Impacts of woody encroachment on the fate of soil CO_2 in grassland watersheds

by

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B.S., California State Polytechnic University, Humboldt, 2016

A THESIS

submitted in partial fulfillment of the requirements for the degree

MASTER OF SCIENCE

Department of Geology
College of Arts and Sciences

KANSAS STATE UNIVERSITY
Manhattan, Kansas

2023

Approved by:

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Abstract

Woody vegetation is encroaching into grasslands worldwide. Previous research has shown that woody encroachment impacts stream flow, nutrient concentrations, and suspended solid loads. However, little is known about deeper subsurface impacts, including impacts to groundwater residence time and composition. We examined these impacts at Konza Prairie Biological Station, a native tallgrass prairie in the Flint Hills of Kansas, USA. Previous research in the study area has found that groundwater CO_2 levels are rising, and we hypothesize that woody encroachment may be a driver. To help test this hypothesis, we compared groundwater chemistry and residence time between two watersheds, which differ in levels of woody encroachment (20% and 40%) as a result of differences in watershed burn frequency (1 yr vs 4 yr, respectively). Every three to four weeks during the 2022 water year, we collected groundwater and stream samples from each watershed and analyzed them for major ion chemistry. Geochemical modeling calculations indicate that an average of 4.4 mmol of CO_2 is added per liter of recharge in the more encroached watershed whereas 4.9 mmol of CO_2 is added per liter of recharge in the less encroached watershed. Groundwater residence time tracers, SF_6 and CFCs, collected at four times during the study period do not reveal clear differences between the watersheds. Groundwater residence time varied mostly as a function of the source of groundwater and the time of sample collection and thus do not appear to explain differences in CO_2 inputs between watersheds. Instead, we interpret that differences in CO_2 inputs reflect differences in the residence time of recharge water in the overlying soils. Woody encroachment alters soil root distributions, which in turn can increase soil hydraulic conductivity. If water passes through soils more quickly during recharge, kinetic reaction path modeling indicates that greater weathering occurs deeper in the subsurface rather than in the soil, which decreases the

amount of dissolved inorganic carbon the groundwater can store, consistent with our measured groundwater chemistries. These findings suggest that woody encroachment is not driving the increase in groundwater CO_2 inputs over time but is instead causing differences in CO_2 levels between watersheds through its impact on soil hydraulic properties.

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Acknowledgements

I would like to thank my parents who have been nothing but supportive throughout this whole process. Thank you for raising me in a compassionate environment where I was pushed outdoors and encouraged to do things, I didn't think I was capable of. Thank you for the kind and encouraging words not only during this process but in every phase of my life. I would like to thank my husband, Nate, for the pep talks and always lending an ear to my weird geology rants.

I would like to thank my high school earth science teacher, Jeffrey Hines, for leading me into the world of STEM. I still have many fond memories of the earth science experiments you had us conduct in class. Thank you for making science fun. I want to thank my graduate advisor, Dr. Matthew Kirk. Your help and knowledge are invaluable. You have helped me grow professionally and personally. Thank you for teaching me to say "no".

Chapter 1 - Introduction

Grasslands are the largest ecosystem on the planet, covering 40% of the terrestrial environment (Sala et al. 2000). They provide important ecological services, including nutrient cycling, carbon sequestration, biotic and abiotic biodiversity, and usable fresh water sources. According to the U.S. Geological Survey, 62% of North America's grassland biome has been lost. Land use changes, invasive plants, fires, woody encroachment, and climate change are key threats to grassland ecosystems (Comer et al. 2018). Woody encroachment, particularly in grasslands, is a global phenomenon (Acharya et al. 2018; Ratajczak et al. 2011). In North America, woody encroachment has been increasing in grasslands at a 1-2% annual rate since the 1960’s (Symstad and Leis 2017). This gradual change in vegetation type has the potential to affect subsurface systems.

Woody vegetation and grasses have different rooting structures and resource requirements, thus affecting the bedrock and soil structure, water content and mineral abundances. Plant roots create preferential flow paths for water (Ghestem, Sidle, and Stokes 2011; Sullivan et al. 2022). Grasses have dense long fibrous roots that spread out laterally in shallow soil in order to maximize water and nutrient uptake (Nippert et al. 2012). Woody vegetation has thick woody roots that access deeper water sources while breaking through bedrock (Scott et al. 2006; Nippert and Knapp 2007; Brantley et al. 2017). Those woody roots in turn create deeper pathways for meteoric water and increasing bedrock weathering (Brantley et al. 2017; Wen et al. 2021). Woody vegetation accesses deep water as well as shallow soil water, putting it in direct competition with neighboring grasses (Nippert and Knapp 2007; Brantley et al. 2017).

Coupled with these changes in soil structure, woody plants have the potential to alter soil CO_2 levels and thereby affect subsurface chemical weathering (Macpherson et al. 2008; Macpherson and Sullivan 2019; Macpherson et al. 2019; Leite et al. 2023). Woody roots have different transpiration rates compared to grasses and may also differ in terms of root exudates that feed soil microorganisms. CO_2 generated by root respiration and microbial organic matter degradation can dissolve in water and form carbonic acid, which then drives chemical weathering in the subsurface. Chemical weathering helps neutralize acids and add solute mass to groundwater. Thus, changes in soil CO_2 abundance, as a result of woody encroachment, have the potential to alter water quality and rates of landscape evolution.

Woody root systems increase soil pathways for CO_2. For this reason, we hypothesize that woody encroachment can cause an increase in concentrations of CO_2 and mineral weathering products in groundwater. We tested this hypothesis at Konza Prairie Biological Station (KPBS, hereafter referred to as Konza Prairie). Konza Prairie is a tallgrass prairie designated research area with 50 individual watersheds that are experiencing various stages of woody encroachment. The extent of wood encroachment varies between watersheds due to prescribed burn patterns. More frequent fires limit woody encroachment, while less frequent fires allow for the expanse of woody encroachment. Recent studies have documented an increase in groundwater CO_2 at Konza Prairie (Macpherson et al. 2008; Macpherson and Sullivan 2019; Macpherson et al. 2019). Rising atmospheric CO_2 is not considered a cause of the increase in subsurface CO_2 because atmospheric concentrations are 1-2 orders of magnitude lower in soils and groundwater (Macpherson et al. 2019). The increase in CO_2 at Konza Prairie may be caused by a change in precipitation patterns, an increase in microbial activity due to climate warming, and a shift in organic matter from C4 grasses to C3 woody vegetation (Nippert and Knapp 2007; Macpherson et al. 2019).

To determine the impact woody vegetation has on groundwater chemistry, residence time and CO_2 concentrations, sampling efforts focused on two watersheds, N1B and N4D. Watersheds N1B is burned annually and has 20% woody cover and N4D is burned every 4 years and has 40% woody cover. N1B is our less encroached watershed and N4D is our more encroached watershed. Sampling occurred every three to four weeks during the 2022 water year. Our findings shed light on the long-term consequences of woody encroachment for groundwater composition and CO_2 transport and has implications for impacts to stream flow in headwater streams.

Chapter 2 - Study Area

The Konza Prairie is a mesic grassland in the Flint Hills region of Kansas, USA. It is co-owned by the Nature Conservancy and Kansas State University as a long term ecological research (LTER) area. The Konza Prairie was established in the 1970s and has been continuously funded by the National Science Foundation (NSF) since 1981. A 3,487-hectare dedicated research area, Konza Prairie science focuses on climate, grazing and fire variability of a native tallgrass prairie. The Konza Prairie is divided into research watersheds with varying grazing treatments (native, bison, cattle or none) and prescribed burn plans (1-y, 2-y, 4-y, or 20-y) (Fig. 1).

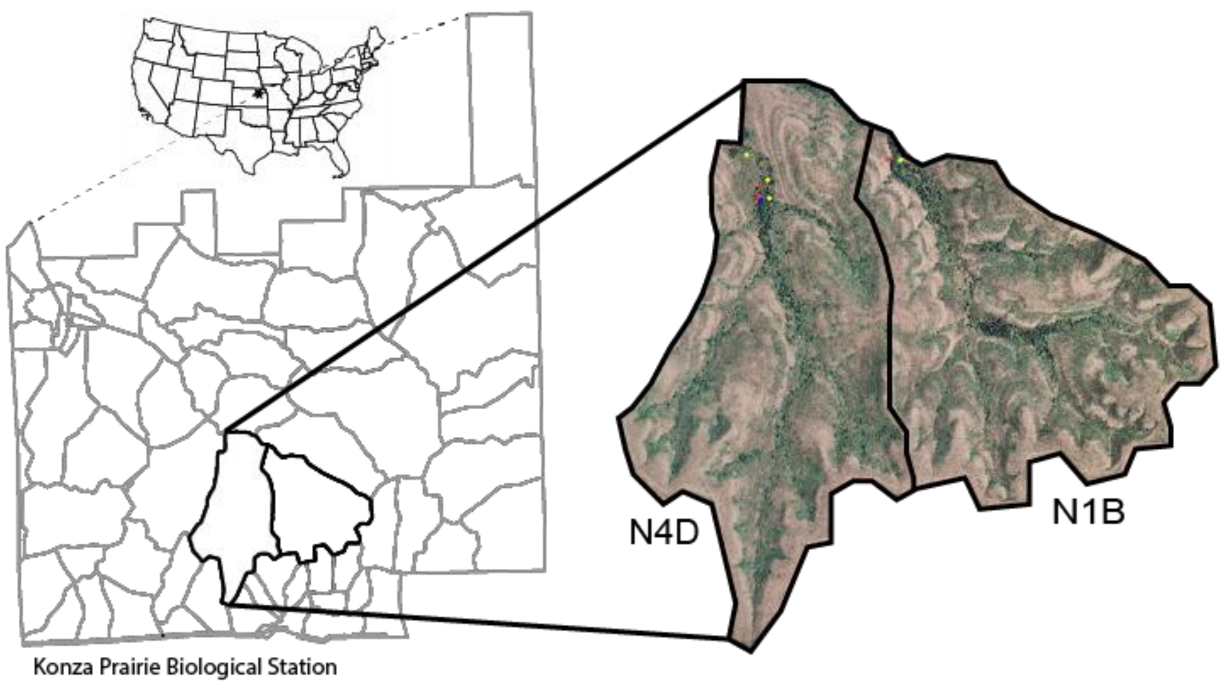

Figure 1. Map of Konza Prairie Biological station and watersheds N4D and N1B. Sampling locations are labeled by colored circles; streams in yellow, wells screened in the Eiss are blue and wells screened in the Morrill are red.

Konza Prairie has warm wet summers and cold dry winters indicative of a mid-continental climate. Mean annual temperature is 11.7 ℃ (1983-2020). Precipitation events occur mostly during the growing season (April-September) averaging annually (1982-2020) at 812 mm.

Konza Prairie is historically a tallgrass prairie with continuous gallery forests around riparian areas (Abrams 1986). The dominant vegetation is a diverse group of C4 grasses, the most abundant of which are Big Bluestem (*Andropogon gerardii),* Little Bluestem *(Schizachyrium scoparium),* switchgrass (*Panicum virgatum)*, and indiangrass (*Sorghastrum nutans*) (Keen et al. 2022; Dodds et al. 2023). Land management practices, suppressing wildfires allowed woody vegetation to become more abundant across the prairie (Knight, Briggs, and Nellis 1994; Knapp, Conard, and Blair 1998; Briggs et al. 2005). Common woody vegetation in Konza Prairie is bur oak (*Quercus macrocarpa),* chinquapin oak (*Quercus muehlenbergii*), and rough-leaf dogwood (*Cornus drummondii*) (Keen et al. 2022; Dodds et al. 2023). The expansion of rough-leaf dogwood in Konza Prairie has been well documented and is the major player in woody expansion at this site.

Woody encroachment in Konza Prairie has been steadily increasing both in burned and unburned watersheds, regardless of burn frequency (Briggs et al. 2005; Ratajczak et al. 2014). Encroachment was first documented via aerial photography at Konza Prairie in 1939 (Knight, Briggs, and Nellis 1994) and continues to be studied and measured. Once woody encroachment is established it is difficult to reverse (Dodds et al. 2023). Fire frequency patterns are linked to woody encroachment expanse across Konza Prairie. A fire frequency of 3 to 4 years was thought to be the historical burn frequency, maintaining gallery forest and grassland, before settlement by colonists (Briggs et al. 2005; Ratajczak et al. 2011). In the 1970's, a burn plan was implemented across Konza Prairie. The watersheds of interest are both experiencing different levels of woody encroachment. N4D is considered more encroached and N1B is considered less encroached.

Soils at Konza Prairie are well-drained silty clay and silty clay loam. Soils in N4D have been described as deep, moderately well-drained and moderately permeable (Tsypin and Macpherson 2012). Soil depth ranges in the upland from 5 cm to 2 m thick, in the lowland soil depth is typically 2.5 m (Nippert et al. 2012). Soils at Konza Prairie are thickest in valleys and at the base of slopes, and thinnest on limestone outcrops along the hill slopes and on the uplands (Macpherson 1996; Tsypin and Macpherson 2012). Limestone fragments are abundant in soils across most watersheds.

Underlying the soils at Konza Prairie bedrock composed of alternating limestone and mudstone. The limestone is of Permian -age that forms flat tops with a sloping mudstone hill, creating a stair stepping appearance (Macpherson et al. 2008). The aquifers in the area are sandwich-type (White 2012) neo-karst aquifers found mostly within the limestone bedrock. Three aquifers of focus are the Morrill (Mor) Limestone aquifer, the upper Eiss (Eiss2) Limestone aquifer and the lower Eiss (Eiss1) Limestone aquifer. The Mor being the deeper of the three, with Eiss1 in the middle and Eiss2 being the shallowest (Macpherson 1996) (Fig. 2).

Streams in each watershed are connected to the groundwater through a “fill and spill” hydrologic process (Hatley et al. 2023). In a recent study of N4D streamflow, Hatley et al. (2023) found that groundwater accounted for 96% of streamflow during the study period (spring – summer, 2021). Early season stream flow at the site appears to be dominated by relatively young groundwater (<3 months old) that had discharged from the Upper Eiss Limestone (Ls). Late season stream flow is predominantly older Mor water (Hatley et al. 2023; Swenson et al. 2023).

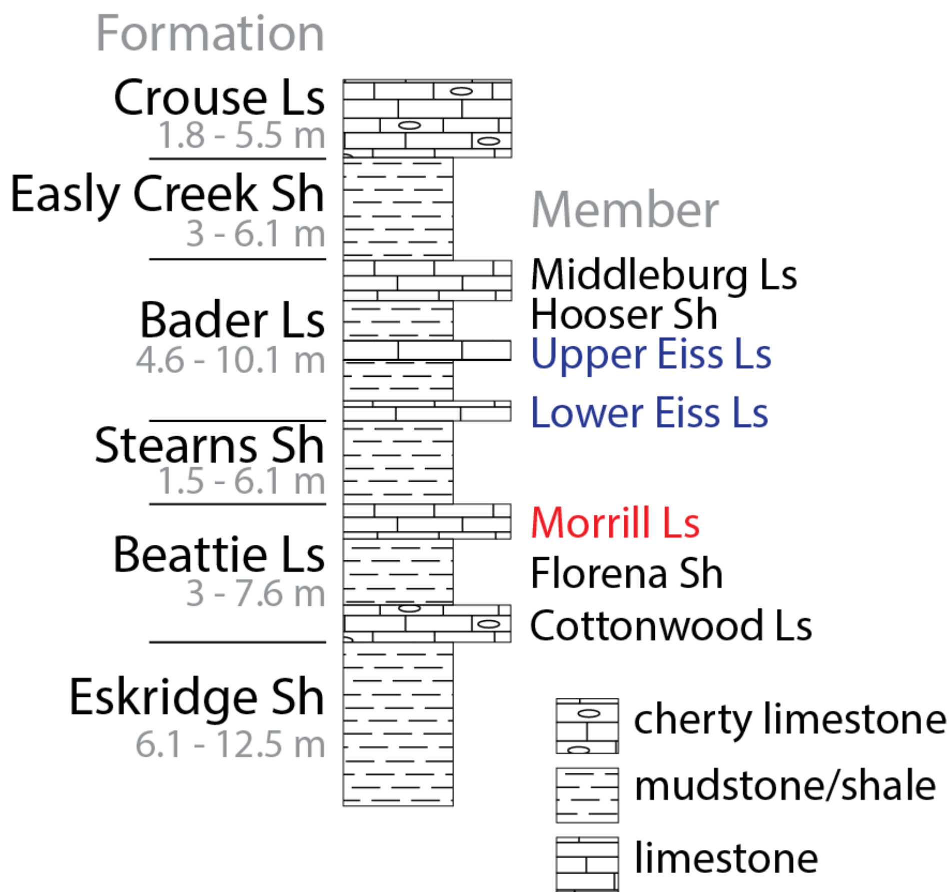

Figure 2 Stratigraphic column of bedrock units within Konza Prairie. Wells examined in this study were screened in the Upper Eiss Limestone Member (Eiss2) and Lower Eiss Limestone Member (Eiss1) of the Bader Formation, and the Morrill Limestone Member (Mor) of the Beattie Formation, Council Grove Group, Permian System. Limestone is abbreviated Ls in the figure. The range of unit thickness is shown in grey beneath each unit's name. This figure is based on Fig. 2a in Macpherson (1996).

During the summer of 2020 five new wells were installed in watershed N1B, the first to be installed in N1B. Studies previously conducted in N1B include hydrologic, biotic and abiotic, nutrient, ecological and land management studies (KNZ Data Catalog). Previous work in N4D dates to the 1990s, when 31 wells were installed. Ground and surface water chemistry data have been collected consistently since then. Research in N4D is similar to that of N1B.

Chapter 3 - Methods

For this study we sampled water from two adjacent watersheds with varying fire frequencies. Watershed N4D is burned every 4-years, with its last fire treatment on April 12, 2021. N1B is burned annually and was burned once during our sampling period, March 28, 2022. Five groundwater monitoring wells and three stream locations were sampled from N4D. Three wells 3-5Mor, 3-5-1Mor and 4-6Mor are screened in the Morrill Ls. The other two wells are screened in the Eiss Ls: 4-6Eiss1 in the Lower Eiss Ls and 4-6Eiss2 in the Upper Eiss Ls. In 2020 the first wells were constructed in N1B, five in total. Four of the five wells either did not provide sufficient water for sampling or had abnormal pH and conductivity values, attributed to contamination from well construction materials. In N1B we sampled from one monitoring well (1-1Mor, screened in the Morrill limestone) and one stream location.

We sampled every three to four weeks from November 28th, 2021, to December 2nd, 2022, thus spanning the 2022 water year. During that time, groundwater was sampled from wells 17 times and streams were sampled when they contained water. Stream samples could only be collected from the 1-1 stream sites of each watershed when the full stream reach within each was flowing. We were able to sample 1-1 stream locations in N1B and N4D five and six times, respectively. However, we sampled at 3-1 and 4-1 stream locations in N4D more frequently because they are found in places where groundwater discharges into the stream channel throughout most of the year. Groundwater age was determined by collecting water samples used to measure concentrations of sulfur hexafluoride (SF_6) and chlorofluorocarbons (CFCs). Groundwater age tracer samples were collected four times between March 2nd, 2022, and October 30th, 2022.

3.1 Field Methods

To characterize variation in groundwater and surface water composition during the 2022 water year, we collected samples from six wells and four stream locations every three to four weeks. Five of the wells and three of the surface water sites are located in watershed N4D. The remaining well and surface water site are in N1B. Surface water sampling was subject to water flow and were collected along the same location of the stream at each visit.

