have relatively low flux rates for volcanic lakes, because Newberry
Volcano is not highly active. In an active volcano, temporal variations in CO$_2$ fluxes are due to changes in volcanic activity and can be used to predict and mitigate volcanic risk (Mazot and Bernard, 2015). By considering normalized emissions rates and the surface area and pH of the ~769 volcanic lakes on Earth, Pérez et. al (2011) estimated global CO$_2$ emissions from all volcanic lakes at 117 Mt per year, and 43252.5 tonnes of which comes from the Newberry lakes.

5.3.2 SGS Analysis

The average of the 1000 equiprobable sequential Gaussian simulations from East Lake 2015, 2016, and combined data show similar trends in spatial distributions of flux rates (Figures 5.12-5.14). These results can be used to reveal spatial trends in high CO$_2$ fluxes and the presence of possible faults related to tectonic structures (Mazot and Bernard, 2015). The 2015 and combined maps show hotspots around the drowned crater area and a NE-SW fissure trend, neither of which are significant on the 2016 flux map. All maps show higher flux rates around the hot springs in the southeast corner of the lake, though most extreme in the 2016 simulation. The 2016 and combined simulations also show higher flux rates along the whole east coast of the lake, including the hot springs, East Lake Resort docks, and shallow pool at the northeast corner. Sampling preferentially occurred in this area in both years due to its proximity to the East Lake Resort, so elevated values could be a result of more frequent measurements.
Figure 5.12: Map of SGS-generated fluxes in moles m$^{-2}$ day$^{-1}$ based on field flux measurements over East Lake from 2015. Average of 1000 simulations.

Figure 5.13: Map of SGS-generated fluxes in moles m$^{-2}$ day$^{-1}$ based on field flux measurements over East Lake from 2016. Average of 1000 simulations.
Figure XX: Map of SGS-generated fluxes in moles m\(^{-2}\) day\(^{-1}\) based on compiled field flux measurements from 2015 and 2016. Average of 1000 simulations.

To estimate the average flux rate and the total diffuse CO\(_2\) output for the lakes, the average contributions of each cell obtained after 1000 SGS simulations were considered. A histogram of 2015 and 2016 SGS-generated flux points shows almost all values between 0 and 0.5 moles m\(^{-2}\) day\(^{-1}\), though there is a wide spread of values going up to 1.5 moles m\(^{-2}\) day\(^{-1}\) (Figures 5.14 and 5.15). The average flux for East Lake was computed at 0.262, 0.247, and 0.219 moles m\(^{-2}\) day\(^{-1}\) in 2015, 2016, and both years combined, respectively. Most field flux measurements from 2015 and 2015 fall between 0.2 and 0.3 moles m\(^{-2}\) day\(^{-1}\), so the simulation reflects empirical data well (Figure 4.31). Based on the SGS-generated flux rates, East Lake’s surface evades an estimated 41-49 tonnes of CO\(_2\) per day, significantly less than the 72.5
tonnes of CO₂ per day estimated by averaging 2016 empirical flux rates. This discrepancy could be the result of a few extremely high outliers in 2016 that skewed the dataset.

Figure 5.14: Histograms of CO₂ flux points generated through SGS based on 2015 (left) and 2016 (right) empirical data. Note the difference in axes scales.

Figure 5.15: Histogram of CO₂ flux points generated through SGS based on empirical data compiled from 2015 and 2016.
Figure 5.16: Normal probability plot of CO₂ flux points generated through SGS based on empirical data compiled from 2015 and 2016. Theoretical quantiles are plotted on the x-axis, and empirical quantiles are on the y-axis.

The histograms and probability plots show that the SGS-generated data have the same statistical characteristics of the original data, and the variograms show that the SGS data reproduce the spatial characteristics of the field conditions. Normal probability plots from 2015, 2016, and combined years (Figure 5.16) were generated to distinguish different geochemical populations by compares the quantiles of the observed data with the quantiles we would expect if normality is assumed (López et. al, 2004). All three look similar and indicate that the field and SGS-generated data sets deviate from normality in the same way as the histograms.

The experimental variograms were fitted with a spherical variogram model and applied to the normal score transformed CO₂ flux data (Figures 5.17-5.19). In a variogram, the nugget parameter is the height of the jump to the origin. The nugget
parameters for data from 2015, 2016, and both years were 0.0007, 0.0128, and 0.007, respectively. All of these nuggets are relatively low, indicating a high instance of correlation in values between points that are spatially proximal. These variograms support the assumptions of SGS that data points spatially closer together are more related and thus have more similar values. As the distance between points increases, they vary more in values, as demonstrated by increased variogram variance, or Cressie’s semivariance, with increased distance in all three variograms. A sill was reached in all three variograms, and at that distance there is no correlation between points; thus increased distance does not increase variance.

Figure 5.17: Experimental variogram and variogram model applied to the normal score transformed CO₂ flux data from East Lake in 2015.
Figure 5.18: Experimental variogram and variogram model applied to the normal score transformed CO$_2$ flux data from East Lake in 2016.

Figure 5.19: Experimental variogram and variogram model applied to the normal score transformed CO$_2$ flux data from East Lake in 2015 and 2016.

SGS was also run for the 11 flux measurements over Paulina Lake, but the data was too sparse. The matrix is singular, meaning that the data does not allow for any model to be fit. Thus only descriptives of the raw data are appropriate, so the distribution of flux rates over Paulina Lake should only be considered in terms of Figure 4.32 (Jiang, 2017).
5.3.3 Theoretical Flux

The efflux of CO$_2$ from East Lake is the result of an imbalance in CO$_2$ pressure between the surface lake water and the ambient air. The pressure of CO$_2$ in the air above East Lake is significantly lower than the PCO$_2$ pressure of CO2 inside the lake, especially because the caldera is about two kilometers above sea level and the atmospheric pressure is ~0.82 atm. The partial pressure calculated for the lake water is labelled here the “virtual pCO2”, which is the PCO$_2$ that would occur if a vapor bubble formed in the surface waters, or the PCO$_2$ needed to explain the dissolved carbonate contents of the waters with its measured alkalinity. Aqueous CO$_2$ concentrations for East Lake waters were calculated in Web-PHREEQ based on the measured pH and alkalinity. The concentrations were corrected from lab to field water temperatures. Aqueous CO$_2$ was assumed to be the only carbonate species that participates in diffusive degassing (López et al, 2004). To get PCO$_2$(water), the CO$_2$ levels were corrected for the temperature dependence of CO$_2$ solubility in pure water based on Henry’s Law (Sander, 2015). Following Henry’s Law,

$$PCO_2 = \frac{[CO_2]}{K_H} \quad \text{(Lower, 1996)}$$

Equation 5.2

where $K_H$ is the temperature-dependent Henery’s Law constant and PCO$_2$ is in atm. PCO$_2$(air) was estimated based on ambient PCO$_2$ concentrations scaled to 0.82 atm, $\Delta$PCO$_2$ was determined by PCO$_2$(water) - PCO$_2$(air).
As derived in Wannikhof, 1992, the flux of CO$_2$ gas as it diffuses from a body of water per unit area can be approximated by an equation that is similar to Fick’s 1$^{st}$ Law equation:

\[ F = k \Delta PCO_2 \quad \text{(Wanninkhof, 1992)} \]

Equation 5.3

where \( k \) is the gas transfer coefficient, which is dependent on wind speed, temperature, and water viscosity. Based on the temperature and wind speeds over East Lake, \( k \) factor calculation is scaled by the Schmidt number (Sc) equation

\[ Sc = A - Bt + Ct^2 - Dt^3 \]

Equation 5.4

where \( t \) is temperature in degrees Celcius and \( A, B, C, \) and \( D \) are constants provided by Wanninkhof, 1992. The Schmidt number is the kinematic viscosity of water at the field temperature divided by the diffusivity of CO$_2$ at that temperature (Mazot and Bernard, 2015). It considers the differences between the vertical and horizontal diffusive properties of a substance under specific conditions. Only East Lake surface water samples were considered for theoretical flux, because this is the location of diffusive gas loss. Surface water temperature measurements where not taken at the time of sampling in May and November 2016. For calculations, late May water temperatures were assumed to be the same as June (15ºC), and November water temperatures were approximated at 19ºC based on temperature data presented in
Lefkowitz et. al (2016). A Schmidt number of 776.85 was determined for 15ºC and 630.02 for 19ºC.

Wanninkhof derived different flux calculations depending on whether wind speeds are above or below 3.5 m/s. East Lake’s surface has wind speeds both above and below this threshold during the periods surveyed (Weather Underground; Capece, 2016), so both equations apply. The gas transfer coefficient for wind speeds lower than 3.5 m/s is

\[ k = \left[ 2.5 \left( 0.5246 + 1.6256 \times 10^{-2} T + 4.9946 \times 10^{-4} T^2 \right) + 0.3u^2 \right] \left( \frac{Sc}{600} \right)^{-1/2} \]

Equation 5.5

where \( T \) is temperature in degrees Celcius and \( u \) is the wind speed in m/s. To calculate the gas transfer coefficient for wind speeds above 3.5 m/s, Wannikhof provides

\[ k = 0.39 \, u^2 \left( \frac{Sc}{600} \right)^{-1/2} \]

Equation 5.6

where the Sc number reflects the effects of temperature. June 2016 weather data from the Bend Municipal Airport gives mean wind speeds of around 1.9 m/s and maximum wind speeds were around 8.9 m/s (Weather Underground).
Table 5.1: Theoretical CO₂ fluxes in mol m⁻² day⁻¹ from East Lake based on ΔPCO₂ and temperature with variations in atmospheric parameters during 2011, 2012, 2014, 2016, and 2016. Mean values use a wind speed of 1.9 m/s and max values use a wind speed of 8.9 m/s.

Of the 2016 data, May had the highest ΔPCO₂ (0.0544 atm) and thus the highest flux rate (mean 0.125 mol m⁻² day⁻¹). This is likely because the May samples were taken soon after the lake thawed and turned over, and still had residual DIC that
had built up over the winter. The June samples were taken just a few weeks later, once the residual winter carbon had been released and the lake had returned to normal summer DIC concentrations. June and November had similar mean theoretical flux rates (0.0827 and 0.0888 mol m$^{-2}$ day$^{-1}$, respectively), indicating flux rates are similar throughout the summer, so field flux data from late June 2015 and early June 2016 is representative of fluxes throughout the summer and fall. Field and SGS-generated flux rates for 2015 and 2016 fall between the mean and maximum theoretical flux rates, indicated that the model simulates field conditions well. Higher mean field fluxes than theoretical fluxes can be attributed to higher wind speeds at East Lake during sampling than the mean wind speed in Bend, which is at a significantly lower elevation. Based on the mean and max theoretical flux rates from all months of 2016, East Lake evades an average of 20.05 tonnes CO$_2$ day$^{-1}$ and 239.47 tonnes CO$_2$ day$^{-1}$ on the most windy days. By averaging the mean and max theoretical flux rates from all years, it was estimated that the East Lake evasion rate is approximately 11.44 to 92.23 tonnes CO$_2$ day$^{-1}$.

Paulina Lake flux rates were determined using the same Wannikhof 1992 methodology as East Lake. Wind speeds of 1.9-8.9 m/s were approximated based on Bend Municipal Airport reports from the day of Paulina Lake sampling (Weather Underground). Wind speeds over Paulina Lake are likely higher than in Bend and similar to or slightly lower than East Lake (Morgan et. al, 1997). A Sc number of 820.91 was determined based on a surface water temperature of 14°C. The mean k value for Paulina Lake water is 2.19, and the maximum value is 26.65. The model indicates that surface waters have a mean flux rate of 0.003 and maximum flux rate of
0.041 mol/m2/day. Paulina Lake flux measurements ranged from 0.04-0.35 mol/m2/day with an average of 0.17 mol/m2/day, though many fewer points were taken with less spread around the lake than East Lake. The unknown wind speed variable could contribute to the model’s gross underestimation of flux values. Paulina Lake waters had a large range in calculated concentrations of CO₂ (aq) at different depths, and surface waters had one to two orders of magnitude less CO₂ than waters at ten meters and deeper.

5.3.4 Boundary Layer Model

As CO₂ degasses from the lake into the atmosphere, it passes through a thin stagnant film referred to as a “boundary layer” at the water-air interface (López et al., 2004) (Figure XX). The boundary layer is only a few µm thick, and its thickness is proportionate to its resistance to gas transfer (Wannikhof, 1992). Turbulent mixing decreases strongly towards this interface, and most of the concentration change in a system is confined to this layer (Jähne et. al, 1988). Surface waters and ambient air are assumed to be homogeneous in composition due to mixing (Emerson, 1975). The transfer out of the layer (flux) is only through molecular diffusivity, which is assumed to be the rate limiting step in water-air gas transfer (Broecker and Peng, 1974). The transfer velocity is related to the wind speed (Jähne et. al 1988). A boundary layer model can be used to calculate the CO₂ diffusive degassing between the water layer and ambient air (Mazot and Bernard, 2015). This model presents a different way to quantify the transfer coefficient that governs water-air gas exchange than the Wanninkhof (1992) model. In the Newberry Lakes, CO₂ degassing is the result of a
large PCO₂ difference between the water and ambient air. The boundary layer would have a CO₂ concentration between that of the water and air (Broecker and Peng, 1974), regulating the water-air ∆PCO₂ and flux rates.

In developing flux models, one must consider that CO₂ can react at the interface with hydroxide ions and water, forming carbonate or bicarbonate and enhancing carbon isotope fractionation. This enhances the CO₂ uptake and thus bypasses the rate-limiting step of gas exchange of molecular diffusion through the boundary layer (Wanninkhof, 1985). However, because East Lake waters have a pH lower than 9.0, chemically enhancement through hydration reactions was assumed to be negligible (King et. al, 1992; Wanninkhof and Knox, 1996).

