PROCESSES GOVERNING CARBON DIOXIDE EXCHANGE BETWEEN THE
ATMOSPHERE AND HYDROMAGNESITE-MAGNESITE PLAYAS IN ATLIN,
BRITISH COLUMBIA

by

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B.Sc., The University of Ottawa, 2019

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
in
THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES
(Geological Sciences)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

June 2022

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Processes Governing Carbon Dioxide Exchange Between the Atmosphere and Hydromagnesite-Magnesite Playas in Atlin, British Columbia

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Abstract

The hydromagnesite-magnesite playas in Atlin, BC provide a unique opportunity for studying the carbonate-bicarbonate system and carbonate mineral stability at the Earth’s surface. Based on analysis of pore water samples and mineralogical data, Power et al. (2014) concluded that the playas degas CO$_2$ from Mg-HCO$_3$-rich groundwater and in-situ carbonate mineral precipitation, but CO$_2$ emissions were not quantified directly. In this thesis, eddy covariance (EC) and dynamic closed chamber (DCC) systems were co-located to directly quantify rates and characterize processes governing the CO$_2$ flux across the playa-atmosphere interface. Data were collected continuously over 27 days in 2020 and 14 days in 2021.

The results from the DCC method show distinct diurnal oscillations of CO$_2$ fluxes, with average daytime fluxes of $+0.15\pm0.34$ μmol m$^{-2}$ s$^{-1}$ (2020) and $+0.15\pm0.19$ μmol m$^{-2}$ s$^{-1}$ (2021) and nighttime fluxes of $-0.24\pm0.31$ μmol m$^{-2}$ s$^{-1}$ (2020) and $+0.04\pm0.18$ μmol m$^{-2}$ s$^{-1}$ (2021) (positive upward and negative downward). Fluxes measured via the DCC method indicate minimal net exchange of carbon across the playa-atmosphere interface during the monitoring period. These observations imply that DCC-measured CO$_2$ fluxes are governed predominantly by changes in CO$_2$ solubility in alkaline porewater related to diurnal temperature fluctuations and variations in CO$_2$ concentrations in ambient air above the ground surface. However, EC measurements show a continuous positive flux averaging $+1.38\pm0.62$ μmol m$^{-2}$ s$^{-1}$ (2020) and $+1.07\pm0.43$ μmol m$^{-2}$ s$^{-1}$ (2021). The net CO$_2$ flux measured by EC was attributed to a source undetected by the DCCs with possible contributions from soil respiration at the playa margins or surrounding forests, or directly released via preferential pathways from a deeper source within the playa. The use of two complementary flux measurement methods revealed that CO$_2$ fluxes vary as a function of scale.
and location at this site. These findings provide insights on CO$_2$ flux dynamics in sparsely vegetated arid and semi-arid regions and the application of these methods for monitoring and verification of *ex-situ* carbon mineralization at sites with enhanced mineral weathering. The complex interactions between minerals, fluids and the atmosphere make Atlin an ideal site to test complementary methods for measuring CO$_2$ fluxes.
Lay Summary

The carbonate deposits at Atlin, BC, known as hydromagnesite-magnesite playas, are unique in this world. The playas have been forming from carbon dissolved in the groundwater for millennia and are exposed to the elements at the Earth’s surface. Since carbon is present in the groundwater and minerals, CO$_2$ gas can be exchanged with the atmosphere. To our knowledge, there is minimal research focused on measuring CO$_2$ exchange between unvegetated mineral soils, such as the Atlin playa, and the atmosphere. An understanding of physical and chemical processes and their importance towards the carbon cycle is currently lacking. This thesis studied CO$_2$ exchange between the playa and the atmosphere using chamber-based and micrometeorological methods. The findings of this thesis provide insights into the factors controlling CO$_2$ fluxes and guidance for future application of these flux methods to measure CO$_2$ capture and storage in similar systems.
Preface

This thesis is original, unpublished work and is a part of the University of British Columbia (UBC). The work done as a part of this thesis was designed by the author, Dr. K. Ulrich Mayer, and Dr. Gregory Dipple. All the field data and samples were collected by the author, Frances Jones, and Bethany Ladd. The modelling work in chapter 4 was designed by the author, Dr. K. Ulrich Mayer and Katherine Raymond and the simulations were set and run by Katherine Raymond. All chapters are written by the author and reviewed by Dr. K. Ulrich Mayer, Dr. Gregory Dipple, and Dr. T. Andrew Black.

Compositional and isotopic analyses of CO₂ gas samples were performed in the Ján Veizer Stable Isotope Laboratory at the University of Ottawa. Radiocarbon analysis was performed at the A. E. Lalonde AMS Laboratory at the University of Ottawa.
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List of Abbreviations

BC  – British Columbia
CO₂ – Carbon dioxide
DCC – Dynamic closed chambers
DIC – Dissolved inorganic carbon
DOY – Day of year
EC  – Eddy covariance
ID  – Inner diameter
IPCC – International Panel on Climate Change
LTC – Long-term chamber
PPM – Parts per million
SVC – Survey chamber
TIC – Total inorganic carbon
VWC – Volumetric water content
Acknowledgements

This study was conducted on the traditional territory of the Taku River Tlingit First Nation. The Atlin town is known as Wéinaa, which means Alkali Place. I am grateful to have had the opportunity to work on the alkali flats (hydromagnesite-magnesite playas).

I am incredibly grateful for the support and guidance from my supervisor Uli Mayer. Conducting a field-based thesis project during a pandemic has been interesting and stressful, so thank you for your patience and encouragement. Thank you to my committee members who were helpful towards the completion of my thesis. Greg Dipple, thank you for providing the big picture ideas and unwavering enthusiasm towards the project. Further, thanks to Andy Black for your methodological insights and answers to my endless questions. I feel fortunate to have been surrounded by this incredible team of researchers and professors.

I am grateful to have received funding provided by NSERC CGS-M and Geoscience BC to support my thesis work.

A special thank you to my research partner Fran Jones for being there every step of the way. From fieldwork to data analysis, your support and help means the world to me. Thanks to Bethany Ladd for field and emotional support. Thanks, Fran, and Bethany for bearing through the midnight isotope sampling, and equipment installation and troubleshooting in the pouring rain. Thanks to Katherine Raymond for the modelling help and being a great friend right from the start of my MSc. program. Also, I am grateful to the CarbMin Lab group for being a great environment for discussion and support.

I cannot thank enough my partner Fred and my parents for their unfailing support and encouragement throughout my years of education. A special shoutout my kitten Freesia for her help editing (deleting) and supervising (blocking the computer screen) during the writing process.
Chapter 1: Introduction

1.1 Background

The accumulation of carbon dioxide (CO$_2$) from anthropogenic emissions has been strongly linked to climate change (IPCC, 2021). CO$_2$ is responsible for 80% of the change in the atmospheric energy fluxes since 1990, causing global temperature rise (NOAA, 2021). It is the most potent anthropogenic greenhouse gas due to its abundance and residence time in the atmosphere (NOAA, 2021). Strategies to reduce anthropogenic emissions and capture CO$_2$ from the atmosphere are now both necessary to keep atmospheric warming below 2°C and mitigate the worst effects of climate change (Fuss et al., 2018). It is essential to continue studying feedback processes, controlling factors, and monitoring natural and engineered sinks and sources that modulate the carbon cycle in response to global climate change.

CO$_2$ fluxes from terrestrial soils to the atmosphere contribute significantly to the global carbon cycle (reviewed in Oertel et al., 2016). Soil CO$_2$ fluxes are governed by CO$_2$ production and transport processes, which are conventionally associated with biological respiration (i.e., microbial and root) and diffusion, respectively (Baldocchi, 2003; Jassal et al., 2004; Rey, 2015). Non-biological processes contributing to CO$_2$ flux (e.g., rock weathering) are commonly neglected in soils as rates are typically much slower compared to the rates of biological respiration (Reichstein et al., 2012; Rey, 2015). However, over the last decade, researchers have shown that carbonate-bicarbonate equilibria, rock weathering reactions and other physical processes partially modulate the short-term carbon cycle within semi-arid and arid systems (Ball et al., 2009; Cueva et al., 2019; Fa et al., 2016; Hamerlynck et al., 2013; Ma et al., 2013; Schlesinger, 1982; Soper et al., 2017; Stevenson & Verburg, 2006; Xie et al., 2009; Yates et al., 2013). Arid and semi-arid regions are extreme environments with soils that have low-biological activity and large inorganic
carbon reservoirs. These soils have upwards of 10 times the inorganic carbon content (i.e., carbonate minerals and dissolved inorganic carbon) compared to the organic carbon content (Schlesinger, 1982). Ma et al. (2017) demonstrated that biological processes are secondary or negligible compared to the carbonate-bicarbonate equilibria in modulating CO$_2$ exchange in alkaline and saline deserts. Albeit the rates of CO$_2$ exchange are lower than biological respiration, the development of an understanding on carbon exchange with the atmosphere in these environments is important. In this context, the knowledge of the role and controls of inorganic carbon in the carbon cycle is essential (Ma et al., 2017, 2013; Sagi et al., 2021; Schlesinger, 2017; Yates et al., 2013).

The hydromagnesite-magnesite playas, near Atlin, British Columbia, Canada, provide a unique case study of the carbonate-bicarbonate system in a dry subarctic climate. These modern playas are carbonate sediment deposits that consist primarily of magnesite (MgCO$_3$) and hydromagnesite (Mg$_5$(CO$_3$)$_4$(OH)$_2$4H$_2$O) minerals. The playas have been forming since the retreat of the last glaciation, approximately 8000 years BP (Power et al., 2014) and currently occupy 0.17 km$^2$ east of the township. The playa genesis was possible due to Mg-HCO$_3$-rich shallow groundwater discharging into the local wetlands, combined with various physicochemical and biological processes that together produced geochemical conditions favouring carbonate mineral precipitation (Power et al., 2014). Currently, there are ca 116,000 tons of pure carbonate minerals at the Earth’s surface at the Atlin site (Grant, 1987).

Previous work was conducted to construct a depositional model of the hydromagnesite-magnesite playas and to understand the formation kinetics of magnesite minerals in a low-temperature environment (Power et al., 2019, 2014, 2009). Researchers hypothesized that CO$_2$(g) exchange occurs across the playa-atmosphere interface due to the degassing from the HCO$_3$-rich
groundwater and *in-situ* mineral precipitation (Mavromatis et al., 2021; Power et al., 2019, 2014). Power et al (2014, 2019) found an enrichment in $^{13}$C isotopic signature in the unsaturated zone waters and carbonate minerals relative to the groundwater, which provides evidence for degassing of CO$_2$ and exchange with the atmosphere. A study of CO$_2$ fluxes above the playa surface will complement and build upon the work previously conducted on the mineral and aqueous phases. This site will also provide insights into the processes governing CO$_2$ exchange in a predominantly abiotic carbonate mineral system.

### 1.2 CO$_2$ Flux at the Atlin Site

At the Atlin playas, CO$_2$ production and consumption are controlled by chemical reactions occurring near the water table in the unsaturated zone, such as the carbonate-bicarbonate equilibrium:

$$ CO_2(g) + H_2O \leftrightarrow H_2CO_3(aq) \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^2- $$  \hspace{1cm} \text{Equation 1.1}

and carbonate mineral precipitation and dissolution (Mavromatis et al., 2021; Power et al., 2019, 2014):

$$ 5Mg^{2+} + 4HCO_3^- + 6H_2O \leftrightarrow Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O(s) + 6H^+ $$  \hspace{1cm} \text{Equation 1.2}

$$ Mg^{2+} + HCO_3^- \leftrightarrow MgCO_3(s) + H^+ $$  \hspace{1cm} \text{Equation 1.3}

Specifically, in Atlin, the shallow groundwater is supersaturated with respect to CO$_2(g)$ from the high bicarbonate (HCO$_3^-$) concentrations. Therefore, when the water reaches atmospheric conditions above the water table (open system), CO$_2$ tends to partition to the gas phase (degas), driving Eq. 1.1 towards the left. Upon CO$_2$ degassing and evaporation in the unsaturated zone, the hydrated magnesium carbonate minerals (e.g., hydromagnesite $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, nesquehonite $Mg(CO_3) \cdot 3H_2O$ and dypingite $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$) become saturated in the porewater (Power et al. 2014). Therefore, CO$_2$ degassing and evaporation (i.e. removing H+...
and H\textsubscript{2}O) can trigger hydrated mineral precipitation to buffer the pH increase and drive Eq. 1.2, e.g. hydromagnesite, to the right (Stumm & Morgan, 1996; Berninger et al., 2014). The rate of hydromagnesite precipitation and hydrated precursor minerals are transport-controlled by the renewal of HCO\textsubscript{3}-rich groundwater and evapoconcentration, and mineral formation occurs in the unsaturated zone closer to the surface (Power et al., 2019). In contrast, magnesite precipitation (Eq. 3) rates are reaction-controlled by the precipitation kinetics and forms closer to the water table via direct precipitation (Power et al., 2019). In natural waters between pH 6.35 and 10.33, the dominant carbon species is bicarbonate; therefore, a mole of acidity (H\textsuperscript{+}) is produced for every mol of magnesite that has precipitated, and approximately 6 moles of acidity are produced for every mol of hydromagnesite that has precipitated (Stumm & Morgan, 1996; Berninger et al., 2014). Thus, Eq 1.1, 1.2 and 1.3 are commonly simplified in the literature showing that carbonate mineral precipitation itself leads to the release of CO\textsubscript{2} (i.e. substituting H\textsuperscript{+} for H\textsubscript{2}O + CO\textsubscript{2(g)}) (Emmerich, 2003; Stumm & Morgan, 1996; Ware et al., 1991).

In this context, CO\textsubscript{2(g)} is expected in the unsaturated zone because of the known HCO\textsubscript{3}-rich groundwater and in-situ carbonate mineral precipitation. However, the rate and amount of CO\textsubscript{2} produced in the gaseous phase are indeterminate due to the complexity of heterogeneous equilibrium reactions, kinetic limitations and buffering capacity of the waters (Hopkinson et al., 2008; Stumm & Morgan, 1996; Ware et al., 1991). The buffering capacity of the water and pH play a crucial role in the number of moles of CO\textsubscript{2(g)} produced per mole of carbonate mineral (Ware et al., 1991).

Although the geochemical reactions discussed above occur within the playa subsurface, physical factors can impact the equilibrium of these reactions at the sediment surface. CO\textsubscript{2} solubility is temperature and pH-dependent; therefore, diurnal, and seasonal temperature
fluctuations can impact the carbonate-bicarbonate equilibrium in basic porewater and result in CO₂ exchange (Eq 1.1). Field observations in alkaline and saline drylands and deserts demonstrate an exchange of CO₂ at the sediment surface correlated with temperature and pH, whereby CO₂ is emitted in the daytime and CO₂ is taken up at nighttime at the soil-atmosphere interface (Ball et al., 2009; Fa et al., 2016; Hamerlynck et al., 2013; Ma et al., 2017, 2013; Parsons et al., 2004; Shanhun et al., 2012; Xie et al., 2009).

The other consideration beyond CO₂ production and consumption is the transport of CO₂ between the sediment pores and the atmosphere. The transport of CO₂ within the subsurface is governed by CO₂ concentration gradients (diffusion), thermal variability (convection), and pressure (advection) (Rey, 2015). The controls on CO₂ transport are generally related to soil properties (e.g., permeability, porosity, tortuosity, water content, temperature) and gas properties (e.g., viscosity, diffusivity). Atmospheric conditions, such as temperature, rainfall, barometric pressure, and wind speed, play an important role in mass, momentum, and energy exchange between the unsaturated zone and the atmosphere. Traditionally, the primary transport process presumed in soil gas exchange is diffusion. However, turbulence-driven advective mass transport, such as pressure pumping and wind speed, can supersede diffusive transport in systems with high porosity (Lewicki et al., 2010; López-Ballesteros et al., 2017; Redeker et al, 2015; Rey, 2015; Takle et al., 2004).

1.3 Methods for CO₂ Tracing

Many techniques can be implemented to estimate soil-atmosphere CO₂ exchange and gain insights into the system-level dynamics of the carbon cycle. Combining techniques such as CO₂
flux measurements and stable and radioactive isotope analysis can be beneficial in answering questions and meeting research objectives regarding the carbon cycle.

1.3.1 Flux Methods

A flux, also known in the literature as flux density, represents an exchange of mass, heat, or energy across a surface over a specified period. The flux can be positive, representing the mass transfer away from the surface to the atmosphere (an emission) or negative representing the mass transfer into the surface from the atmosphere (an uptake). Various methods to measure a CO\textsubscript{2} flux across different surfaces have been used for decades to estimate individual or combined components of the terrestrial carbon budget (e.g., net ecosystem exchange, gross ecosystem photosynthesis, ecosystem, and soil respiration). Flux measurements can be estimated over surfaces of interest on the tens cm to tens of km scales depending on the methodology and in a wide range of environments, such as forests, wetlands, grasslands, agricultural land and urban areas (reviewed in Oertel et al. 2016). Two of these CO\textsubscript{2} flux methods are automated non-steady-state dynamic closed-chambers (DCC) and eddy covariance (EC) systems. DCC and EC methods employ independent approaches to measure the CO\textsubscript{2} flux while having distinct advantages and disadvantages relative to each other. Therefore, in previous studies, EC and DCC methods have been deployed in tandem over homogeneous terrain to increase data reliability and confidence (Gaumont-Guay et al., 2006; Lucas-Moffat et al., 2018; Ma et al., 2012; Norman et al., 1997; Ohkubo et al., 2007; Riederer et al., 2014; Rochette et al., 1997; Wang et al., 2017).

The DCCs method measures the rate of change of CO\textsubscript{2} and H\textsubscript{2}O gas concentrations in a closed headspace directly above the soil-atmosphere interface to compute a CO\textsubscript{2} flux (Rochette et al., 1997). The automation of the DCC method provides consistent and reliable measurements at a
high temporal resolution compared to other chamber-based methods (Savage et al., 2008). However, the flux estimates are spatially limited to the chamber size, the closed headspace can alter the ambient conditions, and the insertion of a base (collar) can disturb the substrate properties (Davidson et al., 2002; Görres et al., 2016).

On the other hand, the EC method is based on statistical micrometeorology and directly measures the turbulent exchange of heat, momentum and gas (e.g. CO₂, H₂O) between the surface and the atmospheric boundary layer (Baldocchi et al., 1988). Turbulence is produced by surface heating, wind shear and obstacles (e.g. trees, logs, irregularities in the soil surface, stones) and is visualized as irregular swirls of air called eddies (Stull, 1988). The CO₂ flux is estimated as the covariance between the vertical velocity (upward ejections or downward sweeps of air) and the concentration of CO₂ (Finnigan, 1979; Lee & Black, 1993). The EC method is a high-frequency, non-invasive and continuous measurement system that incorporates contributions from fluxes over a large source area (0.1 to 10 km²). Estimating fluxes using the EC method requires sophisticated instrumentation and relies on specific conditions to make a valid measurement; the atmospheric boundary layer must have fully developed turbulence, steady-state and non-advevtive conditions, and horizontal homogeneity (Baldocchi et al., 1988; Foken et al., 2004; Verma, 1990). Consequently, data post-processing can be significant due to the strict assumptions, while violating the assumptions can introduce uncertainty and error in the flux measurement (Moncrieff et al., 1996).

Another micrometeorological method that is complementary to the EC method is the flux-gradient method (or above-ground profiles) (Monteith & Unsworth, 2013). This method measures wind speed, air temperature, water vapour pressure, or CO₂ at multiple levels in the atmospheric surface layer. The above-ground profiles can be used to determine flux direction and magnitude,
and CO\textsubscript{2} storage change in the air column. This method was employed before the popularization of the EC method and provides a useful low-cost and robust alternative. However, for gas fluxes, this method employs either one analyzer that switches between levels causing delays and time-gaps or multiple instruments resulting in among sensor bias; both approaches have limitations (Munger et al., 2012). A major advantage of the EC method is that it doesn’t need any assumptions regarding eddy diffusivities, which is required in the flux-gradient method (Lee et al., 2004).

Although DCC and EC are commonly used flux measurement techniques, limited research has been conducted on abiotic mineral soils with high inorganic carbon content. Alkaline desert and dryland valley studies have measured CO\textsubscript{2} fluxes (emissions and uptake) using DCCs (Ball & Virginia, 2015; Ball et al., 2009; Hamerlynck et al., 2013; Ma et al., 2013; Parsons et al., 2004; Xie et al., 2009) and in a few cases EC systems (Emmerich, 2003; Ma et al., 2014; Wohlfahrt et al., 2008). However, shrubs and plants and related microbial and root respiration confound some of the findings relating to the inorganic carbon flux. Researchers have found an approach using soil sterilization to partition the soil CO\textsubscript{2} fluxes between biotic and abiotic sources to isolate the different contributions and controlling factors (Ball et al., 2009; Fa et al., 2016; Ma et al., 2017, 2013; Stevenson & Verburg, 2006; Wang et al., 2020; Yates et al., 2013). Additionally, only once have DCC and EC have been implemented at a field site to measure CO\textsubscript{2} fluxes in engineered mineral systems, above mine rock waste (Kabwe et al., 2005; Kabwe et al., 2006).

1.3.2 Isotopes

Comparison of stable and radioactive isotope compositions between different reservoirs can lend insights into tracking environmental cycles, from source attribution to processes occurring in the environment. The stable isotopes of C, O, H, and Mg and radiocarbon (\textsuperscript{14}C) in the aqueous and
mineral phases at the Atlin playas have been previously characterized by Power et al. (2014, 2019) and Mavromatis et al. (2021). This thesis focuses on CO$_2$ exchange; therefore, the stable and radioactive carbon isotopes, $^{12}$C, $^{13}$C and $^{14}$C, are of interest within the Atlin playa environment.

Stable carbon isotopes ($^{12}$C, $^{13}$C) are a useful tool to resolve CO$_2$ sources and environmental processes. The internationally recognized delta notation $\delta$ (‰) is common for reporting carbon isotope ratios in materials, expressed as the heavy-to-light isotope ratio in parts per thousand deviations relative to a worldwide standard.

$$\delta^{13}C (‰) = \left( \frac{^{13}C_{\text{sample}}}{^{13}C_{\text{std}}} - 1 \right) \times 1000$$  \hspace{1cm} \text{Equation 1.4}

A positive $\delta^{13}C$ value indicates that the sample is more enriched in the heavier isotope ($^{13}$C) compared to the standard. In contrast, a negative $\delta^{13}C$ value indicates that the sample is depleted in the heavier isotope ($^{13}$C) compared to the standard. The carbon reservoirs in the playa environment (e.g., groundwater, carbonates in the playa, atmospheric air) have unique and well-separated signatures due to fractionation, distillation, and mixing processes. CO$_2$(g) derived from biological respiration in forest soils will be highly depleted (e.g. -21 to -30 ‰ from a Pacific Northwest forest) (Fessenden & Ehleringer, 2003) and from the atmospheric air will be slightly depleted (-8 to -10 ‰) (Keeling et al., 2021). It is expected that CO$_2$(g) derived from the carbonate playa porewater and hydromagnesite minerals is slightly depleted according to equilibrium fractionation (-3 to -6 ‰) (Power et al. 2019). Similar values for $^{13}$C-CO$_2$ (-1‰ and -5‰) have been reported by Stevenson and Verburg (2006) and Soper et al. (2017) for CO$_2$ derived from carbonates in desert soils.