During sampling, we measured the depth to water (DTW) and total depth (TD) of each well using a Solinist water level meter. We then bailed each well until the saturated volume had been removed at least two times, consistent with long term data collection at the site (Macpherson 2023). Fresh sample water was drawn from the well using a bailer and emptied into a sample bottle using a bottom emptying device (BED). We filtered all water samples using 0.45 µm syringe filters and 60 mL syringes. Separate samples for anion and cation were collected in 30-60 mL plastic bottles and isotopes in 5-20 mL glass vials. All samples were labeled with the site name, date, and watershed and stored on ice in a cooler while on site.

While sampling, we measured the pH, temperature, dissolved oxygen (DO) concentration and conductivity of our water samples using Oakton PC 450 pH and conductivity probes and a Professional Series YSI Pro 2030 DO probe. Measurements were taken while the probes were submerged in sample water. All probes were calibrated before daily use and were rinsed with deionized water between wells and stream sites. Additional notes were collected such as water flow, clarity, debris and the day's weather.

In addition to these samples, during four sampling visits distributed across the 2022 water year, we collected additional samples for analysis of groundwater residence time. These samples were collected from three wells (4-6Mor, 3-5-1Mor, and 4-6Eiss2) in N4D and one well (1-

1Mor) in N1B. These sites were selected for their ability to recharge quickly and sustain enough water required for exhaustive sampling.

Atmospheric trace samples were collected in triplicate at each site and stored in 16 oz glass sample bottles with aluminum foil lined lids. To limit potential exchange between samples and the atmosphere, we collected the samples while submerged in the water being sampled. Specifically, we placed the sample bottles in a larger container and filled them both to overflowing with our bailer BED. Once the sample bottle had overflowed three times its capacity, it was capped underwater and checked for bubbles. The bottles were labeled and stored in a cooler with ice in the field and a refrigerator in the lab until analysis.

3.2 Laboratory Analysis

All samples were analyzed within a month of collection. Alkalinity and major ion concentrations were measured within a week of sample collection. We measured alkalinity initially using Gran alkalinity titrations (samples from October 31, 2021, to February 27th, 2022) with a glass burette with 0.02 N sulfuric acid titrant. Then, for the remainder of the samples, we used end-point (pH 4.5) titrations using a ThermoScientific OrionStarT910 pH Titrator with 0.02 N sulfuric acid titrant. We measured major ion concentrations (Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, F^-, Cl^-, Br^-, NO_3^-, PO_4^{2-}, SO_4^{2-}) using Thermo Scientific ICS-1100 Ion Chromatographs.

Stable water isotopes, specifically oxygen ($\delta^{18}O$) and hydrogen (δD) isotopic ratios, were measured at 0.1 and 0.5 ‰ precision, respectively, using a Picarro L-i2130 water analyzer in the Stable Isotope Mass Spectrometer Laboratory at the Kansas State University Division of Biology. Results are expressed in delta notation relative to Vienna Standard Mean Ocean Water (VSMOW).

Atmospheric age trace samples were analyzed at the University of Miami, Florida Rosenstiel School of Marine, Atmospheric, and Earth Science Tritium Laboratory using a purge-and-trap chromatograph with electron capture detection. Concentrations were provided for SF_6, CFC-12, CFC-11 and CFC-113 as age before sampling date (Appendix E). These atmospheric tracers are useful in determining age since recharge because their atmospheric concentrations are well known and have changed over time. For our groundwater we decided that SF_6 would be a better age tracer. CFC-11 and CFC-113 atmospheric concentrations have been decreasing since 1994 and CFC-12 has been decreasing since 2003, making it possible to obtain more than one recharge age. SF_6 on the other hand is steadily increasing in the atmosphere and there are no known mechanisms of deterioration. If our water is younger than 52 years old, SF_6 should provide a reliable age. From previous research we assume our groundwater was relatively young (Andrews et al. 2021). Values that were detected above current atmospheric levels of SF_6 and CFCs were considered supersaturated and not usable. To determine ages using SF_6 and CFCs we needed to calculate water recharge temperatures. We calculated recharge temperatures for days when it rained during the past four decades at Konza Prairie using data available in the Konza Data Catalog (Nippert 2023a; 2023b). We used 0.975, 0.5 and 0.025 (27.25, 13.75 and 1.5 ℃) percentiles to provide a range of possible groundwater ages.

3.3 Geochemical Modeling

We used Geochemist's workbench (GWB) geochemical modeling software (Community Edition 17.0) for speciation calculations used to assess concentrations of dissolved CO_2 and mineral saturation indices (SI). The calculations were constrained by all available measured chemistry, including field pH and temperature, major ion concentrations, and carbonate alkalinity. SI indicates whether water is supersaturated (SI>0), undersaturated (SI<0) or at equilibrium (SI=0) with respect to the surrounding minerals. We used SI to determine if our water is favored to precipitate or dissolve calcite and dolomite based on the solutions nearness to equilibrium with bedrock (Appendix C).

Chapter 4 - Results

4.1 Water Chemistry

Values measured for field parameters highlight differences between groundwater aquifers as well as differences between streams and groundwater (Appendix A, Table 1). Water samples showed variation between temperature, pH, DO and alkalinity across watersheds, and between surface and groundwater (Fig. 3 and 4). Temperature changes at surface and groundwater locations followed seasonal trends.

Following seasonal trends, groundwater was warmer than surface water in the winter and cooler in the summer in both N1B and N4D (Fig. 4E). On average in N4D, temperature (avg. 14.2 and 13.3 °C) and alkalinity (avg. 311.0 and 300.9 mg/L as $CaCO_3$) were higher in groundwater than surface water, respectively. In contrast, DO concentrations (avg. 6.1 and 8.5 mg/L) and pH values (avg. 7.2 and 7.8) were lower in groundwater than surface water, respectively (Fig. 4C). In N1B groundwater had higher on average alkalinity and lower temperature, DO and pH than surface water. Mor in N4D experienced, on average, cooler temperatures (Fig. 3F) with higher alkalinity (Fig. 3B and 4A) and DO measurements than Eiss sites. The pH of Eiss and Mor groundwater were quite similar to one another, averaging 7.2 (Fig. 3D). Between N1B and N4D, Mor in N1B on average had greater temperature (avg. 14.4 °C), DO (avg. 6.6 mg/L) and alkalinity (avg. 336.7 mg/L as $CaCO_3$). With a higher pH (avg. 7.2) in Mor at N4D.

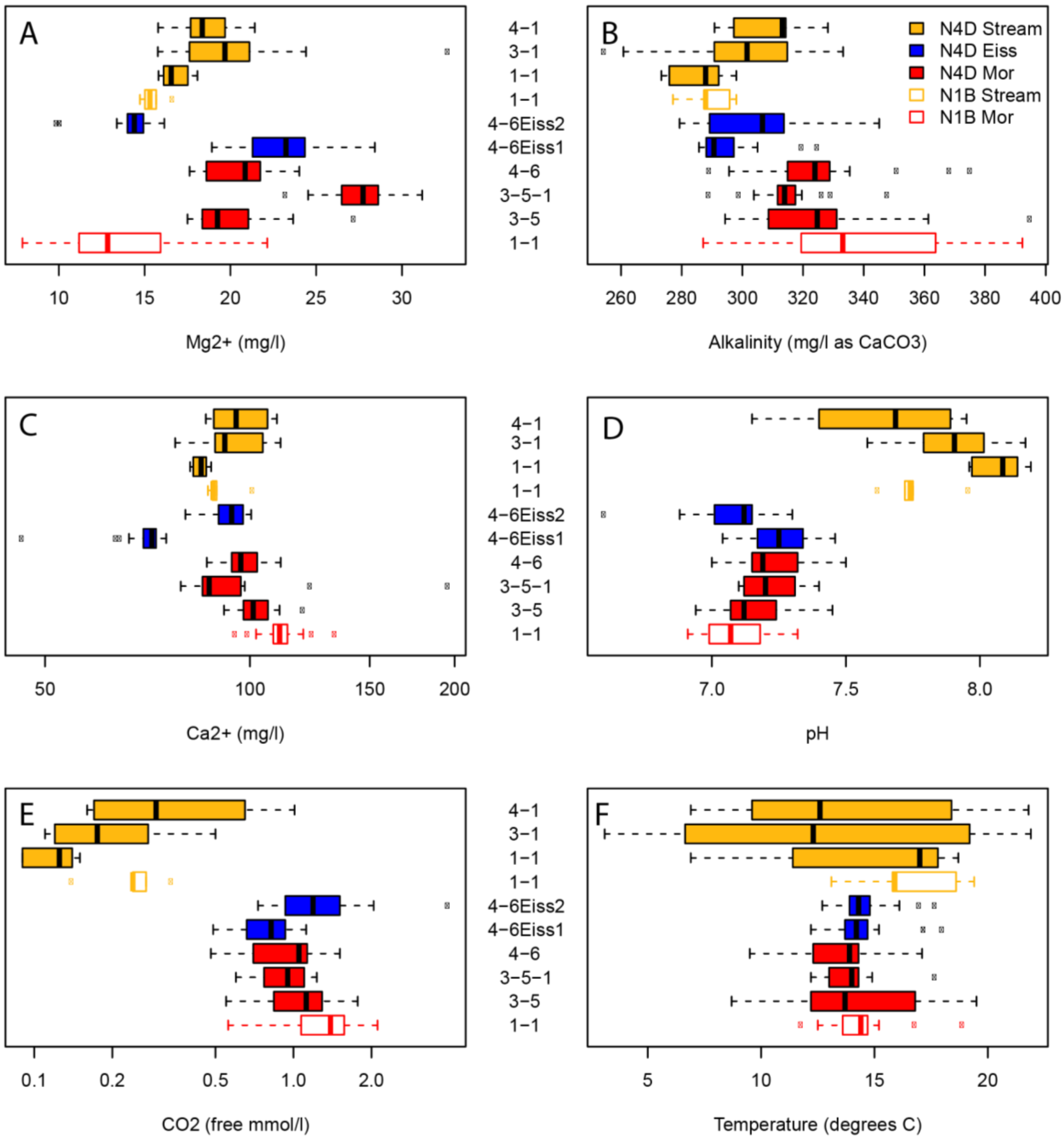

Figure 3 Boxplot data representing stream water (yellow) and groundwater from the Morrill Ls (red) and Eiss Ls (blue) in N1B (empty) and N4D (filled). Measurements of A) magnesium concentrations mg/l, B) alkalinity mg/L as $CaCO_3$, C) calcium concentrations mg/l, D) pH, E) CO_2 concentration mM, and F) temperature °C. Boxplot hinges represent the first and third quartiles with whiskers extend to 1.5 times the interquartile range. Individual points mark outlier samples that were greater or less than 1.5 times the interquartile range.

Comparison Mg^{2+}	P-Value	Significant
1-1 Mor to 3-5 Mor	<0.0001	Yes
1-1 Mor to 3-5-1 Mor	<0.0001	Yes
1-1 Mor to 4-6 Mor	<0.0002	Yes
1-1 Mor to 4-6 Eiss1	<0.0001	Yes
1-1 Mor to 4-6 Eiss2	0.2743	No
1-1 Stream N1B to 1-1 Stream N4D	0.026	Yes

Comparison Alkalinity	P-Value	Significant
1-1 Mor to 3-5 Mor	0.2346	No
1-1 Mor to 3-5-1 Mor	0.0156	Yes
1-1 Mor to 4-6 Mor	0.2415	No
1-1 Mor to 4-6 Eiss1	<0.0001	Yes
1-1 Mor to 4-6 Eiss2	0.0017	Yes
1-1 Stream N1B to 1-1 Stream N4D	0.5736	No

Comparison Ca^{2+}	P-Value	Significant
1-1 Mor to 3-5 Mor	0.0009	Yes
1-1 Mor to 3-5-1 Mor	<0.0001	Yes
1-1 Mor to 4-6 Mor	<0.0001	Yes
1-1 Mor to 4-6 Eiss1	<0.0001	Yes
1-1 Mor to 4-6 Eiss2	<0.0001	Yes
1-1 Stream N1B to 1-1 Stream N4D	0.0087	Yes

Comparison pH	P-Value	Significant
1-1 Mor to 3-5 Mor	0.074	No
1-1 Mor to 3-5-1 Mor	0.003	Yes
1-1 Mor to 4-6 Mor	0.005	Yes
1-1 Mor to 4-6 Eiss1	0.001	Yes
1-1 Mor to 4-6 Eiss2	0.912	No
1-1 Stream N1B to 1-1 Stream N4D	0.007	Yes

Comparison CO_2	P-Value	Significant
1-1 Mor to 3-5 Mor	0.0715	No
1-1 Mor to 3-5-1 Mor	0.0014	Yes
1-1 Mor to 4-6 Mor	0.003	Yes
1-1 Mor to 4-6 Eiss1	<0.0001	Yes
1-1 Mor to 4-6 Eiss2	0.3178	No
1-1 Stream N1B to 1-1 Stream N4D	0.0108	Yes

Comparison Temperature	P-Value	Significant
1-1 Mor to 3-5 Mor	0.7401	No
1-1 Mor to 3-5-1 Mor	0.2933	No
1-1 Mor to 4-6 Mor	0.1843	No
1-1 Mor to 4-6 Eiss1	0.8985	No
1-1 Mor to 4-6 Eiss2	0.7146	No
1-1 Stream N1B to 1-1 Stream N4D	0.7922	No

Table 1 Statistical significance of measured field parameters, major ions and calculated CO_2 between a single groundwater location (1-1 Mor) from N1B to all groundwater locations in N4D, as well as comparing downstream locations between watersheds. Due to a variety of samples between locations, Mann-Whitney tests were used to determine the level of significance.

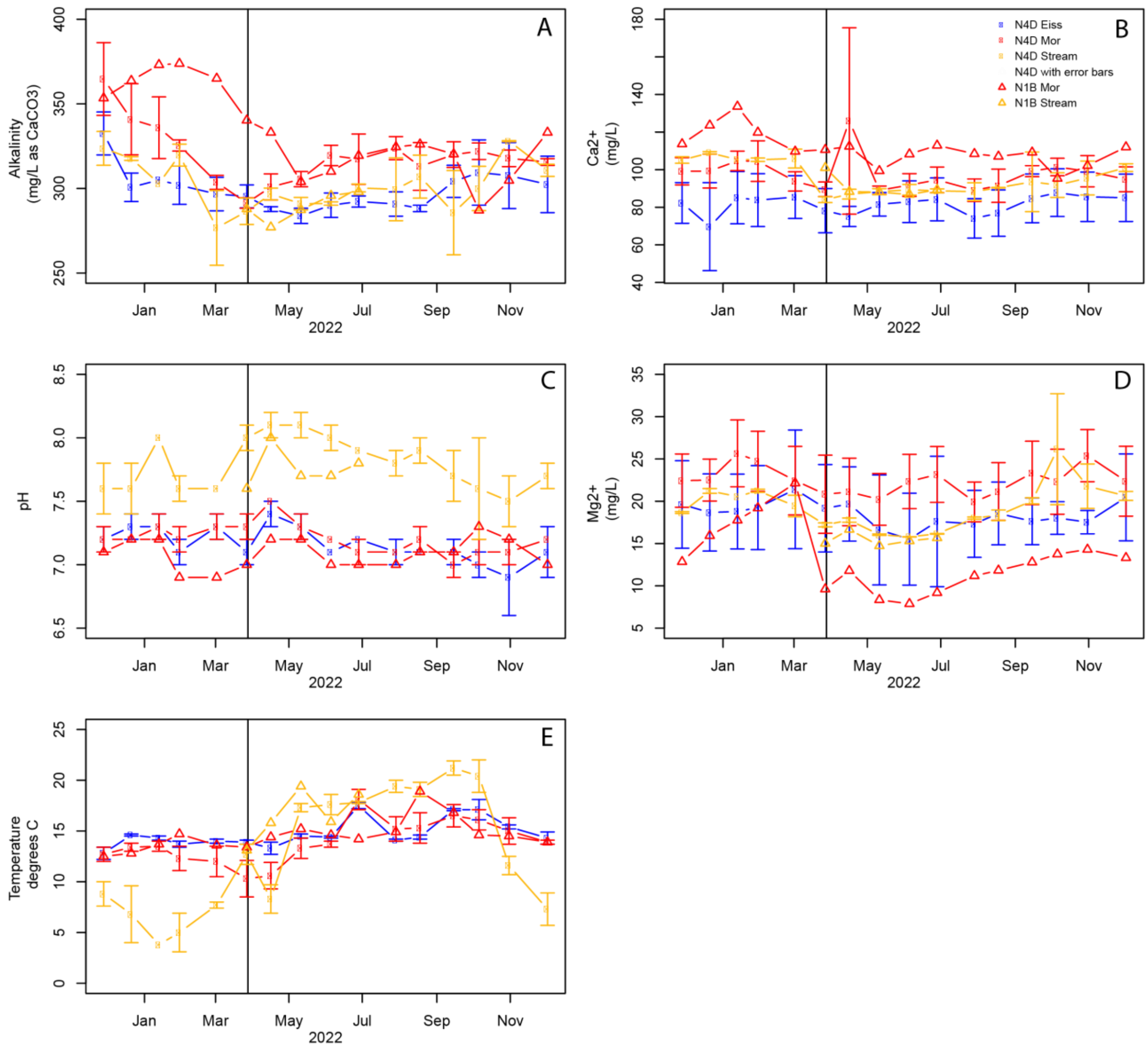

Figure 4 Timeseries plots of field parameters and major ions for groundwater and stream water. A) Alkalinity (mg/L as $CaCO_3$), B) Ca^{2+} (mg/L), C) pH, D) Mg^{2+}(mg/L) and E) temperature (°C). Averages for N4D Eiss (filled blue circles), N4D Mor (filled red circles), N4D streams (filled yellow circles), N1B Mor (open red triangles) and N1B streams (open yellow triangles). Error bars of standard deviation are provided for data points that were generated using averages. Black vertical lines indicate N1B burn date (March 28th, 2022).

The bulk chemical composition of all groundwater and stream samples were similar. The most abundant ions detected were Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, SO_4^{2-} and Cl^-. Other ions detected are not pertinent to this study, however concentrations of all ions are available in Appendix A, Tables 2 and 3. Concentrations of major ions varied slightly between groundwater Mor and Eiss, watersheds N1B and N4D, as well as surface and groundwater samples (Fig. 3 and 4). In N4D, surface water had higher concentrations of Ca^{2+} (avg. 94.1 and 90.2 mg/L) and SO_4^{2-} (avg. 37.2 and 25.8 mg/L) with lower concentrations of Mg^{2+} (avg. 18.9 and 20.6 mg/L) than groundwater, respectively (Fig. 3C and 3A). Surface and groundwater concentrations of Mg^{2+}, Ca^{2+}, and SO_4^2 in N1B were reverse of N4D. With higher on average concentrations of Ca^{2+} (avg. 111.3 and 90.7 mg/L) and SO_4^2 (avg. 21.1 and 20.7 mg/L) and lower Mg^{2+} (avg. 13.6 and 15.5 mg/L) concentrations in groundwater than surface water, respectively. When comparing Ca^{2+} and Mg^{2+}, concentrations at 1-1 streams in both watersheds, there was a significant difference between concentrations (P = 0.008 and P = 0.026, respectively) (Table 1). Mor samples in N4D had consistently higher levels of Mg^{2+} and SO_4^{2-} (Fig. 4D). Concentrations of Ca^{2+} in Mor at N4D are consistently greater (avg. 98.8 mg/L) than Eiss (avg. 81.5 mg/L) (Fig 3C and Fig. 4B). 4-6Eiss2 and 1-1Mor have very similar Mg^{2+} and Ca^{2+} concentrations. Sodium and chloride were the only ions with higher concentrations in Eiss than in Mor. Both Mg^{2+} (avg. 22.7 and 13.6 mg/L) and SO_4^2 (avg. 36.8 and 21.1 mg/L) concentrations are greater at Mor in N4D than N1B, respectively. While Ca^{2+} of Mor is lower in N4D (avg. 98.8 mg/L) than N1B (avg. 111.3 mg/L). All groundwater locations in N4D had significantly lower concentrations of Ca^{2+} when compared to the one well sampled in N1B (Table 1).