The boundary layer over East Lake is an estimated 24-202 µm thick, based on a wind speed of 8.9 to 1.9 m/s, using an empirical relationship with wind speed derived in Kling et. al, 1992 for lakes around the world. The regression equation of
\[
\log_{10} (z) = 2.56 - 0.133u \quad \text{(Kling et. al, 1992)}
\]

was used, where \( z \) is the boundary layer thickness in \( \mu m \) and \( u \) is the wind speed in m/s. Kling et. al, 1992 found that theoretical CO\(_2\) flux rates can also be determined using the boundary layer and similar variables as Wanninkhof 1992, based on the equation

\[
F = \frac{D}{z} \Delta CO_2 \quad \text{(Kling et. al, 1992)}
\]

where \( z \) is the boundary layer thickness, and \( \Delta CO_2 \) is the difference in concentration of CO\(_2\) in the atmosphere and water. \( D \) is the temperature-dependent molecular diffusivity of CO\(_2\) in cm\(^2\)/sec based on Himmelbau 1964, which is \( 1.5 \times 10^5 \) cm\(^2\)/sec at 15\(^\circ\)C. The concentration of CO\(_2\) and PCO\(_2\) from the two theoretical flux determination methods are identical, and the PCO\(_2\) (aq) was corrected using the temperature-appropriate Henry’s Law constant and the lower atmospheric pressure at the high elevation (Sander, 2015). \( D/z \) acts as a variable that takes wind speeds and temperatures into account, similar to the \( k \) factor in the Wanninkhof (1992) model, but the two models take the parameters into account differently.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Flux Mean</th>
<th>Flux Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>EL1A 0M May</td>
<td>0.04</td>
<td>0.36</td>
</tr>
<tr>
<td>EL2B 0M May</td>
<td>0.03</td>
<td>0.27</td>
</tr>
<tr>
<td>EL3A 0M May</td>
<td>0.04</td>
<td>0.40</td>
</tr>
<tr>
<td>HPEL1 0M June</td>
<td>0.02</td>
<td>0.21</td>
</tr>
<tr>
<td>HPEL2 0M June</td>
<td>0.03</td>
<td>0.24</td>
</tr>
<tr>
<td>EL1A 0M Nov</td>
<td>0.06</td>
<td>0.47</td>
</tr>
<tr>
<td>EL2B 0M Nov</td>
<td>0.02</td>
<td>0.19</td>
</tr>
<tr>
<td>EL3A 0M Nov</td>
<td>0.02</td>
<td>0.18</td>
</tr>
<tr>
<td>EL1A-2 0M Nov</td>
<td>0.02</td>
<td>0.19</td>
</tr>
<tr>
<td>EL2B-2 0M Nov</td>
<td>0.02</td>
<td>0.18</td>
</tr>
<tr>
<td>2016 MONTHLY AVERAGES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average May 2016</td>
<td>0.04</td>
<td>0.34</td>
</tr>
<tr>
<td>Average June 2016</td>
<td>0.03</td>
<td>0.23</td>
</tr>
<tr>
<td>Average November 2016</td>
<td>0.03</td>
<td>0.24</td>
</tr>
<tr>
<td>Average 2016 All Months</td>
<td>0.03</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Table 5.2: Theoretical CO2 fluxes in mol m$^{-2}$ day$^{-1}$ from East Lake based on estimated boundary layer thickness, ΔPCO2, and temperature. Mean values use a wind speed of 1.9 m/s and max values use a wind speed of 8.9 m/s.

The Kling et. al (1992) boundary layer-based theoretical flux equation resulted in mean theoretical flux rates significantly lower than empirical fluxes and fluxes estimated in using SGS and Wanninkhof 1992 (Table 5.2). Maximum boundary layer-based theoretical flux rates are very similar to empirical flux rates and SGS simulation estimations and higher than theoretical flux rates from Wanninkhof 1992. Based on the mean and maximum boundary layer-based theoretical flux rates from 2016, East Lake evades around 6.46 to 55.03 tonnes CO2 day$^{-1}$. The upper bounds of this range is very similar to East Lake CO2 evasion rates calculated from field measurements and SGS simulations.

Paulina Lake tends to have lower fluxes than East Lake. Based on the lake’s ΔPCO2, the Kling et. al, 1992 model predicts a flux rate ~0.001-0.009 mol m$^{-2}$ day$^{-1}$
for Paulina Lake, though it is likely higher because real wind speeds are probably faster. The boundary layer model gives similar fluxes as the theoretical flux model (0.003-0.041 mol m$^{-2}$ day$^{-1}$) and significantly lower flux rates than field measurements (0.04-0.35 mol m$^{-2}$ day$^{-1}$).

There are multiple reasons as to why the mean flux rates estimated in the boundary layer model are significantly lower than field degassing measurements. As previously mentioned, field wind speeds are slightly higher than those reported in Bend and used in the model, resulting in thicker boundary layers and decreased flux rates. Additionally, based on empirical flux measurements and gas exchange coefficient estimates from other papers, the equation to determine the boundary layer thickness often gives estimates that are four to eight times too large, resulting in calculated CO$_2$ fluxes that are too small, as is the case for East Lake (Kling et. al, 1992). Also, it is extremely difficult to measure the properties of a layer at a moving wavy interface only a few µm thick, so all of the properities and constraints of boundary layers are not well defined (Jähne et. al, 1988).

Another potential reason why both models give mean flux rates orders of magnitude smaller than mean field flux rates is that the lakes usually have much thicker boundary layers than were present during build-up measurements. It is possible that the CO$_2$-rich boundary layer was mixed and partially or completely destroyed by the accumulation chamber deployment and the intense wave action. The boundary layer’s $\Delta$PCO$_2$(water-air)-regulating properties were then rendered near obsolete, leading to inflated degassing rates. This theory is supported by the fact that maximum boundary layer-based theoretical flux rates, which assume a very thin boundary layer
(24µm) are more similar to empirical flux rates. Real degassing rates from the lakes are likely between those given by the models and field measurements, due to errors in both approaches’ methodologies and assumptions.

In the field draw-down phase of the draw-down build-up experiments, the chamber fan would have mixed up the boundary layer and the CO$_2$ trap would have pumped most of its CO$_2$ out. Once the air CO$_2$ concentration had decreased significantly, during the build-up portion, the measured flux rate was 0.2-0.97 mol m$^{-2}$ day$^{-1}$, which slightly higher than the average East Lake 2016 field rate of 0.3 mol m$^{-2}$ day$^{-1}$. This increase in flux rate with the removal of most ambient CO$_2$ and the boundary layer suggests that the ΔPCO$_2$ has a significant impact on flux rate in the field, supports models, and suggests that field flux measurements are slightly exaggerated.

### 5.3.5 Lab Lake

The empirical flux of CO$_2$ evading from Lab Lake was 1.95 mol m$^{-2}$ day$^{-1}$ (Figure XX, from lab lake flux in Results), which is significantly higher than most East Lake locations, except for a few hot springs site and outliers. Lab Lake had about double the ΔPCO$_2$ of East Lake partially accounting for the inflation of flux rate. A theoretical flux was calculated for Lab Lake using the same Wanninkhof (1992) methodology as used for the two Newberry lakes (Equations 5.2-5.6). The PCO$_2$ in the Lab Lake water was calculated with Web-PHREEQ and the temperature-dependent Henry’s Law constant. The initial PCO$_2$ in the solution was 0.0817 atm, and it decreased less than 0.005 atm over the whole experiment. The stirrer moved so
quickly that the wind speed was assumed to be equivalent to the highest recorded speeds in Bend in June 2016, 8.9 m/s. Because the windspeed was above 3.5 m/s, equation XX was used to determine the k value of 31.19. The Sc number at the lab temperature was 599.42. The theoretical flux was calculated to be 2.43 mol m$^{-2}$ day$^{-1}$, which is slightly higher than the empirical experiment flux. However, the k factor and thus the flux rate are highly dependent on the wind speed, and the speed of the stirrer is not known. A stirrer rate of 8 m/s, which is a probable speed, gives a theoretical flux rate of 1.95 mol m$^{-2}$ day$^{-1}$, identical to the empirical flux rate. The cell was so small and the two stirrer fans were so close together and fast that is is unlikely that a boundary layer formed.

While this Lab Lake run had eight liters of water and approximately five liters of headspace, future runs will have a significantly lower water to headspace ratio in order to decrease the rate at which the headspace fills and to get gas samples at smaller intervals. Additionally, although stoichiometric calculations were performed based on the amount of acid added in titrations of water with various amount of bicarbonate with endpoints of 6.5 pH, the final Lab Lake solution had a lower pH and alkalinity (defined at HCO$_3^-$ + 2CO$_3^{2-}$ - H$^+$) than East Lake. Future runs should have less HCl and more bicarbonate to make the solution more alkaline correct for this discrepancy. If the alkalinity of East Lake is achieved future Lab Lake waters, carbon would be found more as HCO$_3^-$ than CO$_2$ (aq), resulting in decreased internal PCO$_2$ of the water, ΔPCO$_2$ (water-air), and flux rates. This serves as further support for the notion of a boundary layer with an extremely high concentration of CO$_2$ and regulates ΔPCO$_2$. 
Another major difference between Lab Lake and East Lake is that East Lake air is constantly around 400 ppm CO₂, while the Lab Lake headspace increased from ~40-3100 ppm. Carbon and oxygen isotopes fractionate differently under different conditions, and future Lab Lake experiments should be run to monitor fractionation during degassing while holding the CO₂ of the headspace constant, such as at 400 and 2000 ppm CO₂ to simulate field ambient and boundary layer conditions.

5.3.6 Steady-State Model

Kiddie pool experiments were performed to confirm the draw-down build-up experiment methodology and equipment and to verify flux measurements from field and Lab Lake experiments. A steady-state box model can be used to model field and lab draw-down and build-up flux rates and CO₂ concentrations. The CO₂ flowing into the chamber acts as a conservative species in a perfectly mixed reservoir (Varekamp, 1988). Based on the fundamental equation of box modelling, the change in the total mass at any time can be expressed as

\[
\frac{dM}{dt} = IN - OUT = F(IN) - F.OUT = F(IN) - kM \tag{5.9}
\]

where \(F(IN)\) and \(F(OUT)\) are respectively the fluxes of carbon into and out of the chamber (Varekamp, 2003). \(K\) is the rate constant or the fraction of the resident carbon removed per unit time, and \(M\) is the resident amount of carbon in the chamber. When the concentration of CO₂ in the chamber is constant, the system is at steady
state, and F(IN)=F(OUT). By solving the above differential equation with the boundary condition that t=0, this equation is produced:

\[
C(t) = C_{ss} (1-e^{-k1t}) + C_{init} * e^{-k2t} \quad \text{(Varekamp, 1988)}
\]

Equation 5.10

where \( C_{ss} \) is the steady state concentration. If \( C_{init}=0 \), as in the chamber initially was void of carbon, the second portion of the equation disappears, and \( C(t) \) shows an asymptote towards a constant carbon concentration at \( C_{ss} \). If all of the carbon is being pumped out of the chamber, \( C_{ss}=0 \), and the first portion of the equation disappears. In that case, \( C(t) \) decreases until it reaches an asymptote at zero (Varekamp, 2003).

These box modelling equations were applied to the kiddie pool experimental setup, and the model results were compared to empirical kiddie pool results to confirm the mechanisms before applying them to field data. During both the draw-down and build-up portions of the kiddie pool experiments, F(IN) is the rate of CO2 degassing from the water into the chamber. In draw-down experiments, F(OUT) is rate at which gas is pumped out of the chamber. The accumulation chamber has a one-way equilibration valve, which re-equilibrates the internal chamber gas pressure with ambient air pressure. When internal pressure exceeds ambient pressure, the valve allows gas molecules to escape the chamber. In build-up experiments, the F(OUT) is the rate at which chamber gas escapes the chamber through the equilibration valve. However, the PCO2 of the CO2 degassed into the chamber is very small compared to total pressure inside the chamber, so negligible amounts of gas escapes. Concentrations can be expressed in either moles and ppm CO2 in
different steps of calculations because all other factors in the Ideal Gas Law remain essentially constant throughout the experiments, so units cancel.

The concentration of CO$_2$ in the chamber during the draw-down portion of the experiment can be represented by Equation 5.10, where $t$ is time in seconds and $C_{\text{initial}}$ is ambient lab air at 500-560 ppm, depending on the run. $C_{ss}$ should equal zero because the pump and CO$_2$ trap are working to remove all CO$_2$ from the system. In reality, small amounts of carbon leaked into the chamber during the experiment, likely through kiddie pool degassing. Leakage occurs at a linear rate of 0.0162 ppm/second, and this small input must be considered in the steady state model, because it prevents $C(t) = C_{ss} = 0$ (Figure 4.35). The fraction of CO$_2$ added to the chamber per second is $k_1 = \text{IF}/M$, where IF is 0.0162 ppm CO$_2$ added per second and $M$ is the total CO$_2$ in the chamber. The CO$_2$ outflow (mol/sec) is the pump flow rate (0.0167-0.05 L/sec, depending on the run) times the concentration of CO$_2$ in the chamber in mol/L. Alternatively, the outflow can be determined by $k_2*M$, where $k_2$ is the rate constant (sec$^{-1}$). $K_2$ can also be determined by dividing the flow rate (L/sec) by the volume of the chamber (11.231 L). Draw-down experiments proceeded until steady state was reached at ~25-43 ppm. As shown in Figure XX, the box model fits the empirical draw-down experiment data well, indicating that the system functions as theoretically expected.
Because both solution continues to degas during the draw-down experiments, $C_{ss}=0$ is never reached in at East Lake or in the Kiddie Pool and Lab Lake experiments. At least the smallest fraction of initial gas remains. Thus, during the draw-down build-up experiments, no matter how long the experiment has been proceeding for, a small amount of ambient air remains in the chamber. Once steady state has been reached during draw-down or re-equilibration with ambient air concentrations, a minute amount of original air is still in the chamber. When considering the isotopic composition of chamber air after draw-down, it is important to consider that ambient air is always as endmember contributing to the mass balance.