Carbon’s radioactive isotope ($^{14}$C) can be implemented as a source tracer in Atlin. Radiocarbon is generated in the upper atmosphere from cosmic ray bombardment of $^{14}$N and
naturally decays over a half-life of 5730 years to $^{14}\text{N}$ (Trumbore, 2009). Modern carbon (100% pMC) is defined using atmospheric levels relative to a 1950 standard before weapons testing contributed a significant source of $^{14}\text{C}$ to naturally occurring $^{14}\text{C}$:

$$\text{pMC} (%) = \left( \frac{^{14}\text{C}_{\text{sample}, -25 \text{‰}}}{0.95^{14}\text{C}_{\text{atm}, -19 \text{‰}}} \right) \times 100$$  \hspace{1cm} \text{Equation 1.5}

Thus, CO$_2$ in the atmosphere and biological environment has generally exceeded 100% pMC after 1950. The current signature of modern carbon in the atmosphere is around 100% pMC due to CO$_2$ emissions from the burning of $^{14}$C-free fossil fuels (Suess, 1955; Zhang et al., 2021), which neutralizes contributions from less frequent bomb testing. In contrast, the CO$_2$ derived from the groundwater at Atlin contains very little modern carbon due to rock-weathering reactions between $^{14}$C-free carbonate rock and a small contribution of modern CO$_2$ from shallow groundwater recharge affected by microbial activity in soils (~10% pMC).

Therefore, pMC analysis represents the incorporation of modern atmospheric CO$_2$ into materials that are derived from the groundwater at Atlin rather than age. Power et al. (2014, 2019) found that the magnesite and hydromagnesite minerals collected from the surface of the Atlin playas contain some modern atmospheric carbon (~50% pMC). The source of CO$_2$ could either be directly from CO$_2$ exchange with the atmosphere, rainfall or both (Power et al., 2019). Measurements of CO$_2$ exchange and CO$_2$ isotopes may provide insights into the shallow subsurface and atmospheric dynamics.

### 1.4 Applications

The EC method is a widely used flux measurement technique used in environmental monitoring, climate model verification and regulatory applications for characterization of global biogeochemical cycles, and natural biological-based carbon sequestration (Burba, 2013).
Importantly, the global network, FLUXNET, which now has over 900 long-term flux tower sites that operate year-round, has worked towards the standardization of the EC method for the last two decades for broader use in climate sciences and gas exchange research (i.e. for CO₂ and water vapour) in natural and agricultural systems (Baldocchi, 2020).

Mineral-based natural and engineered carbon sequestration systems are emerging as promising strategies to capture and store atmospheric CO₂. Carbonate minerals represent a safe sink of CO₂ that has the largest capacity (>10,000 Gt) for carbon storage and will be stable over the longest time scales (>10⁵ years) compared to other carbon sinks (Fuss et al., 2018; IPCC, 2018; Lackner, 2003). Under many circumstances at atmospheric conditions, the reactions necessary for the dissolution of silicate minerals and precipitation of carbonate minerals are very slow, which does not offer a suitable solution for climate change (Lackner et al., 1995; Seifritz, 1990). Nonetheless, due to standard practices at mine sites, finely ground rock stored in tailings facilities increases reactive surface area and reaction speeds. Ex-situ carbon mineralization reactions are thus enabled by the base cations (Ca, Mg) from the dissolution of silicate rock and CO₂ from the atmosphere (Lackner et al., 1995; Seifritz, 1990). The current methods used to determine carbon sequestration rates in mineral-based systems rely on systematic coring at field sites with mineral quantification, isotope analysis and further laboratory tests, which is labour intensive and spatially and temporally limited (Assima et al., 2014; Stubbs et al., 2022; Wilson et al., 2014). New methods are required for monitoring and verifying long-term carbon capture and storage beyond the laboratory scale (Power et al., 2013; Stubbs et al., 2022; Wilson et al., 2014). EC, DCC and flux-gradient methods can fill this gap in large-scale monitoring of carbon capture and mineralization in mine tailing settings.
The hydromagnesite-magnesite playas are a natural analogue to carbon mineralization occurring in ultramafic-hosted mine waste and other engineered systems that have slowed in mineral dissolution (peak reactivity) and are storing carbonate minerals at the Earth’s surface. Therefore, this work can provide insights into using EC and DCC for measuring CO$_2$ fluxes in engineered and natural mineral-based carbon sequestration and storage strategies.

1.5 Thesis Objectives

The hydromagnesite-magnesite playas in Atlin, British Columbia, are a rare magnesium carbonate sediment deposit with a large lateral surface area that can accommodate both an EC and DCC system. This environment provides a unique opportunity to study CO$_2$ fluxes in a predominantly abiotic setting governed by complex interactions between minerals, fluids, and the atmosphere. The specific research objectives within this topic are to:

1. Quantify the rates and direction of CO$_2$ exchange between the carbonate mineral soil and the atmosphere using three methods (EC, DCC, above ground CO$_2$ profiles) (Chapter 3)
2. Characterize the spatial variability of the CO$_2$ fluxes from DCC observations (Chapter 3)
3. Characterize C isotopic composition for CO$_2$ in the unsaturated zone of the playa and the atmosphere directly above the playa, and evaluate its relationship to the known isotopic composition of carbon in minerals and the aqueous phase of the playa (Chapter 3)
4. Characterize short-term temporal variations of CO$_2$ exchange across the playa-carbonate soil surface using statistical analyses and reactive transport modeling constrained by field observations (Chapter 4)
1.6 Thesis Layout

This thesis is organized into five main chapters.

Chapter 1: Introduction

This chapter provides the background information relating to the project motivations and thesis objectives.

Chapter 2: Experimental Methodology

This chapter describes the study location in detail, along with methods used in the field for data collection; this includes the flux methods and the isotope sampling.

Chapter 3: Quantifying CO$_2$ fluxes and spatial variability across the northern hydromagnesite-magnesite playa

This chapter presents the measured CO$_2$ flux rates over the northern playa from the EC, DCC, and profile systems and the spatial variability of the CO$_2$ fluxes using DCC. Results from supporting measurements are included, such as soil properties, micrometeorology, and subsurface gas concentrations. The isotope composition of the CO$_2$ in the playa, transition and forest pore gas and the atmosphere are presented.

Chapter 4: Short-term processes: quantitative analysis of diurnal flux variations from DCC measurements

This chapter discusses the distinct diurnal CO$_2$ flux pattern measured by the DCC method. A reactive transport model is employed to assess individual and combined contributions of climate variables on simulated CO$_2$ fluxes directly compared to the observed 2020 DCC flux.

Chapter 5: Conclusion and future work

This chapter summarizes the main findings of this thesis, along with limitations and recommendations for future work.
Chapter 2: Experimental Methodology

2.1 Introduction

This chapter describes the field site, including a review of the site geology, site description and techniques used for collecting and analyzing surface efflux data, including eddy covariance (EC), automated non-steady-state dynamic closed chamber (DCC) and soil gas sampling methods. There were two summers of data collection: 27 days in August 2020 (DOY 220-246) and 14 days in August 2021 (DOY 218-232). Microsoft Excel (v.16.56) was used for data organization and some plotting. Python (v. 3.7.12) with the JupyterLab interface (v. 1.2.6.) was predominantly used for data analysis and plotting. Methods for reactive transport modelling and a laboratory fridge experiment are described in Appendices A and B, respectively.

2.2 Geological Setting

The study site is near Atlin, in northwestern British Columbia, located 48 km south of the Yukon border (Figure 2.1). In the Atlin region, the bedrock comprises ultramafic and altered ultramafic rocks, including variably serpentinized harzburgite and dunite, which overlies clastic and carbonate sedimentary rocks (Ash & Arksey, 1990; Hansen et al., 2005). The ultramafic material originated in the upper mantle of the oceanic lithosphere and was tectonically emplaced onto the Stikine and Cache Creek terranes of BC (Ash & Arksey, 1990). Post-emplacement, CO$_2$-bearing hydrothermal fluids along a fault and fractures altered the serpentinized-harzburgite rock and formed listwanite (magnesite + quartz) (Ash & Arksey, 1990; Hansen et al., 2005).

The shallow groundwater weathers the ultramafic and carbonated-ultramafic rocks in the subsurface, leaching magnesium (Mg$^{2+}$) and bicarbonate (HCO$_3^-$). Consequently, small lakes and
shallow groundwater in the region are alkaline in composition. The Mg-HCO$_3$ groundwater generally flows from the north and north-northeast and has a pH of 8.2 (Power et al., 2014, 2009).

East of the town of Atlin, BC, are two groups of hydromagnesite-magnesite playas, the northern and southern playas (outlined in Figure 2.1 A.). Power et al. (2014) constructed a depositional model to describe the genesis of the hydromagnesite-magnesite playas. Due to the local effects of the recent retreat of the cordilleran ice sheet, the Mg-HCO$_3$ groundwater seeps into topographic lows feeding wetlands. The alkaline wetlands are colonized by microbial mats and are surrounded by grasses. Wetland waters are super-saturated with respect to calcium-magnesium (Ca-Mg) carbonate minerals and these minerals precipitate sub-aqueously. The Ca-Mg-carbonates progressively infill wetlands, and the environment transitions to carbonate deposits above the water table (sub-aereal) with some grass colonization. The Mg-HCO$_3$ groundwater is drawn into the carbonate sediment vadose zone above the water table through capillary action and undergoes evaporation leading to increases in ion concentrations. The pore water is supersaturated with respect to various hydrous magnesite minerals (lansfordite (MgCO$_3$·5H$_2$O), nesquehonite (MgCO$_3$·3H$_2$O), dypingite (Mg$_5$(OH)$_2$(CO$_3$)$_4$·5H$_2$O) and hydromagnesite (Mg$_5$(OH)$_2$(CO$_3$)$_4$·4H$_2$O) above the water table and the pCO$_2$ is elevated, which favours CO$_2$ degassing and mineral precipitation. The sub-aerial mineral deposits in the unsaturated zone are predominantly composed of magnesite (MgCO$_3$) and hydromagnesite, which form localized mounds of sediment (meter scale). Further lateral and vertical mineral precipitation leads to the amalgamation of multiple localized mounds overtaking the grassland. The amalgamated mounds are the final playa genesis stage (Power et al., 2014). Due to the evaporative conditions and lateral growth, the amalgamated mounds form polygonal desiccation and cauliflower patterns, which result in extensive surface cracks (up to ~2 cm wide and ~40 cm deep). The sediment deposits on
the amalgamated mounds are populated by green cyanobacteria along the desiccation crack walls and host localized grass colonies. The southern playa currently displays four depositional environments representing each stage of genesis: wetland, grassland, localized mounds, and amalgamated mounds. The northern playa primarily displays the amalgamated mound environment with a wetland on the northern end.

2.3 Site Description

The northern playa (59.5818°N, 133.6885°W, at an elevation of 696 m asl) was selected for monitoring of CO$_2$ fluxes with eddy covariance (EC) and dynamic closed chamber (DCC) systems (Figure 2.1). The Atlin region has a subarctic climate with average temperatures of +17°C in the summer and -18°C in the winter. The annual rainfall received in Atlin ranges between 250 and 500 mm (mean ~350 mm) (Environment and Climate Change Canada, n.d.), which is a similar rainfall range to that in semi-arid regions in warmer climatic conditions. The depth to the water table is not known for the northern playa, but the southern amalgamated mound environment shows the depth of the water table to be around 1.25m (Power et al., 2014).

This location was chosen for the large areal extent of the hydromagnesite-magnesite amalgamated mounds largely devoid of vegetation and as distant as possible from the surrounding forest. The historic prevailing wind direction from the south was considered for the establishment of the EC tower and chamber monitoring network at a location that best captured the desired fetch (i.e., upwind distance to where there is a significant change in the character of the playa surface) (Figure 2.1 b.). In 2020, eight long-term DCCs (LTCs) were set in pairs at 5-metre intervals 5 metres south of the EC tower (Figures 2.2, 2.3.a.) and surrounded by a grid of 22 soil collars for survey DCC (SVCs) flux measurements. In 2021, eight LTCs were set in pairs 10 metres southeast
of the EC tower and then at 5-metre intervals towards the southeast and surrounded by a grid of 51 soil collars for SVC flux measurements (Figures 2.2, 2.3.b.). SVC collars were co-located 30-cm from the LTC for checks.

Figure 2.1. A. The hydromagnesite-magnesite playas northeast-east of Atlin, northwestern British Columbia. The location of the eddy-covariance tower is marked by a yellow star (59.5818ºN, 133.6885ºW). B. Aerial photo of the site (yellow inset on map A.).

Figure 2.2. Photograph of the installed monitoring network (2020). From left to right: in the forefront there are the long-term DCCs (LTCs) and the survey DCCs (SVCs), and in the background there are the EC tower and the photovoltaic array (PV). The red tent housed the battery bank and solar controllers.
Figure 2.3. The experimental monitoring network includes the EC tower and DCCs (LTC and SVC); a. 2020 and b. 2021. The check chambers are also shown on this map.
2.4 Materials and Methods

2.4.1 Sediment and physical properties

Sediment samples were collected with a 25.4 cm long (25.4-mm ID) handheld soil sampler (1055/EP, LaMotte, Chestertown, MD) at 1-10-cm and 10-20-cm depths and stored in 50-mL sterile falcon tubes with a parafilm seal to prevent the loss of moisture. The volume of the sample was calculated from the dimensions of the handheld sampler. In 2020, approximately five rounds of sampling were conducted over the course of the field campaign collecting samples 30-cm away from each long-term chamber collar, resulting in 70 total samples. The samples were returned to the laboratory, weighed, oven-dried at 45°C for 24 hr, which is a lower temperature compared to other techniques to avoid changes in the hydrous mineral content (Hopkinson et al., 2008). Then, the sample was weighed again to measure dry soil bulk density and volumetric water content. The particle density on a single sample was measured using a pycnometer (AccuPyc II 1340, Micromeritics, Norcross, GA) to estimate the porosity from the dry bulk density data.

All the soil samples were then homogenized into one bucket to run a few additional tests. Three aliquots were analyzed for organic and inorganic carbon fractions at ALS laboratories (North Vancouver, BC). The organic carbon fraction was determined via acidification with HCl (50%) to volatilize inorganic carbon phases, and total carbon was analyzed via an induction furnace. The inorganic carbon was estimated from the difference between the two previous methods. Particle size distribution (PSD) was determined using a Mastersizer 2000 instrument (Malvern Panalytical, Malvern, United Kingdom). Quantitative phase analysis was conducted on an aliquot of micronized soil using thermogravimetric analysis (TGA) and Rietveld refinement of x-ray diffraction data (XRD). Details of sample preparation and examination for XRD can be found in Wilson et al. (2014).
2.4.2 CO2 Flux Methods

2.4.2.1 Dynamic Closed-Chamber Method

DCCs were used to quantify CO2 fluxes based on measurements of the rate change of CO2 concentration in the chamber headspace. The long-term chamber (LTC) (LI-8100-101, LI-COR Inc., Lincoln, NE) system consisted of a dome on a rectangular base atop a polyvinyl chloride (PVC) collar (20 cm inner diameter (ID) by 15 cm tall), 15m Bev-A-Line® (4.3mm ID) tubing, an infrared gas analyzer unit (IRGA, LI-8100A LI-COR Inc.), and a multiplexer (LI-8150 LI-COR Inc.) (Figure 2.4 A). To make a measurement the dome was moved automatically horizontally and lowered on to the collar (Figure 2.4 A.). The collars with a bevelled edge were inserted using a wood 4x4 (20-cm long) and a mallet into the sediment (~9-13 cm) approximately 1-hour prior to the initiation of sampling, which is considered sufficient time for low-biomass sediment soils to recover from the disturbance (Ball & Virginia, 2015). For each collar (LTC and SVC), the height above the sediment surface (offset) was individually measured at three internal locations and averaged to accurately estimate the headspace volume. The geometric volume used for the flux calculation was calculated based on the volume of the chamber, collar offset, tubing and IRGA. Four LTCs were collocated with in-soil volumetric water content probes 0 to 5 cm depth (ECH2O Model EC-5, Decagon Devices Inc.) and temperature thermistor probes 0 to 5 cm depth (8150-203, LI-COR Inc.). Each chamber recorded an observation every 30-min in a round-robin fashion, providing a temporal record of CO2 fluxes at the ground surface at the eight selected locations.

Additionally, PVC collars (20 cm ID by 15 cm tall) were set in a grid upwind of the EC tower to provide a measurement of the spatial distribution of the fluxes using survey chambers (SVCs) (Figure 2.3). The SVC collars were inserted into the sediment (~9-13 cm) 1-day prior to the initiation of sampling. The grid was sampled using a portable survey chamber (SVC) in
combination with an IRGA (LI-8100-103 and LI-8100A, respectively, LI-COR Inc.) (Figure 2.4 B). The survey grid in 2020 consisted of 22 soil collars permanently installed in the ground. In addition, there were 12 soil collars emplaced at other selected locations, including on the forest floor and in the transition zone between grassland and carbonate materials. Twenty-five rounds of flux observations were made at each survey collar and 12 rounds at the selectively located SVC collars. The grid in 2021 consisted of 51 soil collars permanently installed in the ground. Eight rounds of survey measurements were completed on this grid. Additionally, on four days in 2020 and three days in 2021, survey-mode observations were made 30-cm from the long-term chambers as checks on the LTC flux measurements and to assess the short-range spatial variability of the sampling (Figure 2.5).

The analyzer unit housing the IRGA controls the automated chamber for the LTC and SVC observations. Opaque domes temporarily seal over the collars creating a closed environment for the observation. Air in the headspace circulates between the chamber and the IRGA with an internal pump, creating small-scale eddies to ensure well-mixed conditions in the system. Each chamber is equipped with a vent to the atmosphere preventing a pressure difference between the headspace and the surrounding atmosphere from affecting the flux measurement. The IRGA measures the headspace concentrations of CO$_2$ and H$_2$O$_{(g)}$ over time and subsequently corrects the concentrations of CO$_2$ for evaporating H$_2$O$_{(g)}$ causing water vapour dilution (Welles et al., 2001). This corrected gas concentration is known in the literature as the molar mixing ratio (mol (mol of dry air)$^{-1}$), which is a conserved gas quantity during changes in pressure, temperature, and water vapour pressure (Foken et al., 2012).
Figure 2.4 Images and conceptual diagrams on the operation of long-term (LTC) (A. top and bottom) and survey (SVC) (B. Top and bottom) DCC systems.

Figure 2.5. Long-term chamber and survey chamber comparisons and validations, panel a. 2020, and b. 2021.
Based on qualitative tests, the chosen chamber closure length was 120 seconds. The chamber tubing was purged prior to and after the observations for 30 seconds. There was a 4-minute pause at the end of each LTC cycle to ensure the system would maintain the 30-min interval (48 measurements per day at each location). These specific settings were used for all long-term chamber-based measurements. Observed linear increases in concentration between 30 and 120 s after chamber closure were used to obtain the rate of change of CO$_2$ mixing ratio over time (Figure 2.6). A linear regression fit tends to be ideal for low flux levels (LI-COR Inc., Ball & Virginia, 2015) and reduces the risk of overestimating the fluxes (Jassal et al, 2012). The rate change of the CO$_2$ mixing ratio ($S_c$) was used in the following equation to compute the CO$_2$ flux ($\mu$mol m$^{-2}$ s$^{-1}$) at the ground surface:

$$F_{CO_2} = \frac{V P_0 (1 - W_0) \frac{\partial S_c}{\partial t}}{RST_0}$$

Equation 2.1.

where $P_0$ is the initial barometric pressure (Pa), $T_0$ is the initial absolute air temperature (K), $W_0$ is the initial water vapour mole fraction (mol mol$^{-1}$), $R$ is the gas constant (8.314 Pa m$^3$ K$^{-1}$ mol$^{-1}$), $S$ is the surface area in the chamber collar (m$^2$), $V$ is the total geometric volume (m$^3$), and $\frac{\partial S_c}{\partial t}$ is the rate change of CO$_2$ mixing ratio ($\mu$mol (mol dry air)$^{-1}$ s$^{-1}$). Evaporation (i.e., water vapour flux) was determined using the equation 2.1 and substituting the rate change in the water vapour mol fraction, $\frac{\partial H}{\partial t}$, which was determined from an exponential regression between 10 and 30 seconds after chamber closure (Cohen et al., 2015).
Figure 2.6. Soil CO$_2$ flux from LTC 8 on 19 August 2021, at 10:00 (blue) and 16:00 (red). The observation length was 120 s, and the linear regression fit was evaluated after a dead band period of 30 seconds over 90 seconds ($\Delta t$). The open circles are the data points collected every second by the analyzer unit. This demonstrates two flux examples, 0.16 μmol m$^{-2}$ s$^{-1}$ ($\Delta S_c = 2.3$ ppm) and 1 μmol m$^{-2}$ s$^{-1}$ ($\Delta S_c = 14.7$ ppm).

2.4.2.1.1 Data Post-Processing, Screening, and Analysis

SoilFlux Pro® software (version 4.2.1.) and python were used for data post-processing. Every LTC chamber measurement were scanned and filtered for poor quality by evaluating the root-mean-square error (RMSE) of the $dS_c/dt$ regression (Görres et al., 2014). The RMSE is a statistical tool to assess regression model fit by the difference between the predicted model value and the observed value. If the RMSE of the $dS_c/dt$ measurement was higher than the mean RMSE plus one standard deviation for individual LTC time-series during the field campaign, the flux measurement was excluded. Rather than screening via a coefficient of determination ($R^2$), the RMSE technique is less biased toward filtering low flux measurements (Görres et al., 2014; Görres et al., 2016; Jassal et al., 2012; Savage et al, 2008). This removed 12.5% in 2020 and 9.5% in 2021 of the LTC data, excluding a 2-day power outage in 2021 (25% data loss). The averages,
minimums, and maximums of the LTC CO₂ flux measurements were calculated for the duration of each of the two field seasons (2020 and 2021).

