Comparing Eddy Covariance and Dynamic Closed-Chamber Methods for Measuring CO_2 Fluxes Above the Hydromagnesite-Magnesite Playas near Atlin, Northwestern British Columbia.

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Abstract (266 words)

The hydromagnesite-magnesite playas of Atlin (British Columbia) are a natural analogue for carbon dioxide (CO_2) exchange between mine waste and the atmosphere. The playas provide an opportunity to test methods for measuring atmospheric CO_2 fluxes in a geologic setting similar to mine tailings, which could then inform verification protocols for measuring carbon capture by ultramafic materials. Eddy covariance (EC) and dynamic closed chamber (DCC) methods were used in tandem at this site to detect and validate CO_2 flux measurements. Data were collected continuously over 27 days in August 2020. Combined with biometeorological information, preliminary results show EC and DCC CO_2 daytime flux averages of +0.98±0.55 μmol $m^{-2}s^{-1}$ and +0.17±0.31 μmol$m^{-2}s^{-1}$, and nighttime flux averages of +1.21±0.54 μmol$m^{-2}s^{-1}$ and -0.13±0.25μmol$m^{-2}s^{-1}$, respectively. The data show that CO_2 fluxes on the playa are influenced by climate variables, such as temperature, barometric pressure, wind speed and ambient CO_2 concentration. Additionally, pore gas was collected to identify the origin and composition of the CO_2. Radiocarbon analysis of pore gas, taken at the 65- and 85-cm depths, shows an age range of 14,000-19,000 BP and percentage of modern carbon between 8-17% (pMC), an old signature comparable to the groundwater and carbonate in minerals taken from the same depth. These preliminary results demonstrate that EC and DCC methods show considerable promise; however, further data analysis is needed to better understand the complexities of the underlying processes and to explain differences in the observed CO_2 fluxes. The next steps are to implement these methods on ultramafic mine tailings that actively sequester carbon, with the aim of improving monitoring and verification processes for carbon sequestration.

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Introduction

The investigation of CO_2 exchange between the soil and atmosphere in a geological setting is limited in the literature. Eddy covariance (EC) and dynamic closed-chamber (DCC) systems, two widely accepted environmental monitoring technologies used in agricultural science and ecosystem science, can potentially be employed in a geological context to measure CO_2 exchange rates. Pairing EC and DCC methods, to target low carbon emissions at mine sites where the ore is hosted in ultramafic rock, may provide the quantification, validation and verification needed to determine CO_2 capture. This field site, in Atlin northwestern BC, is of interest because it provides insights on conditions favourable for ex situ carbon mineralization and provides an analogue to measure CO_2 exchange with the atmosphere. It has been proposed that, due to the high concentration of carbonate in the alkaline groundwater in the playa deposits, carbonate minerals will precipitate and CO_2 will degas[1].

The study objectives are to…

1. Quantify and compare CO_2 flux rates occurring at this site using both EC and DCC methods; and
2. Identify the origin and composition of the CO_2 exchanged across the soil atmosphere interface.

Site Description:

The instruments were installed on the north playa, shown in Figure 1 as 'monitoring location'. This location for pairing the EC and DCC systems was chosen due to the large areal extent of hydromagnesite-magnesite playa, the reduced surface roughness, as well as the absence of grassland influence. Data were collected over 27 days during August 2020. Long-term DCC were set in pairs at 5 m intervals toward the south of the EC tower surrounded by a grid of 22 soil collars for survey DCC measurements.