The build-up experiments start at this steady-state concentration reached during the draw-down portion ($C_{\text{init}} = \sim 25-43$ ppm). Inflow of CO$_2$ in mol/sec is the pump flow rate (0.0167-0.05 L/sec, depending on the run) times the concentration of
CO₂ in the incoming ambient air in mol/L. In accordance with the experimental
design, CO₂ is pumped into the kiddie pool and thus chamber, and the rest of the
chamber gas is pumped around through the LICOR and back into the chamber. The
experiment reached steady state at 500 ppm, when the concentration of CO₂ in the
chamber roughly equaled the concentration in ambient air (Figure 5.22).

![Lab build-up experiment vs. model](image)

Figure 5.22: Model versus empirical CO₂ concentration during one run of build-up
kiddie pool experiment.

Similar equations can be applied to East Lake field draw-down build-up
experiments that also use the accumulation chamber with the equilibration valve.
Equation XX was used, where C\text{initial} was the CO₂ concentration at the end of the
draw-down and C_{ss} was 500 ppm, the concentration at which most build-up runs
leveled off. The k₂ value for each experiment was determined by averaging the k₂
over each of the timesteps of the experiment, which is the inflow rate of CO₂ divided
by the total amount of CO₂ in the chamber. The steady-state models had nearly identical slopes to empirical results from all three East Lake draw-down build-up experiments (blue and red lines in Figures 5.23-5.25, Table 5.3). In theory, the mechanism continues until the system is at steady state and F(IN)=F(OUT), but often the experiments were ended before equilibrium was reached.

Figure 5.23: Empirical and model flux results for first East Lake build-up draw-down experiment. Formulas for the regression lines are given.
Figure 5.24: Empirical and model flux results for second East Lake build-up draw-down experiment.

Figure 5.25: Empirical and model flux results for third East Lake build-up draw-down experiment. Formulas for the regression lines are given.
Draw-down build-up experiments alter field conditions in a few important ways. The initial CO₂ concentration and PCO₂ in the chamber is less than ambient air, so the ∆PCO₂ is lower than when East Lake degasses normally. When C_{init} was set to zero and just the build-up toward steady state was considered in the model, ppm CO₂ increased quicker (“Just Inflow” in Figures 5.23-5.25, and “Model, 0ppm” in Table 5.3). When C_{init} was set to 407 ppm, approximately the concentration of CO₂ in the ambient air, the slope decreased (“Model, 407 ppm” in Table 5.3). This indicates indicating that the flux rates during the draw-down build-up experiments are slightly larger than actually happens at East Lake, and should not be used to approximate total CO₂ evaded from the lake.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Empirical</th>
<th>Model</th>
<th>Model, 0 ppm</th>
<th>Model, 407 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDBU1</td>
<td>0.33</td>
<td>0.33</td>
<td>0.56</td>
<td>0.10</td>
</tr>
<tr>
<td>DDBU2</td>
<td>0.89</td>
<td>0.80</td>
<td>1.31</td>
<td>0.24</td>
</tr>
<tr>
<td>DDBU3</td>
<td>0.72</td>
<td>0.76</td>
<td>0.95</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 5.3: Slopes of CO₂ addition to accumulation chamber, in ppm/second, for the build-up portion of the three draw-down build-up experiments based on the regression lines. “Empirical” is field experimental results, “Model” is simulation results using field initial concentrations, “Model, 0 ppm” is simulation starting with no CO₂ in the chamber, and “Model, 407 ppm” is simulation starting at 407 ppm CO₂ in the chamber.

Regular accumulation chamber runs are more similar to real degassing conditions in these respects, and similar steady-state equations can be applied to model the fluxes. Build-up runs start with ambient CO₂ concentrations inside the chamber. While draw-down build-up experiments evolve toward a steady state with equal CO₂ concentrations inside and outside the chamber (~500 ppm), regular build-up runs trend toward equal CO₂ concentrations in the lake gas and in the chamber.
(≈1,000,000 ppm, or 100% CO₂). As the lake degasses CO₂, the chamber becomes very slightly overpressurized, and the same number of moles of gas that enter the chamber leave through the equilibration valve. While the entering lake gas is entirely CO₂, the escaping gas has the composition of the chamber air, with initially only ≈400-600 ppm CO₂. Although the total number of moles in the chamber remains the same through the measurement, the molar fraction of CO₂ in the gas increases as the experiment progresses. The system is at steady-state when F(IN)_{CO2}=F(OUT)_{CO2}, which can only occur once the accumulation chamber gas is comprised entirely of CO₂. The concentration of CO₂ in the escaping gas is multiple orders of magnitude smaller than the concentration of the invading gas, so the rate of F(OUT)_{CO2} is very small and the experiment would take an extremely long time to reach steady state. However, over the course of the flux measurements, chamber concentrations only reach around 600 ppm, so the system does not even come close to steady state and the equilibration valve does not play an important role. Although the rate of CO₂ loss through the equilibration valve is negligible compared to the rate of CO₂ degassed into the chamber, these models indicate that measurements taken over very long periods of time with accumulation chambers with pressure equilibration valves give slightly lower CO₂ flux rates than actual lake gas fluxes in an open system.
Figure 5.26: Empirical and model flux results for regular East Lake build-up accumulation chamber measurement. This is an example of one measurement, but the model has a similar fit to all field samples of the same type.

5.4 CO2 Gas Isotopic Composition and Fractionation

5.4.1 East Lake $\delta^{13}$C and $\delta^{18}$O CO$_2$ Gas

In addition to measuring the flux rate of CO$_2$ degassing, it is important to consider its carbon and oxygen isotopic composition in order to understand its effects on the isotopic composition of lake DIC. The isotopes of the evading lake gas can be used to trace the role volcanic lake degassing plays in the limnological carbon cycle and the atmospheric CO$_2$ budget. Monitoring the isotopic composition and
fractionation of species involved in volcanic degassing can shed light on degassing processes and changes in volcanic activity (Christenson and Tassi, 2015).

Figure 5.27: The $\delta^{13}C$ in CO$_2$ gas versus CO$_2$ concentration in gas and air samples from East Lake in 2015 and 2016.

To determine whether $\delta^{13}C$ CO2 is affected by the CO$_2$ concentration, the carbon isotopic compositions and concentrations of CO$_2$ gas from East Lake draw-down build-up experiments, flux chamber, air above lake, and hot springs bubbles from 2015 and 2016 were compared (Figure 5.27). The large blue square represents the pure theoretical ambient air endmember with a typical atmospheric composition of 400 ppm and $\delta^{13}C \sim -8.5$‰ (NOAA). Other blue squares are ambient air above the lake, which are probably binary mixtures of diffuse lake gas and atmospheric CO$_2$, and had a spread of values ranging from -17‰ to -9‰. Yellow and orange circles are
the compositions of flux chamber gas, which are also binary mixtures of ambient gases and lake gas. Purple circles are gas samples collected directly from lake and hot spring bubbles. These samples closely reflect East Lake’s geothermal input. The 2016 samples are largely CO\textsubscript{2} with \(\delta^{13}C\) of -6.5 to -7‰; the 2015 samples varied more in concentration and isotopic composition. The two sets of red brackets represent the \(\delta^{13}C\) range of calculated isotopic composition of the lake gas (-10.5‰) and the geothermal input (-7‰), which is the gaseous CO\textsubscript{2} entering East Lake through its volcanic system.

Filled red circles indicate the three draw-down build-up experiments completed in 2016. For these experiments, the CO\textsubscript{2} in the accumulation chamber started with values identical to ambient gas (around 400 ppm and probably ~10.5 \(\%\)). The marker with the lower concentration of each pair are draw-down gas values, which were collected directly after the chamber had reached steady state and probably contain over 99% lake gas. The blue dashed line indicates the change in concentration and isotopic composition as the lake further degasses during the build-up portion of the experiment (no pumpdown). The red circle with the higher concentration shows the \(\delta^{13}C\) CO\textsubscript{2} in the chamber after the build-up portion of the experiment. The concentration has increased proportionate to the flux rate and the duration of the buildup. At the end of the draw-down and at the the end of the build-up, the chamber should have contained almost entirely lake gas. The amount of CO\textsubscript{2} degassed during the measurements is minuscule compared to total carbon in the surface water and surface carbon is constantly replenished from the hypolimnion. Through the draw-down build-up experiments, the \(\delta^{13}C\) CO\textsubscript{2(aq)} was constant, so the
equilibrium $\delta^{13}C_{CO_2{(gas)}}$ should also be constant. Thus, all the draw-down and draw-down build-up red dots should have identical $\delta^{13}C_{CO_2{(gas)}}$ values ($\sim$10.5‰), which is equivalent to the $\delta^{13}C$ of the gas evading from the lake, and the slope of the blue dashed lines should be zero.

The observed differences in $\delta^{13}C_{CO_2}$ measured at the beginning and end of the buildup portion of the experiment can be attributed to a nonequilibrium fractionation, such as kinetic fractionation, or experimental error. The $\delta^{13}C$ of the evolving gas depends on the temperature, the $\Delta$PCO$_2$, and the $\delta^{13}C$ of gas present and $\delta^{13}C_{CO_2{(aq)}}$. CO$_2$ isotopes experience more intense kinetic fractionation at higher $\Delta$PCO2, so the effects of fractionation in the chamber are larger at the beginning of the buildup. Thus, for each of the three trials, the final value after the build-up portion is expected to be the most similar to the isotopic composition of the gas evading the lake under normal air concentration conditions ($\sim$400-500 ppm). Also, it is possible that some atmospheric air going into the accumulation chamber during two of the experiments, when the waves and wind caused the boat to hit the East Lake Resort dock.

Nonequilibration fractionation during CO$_2$ degassing would also contribute to the observed strong gradient in $\delta^{13}C_{DIC}$ with depth East Lake (Figure 4.29). Nonequilibration fractionation is not the sole cause of East Lake’s strong $\delta^{13}C_{DIC}$ gradient with depth, because Paulina Lake’s gradient is not as strong, but it would enhance the effects of the removal of light carbon isotopes through equilibrium degassing and photosynthesis. The $\delta^{13}C_{CO_2{(aq)}}$ is around -2‰ in East Lake surface waters (Figure 5.5a). If the equilibrium fractionation is -1.1‰ for CO$_2{(aq)}$ to
CO₂(gas), then the evading lake gas is expected to have \( \delta^{13}C \approx -3.1\%o \) (Vogel et. al, 1970). However, lake gas has \( \approx -10.5\%o \ \delta^{13}C \) CO₂ (Figure 5.5a, colorful plot of \( \delta^{13}C \) all East Lake air samples). No accumulation chamber CO₂ samples have \( \delta^{13}C \) as heavy as -3.1\%. We infer an additional non-equilibrium fractionation component during degassing, based on both the change in \( \delta^{13}C \) CO₂(gas) with \( \Delta PCO₂ \) during draw-down build-up experiments and based on the discrepancy in \( \delta^{13}C \) CO₂_{aq} and \( \delta^{13}C \) CO₂_{gas}.

Figure 5.28: Screenshot of ArcGIS Online map of \( \delta^{14}C \) of CO₂ from chamber samples taken over East Lake and Paulina Lake in 2016. The interactive webmap can be seen here: https://arcg.is/1qOr8i. By clicking on any point, one can see the exact GPS coordinates, concentration of CO₂, 1000 over concentration of CO₂, δ18O, and \( \delta^{13}C \).
Figure 5.29: Screenshot of ArcGIS Online map of δ18O of CO₂ from chamber samples taken over East Lake in 2016. The interactive webmap can be seen here: https://arcg.is/1njC1C. By clicking on any point, one can see the exact GPS coordinates, concentration of CO₂, 1000 over concentration of CO₂, δ18O, and δ13C.

In 2016, East Lake chamber CO₂ samples had δ13C -11.9 to -8.4‰ and δ18O -21.5 to -13.3‰ (Table 4.3). The heaviest δ13C CO₂ values are near the hot springs. Otherwise, there is no visible trend in δ13C or δ18O with location over the lake or water depth (Figures 5.28 and 5.29). Since the whole lake surface water has the same sources and sinks of carbon, all evading CO₂ should have the same carbon and isotopic composition. The observed variations in δ13C and δ18O CO₂ are thus not caused by location effects, but rather by differences in lake CO₂ concentration and ∆PCO₂ in the accumulation chamber and by nonequilibrium fractionation during CO₂ degassing.

5.4.2 Ambient CO₂

The δ13C CO₂ of ambient air around East Lake has a wide range and is up to ~5‰ lighter than δ13C CO₂ atmospheric air worldwide (Figure 4.4). It is important to
identify the exact $\delta^{13}\text{C}\text{CO}_2$ of ambient air in order to determine the $\delta^{13}\text{C}\text{CO}_2$ of evading lake gas, because accumulation chamber gas samples after regular field build-up measurements are a bianary mixture between lake gas and ambient air.