Further, the fluxes measured in the survey grid were spatially interpolated with an ordinary kriging technique in python. The kriging was conducted with the scikit-gstat package in python (Mälicke et al., 2021). The general formula for estimating a value at an unsampled location (\( F_{CO2}^* \)) is from a weighted sum of nearby observations:

\[
F_{CO2}^*(s_0) = \sum_{i=0}^{N} \lambda_i F_{CO2}(s_i)
\]

where \( s \) is a set of observation points in the grid, \( F_{CO2}^*(s_0) \) is the estimation of the flux at an unobserved location \( s_0 \), \( N \) is the size of the set of observation points, \( F_{CO2}(s_i) \) and \( \lambda_i \) are the flux and weighting factor at the \( i^{th} \) \( s \) location, respectively. The array of weights is derived using a spherical variogram model. The variogram is an effective tool to describe the spatial dependence between observations at a specific separation distance (Mälicke et al., 2021; Rayment & Jarvis, 2000; Vieira et al., 1983). If the observations measured in the grid have a low degree of correlation, the interpolation surface cannot be populated (Rochette et al., 1991; Vieira et al., 1983).

Finally, ordinary least squares multiple regression models were applied to the DCC long-term data from 2020 and 2021. The CO₂ flux was the response variable, and environmental data were the predictor variables. A linear model was chosen as it is commonly used for identifying inferences in relationships occurring in the environment. The predictor variables were normalized to evaluate the magnitude of their individual effects. Pearson’s correlation coefficient (\( r \)) was used to describe individual linear relationships between the flux and all climate parameters.
2.4.2.2 Eddy Covariance Method

The EC system comprised of a 3-D sonic anemometer (model CSAT3B, Campbell Scientific Inc. (CSI), Logan, UT) and an enclosed-path CO₂/H₂O gas analyzer (model LI-7200RS, LI-COR Inc.) (Figure 2.7). The inlet of a 1 m (0.005 m ID) insulated intake tube (model 9972-053, LI-COR Inc.) was mounted 0.07 m north of the sonic anemometer transducer array volume and attached to the support beam. A 7200-101 flow module was installed to provide a high flow rate (15 L min⁻¹) through the gas analyzer ensuring turbulent flow in the sample tube and minimizing high-frequency attenuation (Lenschow & Raupach, 1991; Moore, 1986). An LI-7500 Analyzer Interface Unit was also installed to house the gas analyzer electronics and USB drive for datalogging. The enclosed gas analyzer and the sonic anemometer data were stored and made accessible through a SmartFlux® 2 system (LI-COR Inc.). In 2020, the EC sensors were set at 2.1 m above the soil surface, with measurements made continuously at 10 Hz for the first two weeks. For the last two weeks, the sensors were lowered to 1.65 m, and the sampling frequency was increased to 20 Hz to better align the EC-system sampling footprint with the area covered by DCC measurements. In 2021, the sensor height was set at 1.40 m and measurements made at 20 Hz.

The flux was computed from the covariance between the vertical wind speed and the CO₂ mixing ratio as described in Baldocchi (2003).

\[ F_{CO_2} = \bar{\rho}_a w' S_c' \quad \text{Equation 0.3} \]

where \( \bar{\rho}_a \) is the mean dry-air density, and \( w' S_c' \) is the covariance between \( w \), the vertical wind speed and \( S_c \), the CO₂ mixing ratio. The overbar indicates the mean and the primes (′) indicate the deviation from the mean. Using the mixing ratio (rather than the mole fraction) accounts for the Webb-Pearman-Leuning correction for density effects due to heat and water vapour transfer (Webb et al., 1980).
Figure 2.7 Photograph of the eddy covariance tower. This includes a sonic anemometer and CO\textsubscript{2} analyzer and air intake tube on the left side of the image and micrometeorological sensors which included a 2D sonic anemometer and an air temperature and humidity probe in a radiation shield. Not shown on the image are two soil heat flux plates, soil moisture sensors, a barometer, a rain gauge, and a net radiometer.

Additional soil and micrometeorological instruments at the EC station included two soil heat-flux plates (models HFP01SC and HFP01, Hukseflux, Delft, Netherlands) at 5-cm depth and a soil moisture probe from 0 to 12 cm depth (model CS655, CSI). Additional components of the monitoring system included sensors to measure 2D wind speed and direction (model Windsonic4-L, Gill Instruments, Lymington, United Kingdom) and air temperature and relative humidity (model HMP 155A, Vaisala Oyj, Vantaa, Finland) approximately 20 cm above the EC sensors and varying with the changes in EC sensor height (2.3m, 1.85m and 1.6m, respectively). Barometric pressure sensor (model CS106, Vaisala Oyj) was installed in the datalogger box. A tipping bucket rain gauge (model TE525WS-L, Texas Electronics, Dallas, TX) and incoming and outgoing radiation was measured by net radiometer (CNR4-L, Kipp and Zonen, Delft, Netherlands) both instruments mounted at 1.2-m height on a secondary wood post approximately 10 meters from the...
tower (east in 2020 and north-west in 2021). Data from soil and meteorological sensors were recorded every second by a datalogger (CR1000X, CSI) and stored as 2-minute averaged values. These components were used to record weather conditions and facilitated quantification of the energy balance closure.

2.4.2.2.1 Data Post-Processing and Screening

The open-source EddyPro® software (version 7.0.7), released by LI-COR Inc., was used to process the flux data with a missing sampling allowance of 10%. The CO₂ flux was calculated over a 30-min averaging period and processed as follows: a double rotation of the wind vectors (v and w) to express the vectors relative to main streamlines (u), block averaging, i.e., no de-trending, an automatic time lag optimization correction for the separation between the anemometer and the analyzer unit. The data was de-spiked following Vickers and Mahrt (1997). A correction of high- and low-pass filtering effects was applied according to Moncrieff et al. (1997; 2004).

CO₂ flux data were discarded from the data set if the following criteria were not met. Only data collected for wind directions between 110° and 225° relative to North (0°) were used in 2020 and 2021. The strict wind direction threshold was chosen to restrict the interference from the neighbouring forest. QA/QC was performed on the data using quality flags provided by the EddyPro® software and data categorized as level 1 and 2 were discarded (based on the 0-2 system by Foken et al., 2004). These QC/QA methods apply a flag according to a joint steady-state test and developed turbulent conditions test. Additionally, CO₂ flux as a function of friction velocity ($u_*$) was evaluated. $u_*$ is a velocity scale (= (τ/ρ)^1/2) calculated from the wind shear (τ) near the ground and commonly used as an indicator of atmospheric turbulence intensity (Barr et al., 2013; Hunt et al., 2016; Stull, 1988). Fluxes computed with a $u_*$ less than 0.10 m s⁻¹ were rejected from
the 2020 data and 2021 data (using Hunt et al. (2016), see Appendix C for the approach). Visual outliers (> 4 μmol m⁻² s⁻¹) were manually inspected and found to show non-stationarity of the high-frequency CO₂ mixing ratio data. Three outlier data points were removed, 2 in 2020 and 2 in 2021. The filters and the data lost to each criterion are shown in Table 2.1; 35% of data was retained from 2020 (22.5% daytime and 12.5% nighttime) and 54% from 2021 (31% daytime and 23% nighttime). Data were not gap-filled for this field study.

### Table 2.1 QA/QC criteria and data loss resulting from screening eddy covariance data.

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Threshold for rejection</th>
<th>Reasoning</th>
<th>Data points (n)</th>
<th>Percent of 30-min data failing the criteria (cumulative)</th>
<th>Data points (n)</th>
<th>Percent of 30-min data failing the criteria (cumulative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start date</td>
<td>18:00 2020-08-07 09:00 2020-09-02</td>
<td>Footprint mismatch, fluxes failed standard post-processing, rain, and instrument data gaps</td>
<td>777</td>
<td>64%</td>
<td>306</td>
<td>45%</td>
</tr>
<tr>
<td>End date</td>
<td>10:30 2021-08-06 11:30 2021-08-20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Measurements</td>
<td>1211</td>
<td>674</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>First pass-filtering</th>
<th>2020</th>
<th>2021</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wind direction (WD), data quality and gaps</td>
<td>110° &lt; WD</td>
<td>110° &lt; WD</td>
</tr>
<tr>
<td>WD&gt; 225°</td>
<td>WD&gt; 225°</td>
<td></td>
</tr>
<tr>
<td>QC&gt;0</td>
<td>QC&gt;0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Second pass – filtering</th>
<th>2020</th>
<th>2021</th>
</tr>
</thead>
<tbody>
<tr>
<td>uₜ</td>
<td>$uₜ &lt; 0.10$ (2020)</td>
<td>Insufficient turbulence</td>
</tr>
<tr>
<td>Manual</td>
<td>$uₜ &lt; 0.15$ (2021)</td>
<td></td>
</tr>
<tr>
<td>$F_{CO₂} &gt; 4$ μmol m⁻² s⁻¹</td>
<td>Visual inspection of non-stationarity in the raw high-frequency CO₂ data</td>
<td>788</td>
</tr>
</tbody>
</table>

#### 2.4.2.2 Flux Footprint Modeling

A footprint analysis was used to describe the spatial extent and position of the source area contributing to the turbulent fluxes measured by the EC system. The Kljun footprint method is used in this thesis. Kljun et al. (2015) developed a non-dimensional semi-empirical parameterized footprint function based on the Backwards Lagrangian Stochastic Particle Dispersion model (Kljun
et al., 2004). This model can be applied to a wide range of boundary layer conditions from convective to stable.

The footprint is temporally dependent on atmospheric conditions and surface characteristics. Therefore, a footprint was calculated for every half-hour flux measurement that passed the filtering described above. Input parameters for the footprint model were taken from the EC dataset and surface properties. Boundary layer height was estimated based on Sugiyama & Nasstrom (1999) for stable and neutral conditions. The average boundary layer height throughout the field campaign and used for the footprint calculation was 485 metres. Given the significant difference between the sensor height and the top of the atmospheric boundary layer, the footprint model is relatively insensitive to the boundary layer height (Heidbach et al., 2017). The one-dimension crosswind-integrated footprint and the two-dimensional 80% contour are shown in the results.

2.4.2.3 CO₂ Flux-Gradient Method

A flux-gradient method was implemented in August 2021 to measure CO₂ and H₂O concentrations above the playa. The instruments were located 10 metres north of the EC tower. The system consisted of a CO₂ and H₂O infrared gas analyzer (model LI-850, LI-COR Inc.), a datalogger (model CR1000, CSI), a pump with solenoid valves capable of switching between 4 ports, all within an enclosure. Each port was connected to a 5-m-long (4.3 mm ID) semi-rigid Synflex 1300 Metal-Plastic composite tubing (Eaton Corp. Inc., Beachwood, OH, USA) with a 2-micron stainless steel particle filter (model SS-4FW-2 Swagelok Co., Solon, OH) and inlet cap (model 9972-072, LI-COR Inc.) for the air intake. Air intakes were installed at four levels, 0.22, 0.44, 0.88 and 1.72 m, above the ground on a 4” x 4” wood post. The measurements were made at 1 Hz. The datalogger signalled the solenoid valves to switch between levels continuously.
throughout the field campaign. The switch occurred every 75 seconds. The first 15 seconds of data were removed to ensure the tubing was evacuated and air at the next level was being sampled. The high-frequency data was averaged over 30-min. Time series were plotted for each level and the top and bottom levels (4 and 1). Profiles (CO$_2$ concentration as a function of height) were also plotted at 12-hr averaging intervals.

The CO$_2$ flux ($F_C$) was estimated using the flux-gradient equation for turbulent transport, which is analogous to Fick’s Law for molecular diffusion (Monteith & Unsworth 2013) as follows:

$$F_C = -KD\frac{dS_C}{dz}$$

**Equation 0.4**

where $z$ is the height, $\rho_a$ is the dry-air density (mol m$^{-3}$), and $dS_C/dz$ is the vertical gradient of the mean CO$_2$ mixing ratio (μmol (mol of dry air)$^{-1}$ m$^{-1}$). The eddy diffusivity, $K$ (m$^2$ s$^{-1}$), also called the vertical transfer coefficient, was obtained using

$$K = u_k z_m$$

**Equation 2.5**

where $k$ is the von Karman constant (0.40) and $z_m$ is the height of the EC sensors (m). The mixing ratio difference between levels 1 and 4 were used for the flux calculation. The calculation assumes similarity of momentum and scalar diffusivities and atmospheric conditions are generally neutral over the playa.

### 2.4.3 Gas Sampling and Isotopic and Radiocarbon Analysis

#### 2.4.3.1 Sampling

In 2020, a static chamber method was chosen for gas-sample collection (Wozney et al, 2021). Static chambers were placed in excavations dug to three depths (5 cm, 40 cm and 65 cm below ground surface, Figure 2.8), at two locations on the playa. These chambers, consisting of a section
of PVC pipe 30 cm in length (10 cm ID), were inserted 20 cm into the carbonate soil and fitted with a PVC cap equipped with a septum for sample extraction (Figure 2.9 a.). The static chambers were left sealed and undisturbed for a week before initial sampling. The excavations were left open for the duration of chamber installation and sampling.

Therefore, in 2021, a combination of wells and static chambers were used for gas sampling to gain insight into the discrete and spatial variation in gas composition at depth with minimal soil disturbance (Figure 2.10). The static chambers in 2021 consisted of a collar, PVC pipe 20 cm in length (20 cm ID), inserted 18 cm into the ground with a removable lid. The lid consisted of a 5 cm PVC pipe glued to a PVC sheet with the opposite end covered in weather stripping, the PVC sheet was equipped with a septum and reflective sheeting (Figure 2.9 b.). The lid was attached with two butterfly clasps to make a tight seal. The gas samples at depth were collected using soil gas vapour probes with a dedicated tip manufactured by AMS, Inc (American Falls, ID) (Figure 2.10). The probes were driven into the soil with a drive-hammer, backfilled with 10 cm of carbonate material to cover the screen and then filled with quick-setting cement to create a seal. The vapour probe tubing was fit with a gas-tight ball valve at the surface and housed in a protective PVC casing (10cm ID) with a lid. After 24 hours, the pressure in the vapour probes was tested with a hand pump to ensure the air was not entrained during the sampling. The soil gas sampling was conducted by attaching Bev-A-Line (1/4” ID) tubing to the ball-tight valve on the soil vapour probe. The Bev-A-Line tubing was fit to Masterflex® tubing (Cole-Parmer, Quebec, QC) via male-female Luer-lock and barb hose fittings. The gas sample travelled through a peristaltic pump with a flow rate of 50 mL min⁻¹ and through a CO₂ gas analyzer (model LI-820, LI-COR Inc.) to a one-way Luer-lock and a 22-gauge 4”-long needle. The wells and one static chamber were installed at three locations (well depths): the playa (40, 60, 80, 100 cm), the transition zone (40,
60, 80, 100 cm) and the forest (40, and 80 cm) (Figure 2.8.). The isotope results (i.e. pMC and $^{13}$C) from the 2021 static chamber samples were corrected for atmospheric headspace contributions using a mass balance approach discussed in the methods section of Wozney et al. (2021).

Figure 2.8. Schematic of gas sampling locations and types in 2020 and 2021, showing playa (left), the transition zone (middle) and the forest floor (right). The legend shows the symbols used in the results section.

Figure 2.9. Static chamber schematics for soil gas sample collection a. 2020 design, b. 2021 adapted collar-lid design.
Figure 2.10. Gas Vapour Probe with Dedicated GVP Tip (211.00) made by AMS, Inc., with the sampling pipeline. The pipeline includes a gas-tight ball valve, Bev-A-Line tubing (1/4” ID), a peristaltic pump with Masterflex tubing, an infrared gas analyzer (LI-820 LI-COR Inc.), a one-way Luer-lock and a needle, shown here the 22 gauge 4” long needle.

2.4.3.2 $^{13}$C Analysis

In 2020, gas was collected from the septum of the static chambers with a 25 mL gas-tight glass syringe with a 1-inch, 21-gauge needle and 20 mL of sample was inserted into a 12 mL Labco Limited pre-evacuated Exetainer to be analyzed for stable isotopes of CO$_2$. Twenty-five samples for stable-isotope analysis were taken over three days, 19 from the static chambers and six from the bulk atmosphere (~30 cm a.g.s.). In 2021, 30 samples for $^{13}$C were taken alongside the radiocarbon samples in the soil vapour probes, static chambers, and atmosphere, and an additional 75 samples for $^{13}$C and CO$_2$ concentrations were taken from the static chamber headspace every 30 min for 3 h with one 24 h sample. The isotope samples were analyzed at the Jan Veizer Stable Isotope Laboratory in Ottawa, ON.

Briefly, the gas compositional analysis, specifically for CO$_2$ partial pressure, was determined by injecting a 10 mL aliquot of sample from an exetainer into a gas chromatograph (GC) (Model
The analytical accuracy for the gas composition is ±10 ppm with a standard deviation of the calibration gas around ±8 ppm. Stable carbon isotope ratios $^{13}\text{C}/^{12}\text{C}$ of CO$_2$ were measured using gas chromatography isotope ratio mass spectrometry (GC-IRMS). The sample was injected into a GC isolink system to isolate CO$_2$ from the air in either a fixed loop or sample loop depending on the concentration. The CO$_2$ was sequentially transported via a Thermo Conflo IV to the Thermo Delta V GC-IRMS. The results are expressed as δ values using a per mil notation relative to the international V-PDB standard with an associated uncertainty of ±0.2‰ for the 2020 and 2021 samples.

In Power et al. (2014, 2019), the stable isotopic composition ($\delta^{13}\text{C}$) in the mineral phase was converted based on equilibrium fractionation factors to equivalent $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) to compare samples between the solid and aqueous carbon reservoirs. The hydromagnesite isotopic composition was converted to the DIC (b) phase by subtracting the fractionation factor of dypingite, $\varepsilon_{\text{dy}}(b)$: +4.10 ‰, based on Wilson et al. (2010) laboratory experiments. The fractionation factor is not known for hydromagnesite, therefore the fractionation of dypingite, a hydrated precursor to hydromagnesite, is used as a proxy and adjusted to a temperature of 10°C (Power et al., 2019). Similarly, the equilibrium enrichment factor during the fractionation of stable carbon in gas (g) relative to the DIC (b) is $\varepsilon_{\text{g}}(g)$: -9.60 ‰ (at 10°C) (Mook et al., 1974). These enrichment factors were used in this thesis for $^{13}\text{C}$ stable isotope analysis to compare reservoirs while accounting for equilibrium fractionation during phase transition reactions.
2.4.3.3 $^{14}$C Analysis

Due to the low CO$_2$ concentrations in ambient air and gas in the carbonate playa pore spaces, a large air sample volume was required to obtain a measurable yield of pure carbon for radiocarbon ($^{14}$C) analysis. Therefore, a $^{14}$C sampling technique recently developed at the A.E Lalonde AMS Laboratory (Ottawa, ON) was deployed in the field. This method extracts CO$_2$ from air via a barium carbonate mineral trap by bubbling sample air through a barium hydroxide solution (Eq 2.6; Reynolds, 2019).

\[
Ba(OH)_2 + CO_2 \leftrightarrow BaCO_3 + H_2O \quad \text{Equation 2.4}
\]

The AMS laboratory provided nine vials of a 0.4 mL solution of barium hydroxide (Ba(OH)$_2$). Samples were collected, six from static chambers and three from the bulk atmosphere, in 2020. Approximately 1000 mL of gas was extracted from the chambers and 3000 mL from the atmosphere with a 140-mL syringe with a 23 gauge, 3” inch long needle. Then in 2021, 18 vials with 1 mL of Ba(OH)$_2$ solution were provided, and 500-4000 mL of gas was extracted from the soil gas probes depending on the concentration at depth, and 9000 mL from the atmosphere (see data summary in the appendix D). The flow rate from the peristaltic pump was 50 mL min$^{-1}$. No samples were taken by hand with a syringe in 2021.

The butyl septa of the vial were pierced by the needle on the syringe (2020), or sampling pipeline (2021) and the needle was inserted deep enough for the needle tip to be submerged in the Ba(OH)$_2$ solution. After introducing 5 mL of sample soil gas, the exetainer became over-pressureurized, and a release mechanism was inserted into the septum. The pressure release mechanism was made of a 1-inch (2.5-cm) long 21-gauge needle, attached to a 0.45 µm Whatman
disk filter affixed to a modified 1-mL syringe barrel with a 1/4” (ID), with a 1/4” to 1/16” Swagelock reducer with a 35-cm-long stainless steel coil to prevent backflow (see Reynolds, 2019, for diagram of the release mechanism). This release mechanism prevents backflow and diffusion effects from atmospheric air.

The fractions of radiocarbon (reported in pMC from the $F^{14}$C) in CO$_2$ from the gas samples via barium carbonate were analyzed at the A.E. Lalonde accelerator mass spectrometry laboratory in Ottawa, ON, Canada. The laboratory sample preparation protocols are outlined in Reynolds (2019); field blanks and standards were prepared in the laboratory alongside the barium carbonate samples and analyzed in tandem. Briefly, the laboratory preparations include neutralizing the remaining aqueous solution in the exetainer vial with Milli-Q water to avoid atmospheric contamination and then the carbonate is freeze-dried. The samples are then weighed, and a carbon yield is recorded. The carbonate is mixed and homogenized with tantalum at a weight ratio of 1:1.5 (Yang et al., 2018), and the final mixture is pressed into aluminum target bases and loaded into the 200-sample wheel for AMS analysis. The barium carbonate samples were analyzed on the gas source 3.0 MV tandem accelerator mass spectrometer built by High Voltage Engineering (HVE). $^{12,13,14}$C ions are measured at 2.5 MV terminal voltage with Ar stripping. The BaCO$_3$ results are reported as $F^{14}$C and are calculated following procedures in Reimer et al., 2004, with normalization to graphitized OX-II standards. The results are corrected to a blank tantalum target run in tandem and for $^{13/12}$C fractionation. The uncertainties for each BaCO$_3$ result representing the AMS measurement errors are presented in Table D.1 appendix D.
Chapter 3: Quantifying CO₂ Fluxes and the Spatial Variability Across the Northern Hydromagnesite-Magnesite Playa

3.1 Introduction

This thesis chapter presents CO₂ flux rates and spatial variability of the fluxes, and the isotopic composition of the emitted CO₂ gas and CO₂ soil gas. An eddy covariance (EC) system, dynamic-closed chambers (DCC), and meteorological sensors were deployed above the hydromagnesite-magnesite playas from 7 August to 2 September 2020, and again with an additional above-ground CO₂ profile system from 7 August to 20 August 2021. Together, the duration of data collection of the two field campaigns amounted to 6 weeks. Gas samples for isotope analysis were collected from the unsaturated zone of the playa, the transition zone between playa and natural soils, forest soils and directly from the atmosphere above the playa to help constrain the carbon cycle and processes influencing the fluxes across the playa-atmosphere interface. Additionally, information on the surficial (0-20-cm depth) soil characteristics (mineralogy, grain size distribution, density, porosity, and inorganic and organic carbon content) and meteorology are presented in support of the CO₂ flux data. The work on the hydromagnesite-magnesite playas was conducted on the amalgamated mounds environment of the northern playa.