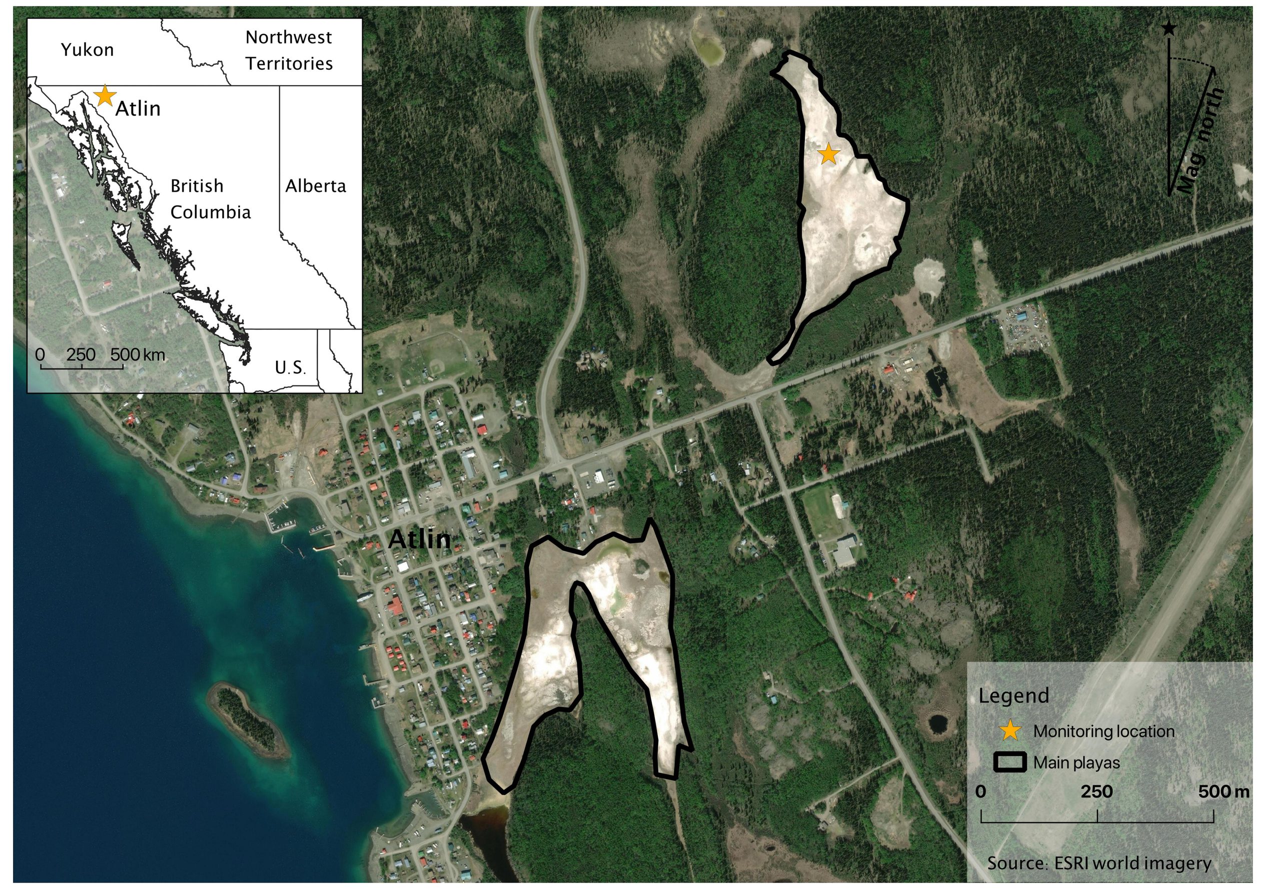


Figure 1. Location of study area in Atlin, northwestern British Columbia.

Geological Setting and Playa Formation:

- The bedrock is composed of ultramafic and altered ultramafic materials originating in the upper mantle of the oceanic lithosphere, and contains Mg-rich harzburgite and dunite. Additionally, serpentinization and carbonation occurred via fluid alterations forming serpentinite and listwanite[2,3].
- The playas formed from progressive infilling of wetlands in topographic lows fed by alkaline shallow groundwater[1,4].
- More specifically, the hydromagnesite-magnesite precipitation and CO_2 degassing occurs from the water table upwelling by the capillary fringe and concentrating the alkaline water[1].