Isotope composition varied little between N4D and N1B for both groundwater and surface water (Appendix B). The oxygen ($\delta^{18}O$) and hydrogen (δD) isotope ratios of the groundwater and surface water for N4D ranged from -4.6 to -6.1‰ VSMOW for $\delta^{18}O$ and -32 to -38‰ VSMOW for δD. Groundwater and surface water $\delta^{18}O$ and δD isotope ratios of N1B ranged from -5 to -5.9 ‰ VSMOW for $\delta^{18}O$ and -34 to -37‰ VSMOW for δD. Isotope ratios measured in the surface water and groundwater samples plotted around average values expected for May and September precipitation (Fig. 5).

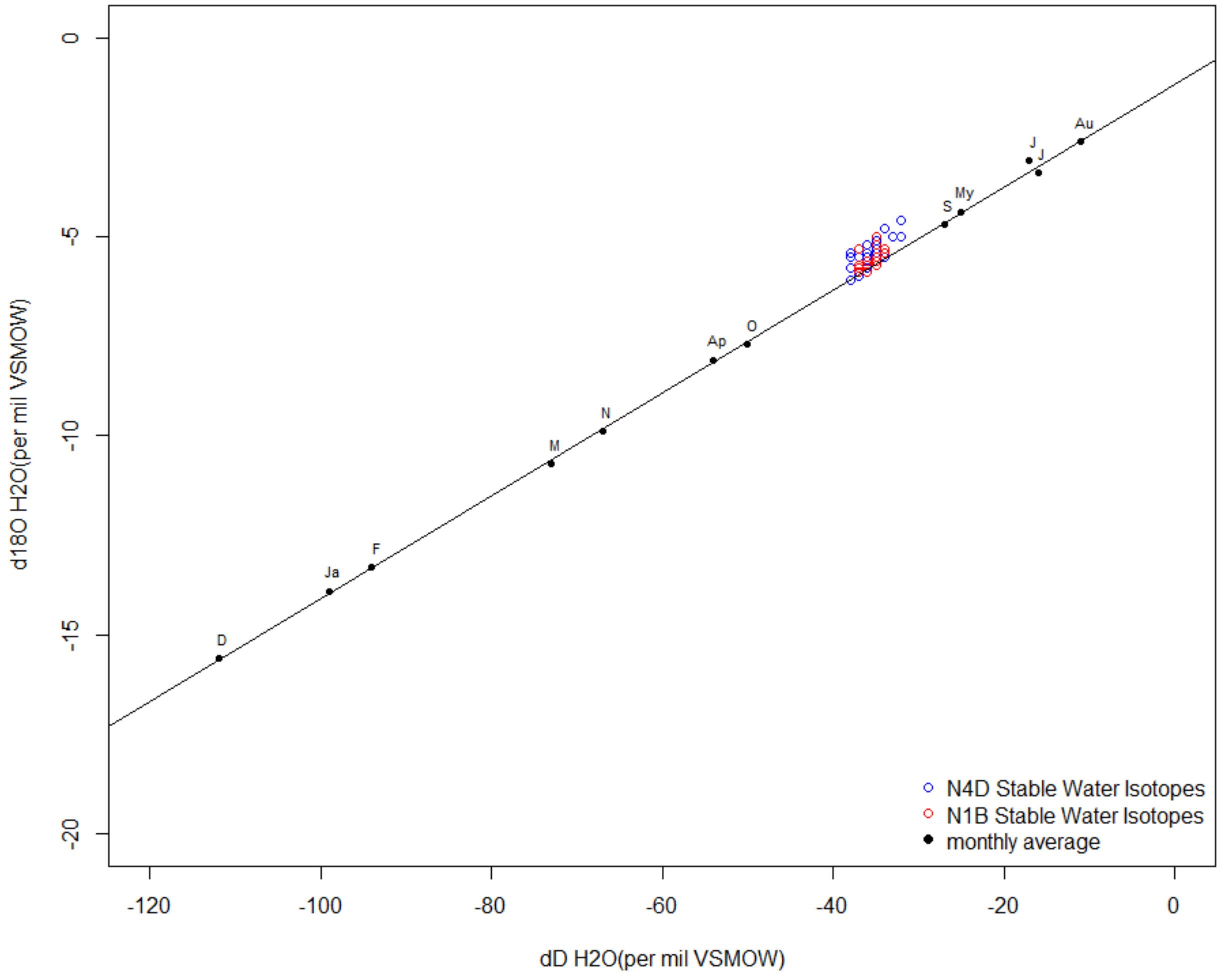

Figure 5 Variation in oxygen ($\delta^{18}O$) and hydrogen (δD) isotope ratios of groundwater and surface water in watersheds N4D (blue circle) and N1B (red circle) at Konza Prairie. Monthly average isotope values collected using the University of Utah Online Isotopes in Precipitation Calculator are shown as black circles. Both are plotted along a black line of best fit from monthly averages.

Based on our SI calculations performed using GWB (Appendix C), stream water in both watersheds favored precipitation of calcite and dolomite and was further from equilibrium than groundwater. The potential for surface water to precipitate calcite and dolomite increases in the summer months (Fig. 6A and 6B). Precipitation of calcite and dolomite was also favored throughout groundwater samples in N1B and N4D although one sample collected from well 4-6Eiss2 indicated that dissolution of calcite (SI= -0.28) and dolomite (SI= -0.27) were favored (October 30, 2022).

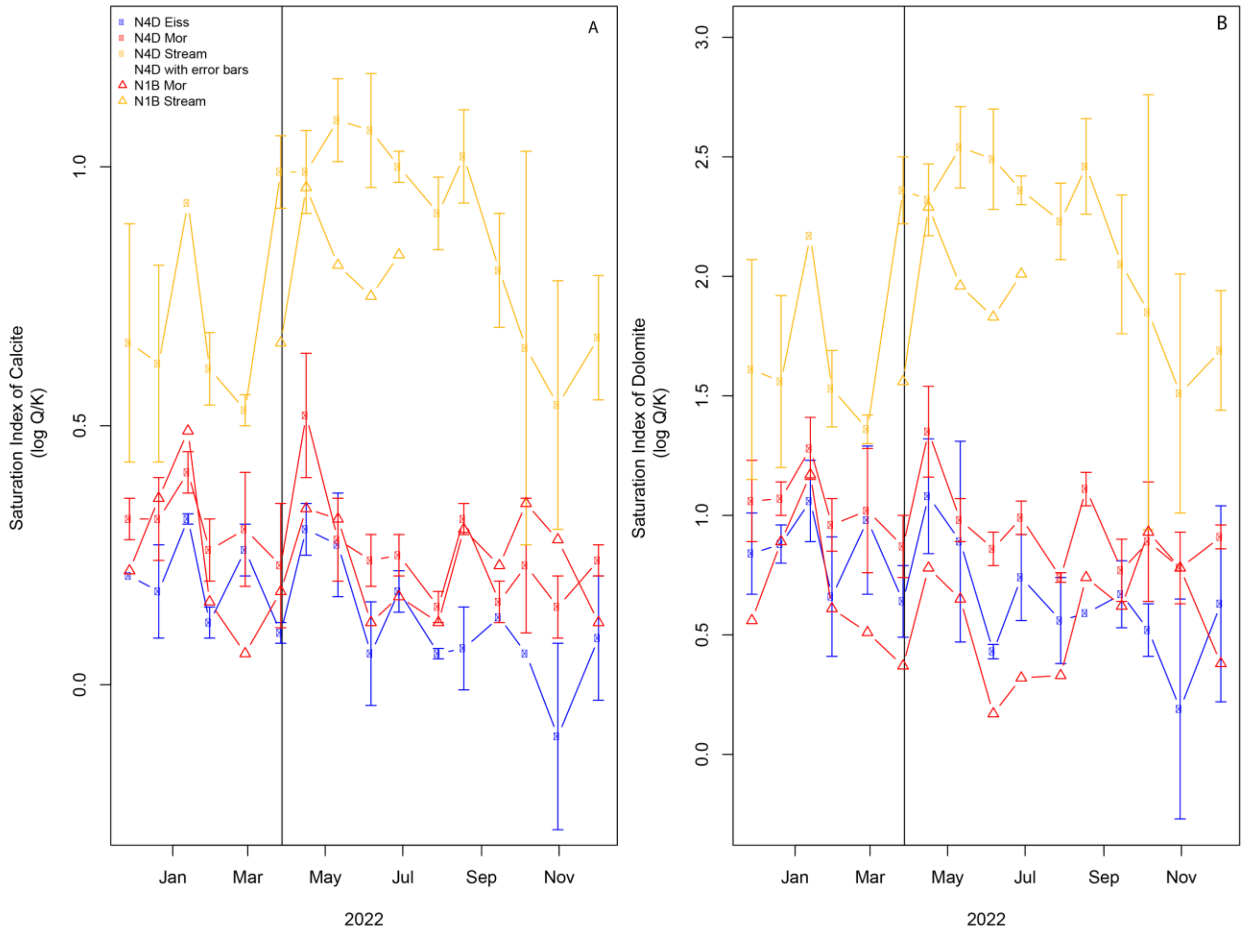

Figure 6 Saturation index over time of calcite (A) and dolomite (B for N1B (empty triangles) and N4D (filled circles) from streams (yellow) and wells (red and blue) sites. Error bars of standard deviation are provided for data points that were generated using averages. Black vertical lines indicate N1B burn date (March 28th, 2022).

4.2 Watershed CO_2

Calculated CO_2 concentrations between N4D and N1B varied between groundwater and surface water locations (Fig. 3E). Seasonal trends in CO_2 were observed predominately in surface water but also at some groundwater locations (Fig. 7). In both watersheds, groundwater generally had much more dissolved CO_2 than surface water. In N4D, surface water and groundwater dissolved CO_2 concentrations averaged 0.3 and 1.1 mM, respectively and in N1B they averaged 0.2 and 1.5 mM. Calculated CO_2 concentrations decrease with distance downstream in watershed N4D. CO_2 concentrations averaged 0.4, 0.2 and 0.1 mM at locations 4-1, 3-1, and 1-1 respectively, while the stream was flowing continuously along the watershed reach. In contrast to the value measured at 1-1 in N4D, the value at location 1-1 in N1B measured 0.2mM (Appendix D). Stream CO_2 calculations in N4D dipped in the spring and summer months and rose again in the fall and winter months (Fig. 7). Stream CO_2 calculations in N1B were initially high but once the watershed was burned dropped, to equal those seen in N4D after which they steadily increased until late summer.

Groundwater Mor and Eiss at N4D had similar CO_2 concentrations, both averaging at 1.1 mM 1-1Mor in watershed N1B had the highest concentrations of CO_2 (2.2 mM) for wells in the Mor Ls. 4-6Eiss2 had the largest concentration of CO_2 (3.9 mM) for Eiss and overall. Using Mann-Whitney test we found there was no significant difference between CO_2 in N4D wells or between 1-1Mor in N1B and 3-5 Mor in N4D (P =0.071). There are significant differences between 1-1Mor in N1B and 4-6Mor in N4D (P=0.003) and 1-1Mor N1B and 3-5-1Mor N4D (P =0.0014) (Table 2). Groundwater locations in N4D see a steady increase in calculated CO_2 concentrations between early May and October. Site 1-1Mor in N1B saw a large jump in calculated CO_2 concentrations between January and February, followed by a gradual decline, with another increase in May to June with another gradual decline until September (Fig. 7).

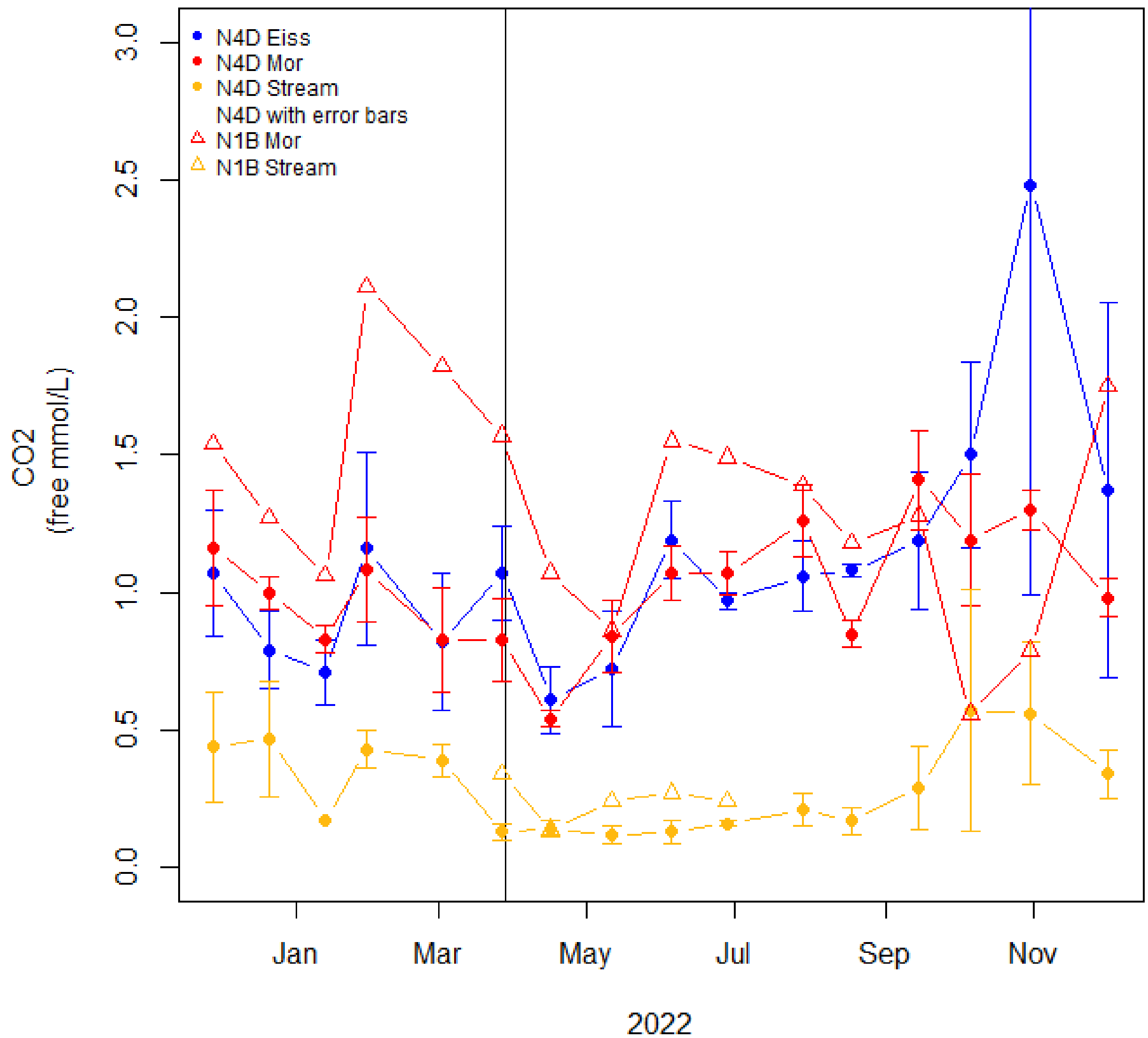

Figure 7 Changes in CO_2 concentrations at groundwater (yellow) and surface water (blue and red) collection sites in N1B (empty triangle) and N4D (filled circle). Error bars of standard deviation are provided for data points that were generated using averages of CO_2 concentrations. Error bar for N4D Eiss in November is truncated to better display the rest of the data. Black vertical line between March and May signifies the date N1B was burned during the study period (March 28th, 2022).

4.3 Atmospheric age tracers

Assuming a recharge temperature of 27.25 °C, our calculations indicate that SF_6 and CFCs would be supersaturated in our samples. At 1.5 °C, 3-5-1 Mor averaged 30 years old, while the three remaining locations averaged 16-17 years old. At the average temperature (avg. 13.7

°C) 3-5-1 Mor averaged 22 years old. For sites 4-6 Mor and 4-6 Eiss2 in N4D the average age since recharge is 7 years and at 1-1Mor in N1B recharge is every 6 years on average (Fig. 8A). Ages obtained using recharge temperature 13.7 °C are more credible because the average annual air temperature at Konza Prairie is 13.4 °C. Residence time for 13.7 °C and 1.5 °C can be found in Appendix E.

CFCs indicate much older groundwater ages. Since CFCs are in decline in the atmosphere it is possible to obtain more than one age. While CFCs were still collected, we did not depend on their ages to represent the groundwater age. However, our different age tracers (CFCs and SF_6) do predict 3-5-1 Mor to be older, and 4-6 Mor, 4-6 Eiss2 and 1-1 Mor N1B to be younger and closer in age (Fig. 8). Our age tracer data also indicates that our groundwater mixes throughout the year creating variability in groundwater age (Fig. 9).

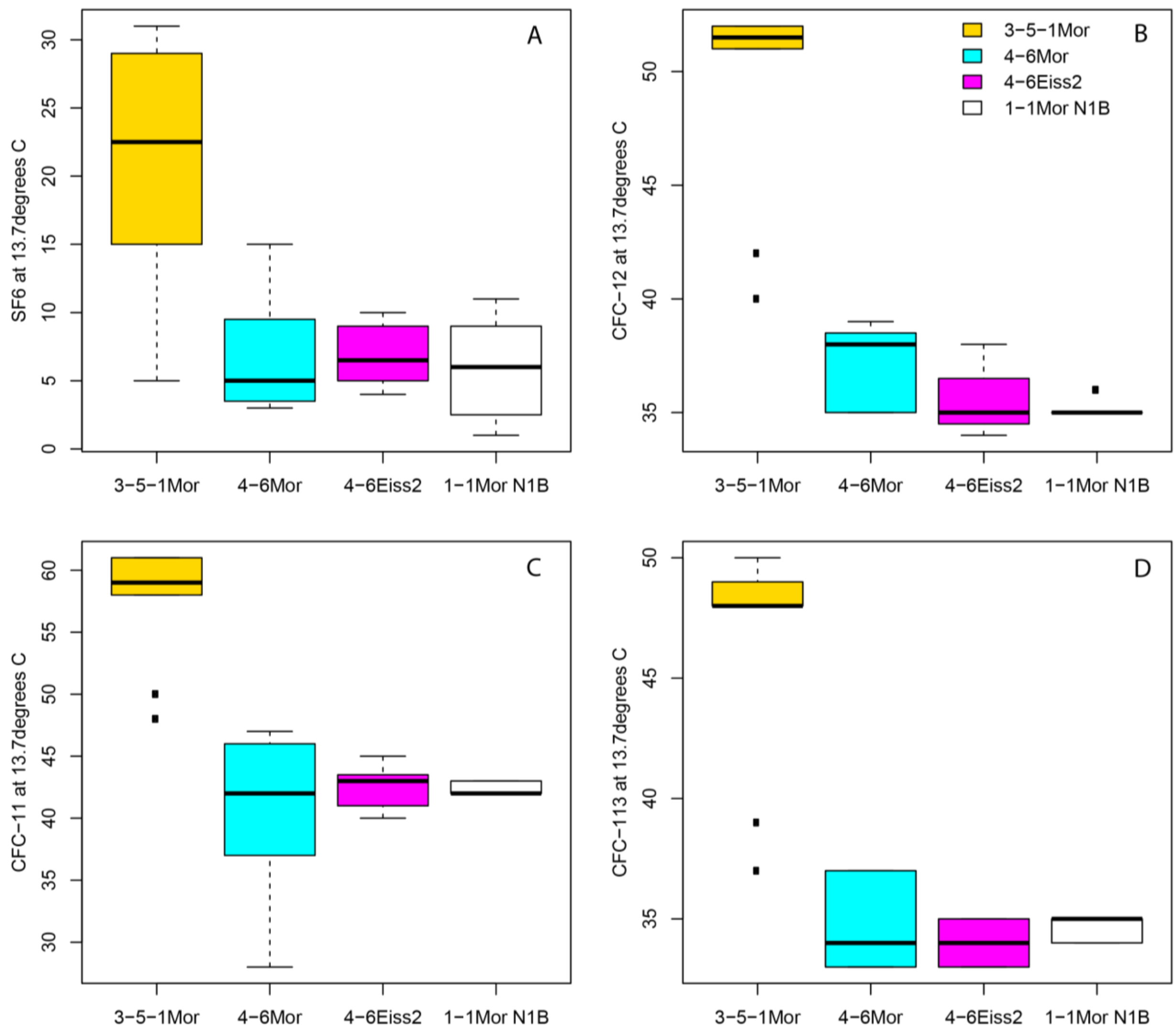

Figure 8 Boxplots of residence time determined at 13.7 °C by A) SF_6, B) CFC-12, D) CFC-11 and D) CFC-113 at four groundwater sampling locations. 3-5-1Mor (yellow), 4-6Mor (cyan) and 4-6Eiss2 (magenta) located in N4D and 1-1Mor (white) located in N1B. Boxplot hinges represent the first and third quartiles with whiskers extend to 1.5 times the interquartile range. Individual points mark outlier samples that were greater or less than 1.5 times the interquartile range.