3.1.1 Chapter Objectives:

- Quantify the rates and direction of CO₂ fluxes between the carbonate mineral soil and the atmosphere using three methods (EC, DCC, above ground CO₂ profiles)
- Characterize the spatial variability of the CO₂ fluxes across the playa from DCC observations
3.2 Results

3.2.1 Playa Characteristics and Alkalinity

The material composing the upper 20 cm of the playa underneath the long-term chamber (LTC) DCC footprint contained 62% hydromagnesite, 12% magnesite, with fractions of ankerite, lansfordite and quartz, determined from Rietveld’s refinement of XRD data (Table 3.1). The remaining 22% was present in the form amorphous mineral phases (determined using a 20 wt% corundum (Al₂O₃) spike). The mineralogical analysis was performed on one homogenized sample obtained from a collection of samples taken within 50 cm of the LTC collars. This XRD result was consistent with previous measurements on material taken from the amalgamated mounds of the south playa, confirming the dominance of hydromagnesite in the overall mineralogy of the playa unsaturated zone (Power et al., 2014). The total carbon content in the material was 10.90%, with 10.58% being inorganic carbon and 0.32% organic carbon (Table 3.2). The playa material is white to light grey and has a high albedo ranging from 0.43 to 0.50 during the daytime, measured using the CNR4-L pyranometers. Polygonal desiccation cracks were common surficial features of the amalgamated mound environment. These features were widespread in the footprint of our study, with the larger cracks extending down to 40 cm deep. The LTC DCCs were set predominantly on the carbonate matrix, avoiding desiccation cracks.

Past work estimated that the near-surface pH of the playa porewater is close to 9, increasing in the vadose zone from pH = 8 at the water table (Power et al., 2019). Measurement of pH was
not performed as part of this study, as it is difficult to extract pore water from the silt-sized (Table 3.2), partially water-saturated playa material. The dry soil bulk density ranged from 0.80-1.34 g cm\(^{-3}\) (average 1.02 ± 0.13, n=70) (Table 3.2). The particle density of minerals present in the playa was 2.38 g cm\(^{-3}\) measured from one homogenized sample. Inferred porosities range from 50 to 70\% (average 61\% ± 5, n=69). The large variability of bulk density and inferred porosity values might be due to sediment disturbance during sampling.

**Table 3.1. Quantitative mineralogy of the northern playa (0-20 cm depth) (n=1) with a 20\% corundum spike using Rietveld refinement.**

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Formula</th>
<th>Abundance (wt% Rietveld)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydromagnesite</td>
<td>(Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O)</td>
<td>62</td>
</tr>
<tr>
<td>Magnesite</td>
<td>((Mg_{0.89}, Fe_{0.11})CO_3)</td>
<td>12</td>
</tr>
<tr>
<td>Ankerite</td>
<td>(Ca(Fe^{2+}, Mg)(CO_3)_2)</td>
<td>1</td>
</tr>
<tr>
<td>Landsfordite</td>
<td>(MgCO_3 \cdot 4H_2O)</td>
<td>2</td>
</tr>
<tr>
<td>Quartz</td>
<td>(SiO_2)</td>
<td>1</td>
</tr>
<tr>
<td>Amorphous</td>
<td>N/A</td>
<td>22</td>
</tr>
</tbody>
</table>

**Table 3.2. Sediment properties of the Atlin northern playa (0-20 cm depth), mean ± 1 standard deviation.**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Source</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g cm(^{-3}))</td>
<td>Sampler core</td>
<td>1.02 ± 0.13 (n=69)</td>
</tr>
<tr>
<td>Particle density (g cm(^{-3}))</td>
<td>Pycnometer</td>
<td>2.38 (n=1)</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>Calculation</td>
<td>61 ± 5 (n=69)</td>
</tr>
<tr>
<td>Soil organic carbon (%)</td>
<td>ALS</td>
<td>0.32 ± 0.02 (n=3)</td>
</tr>
<tr>
<td>Soil inorganic carbon (%)</td>
<td>ALS</td>
<td>10.58 ± 0.03 (n=3)</td>
</tr>
<tr>
<td>P(50) (μm)</td>
<td>Malvern Mastersizer 2000</td>
<td>7.58 (n=1)</td>
</tr>
<tr>
<td>Clay (%)</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>Silt (%)</td>
<td></td>
<td>90</td>
</tr>
<tr>
<td>Sand (%)</td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>
3.2.2 Meteorology

A micrometeorology system was installed alongside the EC sensors to measure climate conditions and assess the energy balance closure. The meteorological conditions were similar in August 2020 and August 2021. The predominant wind direction was from the south-southeast (Figure 3.1). Low wind speeds (<1 m s$^{-1}$), generally at nighttime, prevailed consistently from the north or from the forest to the east and west (Figure 3.1).

Air temperature, soil temperature, downwelling short-wave radiation, evaporation and relative humidity varied diurnally (Figure 3.2.). The air temperature (2-m height) maximum was 18.4 °C and 17.1 °C, the minimum was 1.6 °C and 1.3 °C, the soil temperature (5-cm depth) maximum was 15.5 °C and 15.5 °C, and the corresponding minimum was 3.0 °C and 4.3 °C for 2020 and 2021, respectively. The mean ensemble trends for ambient and soil temperature were similar between 2020 and 2021 over the diurnal cycle (Figures 3.3a. and 3.4a.). Generally, the average soil temperature at 5 cm was cooler than the ambient temperature over the diurnal course (Figure 3.3a. and 3.4a.). It is important to note on still nights the soils were the same temperature or slightly warmer than the ambient air (\(~ 0 - 1 \degree \)C). On specific nights at higher wind speeds (e.g., DOY 221, 223 and 245 in 2020 and DOY 221 to 223 in 2021), dry and relatively warm air flowed over the moist playas resulting in evaporative cooling of the soils, known as oasis effect (Stull, 1988). This effect is shown in the field data with soils that were much cooler than the ambient air (by 2.4 to 3.8 °C), low relative humidity (66.3 % to 67.7 %) and negative sensible heat flux (-19 to -44 W m$^{-2}$) balanced by positive latent heat flux (14 to 51 W m$^{-2}$) (heat fluxes shown in Figure C.3 in Appendix C).

Barometric pressure and rainfall varied with larger-scale climate patterns (Figure 3.2). The barometric pressure varied from 997 to 1016 mbar (2020) and 1003 to 1022 mbar (2021). There
were five rainfall events during the 2020 field campaign and two events during the 2021 field campaign, resulting in a cumulative 23.6 mm (2020) and 29.5 mm (2021) of precipitation. The soil water contents were correlated with rainfall events showing increased volumetric water contents following precipitation. The volumetric water contents were, on average, 5% in 2020 and 40% in 2021, measured at a depth of 0 to 10 cm near the EC tower. Water contents obtained from probes co-located with the LTCs at 0 to 5 cm depth, approximately 10 to 20 meters away from the EC tower, were quantified at 15% in 2020 and 35% in 2021 (n=4, ± 5%). The differences in measured moisture contents between locations may be due to heterogeneities in the playa; however, moisture contents were consistently higher in 2021 relative to 2020. The very low volumetric water content values in 2020 with the 10-cm probe were likely an artifact caused by the introduction of air voids during installation since the playa sediment was quite compact and dry; conditions in which fractures or cracks could form at depth with the sensor insertion (RoTimi Ojo et al., 2015).

Additionally, energy balance closure was estimated by plotting the sum of the turbulent heat fluxes, latent heat (LE) and sensible heat (H), against the available energy (Rn - G - S), where Rn is the net radiation, G is the soil heat flux and S is the change in heat storage in the air column (below the net radiometer) and in the soil. Photosynthetic energy storage is negligible in the playa ecosystem. The energy budget in an ecosystem should be conserved (100%) between available energy, heat storage and turbulent heat fluxes. Any imbalance represents neglected processes, issues with data resolution, and uncertainties (Mauder et al., 2020). Energy balance closures of 64% and 64% were obtained for 2020 and 2021, respectively (Figure 3.5). The estimate was based on the slope of a linear regression fit to data that passed minimum $u_*$ (friction velocity) and quality flag filters. The closure increased to 70% and 72% when the intercept was forced through the origin. The energy balance closure for both years implies fair EC flux quality. The leading reasons
in micrometeorology for the lack of closure are i) (sub)mesoscale transport such as advection, ii) low- and high-frequency loss, and iii) lack of representativeness of the net radiometer and soil heat flux measurements (small area near tower) of the EC source area (i.e., footprint) (Mauder et al., 2020; Wilson et al., 2002).

Figure 3.1 Wind rose showing joint frequency distribution (in percentage) of mean horizontal wind speed and direction for half-hour averages in a. 2020 (n=1211) and b. 2021 (n=675). The yellow star indicates the location of EC systems.
Figure 3.2 Time-series of climate measurements in Atlin 2020 (left panels), and 2021 (right panels). The x-axis shows the day of the year (PDT). From the top panel, a. CO$_2$ and H$_2$O mixing ratios ([CO$_2$] and [H$_2$O]), b. precipitation (P, bars) and cumulative precipitation (CP, black line) with volumetric water content 0-12 cm depth (VWC, blue line) and 0-5 cm depth (VWC, red line), c. temperature (T), d. relative humidity (RH), e. barometric pressure (BP), and f. wind speed (WS, black line) and friction velocity ($u_*$, blue circles). The EC sensors measure the mixing ratios (CO$_2$ and H$_2$O) and *averaged over 30-min intervals. The remaining climate variables from the meteorology sensors were averaged over 2-min intervals.
Figure 3.3. Diurnal course of the climate measurements from the EC tower in 2020 using PDT. The black lines are the daily diurnal trends, and red and blue data points are half-hour ensemble means. From the top left, a. temperatures (T), b. evapotranspiration (ET) and latent heat flux (LE), c. downwelling short wave radiation (S_d), d. relative humidity (RH), e. wind speed (WS), f. CO_2 mixing ratio (CO_2).

Figure 3.4. Diurnal course of the climate measurements from the EC tower in 2021 using PDT. The black lines are the daily diurnal trends, and red and blue data points are half-hour ensemble means. From the top left, a. temperatures (T), b. evapotranspiration (ET) and latent heat flux (LE), c. downwelling short wave radiation (S_d), d. relative humidity (RH), e. wind speed (WS), f. CO_2 mixing ratio (CO_2).
Figure 3.5 Energy balance closure for 2020 (a.) and 2021 (b.). Turbulent heat fluxes were filtered for $u_*$ (below 0.10 m s$^{-1}$ in 2020 and 2021), and QA/QC flags (1,2). The y-axis is the sum of the turbulent fluxes, latent heat ($LE$) and sensible heat ($H$), and the x-axis is the difference between the available energy, net radiation ($R_n$), and ground heat flux and storage ($G+S$). The slope of the linear regression is the closure, 0.64 and 0.64. The closure with forcing the regression through the origin is 0.70 and 0.72.
3.2.3 Rates and Direction of CO\textsubscript{2} Fluxes from DCC and EC

The data from seven long-term chambers (LTC) in 2020 and eight LTCs in 2021 were scanned and filtered for poor quality data by evaluating the root-mean-square-error (RMSE) of the slope fit to the rate change in CO\textsubscript{2} concentration for each 120-second observation (Görres et al., 2014). The filtering threshold was determined for each chamber by the mean RMSE plus 1 standard deviation. The descriptive statistics for each LTC are shown in Table 3.3 and the individual chamber CO\textsubscript{2} flux and RMSE time series can be found in Appendix E. The fluxes obtained from the LTCs were averaged for each half-hourly period to account for spatial variations and facilitate comparison with the EC half-hourly data.

The CO\textsubscript{2} fluxes from the LTCs show a distinct diurnal sinusoidal pattern (Figure 3.6). Specifically, the fluxes obtained from LTCs generally indicate emissions of CO\textsubscript{2} (positive flux) in the daytime and uptake of CO\textsubscript{2} (negative flux) at nighttime. The survey chamber (SVC) flux measurements show good agreement with the emissions of CO\textsubscript{2} in the day measured by the LTCs (Figure 3.6). Peak emissions of CO\textsubscript{2} commonly occurred between 14:00-15:00, and the highest uptake of CO\textsubscript{2} occurred between 2:00-3:00 (Figure 3.7 c.). In 2020, both LTC and SVC measurements indicated CO\textsubscript{2} uptake in the daytime during a heavy rainfall event with ~10 mm of precipitation (DOY 228 to 229) (Figure 3.6). The average flux for the entire duration of the measurement period in 2020 was -0.03 (± 0.37 std) µmol m\textsuperscript{-2} s\textsuperscript{-1} with values ranging from -1.63 µmol m\textsuperscript{-2} s\textsuperscript{-1} at nighttime to 2.14 µmol m\textsuperscript{-2} s\textsuperscript{-1} in the daytime (Table 3.4). In 2020, LTC 2 was excluded from the averaging and diurnal analysis since the raw data trends (dc/dt) demonstrated poor isolation of the closed headspace, i.e., non-linear, and non-exponential trends with a high RMSE compared to the other chambers. This could be due to pervasive cracks in the playa at this location.
location, allowing for gas exchange between the headspace and the atmosphere at the base of the collar.

The magnitude of the flux oscillation was visibly smaller across all LTCs in 2021, with a net average of 0.08 (± 0.21 std) μmol m⁻² s⁻¹ with values ranging from -0.83 μmol m⁻² s⁻¹ to 0.97 μmol m⁻² s⁻¹ (Figure 3.6 and 3.7 d.). As in 2020, the daytime SVC and LTC flux averages were similar in magnitude. Consistent with observations in 2020, rainfall events at the start (DOY 219) and middle (DOY 227) of the monitoring period resulted in negative daytime fluxes. In addition, there was no accumulation of ambient CO₂ above the playa at nighttime from day 220 to 227 (Figure 3.8, mixing ratio < 425ppm). The lack of CO₂ accumulation coincided with high nighttime wind speeds and the corresponding nighttime CO₂ fluxes were near 0 μmol m⁻² s⁻¹.

The EC CO₂ flux measurements do not show a distinct diurnal pattern, as was observed by the LTCs, meaning all fluxes were emissions (positive) (Figure. 3.6 and 3.7 a) and b)). In 2020, the flux average at the 2.01-m height was 1.46 μmol m⁻² s⁻¹ (± 0.58 std, n=194) over 15 days and the flux average at a sensor height of 1.65 m was 1.31 μmol m⁻² s⁻¹ (± 0.64 std, n=229) over 12 days; the dataset for both heights were combined for 2020 averaging, yielding an average value of +1.38 μmol m⁻² s⁻¹ (± 0.62 std, n = 423) over 27 days. The average flux in 2021 was +1.07 (± 0.43 std, n = 363) μmol m⁻² s⁻¹ for the 12-day monitoring period. The flux values ranged between 0.14 μmol m⁻² s⁻¹ to 3.25 μmol m⁻² s⁻¹ (2020) and -0.14 μmol m⁻² s⁻¹ to 3.15 μmol m⁻² s⁻¹ (2021). A limitation of the eddy-covariance method is large data gaps due to filtering for mean wind direction, turbulence, and stationarity (quality flags) and $u_*$ threshold. In 2020 and in 2021, 65% (n=788) and 49% (n= 363) of the flux measurements did not pass the filters, respectively. Note that the EC dataset is not gap-filled due to the short length of the field campaign and minimal nighttime data.
The EC data that passed the filtering were subject to random errors and systematic biases. The random error estimation associated with the sampling procedure was calculated by the Eddy Pro® software using an approach outlined by Finkelstein and Sims (2001). The errors associated with sampling were on average ±0.17 µmol m² s⁻¹ (± 0.13 std) and ±0.13 µmol m² s⁻¹ (± 0.13 std) for 2020 and 2021, respectively. This represents 15% and 12% mean fractional flux sampling error (the random error divided by the flux), which falls within the range of acceptable error for gases (< 20%) (Finkelstein & Sims, 2001). The systematic biases (+/- value) can be estimated from the choice of friction velocity (u*) threshold (-1%) and energy balance closure (+30%) (Morgenstern et al., 2004). For instance, according to Twine et al. (2000) and Wilson et al. (2002), the EC CO₂ fluxes could be systematically low by 36% since the energy balance closure indicates an underestimation of the turbulent fluxes.

In summary, there was a clear and significant difference between the two CO₂ flux methods, EC and DCC, in both flux magnitude and direction (Figure 3.6). The DCC average in the daytime changed to 0.21 µmol m⁻² s⁻¹ (2020) and 0.20 µmol m⁻² s⁻¹ (2021) when evaluated for the same time periods for which EC data was available (Table 3.4). Based on this direct comparison, the fluxes determined by two methods differed by a factor of 6 (2020) and 5 (2021) for daytime conditions. There were only limited instances in the daytime where the two methods converged in estimates of the CO₂ flux across the playa-atmosphere interface (DOY 226, 227, 332 in 2020 and DOY 231, 233 in 2021). The validity of a nighttime comparison is somewhat hindered by limited EC CO₂ flux data caused by low wind speeds and lack of turbulent mixing, and the sign difference between the measured fluxes from the two methods, during nocturnal periods with turbulent mixing (e.g., DOY 221 and 245 in 2020).
Figure 3.6 CO₂ flux time series for long-term chambers (LTC), eddy-covariance (EC) and survey (SVC) measurements. The LTC data (grey symbols) represent mean fluxes from three to eight LTCs after RMSE filtering (± 1 std), black symbols represent fluxes obtained from eddy-covariance measurements, the red symbols represent the survey chamber (SVC) fluxes (± 1 std). The height of the EC sensors (SH) is indicated on the panels. Grey and white vertical bands represent nighttime and daytime, respectively.

Figure 3.7. Diurnal CO₂ flux trends. Semi-transparent grey symbols represent individual fluxes, blue and red symbols represent half-hour ensembles with 1 standard deviation. Panels a. EC 2020, b. EC 2021, c. DCC 2020 (7 LTC), and d. DCC 2021 (8 LTC). The bars at the bottom depict the frequency distribution of each half-hour period. Blue lines and red lines represent overall averages for the whole sampling period.
Table 3.3. Descriptive statistics (mean, standard deviation, minimum value, and maximum value) for LTC CO$_2$ fluxes ($\mu$mol m$^{-2}$ s$^{-1}$).

<table>
<thead>
<tr>
<th>Year</th>
<th>LTC</th>
<th>Mean</th>
<th>Std</th>
<th>n</th>
<th>Min</th>
<th>Max</th>
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<tr>
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<td>1</td>
<td>-0.05</td>
<td>0.25</td>
<td>1002</td>
<td>-0.69</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.34</td>
<td>0.75</td>
<td>1081</td>
<td>-2.10</td>
<td>4.17</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.02</td>
<td>0.32</td>
<td>1019</td>
<td>-0.98</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.09</td>
<td>0.43</td>
<td>1110</td>
<td>-1.55</td>
<td>2.14</td>
</tr>
<tr>
<td></td>
<td>5</td>
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<td>0.22</td>
<td>1168</td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
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<td>0.36</td>
<td>1005</td>
<td>-1.03</td>
<td>1.95</td>
</tr>
<tr>
<td>2021</td>
<td>1</td>
<td>-0.02</td>
<td>0.24</td>
<td>466</td>
<td>-0.66</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
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<td>0.16</td>
<td>445</td>
<td>-0.32</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.08</td>
<td>0.12</td>
<td>464</td>
<td>-0.25</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.13</td>
<td>0.16</td>
<td>456</td>
<td>-0.29</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.06</td>
<td>0.16</td>
<td>485</td>
<td>-0.35</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.16</td>
<td>0.23</td>
<td>435</td>
<td>-0.39</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.03</td>
<td>0.20</td>
<td>456</td>
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<td>0.77</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.09</td>
<td>0.25</td>
<td>460</td>
<td>-0.83</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 3.4. Statistics for each CO$_2$ flux method: total, day and night (mean, standard deviation, range). The + indicate emission and – indicate uptake.

<table>
<thead>
<tr>
<th>Year</th>
<th>Total CO$_2$ Fluxes 0:00-24:00 [\mu$mol$ m$^{-2}$ s$^{-1}$]</th>
<th>Daytime CO$_2$ Fluxes 8:00-20:00 [\mu$mol$ m$^{-2}$ s$^{-1}$]</th>
<th>Nighttime CO$_2$ Fluxes 20:00-8:00 [\mu$mol$ m$^{-2}$ s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Std</td>
<td>Mean</td>
</tr>
<tr>
<td>2020</td>
<td>EC</td>
<td>+1.38</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>-0.03</td>
<td>0.38</td>
</tr>
<tr>
<td>2021</td>
<td>EC</td>
<td>+1.07</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>DCC*</td>
<td>+0.09</td>
<td>0.19</td>
</tr>
</tbody>
</table>

* 2-day data gap, no fill
3.2.4 Above Ground CO$_2$ Profiles and Subsurface Concentrations

At nighttime, there were frequent events of poor turbulent mixing in the atmospheric boundary layer and an accumulation of CO$_2$ was measured above the playa surface (Figures 3.8 and 3.9). The CO$_2$ mixing ratios were inversely proportional to the windspeed, whereby CO$_2$ accumulation above average atmospheric values occurred at the playa’s surface at wind speeds below 1 m s$^{-1}$ (Figure 3.8). The ambient CO$_2$ mixing ratio varied diurnally from 400 ppm in the daytime to an average of 475 ppm (maximum 600 ppm) at nighttime at the playa's surface. CO$_2$ concentrations measured by the profile system between level 1 (0.22 m) and level 4 (1.72 m) differed by over 30 ppm on three of 13 nights (Figures 3.9 and 3.10), with higher values observed near the playa surface.