In each 100-meter-thick layer of air above the East Lake surface, there are approximately 251-279 metric tons of CO$_2$, depending on the temperature (Table 5.4). When flux measurements were taken in June 2016, ambient temperature was around 15$^\circ$C, and it was estimated that 71 metric tons of CO$_2$ are lost from East Lake’s surface daily. Thus, the daily CO$_2$ evasion accounts for over a quarter of the total CO$_2$ in the 100 meters of air above the lake. While the wind speeds directly above the lake are relatively high, up to 8.9 m/s during June 2016 (Weather Underground), much of the regional circulation is contained in the forested elevated sides of the caldera, which rise approximately 200 meters above the lake surface (Figure 5.30). Consequently, at any given time, there is approximately 530 metric tons of CO$_2$ in the air in the East Lake basin depression, and it would take less than eight days of lake degassing to replace all of this ambient air with lake gas. If the residence time of air in the East Lake caldera is eight days or longer, then all of the CO$_2$ in the air in the East Lake caldera could be lake gas. However, if all of the ambient air above the lakes were from lake gas, then CO$_2$ concentrations would be significantly higher than ambient air concentrations worldwide (~407 ppm CO$_2$). The air above the lakes has about 410-500 ppm CO$_2$, based on LICOR readings at the beginning of build-up measurements, so ambient air is still present in the air above the lakes.
<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Moles CO₂</th>
<th>Metric ton CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>632917.709</td>
<td>278.58</td>
</tr>
<tr>
<td>15</td>
<td>600031.321</td>
<td>264.07</td>
</tr>
<tr>
<td>30</td>
<td>5703413.186</td>
<td>251.01</td>
</tr>
</tbody>
</table>

Table 5.4: Amount of CO₂ per 100 meters above East Lake depending on ambient air temperature.

Additionally, it is possible that some of this air above East Lake is interchanged with Paulina Lake. Although the pumice cone towers over the two lakes (upper left profile in figure XX), there are depressions between the two lakes just north and south of the cone (upper right and lower right in figure XX). In general Paulina Lake chamber gas samples have a $\delta^{13}$C $\sim$0.5-1‰ lighter than East Lake ($\sim$ -10.5 to -10‰ in East Lake and $\sim$ -11‰ in Paulina Lake). Ambient air above and around East Lake has a $\delta^{13}$C of $\sim$10.5, though values ranging from -15 to -7‰ have been recorded over the years (Figure XX, Results graph of all $\delta^{13}$C gas values). Very few air samples near East Lake have $\delta^{13}$C heavier than -10‰, but typical atmospheric CO₂ has $\delta^{13}$C $\sim$-8.5 ‰ (NOAA). A basic mixing model suggests that either heavy atmospheric CO₂ is nowhere to be seen, which is unlikely because ambient CO₂ concentrations are not extremely high, or that true lake gas is much lighter than chamber gas.

In future field visits, gas samples should be taken near the Newberry caldera but not above the lakes, such as in the woods or near La Pine, in order to determine the true isotopic composition of ambient air and to add that endmember to the mixing model. Additional measurements of the flux rate and isotopic composition of Paulina Lake gas need to be completed to better constrain these values.
Figure 5.30: Bird’s eye view of 3D imagery of Newberry caldera (bottom left) and East Lake (middle right). Vertical elevation profile of middle of Newberry caldera through pumice cone (upper left), and two west-east vertical elevation profiles of East Lake (upper right and lower right). Elevation is in meters, and both maps are oriented with north facing upwards. Distance scales are in kilometers, and elevation scales are in meters. Profiles and 3D imagery created in SURFER with based on data from Jared and Jeffery, 2016.

5.4.3 Lab Lake

The Lab Lake experiment was completed to understand the isotopic fractionation mechanisms in play during CO₂ degassing in order to better define the East Lake gas and ambient CO₂ endmembers. As discussed above, East Lake δ₁³C CO₂ had two unusual trends: 1) a discrepancy between δ₁³C in CO₂(aq) and CO₂(gas) past equilibrium fractionation, and 2) shift in δ₁³C CO₂(gas) with ΔPCO₂. Similarly, both oxygen and carbon isotopes in Lab Lake CO₂ show offsets both with phase change and with ΔPCO₂ (Figure 5.31). Nonequilibrium processes during degassing,
such as kinetic fractionation, could explain unusual trends in the isotopic composition of East Lake’s \( \text{CO}_2(\text{aq}) \) and \( \text{CO}_2(\text{gas}) \) in East Lake, and Lab Lake serves as a more controlled platform to observe shifts in isotopic compositions. Very few studies have looked at both the \( \delta^{13}\text{C} \) and \( \delta^{18}\text{O} \) \( \text{CO}_2(\text{gas}) \) as it is degassed from a body of water, and the few that do estimate the isotope composition of the evading \( \text{CO}_2 \) based on that composition of the initial solution and the calcite precipitate, usually in speleothems (ex. Wiedner et. al, 2008; Affek and Zaarur, 2014)

Figure 5.31: The \( \delta^{13}\text{C} \) and \( \delta^{18}\text{O} \) of \( \text{CO}_2 \) gas and DIC in East Lake, Lab Lake and ambient gas and water samples. Green symbols are Lab Lake samples, and red and orange symbols are East Lake samples. Circles are gas samples, and squares are water samples. Conventional ambient \( \text{CO}_2 \) \( \delta^{13}\text{C} \) is included for reference. Gas sample \( \delta^{18}\text{O} \) \( \text{CO}_2 \) is compared to the VPDB standard, and water sample \( \delta^{18}\text{O} \) is compared to the VSMOW standard.
During the actual experiment, which ran for about 15 minutes at a linear
degassing rate, 0.0078 g C were degassed from the solution (Section 4.6). Assuming
the degassing rate continued to be linear, an additional 0.0078 g C were degassed
from the solution during the approximately 15 minutes after the experiment it took to
take apart the setup, open the cell, and collect the final solution. The isotopic
composition of this “post-experiment CO₂(aq)” includes the extra few minutes of
degassing after the experiment, but the actual isotopic composition of the CO₂ evaded
during the 15 minutes before the final water sample was taken is not known.

5.4.3.1 δ¹³C CO₂

The relationship between δ¹³C CO₂(aq) and δ¹³C CO₂(gas) in Lab Lake was
calculated to determine whether non-equilibrium fractionation occurred in Lab Lake.
The CO₂(aq) in the Lab Lake solution had δ¹³C -11‰ at the beginning of the
experiment and -9‰ at the end of the “post experiment” degassing, determined using
web-PHREEQ calculations and temperature-dependent carbonate speciation. Lab
Lake CO₂(gas) started slightly heavier in δ¹³C than CO₂(aq), which is unusual for
equilibrium systems. By the end of the experiment, δ¹³C CO₂(gas) became ~2‰ more
negative than δ¹³C CO₂(aq). Similarly, East Lake CO₂(gas) δ¹³C was ~7‰ more
negative than δ¹³C CO₂(aq). Both fractionations exceeded the ~0.8-1.1‰ vapor-
solute equilibrium system fractionations at the lab and field temperatures (Vogel et. al, 1970). East Lake saw a larger discrepancy between CO₂(aq) and CO₂(gas) than
Lab Lake, because it is a bigger reservoir and the degassing is developed over weeks
and months, not mere minutes.
To explore the relationship between CO$_2$(aq) and CO$_2$(gas) in Lab Lake, the final mass balance of total carbon and CO$_2$ was calculated by

\[
\delta^{13}C_{\text{initial}} \times (\text{mass of DIC/total C}) = \\
(\delta^{13}C_{\text{gas}} \times (\text{mass of gas/total C}) + \delta^{13}C_{\text{DIC (final)}} \times (\text{mass of DIC/total C})
\]

Equation 5.11

\[
\delta^{13}C_{\text{-CO}_2\text{aq initial}} \times (\text{mass of CO}_2\text{aq/total CO}_2) = \\
(\delta^{13}C_{\text{-CO}_2\text{gas}} \times (\text{mass of gas/total CO}_2) + \delta^{13}C_{\text{-CO}_2\text{aq final}} \times (\text{mass of final CO}_2\text{aq/total CO}_2)
\]

Equation 5.12

However, both the CO$_2$ and total DIC mass balances are off by 2‰ $\delta^{13}$C. In both, the final system d13C is $\sim$1.8‰ less negative than the initial solution. To compensate for this discrepancy, the evading Lab Lake gas would need to be very light, based on how much isotopically heavier the DIC water gets. If the gas underwent equilibrium fractionation during degassing, based on the $\delta^{13}$C CO$_2$ (aq) of the initial solution as calculated using Web-PHREEQ and speciation calculations, it would be $\sim$12.1‰. But it would take about half of all the carbon in the solution degassing for the solution to be so heavy at the end of the experiment. Alternatively, to achieve the calculated 2‰ shift in $\delta^{13}$C CO$_2$(aq) based on the total mass balance, the total evaded CO$_2$ must ultimately have d13C $\sim$40‰. Although the composition of the post experiment CO$_2$(gas) is not known, Lab Lake gas trended lighter in $\delta^{13}$C.
CO₂ as the experiment progressed, and it is likely that this continued in the few minutes after the experiment. However, it is extremely unlikely that the δ¹³C got as low as -69.2‰ during the post experiment. These calculations confirm that the system is more complicated than simple mass balance equations and equilibrium fractionation factors can account for.

Additionally, like East Lake, Lab Lake δ¹³C CO₂(gas) varied with ΔPCO₂, also suggesting that a non-equilibrium fractionation effect. The ideal gas law was used to calculated the number of moles and pressure of CO₂ in the headspace as a function of time. The PCO₂ of the water was determined using Web-PHREEQ, and the ΔPCO₂ (fluid vs. headspace) using the CO₂ loss in the water and ppm CO₂ gain in the headspace. Linear mixing equations where created using the mass fraction added and isotopic composition of CO₂ in each step to determine the δ¹³C and δ¹⁸O of added gas per time unit as a function of ΔPCO₂. The resulting δ¹⁸O and δ¹³C of the evolving CO₂ show opposite trends in relation to ΔPCO₂. As the experiment progresses, the headspace CO₂ concentration increases, the ΔPCO₂ decreases, the δ¹³C of the evolving CO₂ gas becomes more negative, and the δ¹⁸O evolving CO₂ increases.

With increasing ΔPCO₂, the δ¹³C of the CO₂ added to the cell headspace and thus the δ¹³C of all headspace gas becomes less negative (Figure XX). During the experiment, as the concentration of CO₂ increased and ΔPCO₂ decreased, the δ¹³C in the headspace became more negative, shifting from −−9 to -11‰. Although there is a clear trend of increasing δ¹³C CO₂(gas) with increasing ΔPCO₂, there are a few intervals when the δ¹³C decreases in the headspace, indicating that the δ¹³C of the
CO₂ added in that step was lower than that of the previous step and total headspace gas. These discrepancies are 0.4‰ or lower, within the analytical margin of error.

The linear regression of δ¹³C versus ΔPCO₂ indicates that for every additional atm ΔPCO₂, δ¹³C increases 732.5‰, or for every additional uatm (10⁻⁶ atm), δ¹³C increases 0.0007‰.

At every interval in the experiment that a gas sample was taken, the δ¹³C CO₂(aq) was calculated using an isotope mass balance using the initial δ¹³C CO₂(aq) and the amount and isotopic composition of the evading CO₂(gas) was generated. As the experiment progressed (decreased ΔPCO₂), δ¹³C CO₂(aq) became less negative at a linear rate, showing an opposite trend in δ¹³C with ΔPCO₂ as CO₂(gas) (Figure 5.32).

![Graph showing δ¹³C of CO₂(gas) added to cell headspace, δ¹³C of the total CO₂(gas) in the headspace, and the δ¹³C DIC in the solution based on the mass balance. The isotopic compositions are graphed against the difference in PCO₂ in the solution and in the headspace.](image)

Figure 5.32: The δ¹³C of the CO₂(gas) added to cell headspace, the δ¹³C of the total CO₂(gas) in the headspace, and the δ¹³C DIC in the solution based on the mass balance. The isotopic compositions are graphed against the difference in PCO₂ in the solution and in the headspace.
While Lab Lake and most East Lake chamber gas samples show similar trends in $\delta^{13}C_{CO_2(gas)}$ with ambient CO$_2$ concentration, the draw-down build-up field experiments displayed opposite trends (Figure 5.33). During the draw-down build-up experiments, the chamber started with 100-150 ppm CO$_2$ and finished with around 500 ppm CO$_2$. Because steady state was reached after the long pump-down of CO$_2$, all of the CO$_2$ in the chamber at the beginning and end of the build-up portion of the experiment should be lake gas. However, in two of the three experiments, the final chamber gas at a lower $\Delta$PCO$_2$ had less negative $\delta^{13}C_{CO_2}$ than initial chamber gas (Figure XX, of all East Lake gas samples, way above). Lab Lake CO$_2$, on the other hand, became more depleted in $\delta^{13}C$ as its headspace CO$_2$ concentrations increased.

![Figure 5.33: Relationship between $\delta^{13}C$ and the inverse of the concentration of CO$_2(gas)$ in East Lake and Lab Lake samples.](image)
Additionally, discrepancies in the trend could be due to an influx of room air at the beginning of the experiment during the addition of the fluid or removal of the CO₂ trap. Room air likely has δ¹³C -9‰, and the gas evading from the Lab Lake solution had δ¹³C ~10.8‰ or lighter, based on the final composition of the headspace and CO₂(aq). A mass balance mixing model with δ¹³C -10.8‰ added gas and δ¹³C of the headspace in the previous step shows a strong correlation with the measured δ¹³C of the Lab Lake headspace (Figure 5.34). Mixing models using incoming CO₂(gas) with a δ¹³C slightly smaller or larger than ~10.8‰ also show strong correlations with measured carbon isotopic compositions, so the fit of the model assuming Lab Lake gas δ¹³C ~10.8‰ does not rule out kinetic fractionation.