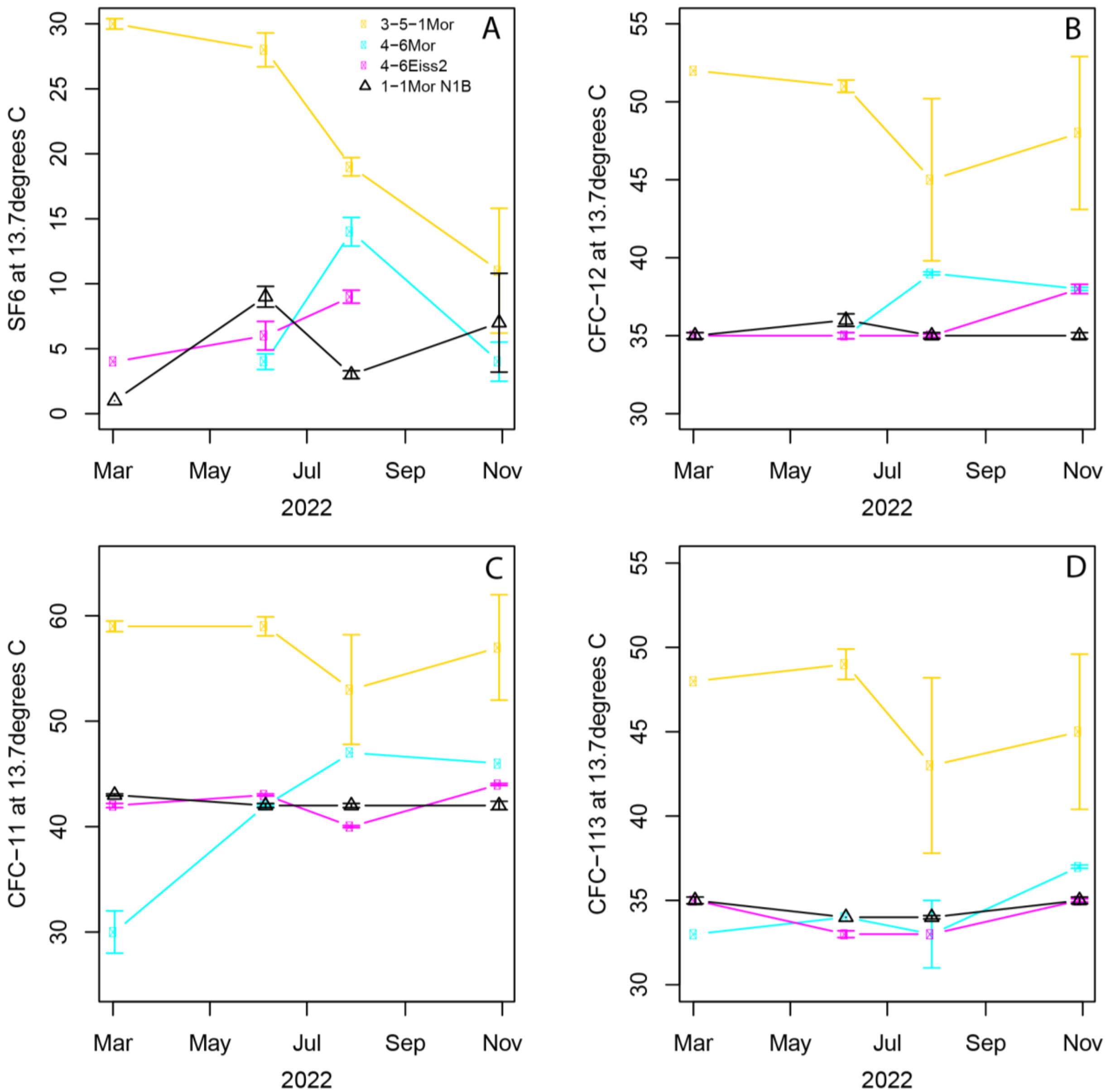

Figure 9 Groundwater residence time at 3-5-1Mor N4D (yellow), 4-6Mor N4D (cyan), 4-6Eiss2 N4D (magenta) and 1-1Mor N1B (black) over the 2022 water year determined at 13.7 °C by A) SF_6, B) CFC-12, C) CFC-11, and D) CFC-113. Averages are given as scatter points and error bars indicate standard deviation.

Chapter 5 - Discussion

The overall goal of this study was to understand the implications of woody encroachment on groundwater chemistry and residence time. To do this we examined chemical concentrations of surface water and groundwater in a more encroachment watershed (N4D) and a less encroached watershed (N1B). To determine residence time, we collected atmospheric tracers. Lastly, we focused on the fate of CO_2 in both watersheds.

Groundwater in N1B had on average higher Ca^{2+} and alkalinity and lower temperature, pH and Mg^{2+} than N4D groundwater (Figs. 3 and 4). Both N4D and N1B groundwater favor precipitation of dolomite and calcite and follow similar trends throughout the sample period (Fig. 6). Dolomite was less favorable in N1B for most of the sample year. As Ca^{2+} and alkalinity peak and dip so does CO_2 in N1B. This pattern occurred less for groundwater in N4D. To better understand how impacts of woody encroachment may be contributing to these differences, we created a simple CO_2 budget to estimate how much CO_2 is added to water during recharge and how much is consumed by mineral weathering in the soil and subsurface of each watershed.

5.1 CO_2 consumed by weathering

We used two approaches to estimate the amount of CO_2 consumed by weathering. For the first approach we calculated CO_2 consumed using chemical reaction equations to determine how much CO_2 would be taken up during dolomite (Eq. 1) and calcite (Eq. 2) dissolution and combined these results (Eq. 3). Dolomite and calcite weather with CO_2 according to the following reactions:

$$\text{Dolomite} + 2\,CO_2\,(aq) + 2\,H_2O \leftrightarrow Ca^{2+} + Mg^{2+} + 4\,HCO_3^- \qquad \text{(Reaction 1)}$$

$$\text{Calcite} + CO_2\,(aq) + H_2O \leftrightarrow Ca^{2+} + 2\,HCO_3^- \qquad \text{(Reaction 2)}$$

Two moles of Mg^{2+} are generated per mole of dolomite consumed (reaction 1). Thus, we can estimate moles of dolomite consumed per liter of water based on the concentration of Mg^{2+}:

$$\text{Dolomite } CO_2 = 2(Mg^{2+}) \qquad \text{(Eq. 1)}$$

where parentheses represent molar concentration. Similarly, we can estimate calcite dissolution based on Ca^{2+} concentration, but we need to account for the Ca^{2+} released by dolomite dissolution. We can do this by recognizing that, per mole of dolomite, one mole of Ca^{2+} and one mole of Mg^{2+} are released (reaction 1). Thus, by subtracting the molar concentration of Mg^{2+} from Ca^{2+} concentration, we isolate Ca^{2+} released by calcite:

$$\text{Calcite } CO_2 = (Ca^{2+}) - (Mg^{2+}) \qquad \text{(Eq. 2)}$$

Summing the amounts of CO_2 from equations 1 and 2 gives an estimate of the total amount of CO_2 consumed by carbonate bedrock weathering per liter of groundwater:

$$CO_2 \text{ Consumed} = \text{Dolomite } CO_2 + \text{Calcite } CO_2 \qquad \text{(Eq. 3)}$$

Based on Macpherson et al (2008) dolomite or high magnesium calcite is not abundant in the bedrock and may be unlikely as the source of dissolved Mg^{2+}. Instead, they interpreted that the Mg^{2+} originates from ion exchange in the mudrock layers. Specifically, some of the Ca^{2+} generated by calcite weathering in the limestone exchanges with Mg^{2+} in clay minerals of the mudrocks:

$$\text{Mg-clay} + Ca^{2+} \leftrightarrow \text{Ca-clay} + Mg^{2+} \qquad \text{(Reaction 3)}$$

Given that Ca^{2+} and Mg^{2+} would exchange in a one-to-one ratio, we can simply use the molar sum of Ca^{2+} and Mg^{2+} as an estimate of the amount of CO_2 consumed by calcite weathering per liter of groundwater:

$$CO_2 \text{ Consumed} = Ca^{2+} + Mg^{2+} \qquad \text{(Eq. 4)}$$

Both approaches give equivalent answers in terms of the amounts of CO_2 consumed by carbonate mineral weathering as well as the amount of alkalinity measured. Thus, the question of which is more representative of our study area is irrelevant to our analysis. Importantly, when we compare the amount to alkalinity predicted by our weathering model to the concentrations we measured, we find excellent agreement (Fig. 10). Thus, our calculations appear to account well for the weathering history of the water samples.

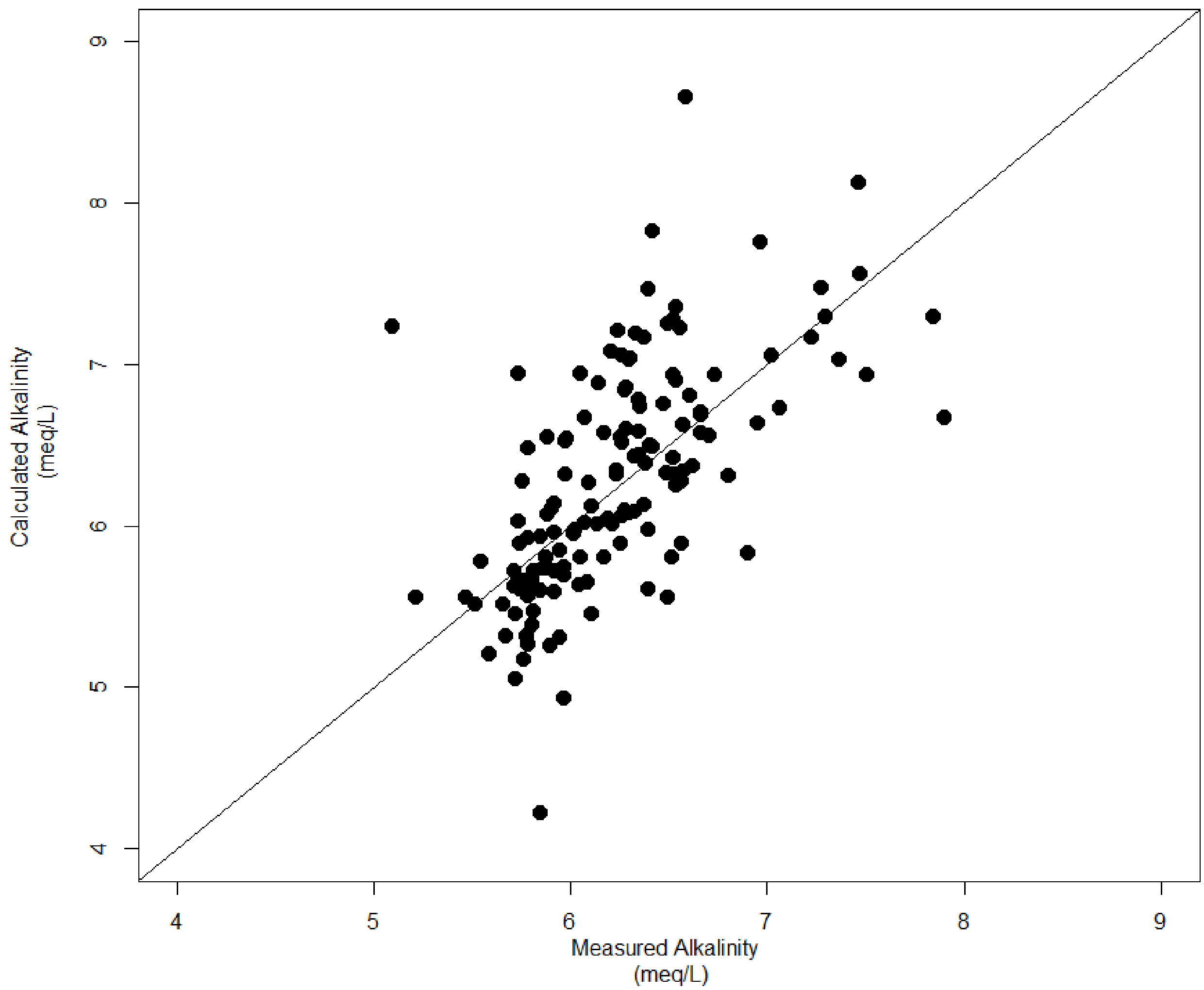

Figure 10 Scatterplot of alkalinity concentrations measured from water samples and calculated alkalinity using consumed CO_2 concentrations determined from our water samples, with a 1:1 line. Outliers may be attributed to a rapid change in alkalinity concentration during sampling and before analysis.

5.2 CO_2 added per liter of recharge water

If we assume that mineral weathering is the primary sink for CO_2 added to recharge water in the watersheds and that little CO_2 is added to the water once it moves into the bedrock, then we can estimate the total CO_2 added per L of recharge as:

$$CO_2 \text{ current} + CO_2 \text{ weathered} = CO_2 \text{ recharge} \quad \text{(Eq. 5)}$$

Using all groundwater Mor samples in N4D and N1B we estimated that the average total amount of soil CO_2 added per liter of recharge is 4.4 and 4.8 mM, respectively. On average in groundwater from wells in the Mor at N4D and N1B, 3.3 mM per liter (~75 %) and 3.3 mM per liter (~68 %) of CO_2 was consumed by bedrock weathering (Fig. 11). These results show differences in carbonate weathering between more and less encroached watersheds. While average concentrations are the same in both N1B and N4D, percentage of CO_2 consumed by weathering is greater in N4D Increased abundances of course roots can enhance preferential flow paths and leave more bedrock exposed to water, potentially increasing the amount of bedrock weathering.

Comparison Dissolved CO_2	P-Value	Significant
1-1 Mor to 3-5 Mor	0.0715	No
1-1 Mor to 3-5-1 Mor	0.0014	Yes
1-1 Mor to 4-6 Mor	0.003	Yes
1-1 Mor to 4-6 Eiss1	<0.0001	Yes
1-1 Mor to 4-6 Eiss2	0.3178	No
1-1 Stream N1B to 1-1 Stream N4D	0.0108	Yes
N1B to N4D of Groundwater	0.0173	Yes

Comparison Consumed CO_2	P-Value	Significant
1-1 Mor to 3-5 Mor	0.5177	No
1-1 Mor to 3-5-1 Mor	0.4134	No
1-1 Mor to 4-6 Mor	0.8919	No
1-1 Mor to 4-6 Eiss1	<0.0001	Yes
1-1 Mor to 4-6 Eiss2	<0.0002	Yes
1-1 Stream N1B to 1-1 Stream N4D	0.1255	No
N1B to N4D of Groundwater	0.8316	No

Comparison Soil CO_2	P-Value	Significant
1-1 Mor to 3-5 Mor	0.2451	No
1-1 Mor to 3-5-1 Mor	0.073	No
1-1 Mor to 4-6 Mor	0.0106	Yes
1-1 Mor to 4-6 Eiss1	<0.0001	Yes
1-1 Mor to 4-6 Eiss2	0.0145	Yes
1-1 Stream N1B to 1-1 Stream N4D	0.0043	Yes
N1B to N4D of Groundwater	0.0307	Yes

Comparison Outgassed CO_2	P-Value	Significant
1-1 Stream N1B to 1-1 Stream N4D	0.1775	No

Table 2 Statistical significance comparing consumed CO_2 and soil CO_2 added at recharge at groundwater location 1-1 Mor from N1B to all groundwater locations in N4D, as well as comparing downstream locations between watersheds. Comparing CO_2 outgassed along downstream locations in N1B and N4D. As well as statistical significance between groundwater averaged groundwater locations (3-5 Mor, 3-5-1 Mor, 4-6 Mor and 4-6 Eiss2) in N4D and one groundwater location (1-1 Mor) in N1B. Due to a variety of samples between locations, Mann-Whitney tests were used to determine the level of significance.

We originally anticipated that watersheds experiencing woody encroachment would have higher concentrations of CO_2. Instead, we found that watersheds that are less encroached have higher concentrations of groundwater CO_2. Our original thought process was that woody roots create deeper pathways and would amass more CO_2 by increased bedrock interactions. Given our data set, less encroached areas retain more CO_2.

In the more encroached watershed, where we saw less groundwater CO_2, increased abundances of course roots can enhance preferential flow paths and allow water to pass more quickly into the bedrock than in the less encroached watershed, potentially increasing the flux of water through the subsurface in the bedrock. Changes in water flux have the potential to alter concentrations, either by diluting or concentrating solutes, and thus have the potential to explain differences we see between watersheds. However, our groundwater residence time analysis does not reveal any clear differences between watersheds. Residence time mostly seems to vary with the geological unit and location within each watershed. Nonetheless, this possibility warrants further research, given the large degree of uncertainty in our residence time data.

As a second possibility, we hypothesize that differences in CO_2 inputs may simply reflect how rapidly the water passes through the soils of each watershed. Higher root abundances in the more encroached watershed could allow more rapid transmission of recharge water into the subsurface, as noted above. Consequently, carbonic acid that forms as soil CO_2 is added to the water has less opportunity to react and equilibrate with carbonate minerals in the soil in the more encroached watershed, which shifts some of the weathering down into the bedrock. Production of CO_2 in the bedrock is likely limited relative to the soil given that the organic matter in the bedrock is ancient. Therefore, CO_2 consumed by mineral buffering in the bedrock is not necessarily able to be replaced. In contrast, in the less encroached watershed, lower soil permeability would increase the residence time of soil water and increase the likelihood that the soil water can equilibrate with carbonate minerals before entering the subsurface. Because soil gas-phases have high partial pressures of CO_2, any CO_2 that is consumed by weathering there can potentially be resupplied by the gas phase. As the water then migrates through the subsurface, its CO_2 concentration would be constant if it already equilibrated with carbonate minerals in the soil. The result is then groundwater that contains more dissolved CO_2, consistent with the differences in groundwater composition that we measured, higher in the less encroached watershed and lower in the more encroached watershed.

5.3 CO_2 Emitted from Streams

While carbonate weathering has the potential to consume more than 70 % of CO_2 present during recharge, some CO_2 is still expected to be lost to the atmosphere during discharge into streams. Understanding CO_2 loss through streams can provide insight into how outgassing may change depending on the amount of below ground weathering due to woody encroachment, or lack thereof. To determine the impact woody encroachment has on CO_2 lost through discharge into our streams we used calculated CO_2 concentrations from streams and groundwater sources in equation 6.

$$CO_2 \text{ loss} = (\text{groundwater } CO_{2\,(aq)}) - (\text{stream } CO_{2(aq)}) \qquad \text{(Eq. 6)}$$

Of CO_2 not consumed by bedrock weathering, it is estimated about 16 % and 10 % is lost through streams in N4D and N1B, correspondingly (Fig. 11). Leaving an estimate 9 % in N4D, and 10 % in N1B, to outgas further downstream of the surface sites focused on in this study. The less encroached watershed consumed less CO_2 by process of bedrock weathering while emitting more CO_2 from surface sites, than the more encroached watershed.