Based on the measured concentrations by the profile system, CO$_2$ fluxes can be determined by modifying Fick’s 1st Law of diffusion by using the eddy diffusivity parameter for applications in the turbulent surface layer under neutral conditions (Eq. 2.4 and 2.5 in Chapter 2) (Monteith & Unsworth, 2013). During periods of strong atmospheric turbulence, the difference between concentrations measured at levels 1 and 4 ranged between -0.1 and 0.75 ppm, corresponding to a turbulent flux of -4.07 and 4.38 $\mu$mol m$^{-2}$ s$^{-1}$ with an average flux of 1.20 $\mu$mol m$^{-2}$ s$^{-1}$ ($\pm$ 0.98 std) (Figures 3.10 panel b) and 3.11). These flux values bracket the EC data, indicating emissions from the playa to the atmospheric boundary layer, even during nights with turbulent mixing (Figure 3.11). Note that the noise in the profile measurements (random negative and very positive fluxes) was due to the system continuously switching between levels; however, the overall pattern and average fluxes were consistent with the EC system data.

Furthermore, gas samples were collected from the subsurface from various depths for concentration and isotope analysis at a single location in 2020 and 2021. The results show a strong
vertical CO$_2$ gradient with concentrations decreasing from 8000 ppm at 1 m depth to around 420 ppm at 5 cm depth (Figure 3.12). The single measurement taken at 5 cm in the daytime (2021) is bracketed the daytime ambient CO$_2$ concentrations and the elevated nocturnal CO$_2$ concentrations. Additionally, we can estimate the effective gas diffusion coefficient as a function of porosity and water contents to infer the CO$_2$ flux through the unsaturated playa from the following set of equations, assuming diffusion was the main gas transport mechanism.

\[
D^* = D_g \theta_g^{10/3} / \eta^2 \quad \text{Equation 0.5}
\]

\[
J = D^* \left( \frac{dC}{dz} \right) \quad \text{Equation 0.6}
\]

where $D^*$, is the effective diffusivity (m$^2$/s), $D_g$ is the diffusion coefficient (m$^2$/s) of CO$_2$ in air, $\theta_g$ is the gas saturation (-), $\eta$ is the porosity (-), $J$ is the CO$_2$ flux (µmol m$^{-2}$/s), $\frac{dC}{dz}$ is the vertical concentration gradient (µmol m$^{-3}$/m).

Porosities and moisture contents were not measured for the deeper subsurface (>20 cm). Therefore, we evaluate a theoretical diffusive flux over a range of water contents and gas-filled pore space with a constant porosity (Table 3.5 and Figure 3.13). The concentration gradients at depth from both 2020 and 2021 below 18 cm yield an upward flux of CO$_2$ of 1.23 to 2.15 µmol m$^{-2}$/s at higher effective diffusivity (10% VWC) and 0.04 to 0.07 µmol m$^{-2}$/s for lower effective diffusivities (40% VWC) (Figure 3.13). The near-surface gradient estimates from 2020 and 2021 (0-18 cm and 0-27 cm) had smaller concentration differences and yield lower upward fluxes ranging between 0.35 µmol m$^{-2}$/s (10% VWC) and 0.01 µmol m$^{-2}$/s (40% VWC). Overall, the fluxes estimated from the subsurface CO$_2$ gradients were in the range of average emissions measured with the EC method for higher effective diffusivities, but for lower effective diffusivities, fluxes correspond well to CO$_2$ exchange rates quantified with the DCCs. These flux estimates are subject to uncertainties due to the lack of knowledge of the soil properties governing the effective
diffusivity, most importantly moisture content, and minimal CO$_2$ concentrations samples taken spatially at depth and temporally. The results can therefore not be used effectively to validate DCC and EC measurements.

Figure 3.8 Time-series (a.) and correlation plot (b.) of ambient CO$_2$ mixing ratio as a function of wind speed measured at the EC tower for 2020 (2.01 m and 1.65 m heights) and 2021 (1.40 m height).

Figure 3.9 A series of ambient CO$_2$ mixing ratio profiles above the hydromagnesite playas. Panel a) 12-hr averaging interval showing a 13-day period, whereby day (black) from 8:00 to 20:00 PST and night (red) from 20:00 to 8:00 PST. Panel b) 2-hr averaging interval between the 19th at 16:00 to 20th at 8:00, showing the accumulation of CO$_2$ above the playa surface under calm conditions.
Figure 3.10 Differences of ambient CO$_2$ mixing ratio between level 1 (0.22m) and level 4 (1.72m). Panel a) complete time series and b) from 08-08 to 11-08.

Figure 3.11 Estimated CO$_2$ flux from Fick’s Law using the mixing ratio gradient between level 1 (0.22m) and level 4 (1.72m) (black) and EC CO$_2$ flux (red).
Figure 3.12. CO₂ concentrations in the subsurface, and two aboveground profiles, daytime (black) and nighttime (red). Panel a. shows all the data focusing on the subsurface concentration gradient, and panel b. focuses on concentration gradients above ground and in the shallow subsurface. The symbols demonstrate the sampling type, x: from the profile system, square: taken directly with the isotope sampling pipeline, circles: from a static chamber, and triangles: from gas vapour probes. Open symbols represent 2020 samples and filled symbols represents 2021 samples.

Table 3.5. Estimates of tortuosity, effective diffusion coefficient and CO₂ flux (J), according to Fick’s 1st Law for the migration of the deep source CO₂ in the playa towards the atmosphere.

<table>
<thead>
<tr>
<th>Carbonate properties</th>
<th>Units</th>
<th>Shallow (0-18 cm)</th>
<th>Deep (60-80 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Low VWC</td>
<td>High VWC</td>
</tr>
<tr>
<td>Diffusivity coefficient, $D_g$</td>
<td>m² s⁻¹</td>
<td>1.60E-05</td>
<td>1.60E-05</td>
</tr>
<tr>
<td>Porosity, $\eta$</td>
<td></td>
<td>-</td>
<td>0.57</td>
</tr>
<tr>
<td>Subsurface gradient, $\frac{\partial C}{\partial z}$</td>
<td>µmol m⁻³</td>
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<td>-1.01E04</td>
</tr>
<tr>
<td>Volumetric water content, $\theta_w$</td>
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<td>0.4</td>
</tr>
<tr>
<td>Volumetric gas content, $\theta_g$</td>
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<td>0.47</td>
<td>0.17</td>
</tr>
<tr>
<td>Tortuosity, $\tau$</td>
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<td>0.05</td>
</tr>
<tr>
<td>Effective diffusivity, $D^*$</td>
<td>m² s⁻¹</td>
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<td>1.16E-07</td>
</tr>
<tr>
<td>Diffusive Flux, $J$</td>
<td>µmol m⁻² s⁻¹</td>
<td>0.35</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Figure 3.13 The CO$_2$ gradient-calculated flux as a function of volumetric water content from multiple concentration intervals in the subsurface. The filled symbols with red lines represent the 2020 samples, the open symbols with black lines represent the 2021 samples. Smaller fluxes with near-surface gradients, while larger fluxes with the stronger gradients at depth.
3.2.5 Spatial Distribution of CO₂ Fluxes

Survey measurements in a grid upwind of the EC tower, provide insights into the discrete spatial distribution of the CO₂ fluxes (Figure 2.2). Although DCC flux measurements only represent fluxes constrained by the dimensions of the PVC collar (314 cm²), techniques such as the coefficient of spatial variation, descriptive statistics and ordinary linear interpolation were implemented to assess the spatial distribution of the fluxes across the site. The interpolation was conducted based on the SVC and the LTC data for 18 days in 2020 and 8 days in 2021 (Figure 3.14). The survey measurements were performed over the span of 2 hrs in 2020 and 3 hours in 2021. Five survey rounds in 2020 did not have sufficient correlation between the CO₂ flux observations to adequately populate the spatial interpolation, due to a high level of variability occurring below the minimum separation distance (5m) (Rochette et al., 1991).

First, descriptive statistics and coefficient of variation (CV) were evaluated to test spatial variability between a group of flux measurements (Table 3.6). The CV was determined based on the absolute value of the standard deviation divided by the mean; a value closer to zero indicates less spatial variability. The measurements in the grid yield a CV ranging from 42% to 814% in 2020 (mean 187%) and from 66% to 183% in 2021 (mean 110%).

First, the grids in 2020 and 2021 suggest some variability in the distribution of the carbonate playa fluxes (Figure 3.14). There were specific locations with measured fluxes that were higher by approximately 1 μmol m⁻² s⁻¹ than the surrounding area (5 m separation), for example, LTC 2 and SVC collar 15 in 2020 (2020-08-11, 2020-08-14, 2020-08-23) and SVC collars 20 and 38 in 2021 (2021-08-09, 2021-08-10, 2021-08-12). Note, 2 out of 22 collars in 2020 and 11 out of 51 collars in the grid in 2021 have at least one small grass patch growing within the area covered by the collars. Out of the 13 locations with small grasses, only three measurements from collars 24, 25
and 29 (2021-08-09, 2021-08-10) produced locally high fluxes, but not to the same magnitude as collar 20 located on barren material on the same days. The overall flux pattern in the grid shows that the higher fluxes occurred at collars devoid of vegetation. Additionally, the surveys in 2020 show a distinction between CO$_2$ uptake and emission patterns in the mornings and afternoons. In the mornings, CO$_2$ uptake or negligible CO$_2$ exchange is dominant (blue), while CO$_2$ emissions occur more commonly in the afternoons (red) (Figure 3.14). The surveys in 2021 were conducted in the late morning until early afternoon and demonstrated predominantly emissions of CO$_2$.

In both years, several survey collars were strategically located outside the grid in the transition zone (n=4) and the forest floor (n=3). These collar locations produced daytime CO$_2$ fluxes (opaque chamber) between 1.11 and 3.60 μmol m$^{-2}$ s$^{-1}$ and 1.85 to 5.37 μmol m$^{-2}$ s$^{-1}$, respectively. Emissions from the transition zone and the forest floor were generally larger than the values measured across the playa.

The EC method integrates the turbulent fluxes over a large area, which smooths spatial flux variations in the measurement area. A flux footprint model provides information on the source area weighted contributions to the measured flux in magnitude and location (Figure 3.15). The EC sensor heights were lowered on the tower three times over the 6-week time series to minimize the size of the footprint, from 2.01 m (DOY 220-235) to 1.65 m (DOY 235-246) in 2020 and then 1.40 m in 2021 (Figure 3.15.; bottom panels). Lowering the sensors to 1.40 m and moving the tower 20 m north in 2021 was done to further compare the two flux methods (DCC and EC), by avoiding the transition zone in the EC footprint. The 2021 total average flux was smaller than the 2020 average by 0.31 μmol m$^{-2}$ s$^{-1}$ with similar temporal variability. Furthermore, according to the FFP flux footprint analysis in the Tovi® software (LI-COR Biosciences, Inc), the 30-min footprint model suggests an average 6% (maximum 16% 2020) and 6% (maximum 19% 2021) footprint
fraction intersecting with the forest and transition zone for the flux estimates that passed filtering (Figure 3.16). There was no general trend in the measured EC flux from both years as a function of footprint fraction overlap with the forest and transition zone (Figure 3.16). The footprint fraction on the playa was 76-95% for both years.

Table 3.6 Descriptive statistics of the CO₂ fluxes measured for each survey grid period.

<table>
<thead>
<tr>
<th>Date</th>
<th>mean</th>
<th>std</th>
<th>n</th>
<th>min</th>
<th>max</th>
<th>CV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2020-08-08 PM</td>
<td>0.40</td>
<td>0.19</td>
<td>22</td>
<td>0.07</td>
<td>0.82</td>
<td>47</td>
</tr>
<tr>
<td>2020-08-10 AM</td>
<td>-0.01</td>
<td>0.10</td>
<td>22</td>
<td>-0.27</td>
<td>0.17</td>
<td>814</td>
</tr>
<tr>
<td>2020-08-10 PM</td>
<td>0.10</td>
<td>0.13</td>
<td>22</td>
<td>-0.31</td>
<td>0.30</td>
<td>136</td>
</tr>
<tr>
<td>2020-08-11 AM</td>
<td>0.57</td>
<td>0.40</td>
<td>22</td>
<td>0.01</td>
<td>1.15</td>
<td>71</td>
</tr>
<tr>
<td>2020-08-12 AM</td>
<td>0.33</td>
<td>0.30</td>
<td>21</td>
<td>-0.02</td>
<td>1.25</td>
<td>92</td>
</tr>
<tr>
<td>2020-08-12 PM</td>
<td>0.53</td>
<td>0.25</td>
<td>23</td>
<td>0.23</td>
<td>1.41</td>
<td>48</td>
</tr>
<tr>
<td>2020-08-13 AM</td>
<td>0.18</td>
<td>0.18</td>
<td>22</td>
<td>-0.01</td>
<td>0.65</td>
<td>100</td>
</tr>
<tr>
<td>2020-08-13 PM</td>
<td>0.70</td>
<td>0.30</td>
<td>20</td>
<td>0.19</td>
<td>1.22</td>
<td>42</td>
</tr>
<tr>
<td>2020-08-14 AM</td>
<td>0.60</td>
<td>0.45</td>
<td>22</td>
<td>-0.01</td>
<td>1.50</td>
<td>75</td>
</tr>
<tr>
<td>2020-08-16 AM</td>
<td>-0.20</td>
<td>0.1</td>
<td>22</td>
<td>-0.43</td>
<td>-0.02</td>
<td>51</td>
</tr>
<tr>
<td>2020-08-19 AM</td>
<td>0.10</td>
<td>0.14</td>
<td>24</td>
<td>-0.09</td>
<td>0.49</td>
<td>136</td>
</tr>
<tr>
<td>2020-08-21 AM</td>
<td>0.02</td>
<td>0.10</td>
<td>21</td>
<td>-0.14</td>
<td>0.25</td>
<td>607</td>
</tr>
<tr>
<td>2020-08-24 AM</td>
<td>-0.05</td>
<td>0.14</td>
<td>25</td>
<td>-0.40</td>
<td>0.21</td>
<td>296</td>
</tr>
<tr>
<td>2020-08-24 PM</td>
<td>0.17</td>
<td>0.22</td>
<td>23</td>
<td>-0.10</td>
<td>0.63</td>
<td>131</td>
</tr>
<tr>
<td>2020-08-26 AM</td>
<td>0.11</td>
<td>0.16</td>
<td>21</td>
<td>-0.03</td>
<td>0.68</td>
<td>147</td>
</tr>
<tr>
<td>2020-08-27 AM</td>
<td>0.23</td>
<td>0.29</td>
<td>24</td>
<td>-0.14</td>
<td>1.16</td>
<td>126</td>
</tr>
<tr>
<td>2020-08-31 AM</td>
<td>-0.04</td>
<td>0.12</td>
<td>20</td>
<td>-0.41</td>
<td>0.08</td>
<td>290</td>
</tr>
<tr>
<td>2020-08-31 PM</td>
<td>0.09</td>
<td>0.13</td>
<td>21</td>
<td>-0.09</td>
<td>0.59</td>
<td>151</td>
</tr>
<tr>
<td>2021-08-09 PM</td>
<td>0.29</td>
<td>0.23</td>
<td>51</td>
<td>-0.13</td>
<td>1.05</td>
<td>81</td>
</tr>
<tr>
<td>2021-08-10 AM</td>
<td>0.31</td>
<td>0.36</td>
<td>51</td>
<td>-0.04</td>
<td>2.61</td>
<td>112</td>
</tr>
<tr>
<td>2021-08-11 PM</td>
<td>0.30</td>
<td>0.25</td>
<td>51</td>
<td>-0.02</td>
<td>1.28</td>
<td>81</td>
</tr>
<tr>
<td>2021-08-12 AM</td>
<td>0.33</td>
<td>0.29</td>
<td>51</td>
<td>0.02</td>
<td>1.97</td>
<td>89</td>
</tr>
<tr>
<td>2021-08-14 AM</td>
<td>0.29</td>
<td>0.19</td>
<td>51</td>
<td>-0.04</td>
<td>1.03</td>
<td>66</td>
</tr>
<tr>
<td>2021-08-17 AM</td>
<td>0.08</td>
<td>0.14</td>
<td>51</td>
<td>-0.28</td>
<td>0.60</td>
<td>183</td>
</tr>
<tr>
<td>2021-08-18 AM</td>
<td>0.05</td>
<td>0.09</td>
<td>51</td>
<td>-0.07</td>
<td>0.39</td>
<td>182</td>
</tr>
<tr>
<td>2021-08-19 AM</td>
<td>0.26</td>
<td>0.23</td>
<td>51</td>
<td>-0.19</td>
<td>1.09</td>
<td>87</td>
</tr>
</tbody>
</table>
Figure 3.14. The spatial distribution of CO$_2$ fluxes derived from survey chamber measurements. Data are shown from eighteen grid surveys in 2020 and eight in 2021. The black dots indicate the location of DCC (SVC & LTC) measurements, and the black triangles indicate the location of the EC tower.
Figure 3.15. 30-min footprints of the source areas in 1D (top panel) and 2D (bottom panels) for EC results that passed the post-processing filters. The top panel shows the 1D crosswind integrated (CWI) footprint as a function of the upwind distance from the EC tower. The coloured lines are the three sensor heights, and the bands are the long-term chamber footprints, black and grey (2020) and green (2021). The bottom panels show an ensemble of 80% contribution contours (black) for the 2D footprint at the three sensor heights and the red oval depicts the long-term chamber footprint.

Figure 3.16. The EC CO₂ flux as a function of the footprint fraction over with the forest and the transition zone, a. 2020 and b. 2021. Zero footprint fraction means that there was no contribution from the forest or transition zone.
3.2.6 Isotopic Composition of CO₂

Isotopes, both stable and radioactive, are commonly measured in earth sciences for source attribution. Stable isotope fractionation processes provide a unique fingerprint to materials. Fractionation is the process of partitioning between the lighter and heavier isotopes during an equilibrium reaction or phase transition in the environment. Accordingly, we use enrichment fractionation factors to relate the stable isotopic composition ($\delta^{13}$C) in the gas phase to the $\delta^{13}$C from hydromagnesite carbonate minerals, the groundwater DIC and pore water DIC, following Power et al. (2014, 2019). The carbon reservoirs in the playa environment are summarized in Table 3.8.

At depth in the playa, below 40cm, the pore gas radiocarbon signature (pMC) from both the vapour gas probes (2021) and static chambers (2020) ranges from 9.0% to 17.3% (average 12.2%) and a $\delta^{13}$C$_{CO2}$ of -4.0‰ to -5.8‰ (VPDB) (average -5 ‰) (Figure 3.17). These isotope signatures were similar to those measured from equilibrium fractionation conversions of the hydromagnesite minerals in the unsaturated zone and the wetland DIC reservoirs, approximately -4 % $\delta^{13}$C$_{CO2}$ and 12% pMC. A static chamber was used in 2021 to assess the composition of pore gas in surficial playa sediments (18-cm depth). The sample was extracted 24 hours after lid closure. The modern carbon and stable carbon signatures were corrected using a mass balance formula for the atmospheric signature in the headspace before closure, see Wozney et al. (2021) for details. The gas sample from the static chamber at the surface had a signature of 76.0% pMC and -9.6‰ $\delta^{13}$C$_{CO2}$ (Figure 3.17, grey circle), falling directly on the mixing line between the playa and the atmospheric carbon reservoirs. The desiccation cracks in the playa add some complexity to the pore gas sampling near the surface as they can extend to a depth of 40 cm.
The pore gas at depth in the playa was similar in isotopic composition to the isotopic signature of the hydromagnesite minerals, both represented as pMC and DIC equivalent $\delta^{13}C$, suggesting the minerals and gas at depth were at equilibrium (Figure 3.18). However, the $\delta^{13}C$ signature in the pore gas towards the surface from 2020 and 2021 is more depleted relative to the groundwater isotopic composition, while the $\delta^{13}C$ signature in the hydromagnesite minerals were more enriched towards the surface. The pore gas signature is more consistent with atmospheric mixing, while the mineral signature is consistent with further evapoconcentration enriching the pore fluid with heavier isotopes. Similarly, the mineral phase has an increasing modern signature closer to the surface from 10% to 50% pMC (Figure 3.18 a.) (Power et al., 2019). The pore gas reflects this trend at depth until the measured pore gas radiocarbon signature increases to 76.0% pMC in a chamber at 18-cm depth, consistent again with atmospheric mixing in the playas.

The isotope samples collected from the forest floor were taken at 80-cm depth, 40-cm depth and in a static chamber near the surface (18-cm depth). All samples had a similar pMC value of 97.9%, 100.0% and 101.6% and $\delta^{13}C_{CO_2}$ values of -21.8, -23.7, and -23.1 ‰, from the deepest to shallowest depths, respectively (Figure 3.17). The pore gas in the transition zone aligns between the signatures seen in the playa and forest soils, with modern carbon signatures near 85% and a depleted $\delta^{13}C_{CO_2}$ value of -16 ‰. The CO$_2$ accumulated in the static chamber (red dot, 18-cm depth) after 24 hrs has a pMC value of 100.6% and has depleted $\delta^{13}C_{CO_2}$ of -19.1‰, falling directly on the binary mixing line between the atmosphere and forest pore gas measurements.

Air samples collected directly above the playa were depleted in $\delta^{13}C_{CO_2}$, approximately -10 ‰ in 2020 and -12‰ in 2021 (presented as $^{13}C$ DIC equivalents in Figure 3.18 b.), compared to the northern latitude atmospheric summer $\delta^{13}C_{CO_2}$ average of -9‰ measured at station PTB 71°N (Keeling et al., 2021). The measured air sample taken in the afternoon (12/08/2021) at 30 cm above
the playa (Figure 3.17 a) had 100.1% pMC signature at a CO\textsubscript{2} concentration of 406 ppm. An additional sample taken at noon (19/08/2021) at the 5-cm depth directly with the tubing connected to the peristaltic pump, CO\textsubscript{2} sensor and sampling needle yielded a signature of -12.68‰ δ\textsuperscript{13}C and 98.3% pMC at 420 ppm; this sample is shallow and prone to atmospheric contamination. Furthermore, the δ\textsuperscript{13}C\textsubscript{CO2} in air samples collected directly above the playa at nighttime (between 2:00 and 5:00 on 16/08/2021 and 5:00 and 8:00 20/08/2021) with calm conditions and CO\textsubscript{2} accumulation above the playa surface. The two samples were slightly depleted around -15.0‰ and -14.2‰ and with a slight enrichment of pMC 101.1% and 100.5% at concentrations of 520 ppm and 460 ppm compared to daytime values (Figure 3.17).

Assuming linear mixing between reservoirs, a value of ~520 ppm between the playa and the atmosphere would yield an isotopic signature of 11.88‰ δ\textsuperscript{13}C\textsubscript{CO2} and 98.6% pMC, while the mixing between the atmosphere and forest pore gas would yield an isotopic signature of 12.22‰ δ\textsuperscript{13}C\textsubscript{CO2} and 100.14% pMC. Nocturnal mixing from the vadose zone playa CO\textsubscript{2} source is not possible due to the depletion in \textsuperscript{13}C and enrichment in pMC at nighttime. According to an isotope mass balance with two-component mixing between air and pore gas following Clark (2015 p. 156), forest soil pore gas contributes 2.5% and 1.5% from δ\textsuperscript{13}CO\textsubscript{2} and 2.5% and 1.2% from pMC for the two nighttime measurements on the playa, respectively. Overall, the accumulation of CO\textsubscript{2} in air samples above the playa has an isotopic signature that was more similar to forest soil pore gas than the playa pore gas.