Figure 5.34: Isotopic composition of evolving headspace gas calculated from a mass balance model using δ¹³C -10.8‰ for Lab Lake gas plotted against measured δ¹³C of Lab Lake headspace gas.
5.4.3.2 $\delta^{18}$O CO$_2$

Oxygen isotopes in dissolved CO2 equilibrate with oxygen isotopes in water in less than a second, which is rapid on both the Lab Lake experiment and East Lake degassing time scales (Affek, 2013; Miller et. al, 1999). The temperature-dependent equilibrium fractionation factors between H$_2$O and CO$_2$(aq) are almost exactly compensated by the difference between the V-PDB-CO$_2$ and V-SMOW scales at the lab temperature (Affek and Yakir, 2003). At the colder field temperature, however, the hydration reaction fractionates $2\%$ more than than shift between the V-PDB and V-SMOW scales, making $\delta^{18}$O CO$_2$(aq) even heavier. Thus, Lab Lake CO$_2$(aq) has the same $\delta^{18}$O as Lab Lake water on V-SMOW, while East Lake CO$_2$(aq) is $2\%$ heavier than $\delta^{18}$O as lake water on V-SMOW. East Lake and Lab Lake gas should have identical $\delta^{18}$O identical to $\delta^{18}$O water on the different scales, but gas from both East Lake and Lab Lake are 10-12\% lighter than water, suggesting a non-equilibrium effect (Figure XX, below).
Figure 5.35: Relationship between δ18O and the inverse of the concentration of CO2 in East Lake and Lab Lake samples.

One potential explanation for the discrepancy in δ18O values between the dissolved and gas phase CO2 is that the oxygen isotopes in CO2(gas) might have reequilibrated with those in ambient water vapor. The δ18O of atmospheric moisture can be calculated by

\[
\delta_A^{18}O(\text{‰}) = 0.39T - 22.8 \quad \text{(Lefkowitz et. al, 2016)}
\]

Equation 5.13

where T is ambient temperature at groundlevel in °C. At field temperature, δA18O is -16.95‰, and at lab temperature, δA18O is -15‰. Both of these oxygen compositions are heavier than East Lake and Lab Lake δ18O CO2(gas), indicating that the oxygen isotopic signatures of East Lake and Lab Lake CO2 were not caused by equilibration
with ambient moisture. Also, humidity during East Lake and Lab Lake sampling was very low.

Figure 5.36: The δ18O of the CO₂ added to cell headspace and the δ18O of the total CO₂ in the headspace per increase in delta PCO₂. Note that experimental time and CO₂ concentration increase from right to left.

Similar to the carbon isotopic composition in evading East Lake and Lab Lake CO₂(gas), the oxygen isotopic composition in overall Lab Lake air and evading Lab Lake gas changes with ΔPCO₂ (Figure 5.36). Although the water δ18O stays constant at -8.9‰, evading Lab Lake gas δ¹⁸O steadily becomes less negative as the reaction proceeds, from -22.5‰ at 300 ppm CO₂ to -9.8‰ at 3100 ppm. This trend of less negative δ¹⁸O CO₂ with larger concentrations is consistent with kinetic fractionation theory and results of other studies looking at CO₂ isotopes under varying concentrations (e.g. Affeck and Zaarur, 2014; Kendall and Caldwell, 1998). Bonds between lighter oxygen isotopes in CO₂ are broken more easily than heavier CO₂
isotopes. Thus light oxygen isotopes react faster and are more prevalent in the initial products, which have low concentrations (Kendall and Caldwell, 1998).

Based on the change in $\delta^{18}$O fractionation between CO$_2$(water)-CO$_2$(gas), for every additional atm $\Delta$PCO$_2$(water-gas), $\delta^{18}$O shifts -3940.4‰ (slope of the regression line in Figure 5.37). Because the fractionation of $\delta^{18}$O CO$_2$ varies with $\Delta$PCO$_2$, this shift is the result of a non-equilibrium fractionation process. Using established equilibrium fractionation factors and the Lab Lake experimental results (Figure XX, delta $\delta^{18}$O water vs headspace), the following equation was determined for $\Delta$PCO$_2$-dependent fractionation of $\delta^{18}$O during degassing of CO$_2$ at 25°C:

$$\varepsilon_{\text{kin}}(\Delta\text{PCO}_2) = -3940.4 * \Delta\text{PCO}_2 + 360.65$$

Equation 5.14

where $\Delta$PCO$_2$ is PCO$_2$(water) – PCO$_2$(air) in atm. Over the course of the Lab Lake experiment, $\varepsilon_{\text{kin}}$ increased from -6‰ to 6‰. In the future, field draw-down build-up experiments should be repeated and gas samples should be taken at more regular intervals at a larger range of CO$_2$(air) concentrations for $\delta^{18}$O analysis to empirically confirm this equation.
Figure 5.37: Difference between $\delta^{18}O$ VSMOW Lab Lake water and $\delta^{18}O$ VPDB CO2 headspace with respect to the difference in pCO2 between the water and the headspace.

Similar to East Lake, the $\delta^{13}C$ and $\delta^{18}O$ of the evading CO2 does not account for the trends in $\delta^{13}C_{(DIC)}$ and $\delta^{18}O_{(H2O)}$ in Lab Lake in a mixing array, confirming that another process is in play. This additional component could be a nonequilibration fractionation, such as kinetic fractionation. The Lab Lake experiment will be rerun multiple times in the coming weeks with more regulated sample collection to better identify carbon and oxygen fractionation during degassing.

Additionally, later experiments should look at the clumping of CO2 isotopes during CO2 degassing to fully understand the isotopic fractionation occurring. When either $\delta^{18}O$ or $\Delta 47$ of CO2(aq) or CO2(gas) show disequilibrium, the other isotopic system does as well, so looking at $\Delta 47$ will also shed light on $\delta^{18}O$ fractionation. Disequilibrium in $\Delta 47$ is often larger and easier to identify than in $\delta^{18}O$, because $\Delta 47$
is independent from $\delta^{18}O$ H$_2$O (Affek, 2013). The effects of the disequilibrium kinetic component of dehydration of bicarbonate into CO$_2$ and CO$_2$ degassing have never been considered regarding $\Delta^{47}$, and it could have major implications for the applications of clumped isotopes.

5.5 Bubble Transport of CO$_2$ in East Lake

The geothermal input of CO$_2$ is East Lake’s main source of carbon and fuels its carbon cycle. East Lake has an internal PCO$_2$(aq) > PCO$_2$(atm), leading to diffusive CO$_2$ loss from its lake surface. This CO$_2$ loss must be replenished by CO$_2$ bubbles rising from the lake bottom that largely dissolve before reaching the water surface. Bubbles are only observed to escape at the surface at the East Lake hot springs. Rising bubbles from the bottom of East Lake to the surface are visible on depth finders and sonars. This bubble injection process from below the lake adds dissolved CO$_2$ to the water through diffusional uptake while the bubbles rise through the water column, acidifying the lake at the same time (Lefkowitz, 2012). In order to understand the $\delta^{13}C$ DIC gradient and how the CO$_2$ gets from the hot springs at the bottom of the lake to the surface water to be consumed by biota and degassed, it is important to understand the bubble transport mechanisms. A derivation of the bubble rise and dissolution processes in East Lake is given below, and will test if bubble rise can indeed resupply the epilimnion with enough CO$_2$ to compensate for the CO$_2$ that diffuses out to the atmosphere.

5.5.1 Theory
Assume a CO$_2$ bubble at some depth $z$ containing $n$ moles with a volume $V$. The internal bubble pressure is hydrostatic, so $P_z = (1+0.1z)$, where $P_z$ is expressed in bars. The temperature at the bottom of the lake is $4^\circ$C, while the upper 15 m are $\sim 14^\circ$C. According to the ideal gas law, $V = nRT / P$, which becomes

$$V = nRT / (1+0.1z)$$

Equation 5.15

The bubble volume $V$ can also be expressed as

$$V = 4/3 \pi R^3$$

Equation 5.16

where $R$ is the bubble radius (note that $R$ is the universal gas constant). We can rephrase the bubble size through its radius $R$ by equating Equations 1 and 2 at a given depth leading to $[nRT / (1+0.1z)] = 4/3 \pi R^3$ which solves for $R_z = [nRT / (4/3 \pi (1+0.1z))]$, which at $T=T1$ becomes

$$R_z = C_1 (1+0.1z)^{-1/3} \quad \text{with} \quad C_1 = [(4/3 \pi) / [nRT]]$$

Equation 5.17

Upon rise, the bubble will expand as a result of decreasing pressure. The bubble size then is a function of depth and the water temperature. The density of the gas decreases with expansion, slightly increasing the buoyancy of the bubble. The bubble rise velocity can be derived in principle from Stokes Law
but this law is only valid at very low Reynolds (Re) numbers. Stokes Law can be used for Re<1, which limits it to bubbles with R < 100 micrometer for rise in water. The Re defines the transition from laminar to turbulent flow regimes and is usually defined as

\[ Re = \frac{\rho v R}{\mu} \]  

Equation 5.19

where the symbols represent respectively the fluid density \( \rho \), the object velocity \( v \), the characteristic size (bubble radius \( R \)), and the fluid’s dynamic viscosity \( \mu \). The upwards velocity of larger bubbles (100 to 1000 micrometer, 800>Re>1) is given approximately by

\[ v = 2 \sqrt{\frac{gR}{0.9}} \]  

Equation 5.20

where \( g \) is the gravitational acceleration. Still larger bubbles travel at speeds roughly independent of their size, because the drag force so strongly deforms the bubble that it becomes ellipsoidal. Common velocities are 28-30 cm/sec for bubbles up to 7.5 mm, whereas still larger bubbles travel at speeds of 35-40 cm/s. The latter usually tend to subdivide into smaller bubbles because of the friction forces acting on a deformable gas medium.
Experimental data of air and CO$_2$ bubbles in pure water show velocities of a few cm/s for small bubbles (10-100 micrometer, following Stokes Law) and 20-30 cm/second for medium (250-1000 micrometer) sized bubbles (Bours et. al, 2008) We fitted a logarithmic function to the available experimental bubble rise data as a function of the diameter d in water at ~20°C and used that in our calculations for East Lake. The best fit equation is

$$V_{\text{rise}} = 5.3326\ln(d) - 22.455$$

Equation 5.21

with the bubble diameter d in micrometers and the bubble rise velocity in cm/second, and this equation is valid for bubble diameters of 10-25,000 micrometer. Uncertainties come from variations in temperature with depth and season, which influences both fluid viscosity and bubble size. Nonetheless, the modeled rise rates are probably accurate within 10%. The bubble expansion from 6.5 bar at the lake bottom to 1 bar at the surface creates roughly a six-fold increase in bubble volume, which is slightly less than a doubling in diameter.
The bubbles lose CO₂ through dissolution (gas exchange with its surrounding water), so the number of moles of CO₂ (n) will decrease during travel, and the bubble will shrink. The rate of dissolution is a function of the CO₂ “overpressure” in the bubble, Δp, compared to the P_{CO₂} in the water. The Δp = P_g – P_w, where P_g is the partial pressure of CO₂ in the bubble (= 1+0.1z bar for pure CO₂) and P_w is the virtual CO₂ pressure in the water (depends on total carbonate and pH). The PCO₂ in the water is on the order of 10^{-2.9} bar (Figures 5.10 and 5.11), so we can neglect the PCO₂(aq) in the Δp expression. The CO₂ invasion rate I from the bubble into the water depends on Δp, temperature, and a resistance coefficient for the specific water-gas combination at unit Δp. Experiments in our lab on CO₂ withdrawal rates at known Δp and room temperature (22°C) in stirred seawater provided an invasion rate of
~0.04 moles m$^{-2}$ year$^{-1}$ microatm$^{-1}$ (Bourse, 2001). The CO$_2$ flux from the bubbles into the water at a given depth, $F_{CO2}(z)$, can then be phrased as

$$F_{CO2}(z) = I \left( \frac{44}{31579200} \right) * (1+0.1z) * 10^6 * 4\pi R^2 \text{ Equation 5.22}$$

With $F_{CO2}$ in grams CO$_2$ per second at depth $z$. Consequently, during bubble rise, two counteracting processes influence bubble size: expansion because of pressure decrease, and shrinkage because of CO$_2$ dissolution.

**5.5.2 Application to East Lake**

Bubble rise evolution in East lake was modeled in Excel, using columns with depth, temperature, number of CO$_2$ moles in an initial ‘bottom bubble’ and Equations 5.15-5.22 for bubble size, rise velocity, and rate of CO$_2$ evasion as a function of depth. We used one meter as the depth step, which was then converted into a time step with the bubble rise velocity at that depth. The number of moles in a bubble at a given depth ($n_z$) is calculated as the number of moles in the bubble one meter deeper minus the CO$_2$ evaded from that bubble into the surrounding water during one meter of travel, expressed in seconds. The CO$_2$ evasion per meter is a function of initial bubble size and depth ($z$); the latter determines PCO$_2$(bubble) and the bubble size, and thus the bubble surface area through which CO$_2$ can evade. The effects of expansion alone and expansion plus shrinkage are shown in Figure 5.39. Obviously, the CO$_2$ dissolution wins out over the expansion in small bubbles, and initial bubbles
<10 micrometer in diameter will not rise very high. Initial bubbles >12 mm will reach the water surface, and setting constraints on the possible initial bubble sizes for East Lake. For East Lake DIC to replenish after degassing, CO2 bubbles much reach the epilimnion. But bubbles are not seen at the lake surface and surface waters are not more concentrated in CO2 than lower in the water column, so bubbles do not reach the surface. We conclude from this modeling that the initial bubble sizes are on the order of 10-12 micrometer, and most bubbles have dissolved before they reach the surface of the lake (Figure 5.39).