CO_2 loss through streams will increase pH of the stream (Fig. 3D and 3E). As pH increases, the stream will favor the precipitation of dolomite and calcite, which is consistent with our measured pH values and calculated saturation indices for carbonate minerals.

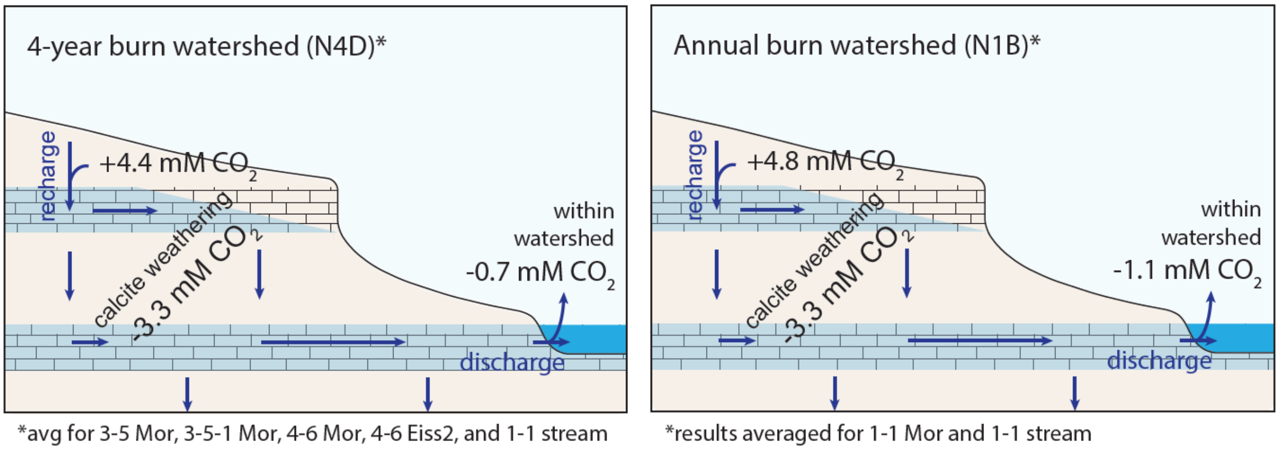

Figure 11 Soil CO_2 is carried to groundwater during recharge, where it can be consumed by chemical weathering. CO_2 discharge has the potential to be lost to the atmosphere. For N4D averages for 3-5Mor, 3-5-1Mor, 4-6Mor, 1-1stream and 1-1stream were used. We estimate that in N4D 75 % of CO_2 is consumed through chemical weathering and 16 % is lost at surface sites. For N1B averages for 1-1Mor and 1-1 Stream were used. In N1B we estimate that 68 % of CO_2 is consumed through chemical weathering and 22 % is lost at surface sites.

5.4 Comparison to other systems

An environment comparable to Konza Prairie is Edwards Plateau, a semi-arid karst environment in west-central Texas. Edwards Plateau resembles that of the Konza Prairie in they share similar karst geology, the streams are predominantly composed of groundwater, and they are both experiencing some woody encroachment (Wilcox and Huang 2010). Studies in Edwards Plateau include effects by woody encroachment on subsurface porosity, groundwater recharge and changes to stream flow. One of these studies concluded that in Edwards Plateau bedrock below woody plants has much higher permeability and can increase over time (Leite et al. 2023). This finding is consistent with our interpretation that woody encroachment is decreasing soil water residence time and driving carbonate weathering to increasingly occur below the soil profile.

Additionally, with increased woody encroachment, Wilcox and Huang, (2010), documented an increase in groundwater and stream water flow, ultimately leading to less surface runoff. Studies examining the relationship between woody encroachment and stream flow loss at Konza Prairie further support those of Wilcox and Huang (2019). Findings by Keen et al., (2022), and Dodds et al., (2023) found an increase in woody vegetation over time accounts for stream loss as well. Both, noting that streamflow is influenced by groundwater that is being affected by woody vegetation. A more recent study by Sadayappan, (2023), further confirms woody encroachment at Konza Prairie is reducing stream flow. Our hypothesis agrees, that preferential flow paths created by woody encroachment is pushing water deeper into the subsurface by driving weathering deeper

Another study at Edwards Plateau removed woody vegetation and based on regression analysis the streamflow was expected to increase 46 mm annually after woody removal (Huang et al. 2006). In other environments, as well as at Konza Prairie, where woody vegetation was removed streamflow did not rebound (Dugas, Hicks, and Wright 1998; Wilcox 2002; Huang et al. 2006; Dodds et al. 2023). At Konza Prairie woody vegetation was removed outside the riparian area with the expectation that stream flow would rebound. Woody vegetation uses more water via transpiration and can access deeper sources of water than grasses, so by removing woody vegetation more water would be available for stream flow. Dodds et al., (2023), did not observe a change in stream flow and attributed this to woody encroachments' ability to permanently change soil structure and preferential flow paths. Consistent with observations made in Edwards Plateau, that as woody plants die the leave behind decaying roots that increase preferential flow (Leite et al. 2023).

Chapter 6 - Concluding Remarks

The subsurface effects by woody encroachment are not well understood despite the possible implications for bedrock weathering and permeability, water quality and stream flow. In this study we used geochemical data collected from groundwater and stream locations during the 2022 water year to create a CO_2 budget for two watersheds with varying degrees of woody encroachment. Our results indicate that woody encroachment is altering soil CO_2 at recharge by modifying soil hydraulic properties which in turn is changing groundwater CO_2 levels. In our less encroached watershed where we hypothesize soil residence time is longer, the potential for increased bedrock weathering is lower. As opposed to our more encroached watershed where water can move quicker, with increased permeability by woody roots, and thus drive bedrock weathering. Even though our atmospheric tracer data did not indicate differences between watersheds, it still showed a relatively young residence age of our groundwater. These results, combined with our observation that the groundwater in our study area is largely equilibrated with carbonate minerals, reflect how rapidly carbonate weathering occurs in karst environments. Taking all the above into account we would expect to see an increase in bedrock weathering across areas experiencing woody encroachment.

Our CO_2 results indicate potential differences in soil residence time between areas with varying degrees of woody encroachment. We hypothesis that the effect woody encroachment has on soil permeability is contributing to stream flow loss. By increasing flow paths and shortening soil residence time woody encroachment is driving recharge water and weathering deeper into the subsurface. Effectively, shifting subsurface flow and changing where soil water is direct. If recharging occurs in deeper groundwater, it could potentially bypass groundwater that is feeding into streams.

Additionally, our estimates show the more encroached watershed consumed a higher percentage (75 %) of CO_2 added by soil recharge by process of bedrock weathering. Followed closely by the less encroached watershed that consumed (68 %) of CO_2 added by soil recharge. Loss of CO_2 through outgassing along streams was much less. CO_2 loss was impacted by surface temperature and influenced the pH and saturation indices of stream water. Ultimately, CO_2 lost through streams is added back into the atmosphere and can contribute to global climate change.

Once grasslands are depleted by woody encroachment there is little hope to restore those grasslands. Bedrock weathering by woody encroachment is irreversible and is a strong component of ecosystem engineering. As we lose our natural grasslands to woody encroachment, it is important to understand this process as it has larger implications for ecohydrological dynamics as well as the ability to alter global atmospheric CO_2 concentrations.

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Appendix A - Geochemical Results

Table 1 Field measurement data for groundwater and surface water sites. Units for DO are mg/l, T are °C, conductivity are microS/cm and alkalinity are meq/l.

Site	Watershed	Date	DO	pH	Temp (°C)	Conductivity	Alkalinity
1-1 Mor	N1B	10/31/2021	7.10	7.08	11.80	841.40	7.84
1-1 Mor	N1B	11/28/2021	9.30	7.06	12.50	824.50	7.06
1-1 Mor	N1B	12/21/2021		7.15	12.80	779.70	7.27
1-1 Mor	N1B	1/13/2022	6.00	7.23	13.70	821.10	7.46
1-1 Mor	N1B	1/30/2022		6.93	14.70	740.50	7.47
1-1 Mor	N1B	2/27/2022	4.60	6.91	13.60	758.90	7.29
1-1 Mor	N1B	3/27/2022	2.60	7.03	13.40	606.30	6.80
1-1 Mor	N1B	4/16/2022		7.18	14.40	659.40	6.66
1-1 Mor	N1B	5/11/2022		7.23	15.20	546.00	6.08
1-1 Mor	N1B	6/6/2022	6.70	6.99	14.60	627.00	6.19
1-1 Mor	N1B	6/28/2022		7.02	14.20	484.40	6.38
1-1 Mor	N1B	7/29/2022	6.20	6.98	14.90	620.90	6.48
1-1 Mor	N1B	8/18/2022	6.60	7.10	18.90	633.60	6.52
1-1 Mor	N1B	9/15/2022	6.70	7.07	16.80	644.20	6.40
1-1 Mor	N1B	10/6/2022	7.80	7.32	14.60	539.50	5.74
1-1 Mor	N1B	10/31/2022	7.50	7.20	14.50	598.30	6.09
1-1 Mor	N1B	12/2/2022	8.70	6.97	13.90	657.60	6.66
1-1 Stream	N1B	3/27/2022	9.8	7.62	13.10	566.00	5.75
1-1 Stream	N1B	4/16/2022		7.96	15.80	616.50	5.54
1-1 Stream	N1B	5/11/2022		7.74	19.40	535.00	5.74
1-1 Stream	N1B	6/6/2022	8.1	7.72	15.90	605.90	5.91
1-1 Stream	N1B	6/28/2022		7.75	18.60	506.00	5.96
3-5 Mor	N4D	10/31/2021	12	7.10	15.20	779.90	6.96
3-5 Mor	N4D	11/28/2021	12.8	7.10	13.70	888.90	7.90
3-5 Mor	N4D	12/21/2021		7.26	13.30	805.70	6.73

Site	Watershed	Date	DO	pH	Temp (°C)	Conductivity	Alkalinity
3-5 Mor	N4D	1/13/2022	9.2	7.24	12.80	1247.00	7.22
3-5 Mor	N4D	1/30/2022		7.12	11.90	654.30	6.41
3-5 Mor	N4D	3/2/2022	9	7.12	11.00	998.70	6.17
3-5 Mor	N4D	3/27/2022	9.3	7.31	8.70	588.80	5.91
3-5 Mor	N4D	4/16/2022		7.45	9.10	627.90	5.90
3-5 Mor	N4D	5/11/2022		7.33	12.20	588.20	6.07
3-5 Mor	N4D	6/5/2022	8.6	7.22	13.60	623.50	6.52
3-5 Mor	N4D	6/28/2022	5.2	7.07	19.50	780.80	6.34
3-5 Mor	N4D	7/29/2022	4.9	7.04	16.70	642.50	6.62
3-5 Mor	N4D	8/18/2022	5.4	7.21	17.40	653.30	5.88
3-5 Mor	N4D	9/15/2022	7.5	6.94	17.40	662.60	6.60
3-5 Mor	N4D	10/6/2022	8.5	6.98	17.20	672.10	6.53
3-5 Mor	N4D	10/31/2022	8.1	7.07	16.80	702.34	6.49
3-5 Mor	N4D	12/2/2022	8.3	7.21	14.10	696.00	6.32
3-5-1 Mor	N4D	10/31/2021	3.8	7.32	12.70	667.00	6.58
3-5-1 Mor	N4D	11/28/2021	6	7.33	12.20	691.60	6.95
3-5-1 Mor	N4D	12/21/2021		7.20	13.00	718.90	6.34
3-5-1 Mor	N4D	1/13/2022	2.1	7.37	13.70	880.00	6.39
3-5-1 Mor	N4D	1/30/2022		7.11	14.00	732.50	6.52
3-5-1 Mor	N4D	3/2/2022	0.9	7.31	14.10	716.10	6.07
3-5-1 Mor	N4D	3/27/2022	1.6	7.11	12.80	671.50	5.78
3-5-1 Mor	N4D	4/16/2022		7.40	12.20	673.40	6.23
3-5-1 Mor	N4D	5/11/2022		7.14	14.50	616.90	6.23
3-5-1 Mor	N4D	6/5/2022	0.6	7.21	14.10	629.00	6.23
3-5-1 Mor	N4D	6/28/2022	1.4	7.17	17.70	825.00	5.98
3-5-1 Mor	N4D	7/29/2022	1.7	7.12	13.80	642.20	6.29
3-5-1 Mor	N4D	8/18/2022	1.4	7.30	14.30	653.90	6.32
3-5-1 Mor	N4D	9/15/2022	1	7.10	14.90	651.30	6.24

Site	Watershed	Date	DO	pH	Temp (°C)	Conductivity	Alkalinity
3-5-1 Mor	N4D	10/6/2022	2.1	7.10	14.70	656.50	6.30
3-5-1 Mor	N4D	10/31/2022	0.8	7.15	14.20	629.90	6.27
3-5-1 Mor	N4D	12/2/2022	1.3	7.21	13.60	646.00	6.25
4-6 Mor	N4D	10/31/2021	12.4	7.09	12.60	699.40	7.50
4-6 Mor	N4D	11/28/2021	11.1	7.19	12.30	725.20	7.02
4-6 Mor	N4D	12/21/2021		7.21	14.00	803.80	7.36
4-6 Mor	N4D	1/13/2022	7.4	7.30	14.10	1147.00	6.53
4-6 Mor	N4D	1/30/2022		7.32	11.10	794.50	6.57
4-6 Mor	N4D	3/2/2022	8.7	7.42	10.80	825.40	5.97
4-6 Mor	N4D	3/27/2022	7.8	7.40	9.50	596.40	5.78
4-6 Mor	N4D	4/16/2022		7.50	10.60	629.60	5.91
4-6 Mor	N4D	5/11/2022		7.33	13.10	588.00	6.02
4-6 Mor	N4D	6/5/2022	6.4	7.15	13.30	629.30	6.41
4-6 Mor	N4D	6/28/2022	4.7	7.17	17.10	662.60	6.70
4-6 Mor	N4D	7/29/2022	4.8	7.12	15.10	667.90	6.51
4-6 Mor	N4D	8/18/2022	8	7.15	14.30	646.10	6.56
4-6 Mor	N4D	9/15/2022	7	7.07	17.10	675.60	6.34
4-6 Mor	N4D	10/6/2022	8.4	7.30	16.30	655.10	6.47
4-6 Mor	N4D	10/31/2022	7.9	7.00	14.10	654.10	6.29
4-6 Mor	N4D	12/2/2022	8.6	7.17	13.90	670.00	6.35
4-6 Eiss1	N4D	10/31/2021	13.4	7.31	12.60	753.60	6.49
4-6 Eiss1	N4D	11/28/2021	4.2	7.28	12.20	655.10	6.39
4-6 Eiss1	N4D	12/21/2021		7.34	14.60	680.00	5.84
4-6 Eiss1	N4D	1/13/2022	3.4	7.40	14.10	1288.00	6.10
4-6 Eiss1	N4D	1/30/2022		7.25	13.40	573.80	5.81
4-6 Eiss1	N4D	3/2/2022	4.6	7.39	14.20	591.30	5.73
4-6 Eiss1	N4D	3/27/2022	7.7	7.20	13.70	560.50	5.77
4-6 Eiss1	N4D	4/16/2022		7.46	13.90	591.80	5.72

Site	Watershed	Date	DO	pH	Temp (°C)	Conductivity	Alkalinity
4-6 Eiss1	N4D	5/11/2022		7.43	14.70	539.70	5.76
4-6 Eiss1	N4D	6/5/2022	7.5	7.04	14.50	807.60	5.94
4-6 Eiss1	N4D	6/28/2022	4.8	7.17	17.20	691.10	5.91
4-6 Eiss1	N4D	7/29/2022	7.5	7.20	14.00	614.80	5.96
4-6 Eiss1	N4D	8/18/2022	7.8	7.11	14.20	563.10	5.72
4-6 Eiss1	N4D	9/15/2022	11.5	7.17	17.20	581.90	5.89
4-6 Eiss1	N4D	10/6/2022	7.6	7.07	18.00	681.80	5.80
4-6 Eiss1	N4D	10/31/2022	5.9	7.15	15.20	671.00	5.76
4-6 Eiss1	N4D	12/2/2022	6.6	7.31	13.70	559.00	5.71
4-6 Eiss2	N4D	10/31/2021	7.5	7.00	13.70	595.70	6.25
4-6 Eiss2	N4D	11/28/2021	8.1	7.12	13.30	591.60	6.90
4-6 Eiss2	N4D	12/21/2021		7.21	14.50	773.40	6.17
4-6 Eiss2	N4D	1/13/2022	3.8	7.25	14.40	760.50	6.10
4-6 Eiss2	N4D	1/30/2022		7.01	13.90	581.70	6.26
4-6 Eiss2	N4D	3/2/2022	3.5	7.15	13.80	814.30	6.13
4-6 Eiss2	N4D	3/27/2022	7.5	7.08	14.00	551.90	6.04
4-6 Eiss2	N4D	4/16/2022		7.30	12.70	579.30	5.78
4-6 Eiss2	N4D	5/11/2022		7.17	14.30	502.80	5.58
4-6 Eiss2	N4D	6/5/2022	4.3	7.12	14.30	680.80	5.65
4-6 Eiss2	N4D	6/28/2022	3.9	7.13	17.70	574.40	5.78
4-6 Eiss2	N4D	7/29/2022	6	7.07	14.10	565.50	5.67
4-6 Eiss2	N4D	8/18/2022	4.1	7.13	14.50	577.00	5.80
4-6 Eiss2	N4D	9/15/2022	3.8	7.01	17.00	595.90	6.27
4-6 Eiss2	N4D	10/6/2022	3.8	6.93	16.10	621.60	6.57
4-6 Eiss2	N4D	10/31/2022	4	6.60	15.50	621.90	6.53
4-6 Eiss2	N4D	12/2/2022	5.5	6.88	14.80	609.70	6.37
1-1 Stream	N4D	3/27/2022	10.6	8.08	11.40	574.90	5.51
1-1 Stream	N4D	4/16/2022		8.09	6.90	599.00	5.84

Site	Watershed	Date	DO	pH	Temp (°C)	Conductivity	Alkalinity
1-1 Stream	N4D	5/11/2022		8.14	17.60	525.10	5.71
1-1 Stream	N4D	6/5/2022	9	8.19	16.40	546.70	5.80
1-1 Stream	N4D	6/28/2022		7.97	17.80	561.50	5.96
1-1 Stream	N4D	7/29/2022	8	7.96	18.70	555.00	5.46
3-1 Stream	N4D	11/28/2021	18.2	7.87	7.60	675.80	6.66
3-1 Stream	N4D	12/21/2021		7.84	4.00	759.60	6.37
3-1 Stream	N4D	1/13/2022	10.8	8.00	3.80	673.30	6.05
3-1 Stream	N4D	1/30/2022		7.58	3.10	748.60	6.52
3-1 Stream	N4D	3/2/2022	4.9	7.61	7.90	681.10	5.09
3-1 Stream	N4D	3/27/2022	9.8	8.11	13.90	585.90	5.78
3-1 Stream	N4D	4/16/2022		8.17	7.80	632.60	6.01
3-1 Stream	N4D	5/11/2022		8.10	16.70	537.10	5.86
3-1 Stream	N4D	6/5/2022	8.8	7.99	18.70	545.70	5.84
3-1 Stream	N4D	6/28/2022		7.90	17.70	572.00	6.05
3-1 Stream	N4D	7/29/2022	7.9	7.83	20.02	604.70	6.21
3-1 Stream	N4D	8/18/2022	9	8.03	19.70	599.40	5.88
3-1 Stream	N4D	9/15/2022	6.3	7.91	20.50	565.30	5.21
3-1 Stream	N4D	10/6/2022	7.1	7.98	21.90	629.10	5.73
3-1 Stream	N4D	10/31/2022	5.3	7.75	10.70	671.50	6.55
3-1 Stream	N4D	12/2/2022	9.8	7.60	5.70	688.10	6.14
4-1 Stream	N4D	11/28/2021	10.3	7.40	9.90	665.90	6.28
4-1 Stream	N4D	12/21/2021		7.38	9.60	730.10	6.33
4-1 Stream	N4D	1/30/2022		7.68	6.90	669.80	6.26
4-1 Stream	N4D	3/2/2022	7.4	7.56	7.40	694.80	5.97
4-1 Stream	N4D	3/27/2022	10.5	7.94	12.70	546.80	5.88
4-1 Stream	N4D	4/16/2022		7.95	10.20	633.90	5.94
4-1 Stream	N4D	5/11/2022		7.92	17.60	535.70	5.87
4-1 Stream	N4D	6/5/2022	8.7	7.89	17.80	549.70	5.81

Site	Watershed	Date	DO	pH	Temp (°C)	Conductivity	Alkalinity
4-1 Stream	N4D	7/29/2022	7.3	7.69	19.60	562.90	6.28
4-1 Stream	N4D	8/18/2022	7.6	7.83	18.40	627.60	6.39
4-1 Stream	N4D	9/15/2022	8.5	7.49	21.80	630.80	6.20
4-1 Stream	N4D	10/6/2022	3.4	7.15	18.80	701.90	6.26
4-1 Stream	N4D	10/31/2022	5.7	7.30	12.50	688.20	6.56
4-1 Stream	N4D	12/2/2022	8.8	7.82	8.80	675.80	6.28

Table 2 Major anion data for groundwater and surface water sites at N4D and N1B. Units are mg/L for all parameters.