Methods

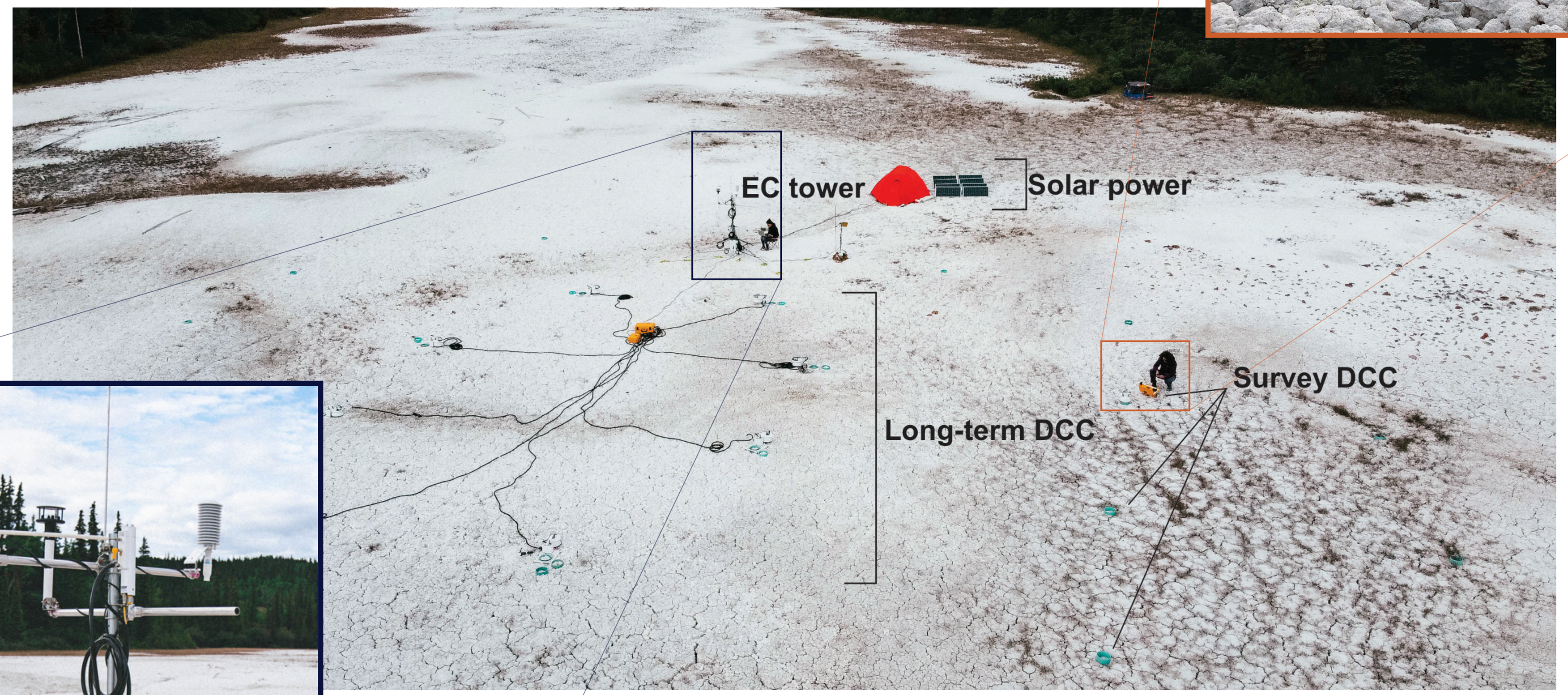
Dynamic Closed Chambers (DCC)

Theory: the rate of CO_2 diffusion or advection is estimated across the soil atmosphere interface.
Application: measure the flux from the change in concentration of CO_2 in the closed chamber headspace over time, and the CO_2 flux (FCO_2) is calculated as follows:

$$F_{CO_2} = \frac{VP_0(1-W_0)}{RST_0}\frac{\partial C}{\partial t} \quad (1)$$

Where,
- P_o is the initial atmospheric pressure
- T_o is the initial absolute air temperature
- W_o is the initial water mole fraction
- R is the gas constant
- S is the ground surface area in the chamber collar
- V is the chamber volume
- dC/dt is the rate of change of water-corrected CO2 mole fraction

Instruments: long-term and survey mode automated chambers from LI-COR Biosciences system (models LI8100A with the LI-8150 and LI-8100A), and PVC pipe collars (inner diameter 20cm).