![Bubble evolution diagram for East Lake, with 'expansion only' on the right-hand side, with initial bubble diameters of resp. 10 and 11 micrometers and on the left-hand side combined expansion and shrinkage because of CO2 dissolution. The annihilation depth for a 10mm diameter initial bubble of CO2 is 15m, for an 11-mm bubble 6 m depth and close to the surface for a 11.6 mm bubble. The rise time for the bubbles from the very lake bottom to annihilation is about 3-4 minutes.](image-url)
We calculated the rate of CO$_2$ uptake in the hypolimnion of the lake (55-15 m depth) and in the epilimnion (upper 15 m). We used the 11.6 mm diameter starting bubble scenario, and its rise velocity decreases as it gets smaller through dissolution and becomes less buoyant (Figure 5.40). The CO$_2$ loss is initially large because of the high PCO$_2$, despite the small bubble surface area (Figure 5.41). For the 11.6 mm starting bubble at 55m depth, a total of 241 microgram CO$_2$ is added to the overlying epilimnion and 9947 microgram CO$_2$ to the hypolimnion. Only the drowned crater area of East Lake is deeper than ~20 m (~20% of lake surface area, Figure 2.3) and this deep crater part is the main zone with escaping bubbles apart from the coastal hot spring zone. The 241 microgram CO$_2$ is spread through horizontal mixing throughout the epilimnion. About 50 tonnes CO$_2$ is added per day to the epilimnion to compensate for the CO$_2$ lost by surface degassing. From the bubble rise analyses, the ratio of CO$_2$ added to the hypolimnion relative to the epilimnion is ~40, thus an amount of ~2,000 tonnes CO$_2$ (not tonnes of carbon) must be added to the hypolimnion each day. The hypolimnionic lake water contains roughly 8,200 tonnes CO$_2$. Thus, the hypothetical addition of 2,000 tonnes CO$_2$ per day is unreasonably large and would be visible in DIC depth profiles.

The bubble rise scenario does not consider CO$_2$ diffusion along a PCO$_2$ gradient or that the CO$_2$ transfer from bubble to water changes the internal PCO$_2$ of the water. It is possible that the bubbles form a boundary layer of CO$_2$-enriched water (Talaia, 2007) which then slows down the transfer of CO$_2$ from the bubble to the surroundings at depth (local pH effect). In that case, a larger fraction of the bubble CO$_2$ reaches the epilimnion than calculated here, depressing the ratio of CO$_2$ added to
the epilimnion to that of the hypolimnion. Additionally, it is possible that East Lake waters mix more than previous anticipated, moving geothermal CO2 from the bottom waters into the surface waters. However, if the lake mixed frequently enough to replenish surface DIC from degassing, observed strong trends in temperature and δ¹³C DIC with depth would have to form unrealistically quickly. All East Lake water profiles have been taken in the crater area to get the full 50-55 m range, so the water chemistry in the shallower part of the lake is not known. It is possible that much of the geothermal input occurs in this region, and because the bubbles would not need to travel as far to reach the epilimnion, less total incoming carbon would be needed to saturate the water column and lead to the observed CO₂ evasion rates. More water mixing could occur in this shallow region, transporting geothermal carbon to the surface waters. This would be reflected in nearly homogenous water chemistry, most notably DIC isotopic composition, throughout the water column. In the upcoming field season, water profiles should be taken all over the lake.
Figure 5.40: Depth-dependent velocity of rise of a bubble with an initial diameter of 11.6 mm.

Figure 5.41: Depth-dependent amount of CO₂ transferred from a bubble with an initial diameter of 11.6 mm.
5.6 Seasonal Carbon Dynamics

5.6.1 Carbon Cycle

The total reservoir of DIC in East Lake as determined based on the 2016 field data and WebPHREEQ calculations is ~3800 tonnes (Figure 5.4). The most significant source of carbon in the lake is the volcanic input and sinks are surface CO2 evasion and in-lake photosynthesis followed by organic matter burial. The amount of carbon in the lake over the years has been relatively constant, so the carbon sources presumably equal the sinks. This makes some sense, because the diffusive CO$_2$ flux depends on the internal PCO$_2$. At a higher PCO$_2$(aq), the lake will degas more, providing a negative feedback. The photosynthesis is probably not simply coupled to the CO$_2$(aq) concentration and will depend on light input, and primary nutrients N and P (as well as Si). The lake is frozen over from November to May, and during this 30-week period, there is probably no surface evasion of CO$_2$ and no burial of organic matter. When the ice melts in late May, the lake turns over and we suspect that the carbon that built up in the lake over the winter will be released at a more rapid rate because of the higher PCO$_2$ in the lake. This degassing may be ‘near-catastrophic’ or just a bit faster.

By averaging the measured CO$_2$ surface evasion rates and using the modeled values from 2015 and 2016, about 16 tonnes of carbon are evaded from the surface of East Lake each day that it is not frozen over, totaling ~112 tonnes per week. The isotopic composition of the lake gas was estimated at $\delta^{13}$C $\sim$10.5‰ (Figure 5.27). Using the carbon concentration in cores from East Lake, together with bulk dry
sediment densities and the $^{210}\text{Pb}$ age scale (Lefkowtiz et al., 2016), ~6.3 tonnes of carbon are buried in the sediment per week of the 22-week summer, which amounts to 140 tonnes per year. The sequestered carbon has $\delta^{13}\text{C} \sim -24\%o$, assuming that the bulk photosynthate (consisting of the three types of organisms: algae, cyanobacteria, and SAV) has the same isotopic composition as the organic carbon in the sediment cores (Capece, 2016). If photosynthetic withdrawal and degassing are the only two major sinks of carbon, then 118.3 tonnes of carbon are lost from the lake each summer week. To hold East Lake at steady state on an annual timescale, a mass balance indicates that the influx of carbon in East Lake must equal 114.33 tonnes of carbon per week year-round, assuming the rate of winter geothermal input is the same as summer input rates. Based on the isotopic composition of the hot springs bubbles (Figure 5.27), the geothermal input has carbon with $\delta^{13}\text{C} \sim -7\%o$. Based on its sources and sinks, the residence time of carbon in East Lake is ~233 days or 0.64 years.

At this rate of geothermal input, the whole lake would have ~3233 more tonnes DIC by the end of the winter than at the beginning of the summer (Figure 5.1). In order for summer lake DIC levels to reach concentrations measured in the field, the additional DIC built up over the winter must be rapidly released. The Wanninkhof (1992) theoretical flux model can be applied to the system to determine the flux rate based on the $\Delta\text{PCO}_2$, temperature, and wind speeds in the spring. By the end of the winter, the whole lake water would have a DIC concentration of 0.00684 mol/L, significantly higher than during the summer. The pH of East Lake waters tend to increase as spring, summer, and fall progress (Figure 5.1), so the pH is likely around 6.4 in the early spring. At this pH, approximately half of dissolved carbonate species
are present as the CO$_2$ species (Lower, 1996). The PCO$_2$ in East Lake water can be estimated by scaling the CO$_2$(aq) concentration by the temperature-dependent Henry’s Law constant. At 4°C with the CO$_2$ built up by the end of the winter, PCO$_2$ in the water would be ~0.1839 atm, so high that bubbles might have formed under the ice in the late winter. The late winter ΔpCO$_2$ between the lake water and ambient air at ~407 ppm is 0.1835 atm, three to five times greater than during the summer (Table 5.1). At 4°C, the Sc number is 1491.26. Wind speeds in Bend in May 2016 average 1.8 m/s and reach a maximum at 12.5 m/s, giving a mean k factor of 1.28 and maximum 38.65 (Weather Underground).

The mean theoretical flux directly after ice melt and spring mixing is 0.24 mol m$^{-2}$ day$^{-1}$, four times higher than the average mean theoretical flux rate from all the summers sampled (0.06 mol m$^{-2}$ day$^{-1}$). The maximum theoretical flux rate during spring mixing is 7.09 mol m$^{-2}$ day$^{-1}$, while the average maximum theoretical flux rate for all the summer sampled is 0.45 mol m$^{-2}$ day$^{-1}$ (Table 5.1). Because East Lake is at a higher altitude as Bend and thus likely has higher wind speeds, real flux rates are likely between mean and maximum values. Based on the surface area of East Lake, 48-1,445 tonnes of CO$_2$ are evaded from the East Lake surface each day after the ice layer melts. With this flux rate range, it would take two days to two months to release the excess 3233 tonnes of carbon built up over the winter. In first couple weeks of spring, the rate of CO$_2$ degassing from the lake is significantly higher than the rest of the season. This release is near catastrophic during the first week after ice melt and spring turnover, when the ΔPCO$_2$ is highest. In the following weeks, flux rates are elevated compared to summer flux rates and gradually decrease until all the built-up
winter DIC has evaded and regular summer flux rates are reached. June 2016 flux measurements likely occurred while some of the built-up winter CO$_2$ was still evading, which could explain why the June 2016 flux rates are 50-100% higher than July 2015 flux rates. The catastrophic release has the same isotopic composition as the lake gas ($\delta^{13}$C $\sim$-10.5‰).

5.6.2 One-Box Carbon Cycle Model

Limnogeologists perform box modelling to quantitatively account for the rates of addition and removal of water and dissolved constituents in a lake. Box modelling assumes that a portion or the whole lake can be considered one “box” because it is so well-mixed that it is homogenous in composition. Constituents are added to or removed from each box at a slower rate than it is mixed, so the box is assumed to be always homogenous. The concentration of a constituent in a box is determined by the initial concentration and the relative rates and magnitudes of inputs and outputs. If the inputs equal the outputs, the box’s concentration remains constant and it is at steady state (Varekamp, 1988; Baker, 1994). A single box model representing the whole lake is the simplest kind of box model. The box model becomes more complicated when inputs and outputs vary seasonally or evolve, as is the case in the Newberry Lakes.

A simple one-box model was created based on the preliminary model in Lena Capece’s 2016 thesis and 2016 field data to see if models could explain the observed heavy $\delta^{13}$C DIC in the surface of East Lake. The model was run over 4.5 years with weekly time steps, a 22-week summer, 30-week winter, and catastrophic release of built up carbon at the end of the winter. Lake DIC was set to 3804 tonnes initially. Due to the mass balance, the total carbon in the lake remains constant over the years.
though varies seasonally, with a minimum of 3721 tonnes at the end of the summer and a maximum of 7037 tonnes after winter buildup (Figure 5.42). Over the course of the summer, due to photosynthetic sequestration and burial, there is a slight decrease in the total amount of carbon in the lake. The carbon builds up during the winter months, because of the continued geothermal input without outflows. After the ice thaws and the catastrophic release in the early summer, the total carbon returns to the initial 3804 tonnes.

![Total Carbon in Whole Lake](image)

Figure 5.42: Total DIC in East Lake over 4.5 years based on simple one-box model.

The carbon isotopic composition was initially set to $\delta^{13}C$ 0‰, and due to the short residence time of carbon in East Lake, the water quickly reached measured isotopic values within one year (Figure 5.43). Consistent with the real lake isotopic composition (Figure 4.29), the bulk lake $\delta^{13}C$ DIC is around 3-4‰ during the summer and becomes very slightly heavier over the years due to the withdrawal of
light carbon from the surface waters during photosynthesis. Because the geothermal input is lighter than the bulk water carbon and there is no surface evasion or photosynthetic removal of preferentially light carbon during the winter, the lake water get substantially lighter during the winter months (as low as $\delta^{13}C -2$ to -1‰). The system is evolving towards isotopic steady state and has almost reach it by the end of the 4.5 years.

Figure 5.43: Trends in $\delta^{13}C$ DIC in East Lake over 4.5 years based on one-box model.

5.6.3 Two-Box Carbon Cycle Model

Two box models are more appropriate for lakes that undergo stratification in the summer time, because their average properties do not fully explain lake processes. Also, in the one-box model above, it is not possible to reproduce gradients in $\delta^{13}C$ (DIC) and DIC concentration in the lake water column, so a two-box model was created. The two boxes are the epilimnion, or the surface water above the thermocline (0-15 m depth), and the hypolimnion, or the bottom water below the
thermocline (15 m to bottom). Based on the volumes and the average carbon concentration in East Lake water, the epilimnion has approximately 2179 tonnes of carbon and the hypolimnion has 1625 tonnes of carbon in the early summer after accumulated winter CO$_2$ had been degassed.

The two-box model takes more nuances of inputs and outputs and seasonal effects into account, which are important due to the episodic mixing and stratification of the lake (Figure 5.44 and 5.45). In addition to input and outputs to the whole lake, two-box models consider fluxes between the two boxes. As describe above, the rate and amount of geothermal CO$_2$ dissolution into the hypolimnion and epilimnion through bubble transport is not well understood, so it was assumed that the geothermal CO$_2$ inputs into both boxes was the same.
The isotopic composition of all the original sources and sinks of carbon is the same in the two-box model as in the one box model. When the geothermal carbon moves from the bottom water to the surface water, it has the same isotopic composition as the geothermal input (-7‰), but the lake carbon that degasses is lighter (-10.5‰) due to equilibrium and kinetic fractionation. The dissolution of the -7‰ geothermal CO₂ in the hypolimnion drives the overall hypolimnion δ¹³C DIC to lighter values, whereas the degassing in the epilimnion drives δ¹³C DIC to heavier values in shallow waters. These two ongoing effects are captured in the two box model.
Figure 5.45: Visualization of two-box East Lake carbon cycle model, created in Insight Maker, a dynamic modeling application. The relationships between the sources and sinks of carbon in the epilimnion and hypolimnion are shown.