Site	Watershed	Date	F^-	Cl^-	Br^-	NO_3^-	SO_4^{2-}
1-1 Mor	N1B	10/31/2021	0.33	1.62	n.a.	0.45	30.60
1-1 Mor	N1B	11/28/2021	0.36	2.18	0.04	0.36	16.19
1-1 Mor	N1B	12/21/2021	0.32	0.93	n.a.	0.63	24.63
1-1 Mor	N1B	1/13/2022	0.36	2.40	n.a.	0.46	36.41
1-1 Mor	N1B	1/30/2022	0.38	1.49	n.a.	0.49	36.91
1-1 Mor	N1B	2/27/2022	0.33	2.46	n.a.	0.08	39.70
1-1 Mor	N1B	3/27/2022	0.36	1.81	n.a.	0.78	10.39
1-1 Mor	N1B	4/16/2022	0.33	0.83	0.19	n.a.	16.85
1-1 Mor	N1B	5/11/2022	0.30	1.60	n.a.	0.45	9.08
1-1 Mor	N1B	6/6/2022	0.33	1.54	n.a.	0.19	7.05
1-1 Mor	N1B	6/28/2022	0.29	2.32	0.02	0.26	6.54
1-1 Mor	N1B	7/29/2022	0.32	2.43	n.a.	0.45	14.66
1-1 Mor	N1B	8/18/2022	0.35	2.57	n.a.	0.58	16.26
1-1 Mor	N1B	9/15/2022	0.33	2.27	n.a.	0.59	22.04
1-1 Mor	N1B	10/6/2022	0.34	2.46	n.a.	0.52	26.15
1-1 Mor	N1B	10/31/2022	0.42	1.45	n.a.	1.00	27.89
1-1 Mor	N1B	12/2/2022	0.32	1.29	n.a.	0.33	16.84
1-1 Stream	N1B	3/27/2022	0.40	2.07	n.a.	0.19	26.62
1-1 Stream	N1B	4/16/2022	0.37	2.26	0.01	n.a.	33.74
1-1 Stream	N1B	5/11/2022	0.38	2.73	n.a.	0.20	17.89
1-1 Stream	N1B	6/6/2022	0.42	2.38	n.a.	0.56	13.11
1-1 Stream	N1B	6/28/2022	0.40	2.89	n.a.	0.30	12.16
3-5 Mor	N4D	10/31/2021	0.40	1.83	0.05	0.02	36.35
3-5 Mor	N4D	11/28/2021	0.40	3.14	n.a.	0.20	38.55
3-5 Mor	N4D	12/21/2021	0.46	15.35	0.03	0.61	37.47
3-5 Mor	N4D	1/13/2022	0.42	3.41	n.a.	0.27	42.44
3-5 Mor	N4D	1/30/2022	0.40	2.00	n.a.	0.14	47.82

Site	Watershed	Date	F^-	Cl^-	Br^-	NO_3^-	SO_4^{2-}
3-5 Mor	N4D	3/2/2022	0.35	2.95	n.a.	0.46	49.20
3-5 Mor	N4D	3/27/2022	0.41	2.47	n.a.	0.17	34.51
3-5 Mor	N4D	4/16/2022	0.39	1.93	0.07	n.a.	34.28
3-5 Mor	N4D	5/11/2022	0.41	2.32	n.a.	0.11	27.02
3-5 Mor	N4D	6/5/2022	0.44	2.91	n.a.	0.11	18.13
3-5 Mor	N4D	6/28/2022	0.42	3.60	n.a.	0.35	13.76
3-5 Mor	N4D	7/29/2022	0.42	3.08	0.01	0.55	19.57
3-5 Mor	N4D	8/18/2022	0.44	4.24	0.02	0.13	24.09
3-5 Mor	N4D	9/15/2022	0.39	2.53	0.04	0.20	31.27
3-5 Mor	N4D	10/6/2022	0.43	4.30	n.a.	0.13	35.60
3-5 Mor	N4D	10/31/2022	0.44	2.93	0.03	0.15	37.91
3-5 Mor	N4D	12/2/2022	0.37	2.45	n.a.	0.33	44.43
3-5-1 Mor	N4D	10/31/2021	0.34	2.36	0.03	0.07	38.01
3-5-1 Mor	N4D	11/28/2021	0.36	3.45	0.04	0.06	38.20
3-5-1 Mor	N4D	12/21/2021	0.40	6.78	0.02	0.18	37.86
3-5-1 Mor	N4D	1/13/2022	0.38	3.54	0.08	0.14	38.18
3-5-1 Mor	N4D	1/30/2022	0.38	2.69	0.03	0.10	43.33
3-5-1 Mor	N4D	3/2/2022	0.34	3.36	n.a.	0.12	39.20
3-5-1 Mor	N4D	3/27/2022	0.37	2.77	0.05	0.14	46.92
3-5-1 Mor	N4D	4/16/2022	0.34	2.30	0.08	n.a.	38.93
3-5-1 Mor	N4D	5/11/2022	0.34	4.07	0.02	0.13	40.06
3-5-1 Mor	N4D	6/5/2022	0.39	3.27	n.a.	n.a.	39.65
3-5-1 Mor	N4D	6/28/2022	0.40	7.64	0.03	1.78	42.02
3-5-1 Mor	N4D	7/29/2022	0.40	3.48	0.01	0.55	37.24
3-5-1 Mor	N4D	8/18/2022	0.39	3.60	0.02	0.45	38.22
3-5-1 Mor	N4D	9/15/2022	0.40	2.88	n.a.	0.37	37.91
3-5-1 Mor	N4D	10/6/2022	0.38	5.09	0.01	1.05	36.81
3-5-1 Mor	N4D	10/31/2022	0.40	2.61	0.03	0.46	41.94
3-5-1 Mor	N4D	12/2/2022	0.37	2.53	n.a.	0.10	42.50

Site	Watershed	Date	F^-	Cl^-	Br^-	NO_3^-	SO_4^{2-}
4-6 Mor	N4D	10/31/2021	0.38	2.88	n.a.	0.48	36.50
4-6 Mor	N4D	11/28/2021	0.41	3.45	0.08	0.40	37.34
4-6 Mor	N4D	12/21/2021	0.42	2.22	0.03	0.42	38.61
4-6 Mor	N4D	1/13/2022	0.42	3.48	n.a.	0.21	35.41
4-6 Mor	N4D	1/30/2022	0.70	3.44	0.04	0.50	45.59
4-6 Mor	N4D	3/2/2022	0.34	3.41	n.a.	0.75	64.26
4-6 Mor	N4D	3/27/2022	0.41	2.40	n.a.	0.11	35.22
4-6 Mor	N4D	4/16/2022	0.39	2.69	0.13	n.a.	34.65
4-6 Mor	N4D	5/11/2022	0.40	3.12	n.a.	0.21	32.16
4-6 Mor	N4D	6/5/2022	0.43	5.82	n.a.	0.40	24.75
4-6 Mor	N4D	6/28/2022	0.44	3.61	n.a.	0.28	18.28
4-6 Mor	N4D	7/29/2022	0.40	4.32	0.01	0.58	24.44
4-6 Mor	N4D	8/18/2022	0.47	4.33	0.02	0.27	27.32
4-6 Mor	N4D	9/15/2022	0.41	7.87	0.03	0.19	32.99
4-6 Mor	N4D	10/6/2022	0.39	4.58	n.a.	0.25	36.75
4-6 Mor	N4D	10/31/2022	0.46	2.66	0.03	0.21	58.08
4-6 Mor	N4D	12/2/2022	0.39	4.62	n.a.	0.34	44.27
4-6 Eiss1	N4D	10/31/2021	0.44	43.90	n.a.	1.58	20.75
4-6 Eiss1	N4D	11/28/2021	0.45	3.33	0.02	1.46	20.68
4-6 Eiss1	N4D	12/21/2021	0.50	2.02	n.a.	1.77	21.75
4-6 Eiss1	N4D	1/13/2022	0.47	69.71	0.03	1.17	19.32
4-6 Eiss1	N4D	1/30/2022	0.51	1.99	n.a.	1.37	22.24
4-6 Eiss1	N4D	3/2/2022	0.49	3.04	n.a.	1.18	23.56
4-6 Eiss1	N4D	3/27/2022	0.06	0.42	n.a.	0.13	5.05
4-6 Eiss1	N4D	4/16/2022	0.45	17.19	0.43	n.a.	23.08
4-6 Eiss1	N4D	5/11/2022	0.43	9.36	n.a.	1.04	21.88
4-6 Eiss1	N4D	6/5/2022	0.47	34.89	0.04	1.28	19.84
4-6 Eiss1	N4D	6/28/2022	0.85	5.02	n.a.	1.76	14.42
4-6 Eiss1	N4D	7/29/2022	0.41	34.53	0.01	1.09	18.15

Site	Watershed	Date	F^-	Cl^-	Br^-	NO_3^-	SO_4^{2-}
4-6 Eiss1	N4D	8/18/2022	0.43	3.18	0.02	1.32	18.99
4-6 Eiss1	N4D	9/15/2022	0.47	7.47	n.a.	1.09	20.78
4-6 Eiss1	N4D	10/6/2022	0.45	5.07	n.a.	1.27	22.74
4-6 Eiss1	N4D	10/31/2022	0.46	2.14	n.a.	1.28	21.22
4-6 Eiss1	N4D	12/2/2022	0.44	2.16	n.a.	1.09	20.90
4-6 Eiss2	N4D	10/31/2021	0.37	1.37	n.a.	0.27	10.32
4-6 Eiss2	N4D	11/28/2021	0.40	2.53	n.a.	0.35	9.87
4-6 Eiss2	N4D	12/21/2021	0.35	1.25	n.a.	0.22	10.32
4-6 Eiss2	N4D	1/13/2022	0.39	2.73	0.03	0.43	9.98
4-6 Eiss2	N4D	1/30/2022	0.42	1.52	n.a.	0.30	10.56
4-6 Eiss2	N4D	3/2/2022	0.36	2.57	n.a.	0.23	10.14
4-6 Eiss2	N4D	3/27/2022	0.39	1.56	n.a.	0.51	10.85
4-6 Eiss2	N4D	4/16/2022	0.38	1.54	0.22	n.a.	12.85
4-6 Eiss2	N4D	5/11/2022	0.38	4.08	n.a.	0.72	7.32
4-6 Eiss2	N4D	6/5/2022	0.37	2.48	n.a.	0.20	6.31
4-6 Eiss2	N4D	6/28/2022	0.39	4.65	0.02	1.45	7.19
4-6 Eiss2	N4D	7/29/2022	0.43	2.64	n.a.	0.51	11.40
4-6 Eiss2	N4D	8/18/2022	0.37	3.36	0.01	0.61	11.74
4-6 Eiss2	N4D	9/15/2022	0.40	1.48	n.a.	0.31	10.15
4-6 Eiss2	N4D	10/6/2022	0.37	2.95	n.a.	0.35	9.46
4-6 Eiss2	N4D	10/31/2022	0.40	2.06	n.a.	0.44	9.40
4-6 Eiss2	N4D	12/2/2022	0.42	1.55	n.a.	0.30	9.88
1-1 Stream	N4D	3/27/2022	0.41	1.95	n.a.	0.04	35.65
1-1 Stream	N4D	4/16/2022	0.39	1.85	0.07	n.a.	39.63
1-1 Stream	N4D	5/11/2022	0.39	1.82	n.a.	0.07	21.21
1-1 Stream	N4D	6/5/2022	0.44	1.98	n.a.	n.a.	13.88
1-1 Stream	N4D	6/28/2022	0.37	2.92	n.a.	0.16	12.60
1-1 Stream	N4D	7/29/2022	0.38	2.67	n.a.	0.12	27.34
3-1 Stream	N4D	11/28/2021	0.40	2.82	0.02	0.07	46.82

Site	Watershed	Date	F^-	Cl^-	Br^-	NO_3^-	SO_4^{2-}
3-1 Stream	N4D	12/21/2021	0.42	1.79	n.a.	0.07	49.93
3-1 Stream	N4D	1/13/2022	0.38	2.84	n.a.	n.a.	55.96
3-1 Stream	N4D	1/30/2022	0.40	1.82	n.a.	0.03	64.01
3-1 Stream	N4D	3/2/2022	0.32	2.75	n.a.	0.11	76.74
3-1 Stream	N4D	3/27/2022	0.40	1.81	n.a.	0.03	35.21
3-1 Stream	N4D	4/16/2022	0.38	1.75	0.03	n.a.	38.09
3-1 Stream	N4D	5/11/2022	0.39	1.85	n.a.	0.08	21.36
3-1 Stream	N4D	6/5/2022	0.43	2.06	n.a.	0.08	14.02
3-1 Stream	N4D	6/28/2022	0.38	2.55	n.a.	0.05	12.63
3-1 Stream	N4D	7/29/2022	0.40	2.86	0.01	0.23	27.21
3-1 Stream	N4D	8/18/2022	0.40	3.04	0.02	0.25	37.57
3-1 Stream	N4D	9/15/2022	0.41	2.14	n.a.	0.21	44.47
3-1 Stream	N4D	10/6/2022	0.39	3.05	n.a.	0.14	60.31
3-1 Stream	N4D	10/31/2022	0.41	2.63	n.a.	0.51	50.43
3-1 Stream	N4D	12/2/2022	0.39	2.11	n.a.	n.a.	21.90
4-1 Stream	N4D	11/28/2021	0.37	2.85	n.a.	0.07	44.29
4-1 Stream	N4D	12/21/2021	0.43	1.76	n.a.	0.04	43.54
4-1 Stream	N4D	1/30/2022	0.40	1.99	0.03	0.21	50.16
4-1 Stream	N4D	3/2/2022	0.35	3.33	n.a.	0.18	52.61
4-1 Stream	N4D	3/27/2022	0.41	1.87	n.a.	0.08	30.65
4-1 Stream	N4D	4/16/2022	0.40	1.64	0.12	n.a.	33.51
4-1 Stream	N4D	5/11/2022	0.40	1.64	n.a.	n.a.	19.53
4-1 Stream	N4D	6/5/2022	0.44	2.07	n.a.	n.a.	12.70
4-1 Stream	N4D	7/29/2022	0.42	2.61	0.01	0.08	21.45
4-1 Stream	N4D	8/18/2022	0.43	3.12	0.02	0.32	29.74
4-1 Stream	N4D	9/15/2022	0.45	1.75	0.04	0.14	36.68
4-1 Stream	N4D	10/6/2022	0.37	3.07	n.a.	0.09	51.87
4-1 Stream	N4D	10/31/2022	0.42	1.86	n.a.	0.27	47.25
4-1 Stream	N4D	12/2/2022	0.39	2.00	n.a.	0.04	57.53

Table 3 Major cation data for groundwater and surface water sites from N4D and N1B. Units are mg/l for all parameters.

Site	Watershed	Date	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}
1-1 Mor	N1B	10/31/2021	4.29	1.17	19.86	113.57	3.82
1-1 Mor	N1B	11/28/2021	2.92	0.83	12.85	113.65	3.73
1-1 Mor	N1B	12/21/2021	3.38	0.84	15.93	123.58	3.63
1-1 Mor	N1B	1/13/2022	3.69	0.72	17.76	133.61	4.41
1-1 Mor	N1B	1/30/2022	4.20	1.01	19.20	119.82	4.00
1-1 Mor	N1B	2/27/2022	4.41	0.80	22.15	109.70	5.28
1-1 Mor	N1B	3/27/2022	2.49	1.42	9.62	110.61	n.a.
1-1 Mor	N1B	4/16/2022	2.89	0.78	11.79	112.37	3.35
1-1 Mor	N1B	5/11/2022	2.66	0.59	8.35	99.36	n.a.
1-1 Mor	N1B	6/6/2022	2.07	0.45	7.88	108.27	n.a.
1-1 Mor	N1B	6/28/2022	2.57	0.66	9.19	112.91	n.a.
1-1 Mor	N1B	7/29/2022	2.84	0.62	11.18	108.43	3.20
1-1 Mor	N1B	8/18/2022	3.75	1.61	11.83	107.04	3.48
1-1 Mor	N1B	9/15/2022	3.98	3.28	12.80	109.21	3.07
1-1 Mor	N1B	10/6/2022	3.34	0.50	13.75	95.32	2.90
1-1 Mor	N1B	10/31/2022	3.72	0.73	14.30	102.13	3.06
1-1 Mor	N1B	12/2/2022	3.24	0.74	13.32	112.02	3.42
1-1 Stream	N1B	3/27/2022	4.15	0.85	15.02	101.00	3.92
1-1 Stream	N1B	4/16/2022	5.05	0.90	16.67	88.30	3.96
1-1 Stream	N1B	5/11/2022	4.44	1.21	14.73	88.09	4.52
1-1 Stream	N1B	6/6/2022	3.85	0.84	15.31	86.76	3.90
1-1 Stream	N1B	6/28/2022	3.83	1.48	15.67	89.35	3.34
3-5 Mor	N4D	10/31/2021	5.26	1.21	27.24	110.57	4.25
3-5 Mor	N4D	11/28/2021	5.07	1.07	19.16	102.15	4.16
3-5 Mor	N4D	12/21/2021	7.63	16.99	19.92	106.33	3.98
3-5 Mor	N4D	1/13/2022	4.90	0.96	23.66	104.72	3.93
3-5 Mor	N4D	1/30/2022	4.75	0.80	22.53	119.78	3.57