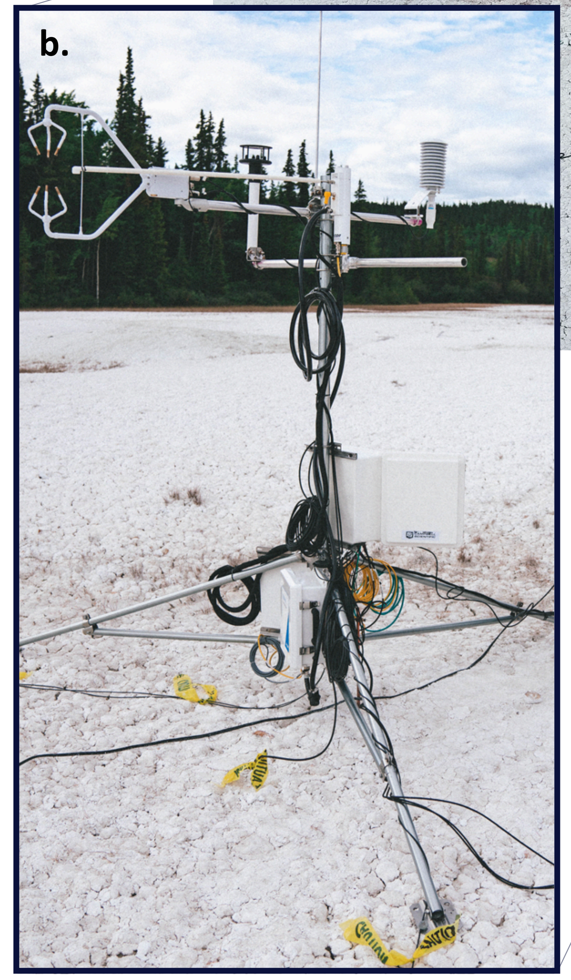


Figure 2. Drone image of the research site facing true north with a. survey DCC and b. EC tower and two researchers for scale.

Eddy Covariance (EC)

Theory: eddies in the atmospheric surface layer transport gases, heat and momentum vertically between the Earth's surface and the atmospheric boundary layer.
Application: measure the flux integrated over the flux footprint area as follows:

$$F_{CO_2} = \rho_a \overline{w'C'} \quad (2)$$

Where,
- w vertical wind speed
- C water-corrected CO_2 mole fraction
- ρ_a dry air density
- the overbar indicates mean
- the primes indicate a fluctuation from the mean

Instruments: CSAT3B 3-D sonic anemometer by Campbell Scientific, Inc. (CSI) and a LI-7200RS enclosed-path CO_2/H_2O gas analyzer by LI-COR Biosciences was initially mounted at 2.01m and on August 21st 2020 was moved down to 1.65m to reduce the extent of the footprint. Other soil and biometeorological instruments (i.e. rain gauge, 2D wind sensor) were installed on the tower.

Radiocarbon and Stable Isotopes Sampling:

- Gas collection: static chambers consisting of a section of PVC pipe 10 cm across and 30 cm in length, which were embedded 20 cm into the carbonate soil and fitted with a PVC cap equipped with a septum for sample extraction.
- Isotopes: 20 mL of sample was injected into a 12 mL Labco Limited pre-evacuated Exetainer® to be analyzed for C13 via Gas Chromatography
- Radiocarbon: 1800mL gas sample was bubbled through a 0.4 mL solution of barium hydroxide {$Ba(OH)_2$}, leading to the sequestration of CO_2 as a barium carbonate precipitate, then prepared and analyzed in the accelerator mass spectrometer at the A.E. Lalonde AMS Facility.