During the summer, the lake stratifies, with the warmer epilimnion and the cooler hypolimnion. Geothermal carbon enters the bottom waters, and some moves toward the surface waters through diffusion and bubbles transport, where it is largely dissolved and then degasses through diffusional escape. Photosynthetic activity is high in the surface waters, and part of the carbon is returned to the hypolimnic water through respiration (from oxygen balance). As discussed above, an estimated 209 tonnes of carbon are photosynthesized annually. Consequently, each summer week, 9.5 tonnes of carbon are removed from the epilimnion by through photosynthesis and sinks to the hypolimnion. Of this organic carbon, 3.23 tonnes are returned to the
hypolimnion through bacterial respiration during decomposition of organic carbon in sediments, as calculated from the oxygen-respiration loop. The remaining 6.27 tonnes of carbon are removed from the bottom water through sedimentation and buried each summer week. Due to photosynthetic fractionation, the epilimnion waters have a lower concentration of carbon during the summer, and the remaining carbon becomes more enriched as the summer progresses. Hypolimnion waters, in contrast, gradually gain light carbon due to respiration and the addition of light geothermal CO₂.

Additionally, as the surface waters warm from May to November, the δ¹³C CO₂ (aq) gets heavier due to a change in temperature-dependent fractionation (Figure 5.5a). Consequently, evading δ¹³C CO₂ (gas) is heavier when waters are warmest, leaving surface DIC δ¹³C lighter. The overall effect of this gradual ~2‰ shift in δ¹³C CO₂ over the course of the whole summer is very small in term of the total reservoir of carbon in the lake, but it is still an important factor to consider.

In the fall, the lake turns over, mixes, and its water becomes homogeneous in concentration and isotopic composition of carbon. The carbon concentration and isotopic composition in the homogenous whole lake water after mixing is determined through a mixing model between the epilimnion and hypolimnion based on their molarity, isotopic composition, and total carbon content at the end of the summer. All waters return to their pre-summer isotopic composition before stratification and the biological pump.

Over the winter, Newberry’s volcanic system continues to bubble CO₂ into East Lake’s hypolimnion, and much of this geothermal CO₂ diffuses into the epilimnion. By the end of the 30-week winter, the epilimnion and hypolimnion waters
have the same molarities of carbon due to bubble transport and diffusion, but because the two boxes have different volumes, an excess of 1,899.5 tonnes of carbon builds up in the epilimnion and 1,530.5 tonnes in the hypolimnion. Because incoming geothermal carbon is isotopically light and no isotopically light CO$_2$ leaves, the models indicates that both surface and bottom waters have light $\delta^{13}$C DIC (~2 to -1.5‰) over the winter (Figure 5.49).

Once the ice layer covering the lake melts in the spring, the surface waters catastrophically release the excess ~3,233 tonnes of carbon built up over the winter. At this point, the lake also turns over, the waters mix, and the whole lake has identical isotopic compositions and concentrations of carbon. The carbon concentration in the whole lake decreases to 0.003683 mol/L carbon after the catastrophic release. Due to the release of isotopically light CO$_2$ during the catastrophic release, the model indicates that the $\delta^{13}$C DIC increases to ~3‰ in the whole lake. Then summer stratification begins, with the full set of sources and sinks of carbon.

Similar with the one-box model and empirical data, the total amount and isotopic composition of the carbon in the surface, bottom, and bulk waters in the two-box model reach near steady state after less than a year regardless of the initial isotopic composition of the waters, due to the short residence time of carbon in the lake. The isotopic composition and total amount of carbon increase very slightly over the years in both the model and field data, though the trend in the field data over time is not well defined (Figure 5.4). After a few more residence times, it is likely that the model would reach steady state and have identical $\delta^{13}$C and amounts of carbon each year.
Figure 5.47: Total DIC in the epilimnion and hypolimnion of East Lake over 4.5 as simulated in a two-box model.

Figure 5.48: Concentration of carbon in the epilimnionic and hypolimnionic waters of East Lake during the 4.5-year modeling period.
The two-box model seasonal trend in $\delta^{13}$C DIC is nearly identical to that of East Lake (Figure 5.50). East Lake water profiles were taken in different months each year, so this model assumes that the lake is at isotopic steady state and does not change over the years. East Lake carbon isotope data from the different months and over the past six years shows a seasonal trend in surface and bottom water composition. In both the model and empirical data, surface and bottom waters are similar in the late spring and become increasingly different over the season. East Lake $\delta^{13}$C DIC is around 1 to 3‰ during the winter months (November-May) at all depths. Once the ice has melted in late May, the lake turns over and the waters become homogenous at 1.5-3‰. The exact timing of the onset of ice melting, spring
turnover, and catastrophic release varies annually, as demonstrated by a range of carbon isotopic compositions in the late spring and early summer.

Figure 5.50: Monthly trend in $\delta^{13}$C DIC in East Lake surface and bottom water. Samples were taken in different months each year.

By mid to late June, photosynthesis has begun and the lake has stratified, with warmer surface water with heavier carbon ($\delta^{13}$C ~5‰) and cooler bottom waters with lighter carbon ($\delta^{13}$C ~2‰). As the summer continues, bottom waters continually become more isotopically light, while the surface waters maintain relatively constant at heavier carbon values. During the hottest part of the summer, mid August, the $\delta^{13}$C DIC becomes slightly more negative because the evading lake CO$_2$ (gas) is heavier in $\delta^{13}$C due to the temperature-dependent fractionation of carbonate species. In the late fall, the lake water once again turns over and then freezes for the winter. Also East
Lake surface waters in May, June, and November 2016 (Figure 5.53) show decreasing total carbon as the summer progresses, which is consistent with the one and two-box models. The model and empirical δ^{13}C DIC values and trends are identical throughout the year, supporting measurements and assumptions included as parameters in the model.

6. Methane

6.1 Background

Methane is one of the most effective greenhouse gases, because although it makes up less than two parts per million by volume (ppmv) of Earth’s atmosphere, it accounts for 20% of total radiative forcing. In aquatic ecosystems, methane serves as a substrate for microbial production. Historically, Archaean microbial methanogenesis is thought to occur in anoxic sedimentary environments, but recently it has been shown that methane often accumulates in aerobic environments. Hypotheses to explain this paradox include the physical transport of methane from anoxic environments or production in microanoxic zones within aerobic areas (Grossart et. al, 2011). It has become more accepted that microbial methanogenesis may also occur in aerobic waters of the oligotrophic ocean, and that ocean waters are more enriched in CH_{4} than equilibrium with the atmosphere would suggest (Karl et. al, 2008; Damn et. al, 2010). Still, only anaerobic methanogenesis is thought to occur in lakes (Wetzel, 2001). Two recent studies suggest that aerobic methanogenesis occurs in the well-oxygenated surface waters of the temperate oligotrophic Lake Stechlin in Germany and a Canadian Lake (Grossart et. al, 2011; Tang et. al, 2014;
Bogard et. al, 2014). While aerobic methanogenesis in the ocean is gaining traction and its implications in the ocean-atmosphere CH₄ cycle are starting to be considered, aerobic methanogenesis in freshwater ecosystems is a novel concept that would drastically change our view of the global CH₄ cycle.

The process of methane production in well-oxygenated surface waters is not well understood for either salt or freshwater systems (Karl et. al, 2008). While geological and anthropogenic emissions are the best-known sources of methane, methane is also produced by methanogens via three major pathways: acetoclastic, methylotrophic, and hydrogenotrophic methane production (Tang et al, 2014). Within these three pathways, exact mechanisms vary based on the dissolved organic substrate used. For example, in the Arctic Ocean, DMSP (dimethylsulfoniopropionate) is used as a methylated substrate for methylotrophic methanogenesis (Damn et. al, 2010). Each pathway is most prevalent under unique conditions and fractionates the C and H isotopes differently, and fractionation factors can be used to qualitatively determine the methanogenesis pathway (Bogard et. al, 2014).

6.2 Results
Figure 6.1: Methane concentration in water depth profile samples collected in East Lake and Paulina Lake in 2014 and 2016. Each 2014 sample was analyzed for methane concentration twice, once during each isotopic analysis.

The concentration of methane in each water sample was calculated from the measured amount of CH$_4$ in the headspace. This was done by dividing the amount of methane in the headspace and water by the volume of water in each exetainer. The total amount of methane in the headspace was determined using the ideal gas law and the methane gas concentration in the headspace. Methane gas in the headspace was assumed to be at equilibrium with dissolved methane in the water, so the amount of methane in the water was obtained by scaling the pressure of methane in the headspace by the Henry’s Law constant and the volume of water. This was done for each sample for the two separate measurements for δD and methane concentration.
and $\delta^{13}C$ and methane concentration and then averaged for all samples taken in 2014 and 2016 (the different samples also had different headspace to water volume ratios).

Figure 6.2: Methane $\delta D$ VSMOW in water depth profile samples collected in East Lake and Paulina Lake in 2014 and 2016.
Geothermal gases are typically rich in methane (Op den Camp et. al, 2009). However, East Lake and Paulina Lake methane concentrations are low for a common geothermal system, though still 10 times higher than in water equilibrated with atmospheric methane without an additional methane source. All seven vertical profiles from the two lakes (four in East Lake, three in Paulina Lake) show similar trends in concentration and isotopic composition of methane with depth (Figures 6.1-6.3). Significantly higher (~6x) concentrations of methane were found in the epilimnion waters (maximum of 36.4 ppmv) than the hypolimnion waters (~1.9 ppmv) of both lakes in both years (Figure 6.1).

In addition to a significant shift in concentration with depth, the isotopic composition of the epilimnion and hypolimnion waters are very different. Surface water methane is extremely depleted in both δD (-354 to -233‰) and δ¹³C (-54 to -44‰).
‰), while deep-water methane is much more enriched in δD (up to -42‰) and δ¹³C (up to -21‰) (Figures 6.2 and 6.3). The trend in isotopic composition with depth is clearer with δD than δ¹³C CH₄, but both show trends of similar, low values from 0 to 10 meters deep (above thermocline) and consistently significantly higher values from 20 to 60 meters (below thermocline). We note that the δD values of the hypolimnion samples all have relatively large error bars (Figure 6.5) because of the low methane concentrations, but we emphasize that the two groups of methane samples have very different isotopic compositions.

Additionally, East Lake hot springs data from 2016 have a CH₄ concentration of 0.3 ppmv, which is much lower than the other shallow waters of East lake, and a δ¹³CᵥPDB of -22.4‰, much higher than the rest of East Lake. Thus, geothermal input cannot explain the trends in methane concentration and isotopic composition, so it is not the main source of methane in the lake.

6.3 Discussion

6.3.1 Statistical Justification

East Lake and Paulina Lake water samples from 2014 and 2016 show different methane concentrations, and different δ¹³C and δD in the epilimnion (above 15m) and hypolimnion (below 15m). Welch Two Sample t-tests were performed on methane concentration, δ¹³C, and δD data to determine whether epilimnionic and hypolimnionic compositions are statistically significantly different.
Table 6.1: Welch Two Sample t-test results comparing the methane concentration and isotopic composition in the epilimnion and hypolimnion of East Lake and Paulina Lake in 2014 and 2016.

All three p-values generated in the Welch Two Sample t-tests are much less than 0.05, indicating that there is a statistically significantly difference in the means of the epilimnion and hypolimnion methane characteristics. Based on the concentration, δD VSMOW, and δ¹³C VPDB of the methane in East Lake and Paulina Lake in 2014 and 2016, the t-test shows that the methane from the epilimnion and hypolimnion came from two different populations.

Figure 6.4: Boxplots of concentrations of CH₄ in waters below and above the thermocline in East Lake and Paulina Lake in 2014 and 2016. Thick black lines are the median of each group. The upper boxes represent 50-75% and lower boxes represent 25-50%.
Figure 6.5: Boxplots of dD CH₄ in waters below and above the thermocline in the two lakes in 2014 and 2016. Thick black lines are the median of each group. The upper boxes represent 50-75% and lower boxes represent 25-50%.

Figure 6.6: Boxplots of δ¹³C CH₄ in waters below and above the thermocline in the two lakes in 2014 and 2016. Thick black lines are the median of each group. The upper boxes represent 50-75% and lower boxes represent 25-50%.
The boxplots in Figures 6.4-6.6 visualize the difference in the qualities of methane from the epilimnion and hypolimnion. The middle two quartiles of the two plots for each analysis never overlap, and there is also little overlap of the whiskers, indicating that the data comes from two independent populations. These visuals and statistical analysis indicate that the methane from the bottom and surface waters of the lakes are unequivocally distinct, and thus probably stem from different sources and were formed through different processes.

6.3.2 Aerobic Methanogenesis

![Figure 6.7: Methane δ¹³C VPDB versus δD VSMOW in East Lake and Paulina Lake water from 2014 and 2016 circled by their likely origins. The light blue circle represents the range of isotopic values expected for methane produced by microbial fermentation, based on the literature. The dark blue, green, and red bubbles present the expected isotopic values for methane produced by geothermal, thermogenic and microbial reduction, respectively. The hypolimnion is component I, and the epilimnion is component II. The small light gray bubbles next to each component number indicate the inferred pure isotopic composition of that end member.](image-url)
The statistically significant differences in methane concentration and isotopic composition in the epilimnion versus the hypolimnion in both lakes in 2014 and 2016 suggest that the methane in the surface and bottom waters have distinct origins or underwent different processes. Trends in the concentration and isotopic composition of the methane are consistent with gradients in temperature and dissolve oxygen concentrations. The upper 25 m of East Lake are well oxygenated (Figure 4.8, section on DO depth profile; Lefkowitz et. al, 2016), while the deeper water is likely hypoxic. Both lakes have a thermocline at 15-20 m depth (Figure 4.1, section on temperature depth profile), and a clear change in methane isotopic signature and concentration occurs around this depth (Figures 6.1-6.3).