Site	Watershed	Date	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	Sr^{2+}
3-5 Mor	N4D	3/2/2022	5.10	0.85	19.58	99.63	4.22
3-5 Mor	N4D	3/27/2022	4.63	0.92	17.50	94.18	3.24
3-5 Mor	N4D	4/16/2022	4.82	0.87	17.97	92.85	3.41
3-5 Mor	N4D	5/11/2022	5.29	1.34	17.65	91.63	4.36
3-5 Mor	N4D	6/5/2022	5.36	1.36	18.66	97.86	4.37
3-5 Mor	N4D	6/28/2022	5.49	3.25	21.05	101.13	3.61
3-5 Mor	N4D	7/29/2022	4.89	1.17	18.36	97.33	3.52
3-5 Mor	N4D	8/18/2022	5.16	2.68	19.23	99.53	4.17
3-5 Mor	N4D	9/15/2022	6.50	1.38	20.14	103.32	3.58
3-5 Mor	N4D	10/6/2022	5.87	2.50	19.25	106.46	3.33
3-5 Mor	N4D	10/31/2022	5.59	2.18	22.50	108.10	3.62
3-5 Mor	N4D	12/2/2022	5.34	1.00	17.74	99.65	3.76
3-5-1 Mor	N4D	10/31/2021	6.39	1.13	30.79	122.83	4.90
3-5-1 Mor	N4D	11/28/2021	7.06	1.76	26.68	89.12	4.65
3-5-1 Mor	N4D	12/21/2021	6.39	1.19	25.85	86.51	4.28
3-5-1 Mor	N4D	1/13/2022	6.29	1.31	31.18	98.29	4.87
3-5-1 Mor	N4D	1/30/2022	6.50	1.24	29.73	96.97	4.56
3-5-1 Mor	N4D	3/2/2022	6.92	1.11	28.17	87.14	5.53
3-5-1 Mor	N4D	3/27/2022	7.17	1.40	27.36	84.68	4.30
3-5-1 Mor	N4D	4/16/2022	6.82	1.28	26.72	195.95	6.10
3-5-1 Mor	N4D	5/11/2022	7.08	3.09	24.53	86.17	n.a.
3-5-1 Mor	N4D	6/5/2022	6.46	1.24	26.49	83.55	5.02
3-5-1 Mor	N4D	6/28/2022	6.98	1.76	27.83	85.19	4.30
3-5-1 Mor	N4D	7/29/2022	6.51	1.36	23.24	83.47	4.29
3-5-1 Mor	N4D	8/18/2022	5.04	n.a.	25.95	79.15	4.87
3-5-1 Mor	N4D	9/15/2022	7.36	1.28	28.62	97.32	4.17
3-5-1 Mor	N4D	10/6/2022	7.56	2.29	27.73	95.26	4.06
3-5-1 Mor	N4D	10/31/2022	6.92	1.16	29.65	88.09	4.14
3-5-1 Mor	N4D	12/2/2022	6.68	1.00	27.77	85.50	4.43

Site	Watershed	Date	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	Sr^{2+}
4-6 Mor	N4D	10/31/2021	5.55	2.24	20.86	104.71	4.15
4-6 Mor	N4D	11/28/2021	5.33	1.11	21.48	106.07	4.30
4-6 Mor	N4D	12/21/2021	5.42	1.25	21.74	105.01	4.01
4-6 Mor	N4D	1/13/2022	5.01	1.19	22.15	110.99	3.91
4-6 Mor	N4D	1/30/2022	5.83	1.86	21.91	96.82	3.62
4-6 Mor	N4D	3/2/2022	5.57	1.35	19.57	94.49	4.33
4-6 Mor	N4D	3/27/2022	4.74	1.09	17.62	89.85	3.36
4-6 Mor	N4D	4/16/2022	5.19	1.59	18.60	88.88	3.59
4-6 Mor	N4D	5/11/2022	5.44	1.35	18.50	89.29	4.82
4-6 Mor	N4D	6/5/2022	6.23	4.61	21.88	94.03	4.51
4-6 Mor	N4D	6/28/2022	6.25	1.40	20.63	97.40	5.74
4-6 Mor	N4D	7/29/2022	5.68	1.66	18.16	86.46	3.74
4-6 Mor	N4D	8/18/2022	6.03	3.13	18.28	95.65	4.33
4-6 Mor	N4D	9/15/2022	7.00	7.35	21.29	96.95	3.78
4-6 Mor	N4D	10/6/2022	6.47	1.75	19.96	102.51	3.72
4-6 Mor	N4D	10/31/2022	6.24	1.21	24.02	101.27	3.89
4-6 Mor	N4D	12/2/2022	6.24	3.75	21.59	99.47	3.88
4-6 Eiss1	N4D	10/31/2021	14.08	48.75	23.38	72.91	3.65
4-6 Eiss1	N4D	11/28/2021	7.46	1.75	24.79	71.47	4.00
4-6 Eiss1	N4D	12/21/2021	7.30	1.34	23.24	46.32	3.68
4-6 Eiss1	N4D	1/13/2022	18.86	74.29	23.21	71.22	4.27
4-6 Eiss1	N4D	1/30/2022	7.30	1.36	24.21	69.74	3.70
4-6 Eiss1	N4D	3/2/2022	7.81	1.40	28.42	74.05	4.49
4-6 Eiss1	N4D	3/27/2022	7.02	1.70	24.34	66.42	3.57
4-6 Eiss1	N4D	4/16/2022	7.61	16.76	24.07	69.76	3.94
4-6 Eiss1	N4D	5/11/2022	10.31	10.09	23.11	75.34	5.01
4-6 Eiss1	N4D	6/5/2022	12.54	25.73	20.95	71.87	4.44
4-6 Eiss1	N4D	6/28/2022	7.00	1.41	25.33	72.81	3.74
4-6 Eiss1	N4D	7/29/2022	13.49	36.41	21.29	63.62	3.78

Site	Watershed	Date	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	Sr^{2+}
4-6 Eiss1	N4D	8/18/2022	6.96	1.80	22.27	64.55	4.03
4-6 Eiss1	N4D	9/15/2022	8.30	7.20	20.39	71.78	3.69
4-6 Eiss1	N4D	10/6/2022	9.08	2.42	19.96	75.10	3.59
4-6 Eiss1	N4D	10/31/2022	7.80	1.57	18.92	72.41	3.66
4-6 Eiss1	N4D	12/2/2022	7.14	1.37	25.61	72.44	3.77
4-6 Eiss2	N4D	10/31/2021	3.79	0.68	14.93	93.48	3.00
4-6 Eiss2	N4D	11/28/2021	3.77	0.67	14.45	93.12	3.29
4-6 Eiss2	N4D	12/21/2021	3.97	0.64	14.11	93.10	3.09
4-6 Eiss2	N4D	1/13/2022	3.70	0.72	14.36	99.05	3.17
4-6 Eiss2	N4D	1/30/2022	3.94	0.60	14.28	97.84	2.93
4-6 Eiss2	N4D	3/2/2022	5.00	1.03	14.40	96.79	3.71
4-6 Eiss2	N4D	3/27/2022	3.46	0.58	14.00	89.96	2.98
4-6 Eiss2	N4D	4/16/2022	3.73	0.73	15.29	80.41	3.24
4-6 Eiss2	N4D	5/11/2022	3.27	1.17	10.11	87.82	n.a.
4-6 Eiss2	N4D	6/5/2022	3.07	1.06	10.09	94.04	n.a.
4-6 Eiss2	N4D	6/28/2022	3.06	1.12	9.90	95.60	2.77
4-6 Eiss2	N4D	7/29/2022	3.42	0.66	13.38	84.59	2.81
4-6 Eiss2	N4D	8/18/2022	3.70	1.34	14.85	89.23	3.29
4-6 Eiss2	N4D	9/15/2022	3.63	0.46	14.87	97.71	2.92
4-6 Eiss2	N4D	10/6/2022	3.79	0.70	16.09	100.45	2.97
4-6 Eiss2	N4D	10/31/2022	4.85	1.10	16.15	98.69	3.02
4-6 Eiss2	N4D	12/2/2022	4.17	0.56	15.32	97.63	3.18
1-1 Stream	N4D	3/27/2022	4.22	1.32	16.99	82.57	3.70
1-1 Stream	N4D	4/16/2022	4.62	0.84	17.52	83.37	3.56
1-1 Stream	N4D	5/11/2022	4.15	0.85	16.11	86.24	4.51
1-1 Stream	N4D	6/5/2022	3.70	0.84	15.81	86.27	3.91
1-1 Stream	N4D	6/28/2022	3.50	0.77	16.11	87.72	3.20
1-1 Stream	N4D	7/29/2022	4.27	0.95	18.08	81.69	4.43
3-1 Stream	N4D	11/28/2021	5.02	0.82	18.78	103.42	4.01

Site	Watershed	Date	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}
3-1 Stream	N4D	12/21/2021	5.16	1.05	21.49	108.29	3.83
3-1 Stream	N4D	1/13/2022	4.71	0.65	20.56	105.38	4.19
3-1 Stream	N4D	1/30/2022	5.33	0.93	21.06	104.39	3.93
3-1 Stream	N4D	3/2/2022	4.96	0.94	20.70	110.94	4.42
3-1 Stream	N4D	3/27/2022	4.22	0.84	17.12	83.42	3.64
3-1 Stream	N4D	4/16/2022	4.70	0.75	18.11	89.38	3.68
3-1 Stream	N4D	5/11/2022	4.11	0.80	16.09	88.44	4.65
3-1 Stream	N4D	6/5/2022	3.72	0.78	15.77	93.11	3.80
3-1 Stream	N4D	6/28/2022	3.55	0.92	16.19	89.77	n.a.
3-1 Stream	N4D	7/29/2022	4.57	1.07	18.13	90.63	3.62
3-1 Stream	N4D	8/18/2022	4.91	0.74	18.97	90.26	3.96
3-1 Stream	N4D	9/15/2022	5.51	1.08	20.40	77.66	3.40
3-1 Stream	N4D	10/6/2022	9.35	3.03	32.72	85.24	3.77
3-1 Stream	N4D	10/31/2022	6.52	2.87	24.41	104.56	4.05
3-1 Stream	N4D	12/2/2022	5.44	0.87	21.16	103.12	4.10
4-1 Stream	N4D	11/28/2021	4.95	0.78	18.55	106.87	3.89
4-1 Stream	N4D	12/21/2021	5.03	0.80	20.94	109.59	3.78
4-1 Stream	N4D	1/30/2022	4.92	0.67	21.42	106.18	3.83
4-1 Stream	N4D	3/2/2022	5.14	1.00	18.17	100.90	4.63
4-1 Stream	N4D	3/27/2022	4.41	0.80	17.53	86.17	3.56
4-1 Stream	N4D	4/16/2022	4.60	0.76	17.68	88.14	3.57
4-1 Stream	N4D	5/11/2022	4.11	0.80	15.94	90.19	4.50
4-1 Stream	N4D	6/5/2022	3.87	1.85	15.79	88.53	3.86
4-1 Stream	N4D	7/29/2022	4.31	0.75	17.83	92.61	3.55
4-1 Stream	N4D	8/18/2022	5.67	1.74	17.71	90.56	4.15
4-1 Stream	N4D	9/15/2022	5.44	0.80	19.69	109.39	3.77
4-1 Stream	N4D	10/6/2022	5.97	1.52	19.59	98.32	3.96
4-1 Stream	N4D	10/31/2022	5.65	1.56	19.14	86.55	3.94
4-1 Stream	N4D	12/2/2022	5.26	0.71	20.10	99.04	3.91

Appendix B - Isotope Data

Table 4 Water isotope data for groundwater and surface water. Oxygen ($\delta^{18}O$) and hydrogen (δD) isotopic values are reported in parts per mil VSMOW.

*sample vial broke or was not collected

Site	Watershed	Date	δD	$\delta^{18}O$
1-1 Mor	N1B	11/28/2021	-36	-5.6
1-1 Mor	N1B	12/21/2021	-36	-5.7
1-1 Mor	N1B	1/13/2022	-37	-5.7
1-1 Mor	N1B	1/30/2022	-37	-5.8
1-1 Mor	N1B	2/27/2022	-37	-5.9
1-1 Mor	N1B	3/27/2022	-35	-5.6
1-1 Mor	N1B	4/16/2022	-36	-5.7
1-1 Mor	N1B	5/11/2022	-35	-5.6
1-1 Mor	N1B	6/6/2022	-34	-5.4
1-1 Mor	N1B	6/28/2022	-35	-5
1-1 Mor	N1B	7/29/2022	-37	-5.3
1-1 Mor	N1B	8/18/2022	-35	-5.5
1-1 Mor	N1B	9/15/2022	-35	-5.6
1-1 Mor	N1B	10/6/2022	-35	-5.6
1-1 Mor	N1B	10/31/2022	-35	-5.6
1-1 Mor	N1B	12/2/2022	-35	-5.6
1-1 Stream	N1B	3/27/2022	-36	-5.9
1-1 Stream	N1B	4/16/2022	-34	-5.3
1-1 Stream	N1B	5/11/2022	-35	-5.7
1-1 Stream	N1B	6/6/2022	-35	-5.6
1-1 Stream	N1B	6/28/2022	-35	-5.2
3-5 Mor	N4D	11/28/2021	-35	-5.6
3-5 Mor	N4D	12/21/2021	-35	-5.5
3-5 Mor	N4D	1/13/2022	-36	-5.6
3-5 Mor	N4D	1/30/2022	-36	-5.7

Site	Watershed	Date	δD	$\delta^{18}O$
3-5 Mor	N4D	3/2/2022	*	*
3-5 Mor	N4D	3/27/2022	-36	-5.8
3-5 Mor	N4D	4/16/2022	-36	-5.7
3-5 Mor	N4D	5/11/2022	-35	-5.7
3-5 Mor	N4D	6/5/2022	-35	-5.6
3-5 Mor	N4D	6/28/2022	-34	-5.4
3-5 Mor	N4D	7/29/2022	-35	-5.3
3-5 Mor	N4D	8/18/2022	-34	-5.4
3-5 Mor	N4D	9/15/2022	-35	-5.5
3-5 Mor	N4D	10/6/2022	-34	-5.5
3-5 Mor	N4D	10/31/2022	-35	-5.5
3-5 Mor	N4D	12/2/2022	-35	-5.6
3-5-1 Mor	N4D	11/28/2021	-37	-5.8
3-5-1 Mor	N4D	12/21/2021	-37	-5.8
3-5-1 Mor	N4D	1/13/2022	-37	-5.9
3-5-1 Mor	N4D	1/30/2022	-37	-5.7
3-5-1 Mor	N4D	3/2/2022	-37	-6
3-5-1 Mor	N4D	3/27/2022	-37	-5.9
3-5-1 Mor	N4D	4/16/2022	-37	-5.8
3-5-1 Mor	N4D	5/11/2022	-37	-5.9
3-5-1 Mor	N4D	6/5/2022	-37	-5.8
3-5-1 Mor	N4D	6/28/2022	-38	-5.8
3-5-1 Mor	N4D	7/29/2022	-38	-5.5
3-5-1 Mor	N4D	8/18/2022	-37	-5.8
3-5-1 Mor	N4D	9/15/2022	-36	-5.8
3-5-1 Mor	N4D	10/6/2022	-37	-5.8
3-5-1 Mor	N4D	10/31/2022	-36	-5.8
3-5-1 Mor	N4D	12/2/2022	-36	-5.8
4-6 Mor	N4D	11/28/2021	-35	-5.6

Site	Watershed	Date	δD	$\delta^{18}O$
4-6 Mor	N4D	12/21/2021	-35	-5.5
4-6 Mor	N4D	1/13/2022	-35	-5.6
4-6 Mor	N4D	1/30/2022	-36	-5.6
4-6 Mor	N4D	3/2/2022	-36	-5.8
4-6 Mor	N4D	3/27/2022	-36	-5.8
4-6 Mor	N4D	4/16/2022	-35	-5.6
4-6 Mor	N4D	5/11/2022	-36	-5.7
4-6 Mor	N4D	6/5/2022	-35	-5.7
4-6 Mor	N4D	6/28/2022	-36	-5.2
4-6 Mor	N4D	7/29/2022	-36	-5.2
4-6 Mor	N4D	8/18/2022	-34	-5.5
4-6 Mor	N4D	9/15/2022	-35	-5.6
4-6 Mor	N4D	10/6/2022	-35	-5.5
4-6 Mor	N4D	10/31/2022	-35	-5.5
4-6 Mor	N4D	12/2/2022	-35	-5.6
4-6 Eiss1	N4D	11/28/2021	-37	-5.8
4-6 Eiss1	N4D	12/21/2021	-37	-5.7
4-6 Eiss1	N4D	1/13/2022	-37	-5.8
4-6 Eiss1	N4D	1/30/2022	-37	-5.8
4-6 Eiss1	N4D	3/2/2022	-38	-6.1
4-6 Eiss1	N4D	3/27/2022	-37	-5.8
4-6 Eiss1	N4D	4/16/2022	-37	-5.8
4-6 Eiss1	N4D	5/11/2022	-37	-5.9
4-6 Eiss1	N4D	6/5/2022	-37	-5.8
4-6 Eiss1	N4D	6/28/2022	-38	-5.4
4-6 Eiss1	N4D	7/29/2022	-37	-5.5
4-6 Eiss1	N4D	8/18/2022	-36	-5.7
4-6 Eiss1	N4D	9/15/2022	-36	-5.6
4-6 Eiss1	N4D	10/6/2022	-36	-5.6

Site	Watershed	Date	δD	$\delta^{18}O$
4-6 Eiss1	N4D	10/31/2022	-36	-5.8
4-6 Eiss1	N4D	12/2/2022	-37	-5.9
4-6 Eiss2	N4D	11/28/2021	-36	-5.7
4-6 Eiss2	N4D	12/21/2021	-36	-5.6
4-6 Eiss2	N4D	1/13/2022	-36	-5.7
4-6 Eiss2	N4D	1/30/2022	-36	-5.7
4-6 Eiss2	N4D	3/2/2022	-36	-5.8
4-6 Eiss2	N4D	3/27/2022	-36	-5.7
4-6 Eiss2	N4D	4/16/2022	-36	-5.8
4-6 Eiss2	N4D	5/11/2022	-34	-5.4
4-6 Eiss2	N4D	6/5/2022	-34	-5.4
4-6 Eiss2	N4D	6/28/2022	-34	-4.8
4-6 Eiss2	N4D	7/29/2022	-36	-5.4
4-6 Eiss2	N4D	8/18/2022	-36	-5.7
4-6 Eiss2	N4D	9/15/2022	-36	-5.7
4-6 Eiss2	N4D	10/6/2022	-35	-5.4
4-6 Eiss2	N4D	10/31/2022	-36	-5.7
4-6 Eiss2	N4D	12/2/2022	-36	-5.7
1-1 Stream	N4D	3/27/2022	-35	-5.6
1-1 Stream	N4D	4/16/2022	-34	-5.4
1-1 Stream	N4D	5/11/2022	-35	-5.7
1-1 Stream	N4D	6/5/2022	-35	-5.6
1-1 Stream	N4D	6/28/2022	-35	-5.2
1-1 Stream	N4D	7/29/2022	-35	-5.2
3-1 Stream	N4D	11/28/2021	-35	-5.5
3-1 Stream	N4D	12/21/2021	-35	-5.6
3-1 Stream	N4D	1/13/2022	-36	-5.6
3-1 Stream	N4D	1/30/2022	-36	-5.7
3-1 Stream	N4D	3/2/2022	-33	-5

Site	Watershed	Date	δD	$\delta^{18}O$
3-1 Stream	N4D	3/27/2022	-35	-5.7
3-1 Stream	N4D	4/16/2022	-35	-5.6
3-1 Stream	N4D	5/11/2022	-35	-5.7
3-1 Stream	N4D	6/5/2022	-35	-5.7
3-1 Stream	N4D	6/28/2022	*	*
3-1 Stream	N4D	7/29/2022	-35	-5.2
3-1 Stream	N4D	8/18/2022	-34	-5.5
3-1 Stream	N4D	9/15/2022	-32	-5
3-1 Stream	N4D	10/6/2022	-32	-4.6
3-1 Stream	N4D	10/31/2022	-35	-5.4
3-1 Stream	N4D	12/2/2022	-35	-5.6
4-1 Stream	N4D	11/28/2021	-35	-5.6
4-1 Stream	N4D	12/21/2021	-35	-5.6
4-1 Stream	N4D	1/30/2022	-36	-5.7
4-1 Stream	N4D	3/2/2022	-36	-5.8
4-1 Stream	N4D	3/27/2022	-35	-5.7
4-1 Stream	N4D	4/16/2022	-35	-5.6
4-1 Stream	N4D	5/11/2022	-35	-5.7
4-1 Stream	N4D	6/5/2022	-36	-5.5
4-1 Stream	N4D	7/29/2022	-35	-5.1
4-1 Stream	N4D	8/18/2022	-35	-5.6
4-1 Stream	N4D	9/15/2022	-34	-5.4
4-1 Stream	N4D	10/6/2022	-35	-5.5
4-1 Stream	N4D	10/31/2022	-35	-5.6
4-1 Stream	N4D	12/2/2022	-36	-5.7

Appendix C - Saturation Index

Table 5 Calcite and dolomite saturation indices (SI) for groundwater and surface water samples. Units for the saturation indices are log Q/K.