Further, a Keeling plot is a valuable tool for CO\textsubscript{2} source attribution of emitted CO\textsubscript{2} by measuring changes in concentrations and δ\textsuperscript{13}C within a closed headspace. Samples were collected in the closed static chambers (playa, transition, forest) to identify the source of CO\textsubscript{2} emitted during the daytime and in the atmosphere at nighttime with elevated CO\textsubscript{2} concentrations. Resolving for
CO₂ sources is most effective when the potential sources have well-defined isotopic compositions (Pataki et al., 2003); in this case, biological respiration (~ -25‰), atmosphere (~ -10 ‰) and playa pore gas (~ -5 ‰) (Table 3.7, Figure 3.19). The static chamber lid was closed, and the headspace was sampled at 30-min intervals for 3 hours, with one additional sample after 24 hours. The δ¹³C samples were plotted against the inverse of CO₂ concentration, and the intercept was solved with the Model II (standard major axis) linear regression (Pataki et al., 2003; Soper et al., 2017). The extrapolated y-intercept of the plot provides information on the source signature, assuming the gas accumulating in the headspace theoretically displaces the background air (atmospheric). The transition zone (n=2) and forest (n=2) chamber regressions and intercepts were significant (p<0.1), showing a δ¹³C_CO₂ signature (intercept) of -20.7‰ and -20.9‰, and -28.9 ‰ and -28.6 ‰, respectively (Figure 3.19). There was no significant regression for the playa chambers (n=4) and the nighttime samples (n=1). However, the playa intercepts suggest no substantial deviation from atmospheric signature with change in concentration in the headspace, indicating negligible emission from the deep playa pore gas source or any biological respiration from organic matter decomposition.

Table 3.7. Carbon reservoirs in the playa environment and their ¹³C and percent modern carbon (pMC) composition. The conversions of ¹³C in equivalent ¹³C_DIC are based on equilibrium fractionation factors.

<table>
<thead>
<tr>
<th>Reservoirs</th>
<th>Depth</th>
<th>[CO₂] ppm</th>
<th>δ¹³C_CO₂ (‰-VPDB)</th>
<th>δ¹³C_DIC (‰-VPDB)</th>
<th>δ¹³C_Hmg-Mg (‰-VPDB)</th>
<th>pMC (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td></td>
<td>-5.7</td>
<td></td>
<td></td>
<td>11.3</td>
<td>Power et al. (2019, 2014)</td>
<td></td>
</tr>
<tr>
<td>Pore water (Southern playa)</td>
<td></td>
<td>1.0</td>
<td></td>
<td></td>
<td>9.9</td>
<td>Power et al. (2019, 2014)</td>
<td></td>
</tr>
<tr>
<td>Pond water (Southern playa)</td>
<td></td>
<td>5.7</td>
<td></td>
<td></td>
<td>11.7</td>
<td>Power et al. (2019, 2014)</td>
<td></td>
</tr>
<tr>
<td>Carbonate Bedrock</td>
<td></td>
<td></td>
<td>-7 to -1</td>
<td></td>
<td>0</td>
<td>Hansen et al. (2005)</td>
<td></td>
</tr>
<tr>
<td>Hydromagnesite</td>
<td>10 cm</td>
<td>4.7</td>
<td>+8.8</td>
<td></td>
<td>14.8</td>
<td>Power et al. (2019, 2014)</td>
<td></td>
</tr>
<tr>
<td>Hydromagnesite (Profile 6)</td>
<td>65 cm</td>
<td>2.7</td>
<td>+6.8</td>
<td></td>
<td>39.6</td>
<td>Power et al. (2019, 2014)</td>
<td></td>
</tr>
<tr>
<td>Magnesite</td>
<td>10 cm</td>
<td>-2.0</td>
<td>+6.0</td>
<td></td>
<td>11.2</td>
<td>Power et al. (2019, 2014)</td>
<td></td>
</tr>
<tr>
<td>Magnesite (Profile 6)</td>
<td>65 cm</td>
<td>0.8</td>
<td>+9.0</td>
<td></td>
<td>11.2</td>
<td>Power et al. (2019, 2014)</td>
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</tr>
<tr>
<td>Local Atmosphere</td>
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<td>-12.0</td>
<td>-3.6</td>
<td></td>
<td>100.1</td>
<td>[2] Zhang et al. (2021)</td>
<td></td>
</tr>
<tr>
<td>Forest soil gas</td>
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<td>-23.1</td>
<td>-13.5</td>
<td></td>
<td>101.6</td>
<td>Measured in this work</td>
<td></td>
</tr>
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</table>
Figure 3.17 Plot of radiocarbon (pMC %) and carbon-13 isotopes ($\delta^{13}$C-CO$_2$ %o) (a.) and correlation plots of concentration and pMC (%) (b.) and $\delta^{13}$C-CO$_2$ (%) (c.). The symbol shape indicates the sampling technique: circles are samples from static chambers, triangles are samples from gas vapour probes, and squares are air samples. The open circles represent the only samples taken in 2020. Grey lines show volumetric mixing between the reservoirs (asterisks) with values and references in Table 3.6.
Figure 3.18. Depth profile in the playa for (a.) percent modern carbon (pMC) (b.) and equivalent δ$^{13}$C$_{DIC}$ for samples from gas samples and mineral phase (hydromagnesite) presented based on DIC equilibrium fractionation of $\varepsilon_b$(g): -9.6 ‰ and $\varepsilon_{dyt}$(b): 4.1 ‰, at 10°C. The open markers are samples from 2020 and filled markers represent gas samples from 2021. The gas samples are further distinguished by shapes: triangles are samples from soil gas vapour probes, circles are samples from static chambers, squares are air samples. The asterisks are mineral phase data taken from Power et al. (2019). The vertical lines are δ$^{13}$C$_{DIC}$ values for the porewater at the water table and the pond water also from Power et al. (2019).

Figure 3.19 Keeling plot for δ$^{13}$C$_{CO_2}$ of the static chamber and nighttime atmospheric measurements. The intercept and $R^2$ values are solved from Model II regression. The solid regressions shown are significant, p<0.1, the dotted regressions are not significant. The chambers on the playa (SC1, SC4, SC5, grey), the transition zone (SC2, red), the forest (SC3, blue), and the atmosphere at night (Night, black).
3.3 Discussion

The hydromagnesite-magnesite playas near Atlin are unique features due to the local geology, playa genesis with a large carbon reservoir at the Earth’s surface. CO₂ production can occur at this site by CO₂ degassing from the HCO₃⁻-rich groundwater and carbonate mineral precipitation (Mavromatis et al., 2021; Power et al., 2019, 2014). CO₂ fluxes and governing processes are not extensively documented for sites similar to the hydromagnesite-magnesite playas. Analysis of DCC measurements indicates a very small net uptake (2020) and a very small net release (2021) of CO₂, while the EC measurements indicate a more substantial net release of CO₂ from the playas (2020 and 2021). Note, that these results represent trends for the month of August exclusively.

The DCC LTC results show a near-zero net flux, subject to diurnal fluctuations, with average daytime emissions of 0.15 μmol m⁻² s⁻¹ and nighttime uptake of 0.23 μmol m⁻² s⁻¹ in 2020. The 2021 DCC results demonstrated a weaker diurnal pattern with average daytime emissions of 0.15 μmol m⁻² s⁻¹ and nighttime emissions of 0.03 μmol m⁻² s⁻¹. This difference could be attributed to variations in volumetric water content in the near-surface playa matrix, which may be explained in part by a large rain event during site installation in 2021. The measured CO₂ fluxes from the DCC method are considerably smaller than biological respiration fluxes typically measured in agricultural and forest soils during the summer months, ~5 to 10 μmol m⁻² s⁻¹ (Griffis et al., 2004; Rochette et al., 1991). However, CO₂ fluxes of this magnitude and diurnal patterns have been measured previously in alkaline desert soils (Ball & Virginia, 2015; Ball et al., 2009; Hamerlynck et al., 2013; Liu et al., 2015; Ma et al., 2013). For example, Ma et al. (2013) reported a similar diurnal pattern with CO₂ fluxes ranging from -0.4 to 0.4 μmol m⁻² s⁻¹, using chambers in sterilized alkaline soils at the Fukang Station of Desert Ecology in China.
In addition to the diurnal CO₂ exchange as seen from the DCC, we found a modern signature (76% pMC) and depleted δ¹³C_CO₂ signature (-9.6‰) in the air within the surface static chamber (18-cm depth), suggesting a source of modern carbon and possible near-surface equilibrium in the pore gas phase with the atmosphere. The δ¹³C signature and pMC trend from 40 cm towards the playa surface suggests a mixing trend with the atmospheric CO₂. As discussed in Power et al. (2019), there is modern carbon in the upper playa carbonate minerals, ~50% pMC, suggesting an exchange of DIC from modern atmospheric CO₂ or rainfall. However, the δ¹³C enrichment in the minerals compared to the δ¹³C pore gas towards the surface complicates the gas-to-mineral reaction interpretations. Constraining the surface processes contributing to the modern incursion of carbon into the minerals is complex. There are uncertainties relating to the interpretations due to the low resolution of sampling in the upper 40 cm of the playa, possible kinetic fractionation effects during CO₂ dissolution (Clark et al., 1992; Wilson et al., 2010), and radioactive decay (¹⁴C half-life of 5720 years). The surface minerals with modern signatures must have formed in part from atmospheric carbon from mineral dissolution and re-precipitation or direct precipitation.

The DCC survey (SVC) grid over the playa was used to assess the discrete spatial variability of the CO₂ flux. Overall, the SVC CO₂ fluxes across the grid were small, with morning surveys demonstrating negative and positive fluxes (-0.2 μmol m⁻² s⁻¹ to 0.6 μmol m⁻² s⁻¹) and afternoon surveys demonstrating positive CO₂ fluxes (0.1 μmol m⁻² s⁻¹ to 0.7 μmol m⁻² s⁻¹). The DCC grid results reveal some locations exhibiting higher fluxes, around 1 μmol m⁻² s⁻¹, than neighbouring points (< 5 m away) and these locations do not show signs of vegetation or organic soil (i.e., SVC collar 15 in 2020 and 20 in 2021). The coefficient of spatial variation (CV) across the grid is, on average, 187% (2020) and 110% (2021). A CV above 100% implies that the standard deviation is larger than the mean, indicating high spatial variability between the measurement locations.
(Rochette et al., 1991). Therefore, the CV values are considered extremely high compared to other sites, for example, 18% to 30% in forest soils (Griffis et al., 2004; Loescher et al., 2006; Norman et al., 1997) or less than 30% on a waste rock pile (Kabwe et al., 2005, 2006). However, the larger CVs occur on days when the average flux was near zero with positive and negative flux observations in the grid. For 5 out of 26 survey rounds between 2020 and 2021, the CVs were around 50% coinciding with flux values that were either all positive or negative in the grid.

Furthermore, subsurface CO₂ concentrations collected at a single location in the middle of the playa in 2020 and 2021 suggest a strong upward CO₂ gradient at depth (i.e., Δ7600 ppm/m 40-100cm). The isotopic composition of the gas at depth (~ 10% pMC and 5 % δ¹³C₂CO₂) was comparable to the pore water and minerals at the site. Therefore, the CO₂ accumulating at depth originated from the groundwater and evapoconcentration, not biological reactions. However, The subsurface gradient decreases towards the surface (Δ2200ppm/m 0-18 cm and 0-27 cm). Accordingly, the estimates of a theoretical diffusive flux through the playa matrix demonstrates a stark drop in the CO₂ flux near-surface above 40 cm, suggesting a decoupling between deep and near-surface playa vadose zone. Similar subsurface CO₂ concentration gradients have been measured in forest soils (e.g. Jassal et al., 2004) and calcite-rich (CaCO₃ - 40%) desert soils (e.g. Hamerlynck et al., 2013). Notably, Jassal et al. (2004) discuss the importance of CO₂ production from microbial respiration in the top 20 cm of forest soils, leading to steep concentration gradients (~Δ4000 ppm 0-20 cm), predominantly responsible for CO₂ effluxes. Hamerlynck et al. (2013) report that most surface effluxes and influxes from carbonate-rich desert soils originate from the top 2 cm. They observed nighttime uptake of CO₂ into the ground regardless of the upward concentration gradient at greater depth (~Δ600 ppm in 20cm), which is comparable to the trends between the above-ground and below-ground playa sediment. One air sample taken at 5cm depth,
shows a concentration of 420 ppm, which is between the daytime atmospheric concentration and the nighttime elevated \( \text{CO}_2 \) concentration in air serving as supporting evidence of gradient reversal for nocturnal uptake measured by the DCC method. However, the lack of resolution, spatially and temporally, of the subsurface concentration profile contributes uncertainty towards the comparison to DCC and EC measurements and the broader carbon cycle within the playa.

While the DCC method measures a \( \text{CO}_2 \) flux directly above the soil-atmosphere interface on a small surface area constrained by the PVC collar (20 cm ID), the EC measures a \( \text{CO}_2 \) flux from a much larger area across the surface boundary layer (100 m’s). The EC method measures net emissions day and night, averaging 1.38 (2020) and 1.07 (2021) \( \mu \text{mol m}^{-2} \text{s}^{-1} \) with no strong diurnal trend. The EC flux was not strongly correlated with any climate variable other than wind speed, implying that other factors, like temperature and moisture, are not limiting \( \text{CO}_2 \) emissions in this system, which are common factors in biological systems (Appendix C) (Goulden et al., 1996). It is possible that the length of the measurement period is too short to determine functional relationships to climate parameters (e.g., temperature and moisture). Additionally, there were 44% (2020) and 20% (2021) fewer nighttime EC data points than in the daytime due to calm atmospheric conditions, which biases average comparisons, assessment of diurnal variations and governing processes controlling the EC flux. It is important to note that the above-ground \( \text{CO}_2 \) profile measurements (2021) agree with the direction and magnitude of the EC flux under turbulent atmospheric conditions. Due to the difference between the EC and DCC in terms of approaches and flux results, the source of \( \text{CO}_2 \) emissions measured by the EC method could not be confirmed with confidence. We hypothesize that the origins of the released carbon as measured by the EC flux could be explained by 1) direct emissions from the playa unsaturated zone through preferential
pathways not captured by the DCC system and 2) emissions driven by biological respiration from localized grass patches, transition grasses and the forest edge.

The first hypothesis supposes the emission of CO\textsubscript{2} from the EC method is supplied by CO\textsubscript{2} degassing from the HCO\textsubscript{3}-rich groundwater and mineral precipitation. We found a strong upward gradient measured in the deep playa subsurface (i.e., Δ7600 ppm/m), but a low net efflux through the carbonate matrix estimated by the DCC method, supported by theoretical gradient diffusion efflux calculations under the assumption of high moisture contents. However, desiccation cracks were pervasive at this site to a depth ranging from a few mm to around 40 cm, which could be preferential pathways or weaknesses in the carbonate matrix facilitating gas migration and CO\textsubscript{2} release. In addition to diffusive transport, the release of CO\textsubscript{2}-rich air from a subsurface reservoir can be affected by advection (i.e. high wind speeds and pressure pumping) (López-Ballesteros et al., 2017; Redeker et al, 2015; Rey, 2015; Sánchez-Cañete et al., 2013). Fluxes measured with the EC system were positively correlated with wind and friction velocity (Appendix C), meaning more substantial fluxes were measured at higher wind speeds, possibly due to ventilation. Subterranean advection from ventilation cannot be confirmed with the current dataset but has been suggested as an important process for EC CO\textsubscript{2} fluxes at an arid grassland site with high-DIC content in the groundwater (López-Ballesteros et al., 2017). The release of CO\textsubscript{2} from ventilation is disabled during periods of low turbulence and high water content (López-Ballesteros et al., 2017; Roland et al., 2013). Consequently, emissions from the deep source would be disabled and not contribute to the elevated ambient CO\textsubscript{2} concentrations and isotopic signature of CO\textsubscript{2} in air on calm nights. Note that advection-dominated transport would result in smaller CO\textsubscript{2} gradients in the subsurface; however, using concentration gradient in the subsurface at a single location in space and time as an indicator of advection has high uncertainties (Laemmel et al., 2017). In this case, it
would be necessary to have permanent soil CO$_2$ and pressure sensors in the vadose zone to assess the CO$_2$ transport. CO$_2$ release from subterranean ventilation can escape DCC detection since the collars generally avoid the desiccation cracks.

Alternatively, the second hypothesis is that CO$_2$ originated from external sources important to the playa, e.g., biological activity associated with the transition grasses and adjacent forest (i.e., respiration and photosynthesis). At our site, the CO$_2$ source strength is much smaller across the carbonate matrix (chambers – daytime 0.3 μmol m$^{-2}$ s$^{-1}$ or ~1 μmol m$^{-2}$ s$^{-1}$ from the specific SVCs exhibiting higher fluxes) compared to soil respiration in the forest (~3.5 to 5 μmol m$^{-2}$ s$^{-1}$) and gross ecosystem photosynthesis (not known for this environment but likely between ~ 0 and 10 μmol m$^{-2}$ s$^{-1}$). The footprint model visually demonstrates the relative contributions of the source areas to the EC flux estimate. According to the footprint analysis using FFP in python and Tovi, the dominant contribution (76-95%) to the EC flux was from the carbonate playa (i.e., the area of interest). However, there is a possibility that outside of the DCC SVC footprint, but within the EC footprint (i.e., 90% source area), biological respiration occurring in localized grass patches, the transition zone and close to the forest edge could be registered and overestimate the EC CO$_2$ flux by 4 to 6 %. For example, assuming CO$_2$ effluxes from soil respiration in the 4 to 6 % footprint fraction is maximum 5.37 μmol m$^{-2}$ s$^{-1}$, this could contribute about 0.21 to 0.32 μmol m$^{-2}$ s$^{-1}$ to the measured EC CO$_2$ flux.

Furthermore, the EC method assumes horizontal homogeneity and non-advective conditions, whereby the measured CO$_2$ flux is derived strictly from 1D vertical turbulent transport. However, in complex terrain (e.g. nearby a forest edge), 2D and 3D effects can gain importance, such as advection or entrainment, which can produce biases in the measured fluxes (Massman & Lee, 2002). At night we found an accumulation of CO$_2$ at the playa surface during periods of weak
atmospheric turbulence. During these periods, the EC method does not produce a valid estimate of the CO₂ flux and the data is discarded. The profile system measured a decrease in concentration with elevation (1.50 m) above the playa at nighttime on the order of 30 ppm, suggesting a pooling of CO₂-dense air near the ground. To achieve a concentration of 520 ppm in the nocturnal boundary layer, the source of CO₂ mixed with the ambient atmosphere (100% PMC and -12‰) resulted in a signature that was depleted in stable carbon (-14.2 ‰ and -15.0‰) and enriched radiocarbon (100.5 % and 101.1 ‰). The two nocturnal samples are more similar to the forest pore gas than the playa pore gas. There is a strong indication that CO₂ in the forest pore gas is emitted from the soil at night mixing with a stagnant atmosphere in the forest and subsequently transported onto the playa. Nocturnal drainage flow is a known phenomenon in biometeorology that can occur on slopes of less than 3° (Foken, 2008) and is an issue for missing carbon in sloped forest carbon budgets (Pypker et al., 2007; Vickers et al., 2012). The pooling of CO₂ can occur on even terrain when the background topography is larger than the fetch and footprint (Massman & Lee, 2002). Additionally, in the daytime under turbulent conditions an overestimation of EC fluxes could be attributed to non-local advection, as found in recent studies (Esters et al., 2021; Kenny et al., 2017). These studies are conducted in freshwater lake environments surrounded by forests, whereby the source strengths are quite different, like at the playa study site. Esters et al. (2021) conducted a study above a frozen lake surface near a forest edge, assuming the frozen lake has zero CO₂ flux. The researchers found that non-local processes (vertical entrainment or horizontal advection) contributed to erroneous CO₂ fluxes up to +0.5 μmol m⁻² s⁻¹ with increasing wind speeds (up to 9 m s⁻¹) at 10 m above the ground. This phenomenon relates positively to wind speed, which was also shown in the EC data. However, confirming the occurrence of non-local advection, during
nighttime and daytime, from the forest biological respiration requires a more targeted experimental design and analysis, which is outside the scope of this thesis.

Overall, the fluxes from EC measurements and vertical above-ground CO$_2$ profiles were distinctly different from DCC measurements at this site. These methods measured different CO$_2$ flux directions at nighttime under weak turbulent conditions and different magnitudes of CO$_2$ flux in the daytime (by 5 to 7 times). EC and DCC methods are paired together for cross-validation over homogeneous terrain; however, these two methods appear to capture different scales of processes occurring in the carbon cycle across the playa-atmosphere environment (Riederer et al., 2014). The DCC method is representative at the local scale, capturing CO$_2$ exchange directly with the playa matrix, which is very small and highly dependent on the diurnal changes of environmental conditions. On the other hand, the EC method captures fluxes on a much larger scale, likely integrating the effects of one or multiple processes ranging from deep CO$_2$ release from preferential pathways to biological carbon sources, which could not be fully resolved using isotope analysis. This finding reinforces the importance of using complementary methods to understand site processes and uncertainties, especially while assessing new sites that have not been widely studied in the literature.
Chapter 4: Short-term processes: quantitative analysis of diurnal flux variations from DCC measurements

4.1 Introduction

This chapter focuses on the short-term diurnal processes governing CO₂ fluxes across the playa-atmosphere interface in Atlin, British Columbia. The previous chapter showed that the average LTC fluxes are near zero with an average daily flux of +0.15 μmol m⁻² s⁻¹ and an average nightly flux of -0.23 μmol m⁻² s⁻¹. Surface CO₂ fluxes are small, despite a strong subsurface upward CO₂ concentration gradient across the carbonate matrix. The controls on soil CO₂ fluxes from biological respiration have been studied for decades (reviewed in Oertel et al., 2016). Commonly, chemical processes (e.g. solubility, rock weathering and adsorption) contributing to the CO₂ flux are negligible in soils from most land cover types (Rey, 2015). However, many studies from sparsely vegetated alkaline deserts demonstrate an inorganically sourced CO₂ flux. This flux is triggered predominantly by temperature changes affecting gas phase exchange, as dictated by Henry’s Law, with the magnitude of the flux controlled by the pore water alkalinity and salinity (e.g., Cueva et al., 2019; Ma et al., 2013; Sagi et al., 2021; Shanhun et al., 2012; Yates et al., 2013). The work presented in this chapter aims to elucidate diurnal controls influencing CO₂ fluxes occurring at the hydromagnesite playa-atmosphere interface measured by the DCC method via a reactive transport modelling analysis.