The observed shifts in methane concentrations and isotopic signatures with depth, DO, and temperature in the water column strongly suggest aerobic bacterial fermentation of methane in the oxic surface waters of East Lake and Paulina Lake. Similar trends have been identified in marine systems, with surface waters supersaturated with isotopically light methane, which was attributed to aerobic methanogenesis through microbial fermentation (Karl et. al, 2008). Deep-water methane concentrations and isotopic signatures are consistent with thermogenic origins (Figure 6.10). Plots of δ¹³C and δD versus 100/CH₄ (Figures 6.8 and 6.9, respectively) provide linear mixing arrays between the two end members: thermogenic methane (-50 to -20‰ δ¹³C) (I) and microbial fermentation methane (-110 to -50‰ δ¹³C) (II) (Op den Camp et. al, 2009). These plots show a strong negative correlation between methane concentration and its isotopic signature. The
less concentrated hypolimnion (I) has a $\delta^{13}C \sim -30$ and $\delta D \sim -150$ CH$_4$, while the methane-rich surface waters (II) have a $\delta^{13}C \sim -50$ and $\delta D$ less than -300 CH$_4$. These values are much lighter than East Lake DIC ($\delta^{13}C \sim 1$ to 6‰) and water ($dD \sim -77$ to -71‰) (Figures 6.8-6.9). The noise in the data array between the two end members I and II, especially in the 2016 data, is likely the result of seasonal water mixing, because the samples were collected in early June, shortly after lake thawing and turnover in May and with just the beginning of summer stratification.

Figure 6.8: The relationship between the carbon isotopic signature of the methane in East Lake in 2014 and 2016 and the inverse concentration of methane in the water multiplied by 100. The horizontal black line indicates the approximate $\delta^{13}C$ of East Lake DIC (~1-6‰).
Figure 6.9: The relationship between the hydrogen/deuterium isotopic signature of the methane in East Lake and Paulina Lake in 2014 and 2016 and the inverse concentration of methane in the water multiplied by 100. The horizontal black line indicates the approximate δD of East Lake water (~ -77 to -71‰).

Bubbles with geothermal gases and local lake water circulation throughout the water column transport thermogenic methane, which comes from subaqueous geothermal inputs, similar to the hot springs CO₂ distributed throughout the water column as DIC. Surface water would then have some thermogenic methane, while aerobic methanogenesis is confined to the well-oxygenated, warmer surface waters. Consequently, II does not represent the pure microbial fermented methane; the actual end member would likely have an even more negative isotopic signature and extend the linear array. Although there is some lake circulation and some bottom-originating thermogenic methane reaches the surface water, sonar images and bubble models (Figures 5.39) show that the geothermal bubbles that transport gases dissolve significantly before reaching the thermocline. The significant difference in isotopic
signature with depth and the deep bubble dissolution indicate that it is highly unlikely that high concentration of methane in the surface water is due to the transport of geothermal bubbles.

East Lake hot spring waters have a much lower methane concentration and much heavier $\delta^{13}C$ than the rest of East Lake. This suggests that the geothermal hot spring gases are not the only or likely dominant source of methane in East Lake or have been modified during thermal requilibration the lake waters. The hot springs are likely the source of hypolimnic methane, but linear mixing arrays indicate that surface water had an additional lighter source of methane.

Figure 6.10: Isotopic composition of carbon in methane versus CO$_2$ in East Lake and Paulina Lake water samples from 2014 and 2016. $\delta^{13}C$ CO$_2$ was determined using Web-PHREEQ, $\delta^{13}C$ DIC, and speciation fractionation factors. $\delta^{13}C$ CO$_2$ for 2014 waters were not known, so 2016 data from the corresponding lake and depth were used to compare to 2014 methane data.
All lake methane had significantly lighter $\delta^{13}$C than lake DIC and CO$_2$, and epilimnion $\delta$D was significantly lighter than local water and lake $\delta$D (Figures 6.8-6.9). Thus, incoming methane likely maintained its isotopic fingerprint and did not reequilibrate with local water. The lakes do not show a clear correlation in $\delta^{13}$C CH$_4$ with $\delta^{13}$C CO$_2$, indicating that the trends in $\delta^{13}$C CH$_4$ is not simply the result of differing isotopic composition of the source carbon (Figure 6.10). Rather, the methane is likely formed from the fermentation from an organic precursor molecule.

The Newberry lakes have similar chemical, biological, and physical characteristics with the ideal conditions for aerobic methanogenesis. Aerobic methanogenesis often occurs in phosphorus-limited, oligotrophic areas in the ocean where cyanobacteria fix nitrogen *in situ* (Karl et. al, 2008). Both Newberry crater lakes are P-limited, with 7-17 ppb P at all depths (Figure XX, P results). The lakes have N-fixing cyanobacteria in the Nostoc balls, and they are low productivity mesotrophic (Johnson et. al, 1985). It has been suggested that microbes in oceans with these conditions can metabolize methylated compounds and release methane aerobically (Karl et. al, 2008; Damn et. al, 2010).

Both the marine systems and freshwater lakes that have been shown to undergo aerobic methanogenesis have less negative $\delta^{13}$C CH$_4$ (~-47 to -43‰) compared to the Newberry lakes (~-50‰) and have a smaller fractionations of $\delta^{13}$C CH$_4$ versus $\delta^{13}$C DIC, suggesting that the Newberry lakes have a different mechanism of aerobic methanogenesis (Holmes et. al, 2000; Tang et. al, 2014; Bogard, et. al, 2014).
Of the many possible biochemical mechanisms for methanogenesis in oxygenated waters described above and in the literature, hydrogenotrophic methanogenesis, which is common among Archaea, most likely formed the methane in the Newberry lakes. East Lake has a ~37‰ $\delta^{13}$C offset in CO$_2$ versus CH$_4$, and Paulina Lake has a ~31‰ offset. Stable carbon isotope fractionation effects during hydrogenotrophic methanogenesis are around -79‰ to -29‰, while offsets for other biochemical pathways are significantly smaller or larger, so the Newberry Lake methane was likely formed by this mechanism (Tang et. al, 2014; Bogard, et. al, 2014). Hydrogenotrophic methanogens would flourish in the Newberry lakes’ CO$_2$-rich water, because they form methane by reducing CO$_2$ with hydrogen as a reducing agent (Bogard et. al, 2014).

Additionally, because the DO data does not extend past 30 meters, it is possible that the parts of the deeper water column are well-oxygenated and that aerobic methanogenesis occurs at all depths and that anaerobic methanotrophic bacteria consume methane in the bottom waters. The bacteria would potentially preferentially consume the depleted fermented methane in the colder, darker hypolimnion waters, leaving behind low concentrations of isotopically enriched methane. However, field and laboratory studies have shown a temporal and spatial uncoupling of methanogenesis and methanotrophy (Grossart et. al, 2011), so it is unlikely that both processes occur in the hypolimnion.

If aerobic methanogenesis does occur in both salt and freshwater environments, it will have significant consequences on the aquatic and global carbon cycles and climate. Pelagic nutrient availability, biological carbon inputs, and the
physical and chemical structure of the water column all affect aquatic algal dynamics and thus oxic methanogenesis and aquatic CH₄ emissions, may be affected by intensifying anthropogenic and climate changes (Bogard, et. al, 2014).

7. Conclusions

The twin Newberry lakes are unique because they have different ionic and isotopic compositions, although they are a mere two kilometers apart and associated with the same geothermal system. Temporal and spatial trends in the dissolved species concentrations and isotopic compositions are indicative of the geothermal inputs and circulation in both lakes. The lakes have the same meteoric inputs, but East Lake gaseous geothermal input is rich in CO₂ and H₂S, while Paulina Lake hydrothermal input has abundant dissolved carbonate and high overall dissolved contents.

East Lake is both a volcanic and a biologically productive lake, so the lake’s carbon dynamics are affected by both of these systems. Geothermal input and surface CO₂ evasion are largely related to the lake’s volcanic origins, while photosynthesis, respiration, and biogenic sedimentation are biological processes. These carbon sources and sinks cause trends in DIC concentration and δ¹³C with depth, so the effects of the biological and volcanic roots enhance each other and create a steep depth gradient in δ¹³C. East Lake δ¹³C (DIC) is much heavier than Paulina Lake, and has a very strong gradient with depth of up to 5‰. East Lake water column gradients in temperature and δ¹³C (DIC) get more pronounced as the summer progresses, due to degassing and photosynthetic removal of isotopically light carbon from surface waters and the addition of light carbon to the bottom waters through geothermal input.
and respiration. The clear water column gradients indicate that the lake remains stratified at the thermocline (15 m) throughout the summer. However, while East Lake’s main source of dissolved species is the subaqueous geothermal input, the water column is nearly homogeneous in DIC, cation, and anion species. CO₂ bubble transport models cannot account for the observed constant DIC with depth, because bottom waters would need be very enriched in DIC to replenish surface water DIC after degassing. Thus, East Lake waters must mix on a local scale more than would be predicted from the thermal stratification and coupled models of mass and heat exchange are needed to simulate these processes. Alternatively, geothermal input could be constrained more in the deep crater area or shallow area of the lake, allowing for regional mixing.

Mixing models of δ¹³C, δ¹⁵N, and C/N organic matter in the lakes indicate that organic carbon in Paulina Lake sediment is comprised of phytoplankton and cyanobacteria, while East Lake sediment is mostly phytoplankton and subaqueous vegetation, with some contribution of cyanobacteria and caldera pine tree needles. Thus, in both lakes, diatoms and related species are dominant photosynthesizers. About two thirds of carbon removed from surface waters through photosynthesis is buried in the lake sediments, while the other third is respired back into the bottom waters.

Carbon dioxide emissions from volcanic lakes were excluded from the global carbon budget until recently (Pérez et. al, 2011). Variations in CO₂ flux over time could be indicative of changes in volcanic activity, and should be monitored to prevent catastrophic CO₂ explosions, like of Lake Nyos and Lake Monoun. Based on
field measurements, SGS interpolations, theoretical flux models, boundary layer
calculations, and steady state models, East Lake and Paulina Lake CO₂ evasion rates
are similar to other volcanic lakes with the same surface area (Mazot and Bernard,
2015). CO₂ flux rates are highest in May and June (71 tonnes per day in East Lake),
soon after lake ice melting and spring turnover, as the built up DIC from the
geothermal input through the winter evades. The lake surfaces have a few μm-thick
boundary layer with constant CO₂ concentration which regulates ΔPCO₂ between the
surface water and ambient air and thus constrains flux rates. East Lake build-up draw-
down experiments provide a novel method for gas flux determinations and allow the
lake CO₂ to be isolated and sampled for isotopic analysis. Diffusive CO₂ loss is an
important term in the carbon mass balance and δ¹³C (DIC) gradient of East Lake and
may be as well in many other organic-rich non-volcanic lakes.

Evading lake CO₂ exhibits unusual carbon and oxygen isotopic compositions
in two ways. Lake gas has more negative δ¹³C and δ¹⁸O than expected based on the
isotopic composition of CO₂(aq) in the lake water and equilibrium fractionation
factors. Additionally, field draw-down build-up experiments show that δ¹³C of
evading CO₂ (gas) varies with different ΔPCO₂ water-gas. Lab Lake experiments
also give unusual δ¹³C and δ¹⁸O CO₂(gas) for the observed δ¹³C CO₂(aq) and
ΔPCO₂. These offsets observed in the field and lab suggest that a non-equilibrium
fractionation process occurs during CO₂ degassing, such as kinetic fractionation.
More field draw-down build-up experiments and Lab Lake experiments will be run in
the coming months to provide new insights on isotopic fractionation during degassing
relative to ΔPCO₂. No previous studies have observed the δ¹³C and δ¹⁸O

200
fractionation in CO$_2$(gas) evading from water, so this non-equilibrium fractionation is poorly defined. If all CO$_2$(gas) evading from aquatic systems fractionates more than expected and differently under different ambient CO$_2$ concentrations, its isotopic signature should be considered when observing trends in $\delta^{13}$C and $\delta^{18}$O CO$_2$(aq) and considered in global atmospheric CO$_2$ models, especially as atmospheric CO$_2$ concentrations rise worldwide.

A quantitative two-box carbon cycle model using the $\delta^{13}$C and amounts of East Lake carbon sources and sinks, including CO$_2$ flux rates, $\delta^{13}$C DIC profiles, $\delta^{13}$C lake gas, and build-up draw-down experiments, reflects observed seasonal and annual trends in DIC concentrations and $\delta^{13}$C DIC in epilimnion and hypolimnion waters. Models and six years of measurements of dissolved species and isotopes suggest that East Lake is at chemical and isotopic steady.

Both East Lake and Paulina Lake surface waters are rich in isotopically-light methane, indicating that aerobic methanogenesis occurs in the oxygen-rich surface waters. In recent years, it has become accepted that aerobic methanogenesis occurs in surface waters, but very few other freshwater environments have this shallow-level CH$_4$ enrichment. The methane produced by aerobic methanogenesis in the other freshwater lakes is isotopically less negative than the methane observed in the Newberry lakes, indicating that have different mechanism of aerobic methanogenesis. Aerobic methanogenesis might be more common than previously considered, and aerobic lake methane degassing might contribute to the global atmospheric methane budget and its isotopic composition. Overall, the carbon dynamics in the Newberry
lakes suggest that both volcanic and non-volcanic lakes are important factors in the
global $\text{CO}_2$ and $\text{CH}_4$ budgets, and thus global climate.
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