Preliminary Results

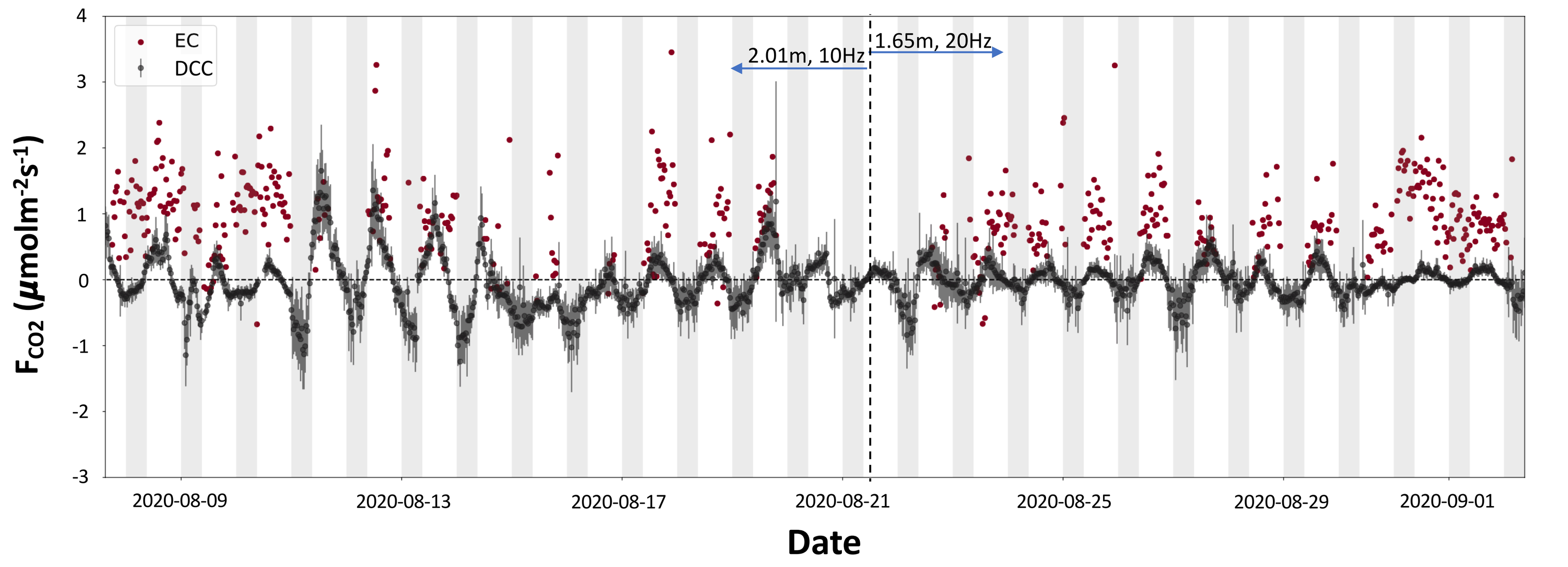


Figure 3. Time-series of the $CO_{2(g)}$ exchange averaged over 30 minutes above the playas from the EC and DCC (±1SDev, n=8). The grey boxes indicate nighttime and the arrows indicate the change in tower height and frequency of sampling, respectively, during the field campaign (dotted line).

Table 1. Composition of the $CO_{2(g)}$ accumulated in static chambers at depth in the playas.

Static Chamber ID	Depth* cm	^{14}C age yr BP	±	F^{14}C	±	δ^{14}C ‰	±	pMC* %	δ^{13}C-CO_2 ‰	δ^{13}C-DIC+ ‰
S1_3	84	14111	86	0.1726	0.0018	-827.37	1.85	17.26	-5.97	3.63
S2_2	64	14869	70	0.1571	0.0014	-842.91	1.36	15.71	-5.90	3.69
S2_3	84	19355	106	0.0899	0.0012	-910.14	1.19	8.99	-4.69	4.91
Atm	0	-	-	-	-	-	-	-	-10.00	-0.41

*pMC = percent modern carbon, which is the activity of the sample relative to the activity of a standard from the 1950's.
+Fractionation factor of +9.60 ‰ at 10°C[5]