4.1.1 Chapter Objective

- Characterize short-term temporal variations of CO₂ exchange across the playa-carbonate soil surface using statistical analyses and reactive transport modeling constrained by field observations.
4.2 Results

4.2.1 Correlations Between CO₂ Fluxes and Climate Variables from the Field Data

A statistical analysis was conducted between CO₂ fluxes and climate predictors using correlation plots and multiple linear regression (MLR) models on the DCC LTC 30-min averages and EC data from 2020 and 2021. This analysis finds environmental predictors that best explain the CO₂ flux. EC data do not demonstrate a daily dependence, nor strong correlations with most climate parameters with the exception of wind speed and latent heat flux and was excluded from the short-term temporal analysis. The CO₂ flux was the response variable, and the following environmental data were the predictor variables considered in the MLR analysis, which include soil temperature (Ts), difference in air and soil temperature (Ta-Ts), barometric pressure (Pa), wind speed (WS), ambient CO₂ concentrations ([CO₂]), and volumetric water content (VWC), and water vapor flux (FH₂O). The predictor variables were normalized to evaluate the effect. Ambient air and soil temperature, and downwelling solar irradiance were highly correlated environmental parameters (r < |0.7|). The predictor variables must be independent of each other to avoid biasing the analysis. Therefore, ambient air temperature and downwelling solar irradiance were not included in the MLR model.

The results of the MLR analysis show a significant dependence was found in 2020 and 2021 (F(7,1190), p<0.05 and F(6,425), p<0.05, respectively) with an adjusted R² of 0.63 and 0.70, respectively (Table 4.3). The climate variables can explain 63% and 70% of the variability in the CO₂ flux across the playa matrix for 2020 and 2021, respectively; however, the flux extremes (above +1 and below -1μmol m⁻² s⁻¹) were not well accounted for by this model. There was a positive correlation between CO₂ fluxes and Ts (r²: 0.35 and 0.27), with standardized coefficients of 0.07 and 0.05 in the MLR for both years (Figures 4.1 a) and 4.2). The Ta-Ts was positively
correlated with the CO$_2$ flux ($r^2$: 0.46 and 0.45) and strong standardized coefficient, 0.11 and 0.05 (Figure 4.1 c)). The CO$_2$ flux was inversely correlated with [CO$_2$] ($r^2$: 0.29 and 0.26) and positively correlated with FH$_2$O ($r^2$: 0.47 and 0.45) (Figure 4.1 e) and d)). The rate change in temperature, WS, Pa, and VWC have coefficients of determination below 0.2. Overall, soil temperature, ambient CO$_2$ concentrations and water vapor flux demonstrate the strongest correlations with the CO$_2$ flux measure by the DCC method.

Table 4.1. Ordinary least-squares linear regression model for the DCC CO$_2$ flux against standardized coefficients and significance shown with asterisks.

<table>
<thead>
<tr>
<th>Predictor variable</th>
<th>Response Variable: 30-min CO$_2$ flux</th>
<th>2020</th>
<th>2021</th>
<th>2020</th>
<th>2021</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td></td>
<td>0.0210**</td>
<td>0.1048***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil Temperature at 5-cm depth (Ts)</td>
<td></td>
<td>0.0724***</td>
<td>0.0468***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Difference in air and soil temperature (Ta-Ts)</td>
<td></td>
<td>0.1145***</td>
<td>0.0519***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water vapor flux (FH$_2$O)</td>
<td></td>
<td>0.0757***</td>
<td>0.0391***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wind speed at 1.4- to 2.01-m height (WS)</td>
<td></td>
<td>-0.0551***</td>
<td>0.0258***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$ Mixing Ratio (CO$_2$)</td>
<td></td>
<td>-0.0652***</td>
<td>-0.0227***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atmospheric pressure (Pa)</td>
<td></td>
<td>-0.0079</td>
<td>0.0382***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volumetric Water Content at 5-cm depth (SWC)</td>
<td></td>
<td>-0.0162**</td>
<td>-0.0461***</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observations (n)</td>
<td></td>
<td>1198</td>
<td>433</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-squared</td>
<td></td>
<td>0.635</td>
<td>0.705</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adjusted R-squared</td>
<td></td>
<td>0.632</td>
<td>0.700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Df regression</td>
<td></td>
<td>7</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Df residuals</td>
<td></td>
<td>1190</td>
<td>425</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: *p<0.1; **p<0.05; ***p<0.01
Figure 4.1. Series of correlation plots of DCC FCO$_2$ in 2020 and 2021 as a function of a) soil temperature at 5-cm depth (Ts), b) the rate change in soil temperature (dTs °C/hour), c) difference in air and soil temperature (Ta-Ts), d) water vapour flux (H$_2$O), e) ambient CO$_2$ mixing ratio ([CO$_2$]), f) atmospheric pressure (Pa), g) volumetric water content at 5-cm depth (VWC), h) wind speed (WS). The correlation regressions shown are significant p<0.001.

Figure 4.2. Time-series of DCC CO$_2$ Flux (grey), soil temperature 5 cm (red) and ambient CO$_2$ concentration (blue). Grey and white vertical bands represent nighttime and daytime, respectively.
4.2.2 Reactive Transport Modelling of CO₂ Exchange using MIN3P

We found strong correlations between the CO₂ flux across the carbonate matrix and the following diurnal environmental variables from the field results: soil temperature, ambient CO₂ concentration, and evaporation. A reactive transport model, MIN3P (MIN3P-HPC version 2.2.1.788), was used to characterize the individual and combined influence of each climate parameter on the diurnal CO₂ flux at the surface boundary of a simplified, yet process-based 1D column model. The model details are in Appendix A.

First, we set up a simple model using inert soil with the same properties as the playa sediment at variable pH and 20% water content. We created mathematical functions to mimic diurnal changes in soil temperature (8 to 16 °C), ambient CO₂ fluctuation (400 to 500 ppm) and daily evaporation patterns (0 to 1 mmol m⁻² s⁻¹) (Figure 4.3). Second, we set up a model for Atlin-specific conditions to compare modelled CO₂ fluxes using the environmental climate data collected in 2020 to the 2020 measured DCC flux. The pH used for the model simulations was 9.1 and 40% soil volumetric water content. The column depth for the Atlin-specific model was 40cm with an imposed concentration at the base constrained by field observations. For these conditions, the net CO₂ flux through the model, from the basal boundary to the surface, is near 0.04 μmol m⁻² s⁻¹, due to a low effective diffusivity associated with high assumed moisture contents. This model setup mimics the conditions as seen in the playas, reproducing the below-ground concentration gradients and average fluxes measured by the DCC system. Additionally, hydromagnesite was included in the model with 62 wt % in the 1D column and a reversible dissolution reaction rate of 5x10⁻¹⁰ mol dm⁻³ s⁻¹. The model also accounted for hydrolysis and aqueous speciation, partitioning of CO₂ between the pore water and soil gas, as well as the temperature-dependence of thermodynamic data.
The modelled fluxes from the basic model show that temperature and ambient CO₂ fluctuations have important individual effects on the simulated CO₂ flux at the model boundary, while the effect of evaporation was negligible (Figure 4.4). Additionally, the magnitude of the flux increases significantly for different initial pH conditions; explored for pH values ranging from 8 to 10. The combined effect for the various cases demonstrates small fluctuations between -0.05 and 0.05 μmol m⁻² s⁻¹ for a pH of 8 and increases to an amplitude between -3.0 and 3.5 μmol m⁻² s⁻¹ at pH 10. These strong differences are due to the much larger TIC reservoir for higher pH values, controlling CO₂ exchange.

The simulated fluxes for the Atlin model agree with the exploratory basic model showing temperature and CO₂ concentrations having the dominant individual impacts on the modelled flux (Figure 4.5). According to the isolated temperature effect, the modelled flux predominantly captures the daytime peaks around 0.5 μmol m⁻² s⁻¹ and the nighttime minimums around -0.5 μmol m⁻² s⁻¹ (Figure 4.5 a.). However, the amplitude of the CO₂ flux at temperature minimums was generally smaller than the temperature maximum. The increase in ambient CO₂ concentration above the playa at night, set as an upper boundary condition in the model, contributes to the modelled nighttime minimums exclusively to a maximum of -0.5 μmol m⁻² s⁻¹ (Figure 4.5 b.). Interestingly, the modelled results agree that nocturnal increases in atmospheric CO₂ outcompete the subsurface concentration gradient (i.e., due to elevated CO₂=2600 ppm at 40 cm) causing a gradient reversal. The modelled CO₂ flux from the isolated effect of evaporation according to the water vapour flux from the field chamber data was very small and does not exhibit a strong diurnal pattern (-0.12 to 0.001 μmol m⁻² s⁻¹) (Figure 4.5 c.).

There was generally good agreement between the field and modelling results in the combination case (Figure 4.5 d.). The model fit was further improved with the addition of
hydromagnesite in the column. The model demonstrated near-surface diurnal fluctuations in total inorganic carbon, pH, and hydromagnesite saturation indices, suggesting CO$_2$ is partitioning between the aqueous and soil gas phase, impacting hydromagnesite mineral stability (Figure A.1 in the appendix A). However, the model fit to the measured data diverges on specific days, e.g., between DOY 224 to 226, and 228 to 229. The most significant discrepancies can be attributed to periods with significant precipitation events. The rainfall event was not modelled due to difficulties with accounting adequately for gas entrapment and displacement. For example, there was a change in the flux behaviour at the large rainfall event, DOY 228 to 229 (rainfall shown in Figure 4.5 d.), where the field results were consistently more negative than the modelled results with enhanced CO$_2$ uptake. However, these short-lived events only temporarily affected the model fit (less than 24 hrs). In addition, the model diverges for observed fluxes above 1 μmol m$^{-2}$ s$^{-1}$ and below -1 μmol m$^{-2}$ s$^{-1}$ e.g., DOY 224-226. This was also the case with the multiple linear regression model. This difference is left unexplained by the measured climate variables. It is likely processes unaccounted for in the modelling explain these higher fluxes measured in the field.

![Figure 4.3](image.png)

Figure 4.3. The climate cycles used in the base basic model from mathematical functions for temperature (left), atmospheric CO$_2$ (middle) and evaporation (right).
Figure 4.4. Basic model showing CO₂ flux over 5 days undergoing individual and combined effects (columns) from simulated changes in temperature, ambient CO₂ and evaporative at three different pH values (rows). Grey and white vertical bands represent nighttime and daytime, respectively.
Figure 4.5. Modeled CO$_2$ fluxes for the hydromagnesite-magnesite playa (black) and field-based measured fluxes (grey) with climate parameters (red), a. case isolating temperature effects, b. case isolating ambient CO$_2$ concentration effects, c. case isolating evaporation effects, d. case combining effects with precipitation shown in blue. Grey and white vertical bands represent nighttime and daytime, respectively.
4.3 Discussion

This thesis chapter provides statistical and modelling evidence for controls governing the short-term CO$_2$ fluxes across the carbonate matrix. We found that the LTC DCC CO$_2$ flux followed a distinct diurnal pattern in 2020 and 2021; daytime emissions were mirrored by nighttime uptake with a long-term near-zero average. Interestingly, alkaline soils with low organic carbon and lacking vegetation demonstrate strong diurnal CO$_2$ fluxes from physical-chemical processes. Inorganic CO$_2$ flux between the soil-atmosphere interface is often overshadowed by biological respiration (i.e., microbes and roots) and is thus considered negligible. Although this flux is relatively small in comparison to soil respiration, it cannot be overlooked in alkaline and saline sediments, where they play a key role in modulating the diurnal carbon cycle. The possible mechanisms governing the inorganic flux are changes in CO$_2$ solubility in pore water as controlled by Henry’s Law, CO$_2$ hydrolysis and complexation, changes in barometric pressure and volume governed by the ideal gas law, and adsorption of CO$_2$ on charged mineral surfaces (Ball et al., 2009; Fa et al., 2016; Gao et al., 2021; Hamerlynck et al., 2013; Ma et al., 2013; Parsons et al., 2004; Yang et al., 2020; Yates et al., 2013).

Statistical analyses of field data demonstrate correlations between climate parameters but cannot reveal the governing mechanisms. Therefore, a reactive transport model, MIN3P, was employed to reproduce the CO$_2$ flux patterns measured at the field site and understand the relative contributions of three climate parameters identified in the correlation and regression analysis. This model accounts for gas exchange based on Henry’s law as a function of temperature and the carbonate-bicarbonate equilibrium with pH dependencies of CO$_2$ solubility. However, the model does not consider changes in barometric pressure or adsorption postulated in the literature as a possible mechanism driving the CO$_2$ flux. The model also accounts for diffusive CO$_2$ transport.
through the pore space as a function of water content and CO$_2$ exchange with the atmosphere under variable boundary conditions.

The soil temperature was the best single predictor variable of the CO$_2$ flux found in the field data. The modelling results agree that temperature fluctuations occurring in the field have an important individual impact on triggering a CO$_2$ exchange across the upper model boundary. Some studies also find the temperature the best predictor of the CO$_2$ flux in alkaline deserts (Liu et al., 2012; Ma et al., 2013; Shanhun et al., 2012), while other studies find the rate change of temperature a stronger predictor (Ball et al., 2009; Liu et al., 2020; Ma et al., 2017; Parsons et al., 2004; Yates et al., 2013). The most common reason for the diurnal exchange of CO$_2$ reported in the literature is the temperature dependence of Henry’s law and CO$_2$ solubility promoting CO$_2$ dissolution and exsolution in the porewater (Cueva et al., 2019; Hamerlynck et al., 2013; Ma et al., 2013; MacIntyre et al., 2019; Sagi et al., 2021; Shanhun et al., 2012).

Moreover, we observed increased CO$_2$ concentrations in the nocturnal boundary layer above the playa creating a diffusion gradient into the playa. This process leads to diffusive mass flux into the pore space and increased CO$_2$ solubility by increasing partial pressure. The field and modelling data demonstrate the importance of the elevated CO$_2$ concentrations above the carbonate playa for nighttime uptake regardless of the upward concentration gradient in the subsurface. Researchers at the Nevada Desert Free-Air CO$_2$ enrichment facility exposed soil in the Mojave desert to elevated CO$_2$ concentrations, 550 ppm day and night, and demonstrated an increase in nighttime uptake to $\sim -0.75 \mu$mol m$^{-2}$ s$^{-1}$ compared to a baseline $\sim -0.2 \mu$mol m$^{-2}$ s$^{-1}$ at 370 ppm (Jasoni, Smith, & Arnone, 2005). Notably, on certain nights with higher wind speeds and the ambient CO$_2$ near 410ppm, the CO$_2$ flux from the DCC was near zero or slightly negative, between -0.2 to 0.05 $\mu$mol m$^{-2}$ s$^{-1}$ (see nights 221 and 245 in 2020 and 221 to 226 in 2021 from Figure 3.7.).
Evaporation as a mechanism for CO₂ emissions in the alkaline desert literature is often not discussed or found to be negligible due to the lower water content of the soils (Fa et al., 2016; Hamerlynck et al., 2013). The field data show a significant correlation between evaporation (i.e. water vapor flux) and CO₂ fluxes for 2020 and 2021. However, the results from reactive transport modeling suggests that evaporation alone does not strongly influence the CO₂ flux. The mechanism behind evaporation as a control on CO₂ emissions is water loss driving the carbonate system (equations 1.2 and 1.3) progress to the right, resulting in mineral precipitation and the release of CO₂ from the inorganic pool. The modelling results should not preclude the possibility that evaporation plays a role in CO₂ emissions and carbonate mineral precipitation from systems with stronger evaporative fluxes.

The magnitude of the CO₂ flux is controlled by soil water content, pH and rate change in temperature. First, increasing water saturation impedes the exchange of gases between the atmosphere and the playa pore space and impacts the surface area available for CO₂ dissolution. The model did not simulate changes in soil water content, and a fixed value was chosen for simplicity. This approach provided a favorable fit, apart from short-lived deviations during major precipitation events. For longer term simulations (seasonal effects), the impact of precipitation and water content are expected to have a more pronounced effect and should be considered. Generally, the effect of water content in soils on CO₂ diffusion is a well-studied parameter in biotic (Herbst et al., 2009) and abiotic soils (Xie et al., 2009). The magnitude of the exchange of CO₂ at the air-water interface also depends on the pH and DIC content of the pore water. The pH in an open system determines the DIC reservoirs, and with a larger DIC reservoir, there can be a larger exchange of CO₂. The pH was not measured during the field campaign but was assumed to be between 8 and 9, in line with previous observations at the site (Power et al., 2014). The basic
MIN3P model results demonstrated the increasing amplitude of the CO$_2$ flux with increasing pH and DIC. These findings are consistent with observations in a range of alkaline soils with varied pH values (Ma et al., 2013; Sagi et al., 2021; Wang et al., 2016; Xie et al., 2009; Zhao et al., 2019). The rate change in temperature is an important control on the magnitude of the flux. Laboratory tests on Atlin playa material demonstrated that the peak fluxes, +1.30 μmol m$^{-2}$ s$^{-1}$ and -1.5 μmol m$^{-2}$ s$^{-1}$, occurred during the highest rate change in temperature, 3°C/15min (Appendix B). A larger flux was also seen in a laboratory test on the Railroad Valley alkaline playa sediment in Nevada (pH 9.8). Yates et al. (2013) found a flux of -16 μmol m$^{-2}$ s$^{-1}$ during the highest rate change temperature of -9°C/15min. Smaller magnitude fluxes were measured in the field at natural rate changes in temperature. On the playas, the flux peaked on average at -0.36 μmol m$^{-2}$ s$^{-1}$ and +0.30 μmol m$^{-2}$ s$^{-1}$ (∼ΔT 2.25°C/1hr), which agrees with a study by Parsons et al. (2004) conducted in a dry valley in Antarctica (pH 9.63) that found a nighttime uptake of -0.10 μmol m$^{-2}$ s$^{-1}$ (∼ΔT 3°C/hr) and a study by Ma et al. (2017) on an alkaline desert in China (pH 9.17) that found a balanced diurnal exchange of ±0.45 μmol m$^{-2}$ s$^{-1}$ (∼ΔT 1.5°C/hr).

Many studies cite carbonate mineral dissolution and reprecipitation as a mechanism sustaining CO$_2$ flux in alkaline soils (Fa et al., 2016; Hamerlynck et al., 2013; Roland et al., 2013; Zhao et al., 2016). The diurnal variations in the temperature and the ambient CO$_2$ drive the mass transfer of CO$_2$ at the air-water interface. The pH of the pore water decreases at night with the uptake of CO$_2$, and then hydromagnesite dissolves acting as a pH buffer which further contributes to the DIC reservoir. The mineral saturation index for hydromagnesite becomes negative in the model alongside CO$_2$ uptake at nighttime (Appendix Figure A.1). The pH increases from warming soil temperatures and CO$_2$ effusion occurring in the late morning. Hydromagnesite precipitates acting again as a buffer, as shown by the increase in saturation indices and precipitation rates.
According to the MIN3P model results, mineral precipitation and dissolution occurs strictly at the surface with a sharp decline by 5 cm depth. The small spatial extent of this process was similarly reported by Hamerlynck et al. (2013) in a field study on CO₂ exchange with the carbonate-rich soils of the Chihuahua desert (< 2 cm from surface). Overall, hydromagnesite dissolves and precipitates in the playa near-surface, which is in line with what is suggested by the modern ¹⁴C measured in the minerals (Figure 3.18).

There are a few limitations to the modelling approach. First, there are additional temperature-related mechanisms that can lead to the ingress or release of CO₂ from soils, which were not considered in the model. For instance, CO₂ adsorption to mineral surfaces, mainly clays, has been shown to have a similar temperature dependence (Davidson et al., 2013). Additionally, thermal convection due to air-soil temperature gradients and thermal compression-expansion of soil air is suggested as possible exchange mechanisms governed by the ideal gas law (Fa et al., 2016; Gao et al., 2021; Hamerlynck et al., 2013; Rey, 2015; Sagi et al., 2021; Yang et al., 2020). The omission of these mechanisms may have contributed to the mismatch between the model and field data (e.g., dates DOY 224-226). As discussed, the reactive transport model produced mismatches with the field data, specifically during periods of rainfall. Future work could incorporate the effect of precipitation events and thermal fluxes across the playa-boundary layer interface.

To conclude, at fixed ambient conditions without additional triggers, the playa sediment and porewater return to equilibrium and the net CO₂ flux is close to zero. Therefore, atmospheric conditions that follow a diurnal pattern, specifically temperature and ambient CO₂ concentrations, maintain a constant state of disequilibrium in the pore space and fluid, and controls cycling of CO₂ fluxes across the playa surface. In the process, the diurnal cycling can lead to the re-dissolution
and re-precipitation of hydromagnesite and incorporation of atmospheric \( \text{CO}_2 \) into its crystal structure. The dependence of the \( \text{CO}_2 \) flux on diurnal climate cycles, regardless of the governing mechanisms, highlights the importance of making continuous and robust measurements over 24hrs to estimate the long-term carbon cycle in these natural systems, especially when the magnitude of fluxes changes on an hourly scale and the direction of fluxes changes based on a diurnal pattern. Only through multi-day monitoring was it possible to identify that the net exchange of \( \text{CO}_2 \) across the playa matrix was near zero during the monitoring periods.
Chapter 5: Conclusions

5.1 Main Findings

This thesis is focused on quantifying CO$_2$ fluxes across the playa-atmosphere interface at the Atlin hydromagnesite-magnesite deposits with EC, DCC and flux-gradient (2021) systems and characterizing the spatial and temporal variability. Additionally, isotope samples were collected to characterize the gaseous C-CO$_2$ phase (i.e., $^{13}$C and $^{14}$C) and relate the findings to previous work on the mineral and aqueous phases. Power et al. (2014, 2019) have done comprehensive work to describe the playa genesis and characterize the aqueous and solid phases and mineral precipitation kinetics. Their work postulated that CO$_2$ degasses from the HCO$_3$-rich groundwater and carbonate mineral precipitation in the unsaturated zone of the amalgamated mounds. The complex interactions between minerals, fluids and the atmosphere make Atlin an interesting site to test methods for measuring CO$_2$ fluxes in predominantly non-vegetated geologic settings. Both EC, above-ground profiles, DCC and C-CO$_2$ isotopes provide valuable information for assessing CO$_2$ exchange with the atmosphere at this site.