Implications

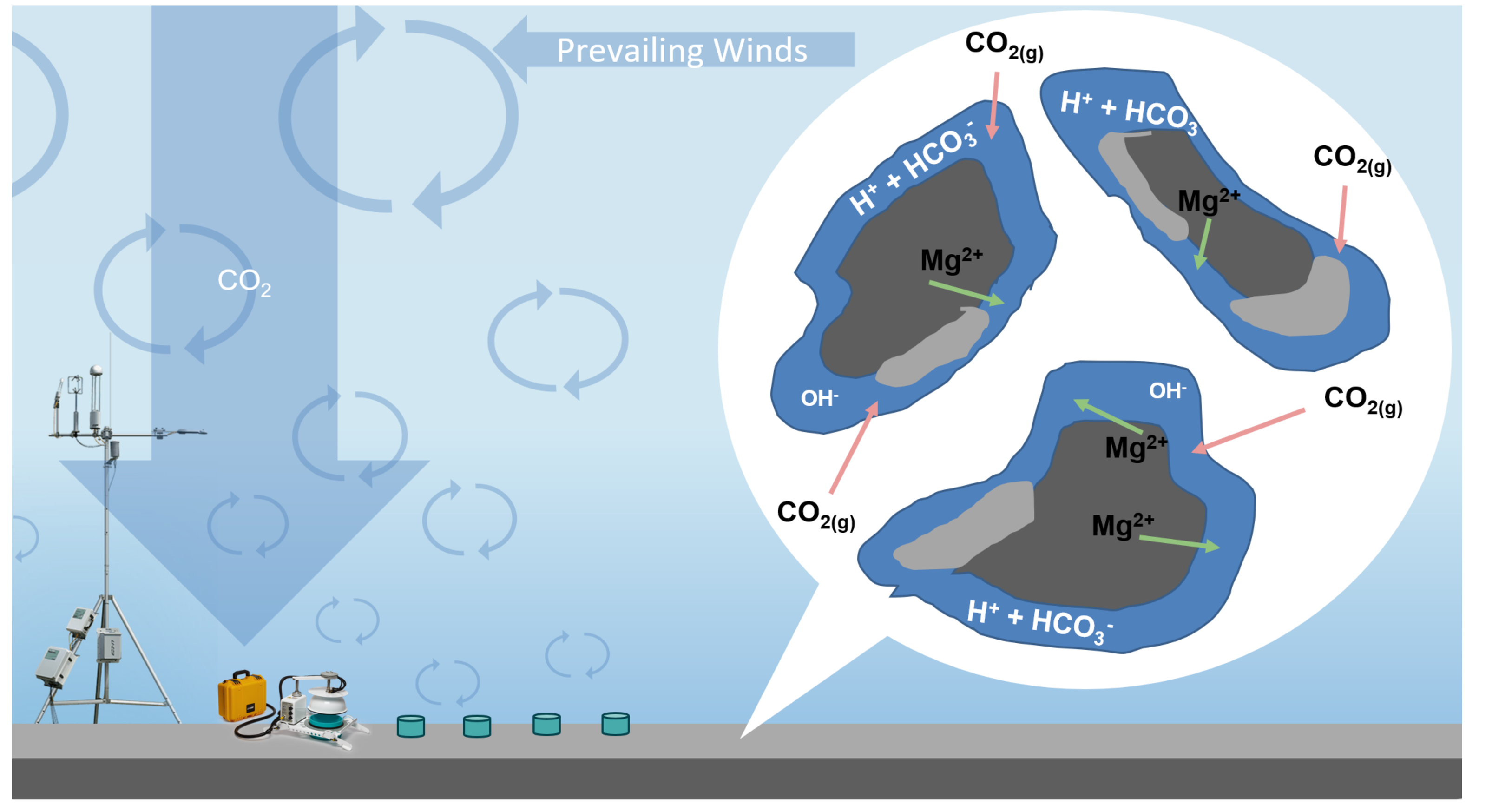


Figure 4. Schematic demonstrating the application of EC and DCC on mine tailings with ultramafic deposits (left) and the geochemical framework for carbon mineralization (right) in the pore spaces of the Mg-rich tailings (dark grey), which reacts with bicarbonate and precipitates magnesium carbonate (light grey) - a stable form of CO_2 capture.

- From this pilot study, EC and DCC methods show considerable promise. Both methods have their distinct advantages and complexities in understanding the exchanges of CO_2 in a geological environment. Data analysis is still in progress.
- The overarching goal of this project is to apply these methods on ultramafic mine tailings to quantify passive carbon uptake and to inform verification protocols for use by mining companies to secure carbon credits and to market low-carbon metals at a premium.

Acknowledgements & References

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Natural Resources Canada

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