These are the main findings of the thesis (summarized in Figure 5.1):

First, we expected the three flux measurement methods to have some agreement but found that fluxes measured with chambers were different from those measured by the EC and profile gradient systems. Net carbon flux as measured by the DCC method is near-zero, 0.04 μmol m$^{-2}$ s$^{-1}$ uptake in 2020 and 0.08 μmol m$^{-2}$ s$^{-1}$ emission in 2021. However, EC flux estimates were on average +1.38 μmol m$^{-2}$ s$^{-1}$ (2020) and +1.07 μmol m$^{-2}$ s$^{-1}$ (2021). The DCC system measures CO$_2$ fluxes on a small scale at the sediment-atmosphere interface with no strong contributions from the CO$_2$ source in the deeper unsaturated zone. In contrast, the EC and profile methods measure fluxes a few meters above the surface and integrate the flux estimate over a larger area. Higher fluxes
observed with the EC method relative to the DCC system may be explained by two scenarios: 1) emissions of CO$_2$ from a CO$_2$-rich subsurface reservoir along preferential pathways not captured by the DCC system and 2) contributions from biological respiration beyond the DCC survey grid, specifically from grassy transition zones and the adjacent forest (Figure 5.1). The results from Chapter 3 emphasize the scales of measurement and heterogeneities of the playa system. It is important to use multiple complementary methods in measuring the flux to understand the carbon cycle at a complex site, such as Atlin.

Second, during periods of atmospheric stability at nighttime, CO$_2$ accumulates above the playa. We speculate that the CO$_2$ source is from horizontal advection of CO$_2$-rich air from soil respiration in the neighbouring forest. The radiocarbon and stable isotope results from two nighttime air samples demonstrate that the likely source of CO$_2$ accumulating above the playa is from respiration in the forest soil. Nocturnal advection from drainage flows of CO$_2$-dense air has previously been observed at forested sites within complex terrain, i.e. sloped landscapes (Feigenwinter et al., 2008; Vickers et al., 2012). The increase in CO$_2$ concentration above the playa at nighttime is strong enough to cause a gradient reversal, where CO$_2$ fluxes measure by the DCC method at the playa-atmosphere interface are more negative. However, further field work and characterization would be needed to confirm the occurrence of nocturnal drainage flows. Chapter 3 and 4 demonstrate the influence of nocturnal CO$_2$ accumulation on the CO$_2$ cycle dynamic above the carbonate playa.

Finally, the field and modelling results demonstrate a distinct diurnal exchange of CO$_2$ at the local scale between the carbonate matrix and the atmosphere (summarized in panel b. of Figure 5.1). Similar flux patterns have been observed in alkaline deserts and drylands. The CO$_2$ emissions in the daytime were balanced by CO$_2$ uptake at nighttime, resulting in a near net-zero average. Thus, observed DCC fluxes indicate that gas migration from the deep subsurface CO$_2$-rich
reservoir through the playa matrix was likely impeded by low diffusivity and has low to minimal biological activity. The carbonate-bicarbonate equilibrium in the alkaline pore water is perpetually disturbed by the diurnal climate cycles, specifically changes in temperature and ambient CO$_2$ concentrations. The magnitude of the flux is dependent on the pH and TIC of the pore water, the soil water content, and the magnitude of the temperature change. The results presented in chapter 4 highlight the importance of collecting measurements with high temporal resolution. It is paramount to quantify the CO$_2$ flux across the whole day to obtain a representative long-term rate for alkaline deserts and carbonate mineral soil systems. In addition, understanding the controls on the inorganic carbon CO$_2$ flux, such as pH and temperature changes, will provide valuable information for predicting the response of these mineral systems to climate change and for gap-filling using a non-biological process-oriented approach.

Figure 5.1 Schematic summarizing the results from this work, including DCC and EC flux measurements and isotope results for CO$_2$(g) samples (left panel a.). The environmental controls and carbonate chemistry relating to the DCC flux are summarized (right panel, b.).
5.2 Future Work and Applications

5.2.1 Hydromagnesite-Magnesite Playas

Based on the findings, I have several recommendations. First, future work at this site should consider longer-term CO₂ flux measurements to capture seasonal and annual variability. Data were collected over 6 weeks; therefore, these findings are only representative for conditions in August on the most mature part of the playa. Long-term measurement periods will allow for daily and annual net exchange estimates and more in-depth uncertainty analysis. Also, long-term measurements of CO₂ fluxes could provide more evidence for the stability of the carbonate reservoir at the Earth's surface with ongoing climate change. Alongside flux measurements, I recommend additional supporting variables in the shallow subsurface (0 to 40 cm depth) to provide more spatial and temporal resolution of the subsurface dynamics, such as CO₂ concentration, soil temperature, moisture content and water samples, and gas vapour probes profiles. These supplemental measurements could help determine the coupling between the atmosphere, surface playa and deep playa.

Second, since the source of CO₂ measured by the EC and flux-gradient methods was not resolved with the current data set, future work at this site could evaluate the flux footprint source area and horizontal advection regarding biological sources. Flux footprint extent can be further studied using a tracer experiment alongside various footprint models. Also, horizontal advection processes can be evaluated using CO₂ and wind speed profile measurements at various distances from the flux tower or running two EC systems at two heights (e.g., 1 m and 3 m) to confirm constant flux with height (i.e., minimal to no advection).

Third, future studies should investigate desiccation cracks for their impact on gas migration and flux measurements. As discussed, desiccation cracks could be a preferential pathway for gas
transport from the CO$_2$-rich subsurface reservoir. Further, the cracks are difficult to study with chamber-based methods as they prevent the complete isolation of the headspace and increase the volume of the closed system. Desiccation cracks could have important implications for flux measurements in evaporative systems, such as arid and sei-arid deserts. However, to my knowledge, very few studies have attempted to investigate the role of desiccation cracks in these environments for gas exchange (Weisbrod et al., 2009).

5.2.2 Beyond the Playas

The hydromagnesite-magnesite playas are a natural analogue to carbon mineralization from atmospheric CO$_2$ in engineered mineral-based systems, such as ultramafic mine tailings facilities with enhanced silicate weathering. A variety of scenarios lead to the possible exchange of CO$_2$ across the playa-atmosphere interface, which has interesting applications for carbon capture and storage in ultramafic rocks. The playas can represent two specific scenarios for engineered systems: 1) ex-situ mine tailings that have reached the full-carbonation potential and are stored at the Earth’s surface, or 2) in-situ CO$_2$ injection in geological formations or into mine waste with surface leakage.

While carbon mineralization in engineered mineral-based systems is emerging as one of the most valuable forms of carbon sequestration and storage, there are no standards for measuring and monitoring atmospheric CO$_2$ uptake under near-surface conditions. Many studies have proven carbonate mineral precipitation occurs from atmospheric CO$_2$ in ultramafic mine tailings, e.g. Mount Keith mine, Woodsreef asbestos mine, Black Lake mine and Clinton Creek mine (Lechat et al., 2016; Pronost et al., 2012; Turvey et al., 2018; Wilson et al., 2009, 2014). However, the current methods used to determine carbon sequestration rates are labour-intensive and have a low
spatial and temporal resolution (Assima et al., 2014; Stubbs et al., 2022; Wilson et al., 2014). To
our knowledge, there is minimal research associated with testing field-based methods that are
efficient and continuous for monitoring and verifying long-term carbon capture and storage within
mineral-based systems beyond the laboratory scale (Power et al., 2013; Stubbs et al., 2022; S. A.
Wilson et al., 2014). Surface-atmosphere CO$_2$ flux measurement techniques, EC, DCC and flux-
gradient methods, provide a feasible solution.

Insights from the playa study towards engineered carbon mineralization systems are two-fold.
First, the short-term influence of climate on the CO$_2$ fluxes in predominantly abiotic alkaline
carbonate sediment highlights the importance of continuous measurements to estimate long-term
carbon exchange rates. Second, EC and profile data, and supporting measurements did not provide
any conclusive evidence on the source of CO$_2$ over the larger surface area above the playa. These
results highlight the possibility that estimates of net CO$_2$ exchange between mine waste and the
atmosphere may be affected by outside sources related to biological processes or desiccation
cracks providing preferential pathways for CO$_2$ migration. Methods must be developed that allow
us to confidently distinguish between carbon fluxes associated with the mine waste and from other
sources. This scenario provides strong incentive to resolve the issue using new supporting
methods, scaling, or flux partitioning approaches.

Future work will assess and develop protocols for this novel application of EC and DCC
methods to measure carbon sequestration during enhanced silicate weathering with carbon
mineralization. Reliable and continuous methods for CO$_2$ monitoring and establishing standards
will be critical for deploying and optimizing carbon mineralization in mineral-based systems as a
strategy to tackle climate change.
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Appendices

Appendix A: Reactive Transport Modelling Methodology

MIN3P-HPC (version 2.2.1.788) was used to investigate the influence of individual and combined environmental variables on the CO$_2$ flux across a carbonate matrix-atmosphere interface. MIN3P is a reactive transport code for applications in variably saturated porous media that accounts for advective-diffusive multi-component transport and geochemical reactions. The governing equations and numerical methods are provided in Mayer et al. (2015) and Su et al. (2021).

In this study, two simulations were completed, first a basic model and second an Atlin-specific model. First, a simulation was conducted in a basic model to test the effect of diurnal changes in climate parameters on the CO$_2$ flux at the surface boundary in an inert quartz matrix under varied pH-conditions. The simulations were completed using a one-dimensional domain representing a 1-m deep vertical profile. Climate variables, such as temperature, ambient CO$_2$ concentrations and evaporation, were provided to the simulation via sinusoidal functions with minimum and maximum values constrained by field observations. Second, an Atlin specific simulation was conducted with field climate data as input. The simulations were completed using a one-dimensional domain representing a 40-cm deep vertical profile of the hydromagnesite-magnesite playa unsaturated zone. Hydromagnesite is assigned to the profile at a volume fraction of 0.124 and a reversible dissolution reaction rate of $5 \times 10^{-10}$ mol dm$^{-3}$ s$^{-1}$ was specified. The results are representative for the time frame in which the DCC data was collected in 2020. A 30-day spin-up was used for the Atlin model to ensure the initial conditions are representative for long-term site conditions, before initiating the transient simulations.
The physical properties of the materials for both simulated profiles were selected based on field data (Table A.1). A transient flux boundary was applied at the upper boundary of the model with imposed atmospheric boundary conditions. Precipitation and infiltration were neglected in the simulations; negative precipitation values were applied to mimic evaporation. A constant hydraulic head of -7 m and -2 m was assigned to the base of the basic and the Atlin specific columns, respectively. These values were used to calibrate the model to representative volumetric water contents of 0.20 and 0.40. The initial conditions and aqueous geochemistry are presented in Table A.2. The aqueous geochemistry is taken from Power et al. (2014) from profile 4 in the southern playa. It is assumed that the results from profile 4 are representative of the amalgamated mounds and can be used to infer conditions for the northern playa.

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<th>Value</th>
<th>Reference</th>
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<td>Residual Saturation [-]</td>
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<tr>
<td>Volumetric water content [-]</td>
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<tr>
<td>Van Genuchten</td>
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<td></td>
</tr>
<tr>
<td>α</td>
<td>0.6</td>
<td>Rosetta</td>
</tr>
<tr>
<td>n</td>
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<td>Rosetta</td>
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<tr>
<td>l</td>
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<td>Clay %</td>
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<td>PSD</td>
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<tr>
<td>Bulk density (g cm⁻³)</td>
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<td>Field measurements</td>
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<td>7-10</td>
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<tr>
<td>pO₂</td>
<td>atm</td>
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<td>mg L⁻¹</td>
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<td>2.43x10⁻⁵</td>
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Figure A.1  Additional reactive transport modeling outputs. Panel a. CO₂ concentration ([CO₂]), b. total inorganic carbon (TIC), c. pH, d. hydromagnesite mineral precipitation/dissolution rate (Rate), e. saturation index (SI) for hydromagnesite. Grey and white vertical bands represent nighttime and daytime, respectively.
Appendix B: Laboratory Experiment Methodology and Results

B.1 Introduction

In addition to the field work and modelling of CO₂ fluxes, laboratory experiment was carried out. Laboratory tests were conducted on the playa carbonate sediment in a fridge to isolate the effect of temperature and temperature changes on the CO₂ flux.

B.2 Methods

The soils collected from the field for soil properties measurements were combined and used in this laboratory control experiment. An aliquot of soil was sterilized in an autoclave for one hour on a dry cycle at 120°C (based on Ball 2009) to minimize biological activity. Q-XRD was conducted before and after the sterilization to assess any changes with the hydrated mineral composition due to heating and pressurizing (e.g., changes in hydromagnesite abundance).

Approximately 1 kg of soil (Atlin, Atlin sterilized and quartz) was mixed with water to reach a gravimetric water content of 15%, and the soil mixture was placed in a PVC collar equipped with a PVC base plate. A survey chamber was placed on the collar in a small fridge, and the analyzer unit with the infrared CO₂ gas analyzer was set up on the laboratory bench. A Vaisala temperature and humidity probe was embedded in the soil. The fridge was set on a timer to turn off for 12hrs to equilibrate with laboratory air temperature (21 °C) and turned on to reach a temperature of 5°C to mimic diurnal temperature fluctuations. The data was processed in Soil Flux Pro® (LI-COR, Inc.) and plotted in python.

B.3 Results

Two tests were conducted, and results are summarized in Table B.1. First, a test was conducted on the carbonate playa material mixed with 15 w/w% DI water to evaluate the change in flux from transient to steady-state temperature conditions. The steepest changes in temperature,
+1°C/15min and -3°C/15min, resulted in the largest fluxes, +1.8 μmol m⁻² s⁻¹ and -1.4 μmol m⁻² s⁻¹ (Figure 4.3), respectively. As the rate change in temperatures slowed and remained constant, the flux trended towards 0 μmol m⁻² s⁻¹ and this behavior is demonstrated at 20°C and 6°C. Second, a test was conducted to evaluate a similar diurnal CO₂ flux from a change in temperature from 5 treatments: Quartz pH 6-7 solution (15% w/w), quartz pH 9 solution (15% w/w), Atlin carbonates unsterilized (15% w/w), Atlin carbonate unsterilized (air dry, residual moisture %), Atlin Sterilized (15% w/w). The quartz with pH 7 water showed no change in the flux due to a diurnal change in temperature, while the pH 9 quartz treatment resulted a minimum negative flux of -0.3 μmol m⁻² s⁻¹ and a maximum positive flux of 0.23 μmol m⁻² s⁻¹ (Figure 4.4). The Atlin playa material, both sterilized and unsterilized, follow the same pattern; however, the flux minimum for the sterilized soil is smaller due to differences in minimum temperatures (4°C compared to 2°C). The air-dried Atlin material surprisingly demonstrated similar fluxes as the two other Atlin treatments, slightly smaller at 0.25 μmol m⁻² s⁻¹; however, the sample flux decreases at a faster rate towards zero. Field data from the Atlin site (2020 DOY 224.83-226.71), at a volumetric water content of 0.1, is superimposed on the 5 treatments to show similarities between the simulated temperature fluctuations and field observations. Similar experiments were conducted by Ball et al. (2009), Ma et al. (2013) and Yang et al. (2020), with similar fundings.

<table>
<thead>
<tr>
<th>Table B.1</th>
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<tr>
<td><strong>Test 1</strong></td>
<td>With Atlin playa material (15% w/w), assess the CO₂ flux change from transient conditions with temperature fluctuations to steady state, at constant ambient (20°C) and cold (5°C) temperature conditions.</td>
</tr>
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</table>
| **Test 2**| Assess diurnal temperature changes in the following material:  
- 15% w/w, quartz, pH 6  
- 15% w/w, quartz, pH 9  
- 15% w/w, Atlin soil  
- 15% w/w, Atlin soil, sterilized  
- Dry Atlin soil |
Figure B.1  Laboratory control tests of CO$_2$ flux (red) in playa soil at 15% w/w as a function of changing temperature (black ambient and grey soil) in a closed mini-fridge.

Figure B.2  Laboratory control tests of CO$_2$ fluxes as a function of temperature fluctuations in a close mini fridge: a) CO$_2$ fluxes  b) temperatures. The grey data are the field values, the black is quartz with pH 7, the orange is quartz with pH 9, the red is Atlin carbonate unsterilized, the green is Atlin carbonate unsterilized dry, and the blue is the Atlin carbonate sterilized.
Appendix C: EC Auxiliary Data

This appendix includes data from the EC sensors and the meteorological data that is not included in the thesis body. The $u_*$ threshold determination is presented in section C.1 and correlation plots between EC FCO$_2$ and the climate measurements and a time series of the stability parameter and the heat fluxes can be found in section C.2.

C.1 $u_*$ Threshold

The $u_*$ threshold was informed by visualizing the correlation plot of the flux ($F_{CO_2}$) against $u_*$ and the standard deviation of the vertical velocity ($\sigma_w$), and then using a moving point test (MPT) following Hunt et al. (2016). The threshold, in Hunt et al (2016), was decided based on the visual assessment of the MPT, not automated by an algorithm (J. Laubach, personal communication, May 4, 2021). The threshold is commonly applied solely on nighttime data that are binned by temperature. Due to the short field campaign and the constant diurnal behaviour in this unique environment, I assessed the $u_*$ threshold using the entire data set, after filtering for quality control parameters and wind direction. Since there was very little difference between the daytime and nighttime relationships between $F_{CO_2}$ and $u_*$ (Fig C.1, left panels), the MPT was applied to the daytime and nighttime data combined (Figure C.2 middle and right panels). There was a strong linear relationship between $F_{CO_2}$ and both $u_*$ and ($\sigma_w$) extending over their full ranges making it difficult to detect a threshold. Consequently, we chose a value that best-removed data that would not correspond to estimates in turbulent conditions. This value was 0.10 m s$^{-1}$ for 2020 and 2021. These values are very similar to those reported in the literature for surfaces with similar aerodynamic roughness, i.e., roughness length, $z_0$ (e.g., Hunt et al., 2016; Soares et al., 2021).
Figure C.1  Assessment of the friction velocity ($u_*$) threshold for CO$_2$ flux data quality control. Left panels: Daytime and nighttime $F_{CO2}$ plotted against $u_*$ for 2020 (top) and 2021 (bottom). Middle panels: Same as left panels without separation of daytime and nighttime data and with the moving point test (MPT) applied to all data. Right panels: Same as middle panels except $F_{CO2}$ is plotted against the standard deviation of the vertical velocity ($\sigma_w$).
C.2 EC Auxiliary Data

This section of the appendix includes correlations between EC FCO₂ and the climate data, and a time series of the stability parameter and turbulent heat fluxes (latent and sensible heat).

Figure C.2 Series of correlation plots of EC FCO₂ in 2020 and 2021. The FCO₂ is plotted against a) soil temperature (Ts), b) the rate change in soil temperature (dTs/hour), c) difference in ambient and soil temperature (Ta-Ts), d) water vapor flux (FH₂O), e) ambient CO₂ mixing ratio ([CO₂]), f) atmospheric pressure (Pa), g) volumetric water content (VWC), h) wind speed (WS).

Figure C.3 Time-series of the stability parameter (z/L, top panel), and latent (LE) and sensible (H) heat fluxes (middle panel) and available energy (Rn) and storage (G+S) (bottom panel).
Appendix D  Isotopes and Radiocarbon Analysis and Data

This appendix includes equations used for calculating static chamber isotope corrections and two-reservoir mixing used for estimating the contributions from the forest for the nighttime air values. The radiocarbon samples with the sample locations, volumes, and measured concentrations are summarized in Table D.1. Table D.1 includes the $\delta^{13}C$ samples taken in tandem.

Mass balance corrections to correct for air initially present in in the chamber headspace of 2021 the static chambers were performed based on the method by Wozney et al. (2021):

$$PE^{14}C_{corr} = \frac{(F^{14}C)_{sample} - (F^{14}C)_{air}^{14}CO_2}{(F^{14}C)_{sample}^{14}CO_2 - (F^{14}C)_{air}^{14}CO_2}$$  \[\text{Equation D.1}\]

$$PE^{14}C_{corr} = \frac{(F^{14}C)_{sample} - (F^{14}C)_{air}^{14}CO_2}{(F^{14}C)_{sample}^{14}CO_2 - 406}$$

$$\delta^{13}C_{corr} = \frac{(\delta^{13}C)_{sample} - (\delta^{13}C)_{air}^{14}CO_2}{(\delta^{13}C)_{sample}^{14}CO_2 - (\delta^{13}C)_{air}^{14}CO_2}$$  \[\text{Equation D.2}\]

$$\delta^{13}C_{corr} = \frac{(\delta^{13}C)_{sample}^{14}CO_2 - (\delta^{13}C)_{air}^{14}CO_2}{(\delta^{13}C)_{sample}^{14}CO_2 - 406}$$

The two-reservoir mixing model of Clark (2015) was used to determine contributions from deep source in the playa and forest to CO$_2$ present above the playa at nighttime.

$$f_{forest \ pore \ gas} \% = \frac{(\delta^{13}C)_{sample}^{14}CO_2 - (\delta^{13}C)_{air}^{14}CO_2}{(\delta^{13}C)_{forest}^{14}CO_2 - (\delta^{13}C)_{air}^{14}CO_2} \times 100$$  \[\text{Equation D.3}\]

Example:

$$f_{forest \ pore \ gas} \% = \frac{(-15.0 \times 530) - (-12.1 \times 406)}{(-22.3 \times 5400) - (-12.1 \times 406)} \times 100 \approx 2.5$$

Example:
### Table D.1  Radiocarbon data with associated δ¹³C result.

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<th>Volume (mL)</th>
<th>[CO₂] (ppm)</th>
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<th>F¹³C Corr*</th>
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* Samples were corrected for atmospheric gas in the original headspace of the larger static chambers using eq. D.1 and D.2. following Wozney et al. 2021
Appendix E: Individual Long-term Chamber Flux Results

This appendix contains the CO₂ fluxes and RMSE of the rate change of CO₂ mixing ratio (ds₂/dt) time series for each LTC. Figure E.1. depicts the 2020 data and Figure E.2. shows the 2021 data. The numbering of the LTCs corresponds with the locations in Figure 2.3.
Figure E.1  Time series of the DCC CO₂ (left panels) and RMSE of ds/dt (right panels) for the 2020 measurement period. Each LTC is shown starting at the top with LTC 1 to LTC 8.
Figure E.2  Time series of the DCC CO\textsubscript{2} (left panels) and RMSE of \(ds/dt\) (right panels) for the 2021 measurement period. Each LTC is shown starting at the top with LTC 1 to LTC 8.