Site	Watershed	Date	Calcite SI	Dolomite SI
1-1 Mor	N1B	10/31/2021	0.27	0.84
1-1 Mor	N1B	11/28/2021	0.22	0.56
1-1 Mor	N1B	12/21/2021	0.36	0.89
1-1 Mor	N1B	1/13/2022	0.49	1.17
1-1 Mor	N1B	1/30/2022	0.16	0.61
1-1 Mor	N1B	2/27/2022	0.06	0.51
1-1 Mor	N1B	3/27/2022	0.18	0.37
1-1 Mor	N1B	4/16/2022	0.34	0.78
1-1 Mor	N1B	5/11/2022	0.32	0.65
1-1 Mor	N1B	6/6/2022	0.12	0.17
1-1 Mor	N1B	6/28/2022	0.17	0.32
1-1 Mor	N1B	7/29/2022	0.12	0.33
1-1 Mor	N1B	8/18/2022	0.30	0.74
1-1 Mor	N1B	9/15/2022	0.23	0.62
1-1 Mor	N1B	10/6/2022	0.35	0.93
1-1 Mor	N1B	10/31/2022	0.28	0.78
1-1 Mor	N1B	12/2/2022	0.12	0.38
1-1 Stream	N1B	3/27/2022	0.66	1.56
1-1 Stream	N1B	4/16/2022	0.96	2.29
1-1 Stream	N1B	5/11/2022	0.81	1.96
1-1 Stream	N1B	6/6/2022	0.75	1.83
1-1 Stream	N1B	6/28/2022	0.83	2.01
3-5 Mor	N4D	10/31/2021	0.26	0.99
3-5 Mor	N4D	11/28/2021	0.27	0.90
3-5 Mor	N4D	12/21/2021	0.38	1.10
3-5 Mor	N4D	1/13/2022	0.36	1.14

Site	Watershed	Date	Calcite SI	Dolomite SI
3-5 Mor	N4D	1/30/2022	0.25	0.83
3-5 Mor	N4D	3/2/2022	0.15	0.65
3-5 Mor	N4D	3/27/2022	0.27	0.85
3-5 Mor	N4D	4/16/2022	0.41	1.15
3-5 Mor	N4D	5/11/2022	0.34	1.03
3-5 Mor	N4D	6/5/2022	0.30	0.96
3-5 Mor	N4D	6/28/2022	0.24	0.90
3-5 Mor	N4D	7/29/2022	0.17	0.71
3-5 Mor	N4D	8/18/2022	0.31	1.01
3-5 Mor	N4D	9/15/2022	0.10	0.59
3-5 Mor	N4D	10/6/2022	0.13	0.62
3-5 Mor	N4D	10/31/2022	0.22	0.85
3-5 Mor	N4D	12/2/2022	0.28	0.88
3-5-1 Mor	N4D	10/31/2021	0.47	1.41
3-5-1 Mor	N4D	11/28/2021	0.38	1.29
3-5-1 Mor	N4D	12/21/2021	0.21	0.96
3-5-1 Mor	N4D	1/13/2022	0.44	1.45
3-5-1 Mor	N4D	1/30/2022	0.19	0.94
3-5-1 Mor	N4D	3/2/2022	0.32	1.22
3-5-1 Mor	N4D	3/27/2022	0.07	0.72
3-5-1 Mor	N4D	4/16/2022	0.70	1.60
3-5-1 Mor	N4D	5/11/2022	0.17	0.86
3-5-1 Mor	N4D	6/5/2022	0.20	0.97
3-5-1 Mor	N4D	6/28/2022	0.22	1.04
3-5-1 Mor	N4D	7/29/2022	0.11	0.74
3-5-1 Mor	N4D	8/18/2022	0.29	1.18
3-5-1 Mor	N4D	9/15/2022	0.18	0.90
3-5-1 Mor	N4D	10/6/2022	0.15	0.85
3-5-1 Mor	N4D	10/31/2022	0.16	0.92

Site	Watershed	Date	Calcite SI	Dolomite SI
3-5-1 Mor	N4D	12/2/2022	0.20	0.98
4-6 Mor	N4D	10/31/2021	0.24	0.84
4-6 Mor	N4D	11/28/2021	0.31	0.99
4-6 Mor	N4D	12/21/2021	0.37	1.13
4-6 Mor	N4D	1/13/2022	0.44	1.25
4-6 Mor	N4D	1/30/2022	0.34	1.10
4-6 Mor	N4D	3/2/2022	0.41	1.20
4-6 Mor	N4D	3/27/2022	0.35	1.03
4-6 Mor	N4D	4/16/2022	0.46	1.30
4-6 Mor	N4D	5/11/2022	0.34	1.06
4-6 Mor	N4D	6/5/2022	0.19	0.82
4-6 Mor	N4D	6/28/2022	0.31	1.04
4-6 Mor	N4D	7/29/2022	0.18	0.76
4-6 Mor	N4D	8/18/2022	0.22	0.81
4-6 Mor	N4D	9/15/2022	0.19	0.81
4-6 Mor	N4D	10/6/2022	0.42	1.22
4-6 Mor	N4D	10/31/2022	0.06	0.58
4-6 Mor	N4D	12/2/2022	0.23	0.88
4-6 Eiss1	N4D	10/31/2021	0.25	1.06
4-6 Eiss1	N4D	11/28/2021	0.21	1.02
4-6 Eiss1	N4D	12/21/2021	0.09	0.96
4-6 Eiss1	N4D	1/13/2022	0.32	1.22
4-6 Eiss1	N4D	1/30/2022	0.15	0.91
4-6 Eiss1	N4D	3/2/2022	0.31	1.29
4-6 Eiss1	N4D	3/27/2022	0.08	0.80
4-6 Eiss1	N4D	4/16/2022	0.35	1.32
4-6 Eiss1	N4D	5/11/2022	0.37	1.31
4-6 Eiss1	N4D	6/5/2022	-0.04	0.46
4-6 Eiss1	N4D	6/28/2022	0.15	0.92

Site	Watershed	Date	Calcite SI	Dolomite SI
4-6 Eiss1	N4D	7/29/2022	0.07	0.75
4-6 Eiss1	N4D	8/18/2022	-0.01	0.58
4-6 Eiss1	N4D	9/15/2022	0.13	0.81
4-6 Eiss1	N4D	10/6/2022	0.05	0.63
4-6 Eiss1	N4D	10/31/2022	0.08	0.66
4-6 Eiss1	N4D	12/2/2022	0.21	1.04
4-6 Eiss2	N4D	10/31/2021	0.06	0.39
4-6 Eiss2	N4D	11/28/2021	0.21	0.67
4-6 Eiss2	N4D	12/21/2021	0.27	0.80
4-6 Eiss2	N4D	1/13/2022	0.33	0.89
4-6 Eiss2	N4D	1/30/2022	0.09	0.41
4-6 Eiss2	N4D	3/2/2022	0.21	0.67
4-6 Eiss2	N4D	3/27/2022	0.11	0.49
4-6 Eiss2	N4D	4/16/2022	0.25	0.84
4-6 Eiss2	N4D	5/11/2022	0.17	0.47
4-6 Eiss2	N4D	6/5/2022	0.15	0.41
4-6 Eiss2	N4D	6/28/2022	0.22	0.56
4-6 Eiss2	N4D	7/29/2022	0.06	0.38
4-6 Eiss2	N4D	8/18/2022	0.15	0.59
4-6 Eiss2	N4D	9/15/2022	0.13	0.54
4-6 Eiss2	N4D	10/6/2022	0.06	0.41
4-6 Eiss2	N4D	10/31/2022	-0.28	-0.27
4-6 Eiss2	N4D	12/2/2022	-0.03	0.21
1-1 Stream	N4D	3/27/2022	0.99	2.35
1-1 Stream	N4D	4/16/2022	0.96	2.28
1-1 Stream	N4D	5/11/2022	1.16	2.70
1-1 Stream	N4D	6/5/2022	1.20	2.76
1-1 Stream	N4D	6/28/2022	1.03	2.41
1-1 Stream	N4D	7/29/2022	0.97	2.38

Site	Watershed	Date	Calcite SI	Dolomite SI
3-1 Stream	N4D	11/28/2021	0.89	2.07
3-1 Stream	N4D	12/21/2021	0.81	1.93
3-1 Stream	N4D	1/13/2022	0.93	2.17
3-1 Stream	N4D	1/30/2022	0.54	1.38
3-1 Stream	N4D	3/2/2022	0.56	1.42
3-1 Stream	N4D	3/27/2022	1.08	2.54
3-1 Stream	N4D	4/16/2022	1.09	2.52
3-1 Stream	N4D	5/11/2022	1.13	2.62
3-1 Stream	N4D	6/5/2022	1.07	2.48
3-1 Stream	N4D	6/28/2022	0.97	2.30
3-1 Stream	N4D	7/29/2022	0.95	2.31
3-1 Stream	N4D	8/18/2022	1.11	2.66
3-1 Stream	N4D	9/15/2022	0.90	2.34
3-1 Stream	N4D	10/6/2022	1.03	2.76
3-1 Stream	N4D	10/31/2022	0.79	2.00
3-1 Stream	N4D	12/2/2022	0.55	1.44
4-1 Stream	N4D	11/28/2021	0.43	1.15
4-1 Stream	N4D	12/21/2021	0.44	1.20
4-1 Stream	N4D	1/30/2022	0.68	1.69
4-1 Stream	N4D	3/2/2022	0.51	1.31
4-1 Stream	N4D	3/27/2022	0.91	2.20
4-1 Stream	N4D	4/16/2022	0.90	2.15
4-1 Stream	N4D	5/11/2022	0.98	2.31
4-1 Stream	N4D	6/5/2022	0.94	2.23
4-1 Stream	N4D	7/29/2022	0.81	2.01
4-1 Stream	N4D	8/18/2022	0.94	2.26
4-1 Stream	N4D	9/15/2022	0.69	1.76
4-1 Stream	N4D	10/6/2022	0.27	0.94
4-1 Stream	N4D	10/31/2022	0.30	1.01

Site	Watershed	Date	Calcite SI	Dolomite SI
4-1 Stream	N4D	12/2/2022	0.79	1.94

Appendix D - Watershed CO_2 Data

Table 6 Dissolved CO_2 concentrations, aqueous CO_2 in groundwater and total soil CO_2 added to recharge water per liter. Units for each are mM.

Site	Watershed	Date	Dissolved CO_2	Aqueous CO_2	Soil CO_2
1-1 Mor	N1B	10/31/2021	3.6509	1.6360	5.2869
1-1 Mor	N1B	11/28/2021	3.3647	1.5350	4.8997
1-1 Mor	N1B	12/21/2021	3.7385	1.2690	5.0075
1-1 Mor	N1B	1/13/2022	4.0649	1.0610	5.1259
1-1 Mor	N1B	1/30/2022	3.7790	2.1090	5.8880
1-1 Mor	N1B	2/27/2022	3.6484	2.1960	5.8444
1-1 Mor	N1B	3/27/2022	3.1559	1.5690	4.7249
1-1 Mor	N1B	4/16/2022	3.2889	1.0670	4.3559
1-1 Mor	N1B	5/11/2022	2.8227	0.8649	3.6876
1-1 Mor	N1B	6/6/2022	3.0253	1.5460	4.5713
1-1 Mor	N1B	6/28/2022	3.1949	1.4900	4.6849
1-1 Mor	N1B	7/29/2022	3.1648	1.6430	4.5378
1-1 Mor	N1B	8/18/2022	3.1579	1.1840	4.3419
1-1 Mor	N1B	9/15/2022	3.2515	3.4570	6.7085
1-1 Mor	N1B	10/6/2022	2.9436	0.6672	3.4988
1-1 Mor	N1B	10/31/2022	3.1363	0.9327	3.9115
1-1 Mor	N1B	12/2/2022	3.3428	1.7470	5.0898
1-1 Stream	N1B	3/27/2022	3.1379	0.3402	3.4781
1-1 Stream	N1B	4/16/2022	2.8889	0.1432	3.0321
1-1 Stream	N1B	5/11/2022	2.8042	0.2367	3.0409
1-1 Stream	N1B	6/6/2022	2.7948	0.2676	3.0624
1-1 Stream	N1B	6/28/2022	2.8739	0.2420	3.1159
3-5 Mor	N4D	10/31/2021	3.8800	1.3160	5.1960
3-5 Mor	N4D	11/28/2021	3.3372	1.5340	4.8712

Site	Watershed	Date	Dissolved CO_2	Aqueous CO_2	Soil CO_2
3-5 Mor	N4D	12/21/2021	3.4724	0.9064	4.3788
3-5 Mor	N4D	1/13/2022	3.5864	1.0250	4.6114
3-5 Mor	N4D	1/30/2022	3.9158	1.2150	5.1308
3-5 Mor	N4D	3/2/2022	3.2915	1.1960	4.4875
3-5 Mor	N4D	3/27/2022	3.0700	0.7702	3.8402
3-5 Mor	N4D	4/16/2022	3.0563	0.5524	3.6087
3-5 Mor	N4D	5/11/2022	3.0120	0.7142	3.7262
3-5 Mor	N4D	6/5/2022	3.2097	0.9647	4.1744
3-5 Mor	N4D	6/28/2022	3.3889	1.2230	4.6119
3-5 Mor	N4D	7/29/2022	3.1832	1.4220	4.6052
3-5 Mor	N4D	8/18/2022	3.2740	0.8440	4.1180
3-5 Mor	N4D	9/15/2022	3.4067	1.7650	5.1717
3-5 Mor	N4D	10/6/2022	3.4480	1.5940	5.0420
3-5 Mor	N4D	10/31/2022	3.6226	1.2910	4.9136
3-5 Mor	N4D	12/2/2022	3.2160	0.9495	4.1655
3-5-1 Mor	N4D	10/31/2021	4.3320	0.7706	5.1026
3-5-1 Mor	N4D	11/28/2021	3.3220	0.8132	4.1352
3-5-1 Mor	N4D	12/21/2021	3.2220	0.9926	4.2146
3-5-1 Mor	N4D	1/13/2022	3.7350	0.6619	4.3969
3-5-1 Mor	N4D	1/30/2022	3.6420	1.2310	4.8730
3-5-1 Mor	N4D	3/2/2022	3.3330	0.7232	4.0562
3-5-1 Mor	N4D	3/27/2022	3.2390	1.1170	4.3560
3-5-1 Mor	N4D	4/16/2022	5.9880	0.5963	6.5843
3-5-1 Mor	N4D	5/11/2022	3.1590	1.0960	4.2550
3-5-1 Mor	N4D	6/5/2022	3.1750	0.9368	4.1118
3-5-1 Mor	N4D	6/28/2022	3.2710	0.9368	4.2078
3-5-1 Mor	N4D	7/29/2022	3.0391	1.1730	4.2121
3-5-1 Mor	N4D	8/18/2022	3.0430	0.7718	3.8148

Site	Watershed	Date	Dissolved CO_2	Aqueous CO_2	Soil CO_2
3-5-1 Mor	N4D	9/15/2022	3.6050	1.1900	4.7950
3-5-1 Mor	N4D	10/6/2022	3.5180	1.2060	4.7240
3-5-1 Mor	N4D	10/31/2022	3.4180	1.0800	4.4980
3-5-1 Mor	N4D	12/2/2022	3.2760	0.9467	4.2227
4-6 Mor	N4D	10/31/2021	3.4711	1.5140	4.9851
4-6 Mor	N4D	11/28/2021	3.5297	1.1290	4.6587
4-6 Mor	N4D	12/21/2021	3.5145	1.1020	4.6165
4-6 Mor	N4D	1/13/2022	3.6802	0.7998	4.4800
4-6 Mor	N4D	1/30/2022	3.3173	0.7938	4.1111
4-6 Mor	N4D	3/2/2022	3.1623	0.5804	3.7427
4-6 Mor	N4D	3/27/2022	2.9670	0.6047	3.5717
4-6 Mor	N4D	4/16/2022	2.9823	0.4811	3.4634
4-6 Mor	N4D	5/11/2022	2.9892	0.6980	3.6872
4-6 Mor	N4D	6/5/2022	3.2463	1.1260	4.3723
4-6 Mor	N4D	6/28/2022	3.2790	1.0580	4.3370
4-6 Mor	N4D	7/29/2022	2.9040	1.1940	4.0980
4-6 Mor	N4D	8/18/2022	3.1382	1.1300	4.2682
4-6 Mor	N4D	9/15/2022	3.2949	1.2620	4.5569
4-6 Mor	N4D	10/6/2022	3.3791	0.7632	4.1423
4-6 Mor	N4D	10/31/2022	3.5153	1.5310	5.0463
4-6 Mor	N4D	12/2/2022	3.3703	1.0470	4.4173
4-6 Eiss1	N4D	10/31/2021	2.7811	0.7936	3.5747
4-6 Eiss1	N4D	11/28/2021	2.8030	0.8471	3.6501
4-6 Eiss1	N4D	12/21/2021	2.1120	0.6586	2.7706
4-6 Eiss1	N4D	1/13/2022	2.7320	0.5902	3.3222
4-6 Eiss1	N4D	1/30/2022	2.7362	0.8119	3.5481
4-6 Eiss1	N4D	3/2/2022	3.0170	0.5700	3.5870
4-6 Eiss1	N4D	3/27/2022	2.6580	0.9030	3.5610

Site	Watershed	Date	Dissolved CO_2	Aqueous CO_2	Soil CO_2
4-6 Eiss1	N4D	4/16/2022	2.7312	0.4876	3.2188
4-6 Eiss1	N4D	5/11/2022	2.8308	0.5190	3.3498
4-6 Eiss1	N4D	6/5/2022	2.6549	1.3230	3.9779
4-6 Eiss1	N4D	6/28/2022	2.8590	0.9394	3.7984
4-6 Eiss1	N4D	7/29/2022	2.4630	0.9259	3.3889
4-6 Eiss1	N4D	8/18/2022	2.5272	1.0970	3.6242
4-6 Eiss1	N4D	9/15/2022	2.6300	0.9388	3.5688
4-6 Eiss1	N4D	10/6/2022	2.6951	1.1520	3.8471
4-6 Eiss1	N4D	10/31/2022	2.5853	0.9898	3.5751
4-6 Eiss1	N4D	12/2/2022	2.8610	0.6904	3.5514
4-6 Eiss2	N4D	10/31/2021	2.9462	1.5460	4.4922
4-6 Eiss2	N4D	11/28/2021	2.9174	1.2990	4.2164
4-6 Eiss2	N4D	12/21/2021	2.9034	0.9286	3.8320
4-6 Eiss2	N4D	1/13/2022	3.0620	0.8346	3.8966
4-6 Eiss2	N4D	1/30/2022	3.0287	1.5060	4.5347
4-6 Eiss2	N4D	3/2/2022	3.0074	1.0680	4.0754
4-6 Eiss2	N4D	3/27/2022	2.8201	1.2380	4.0581
4-6 Eiss2	N4D	4/16/2022	2.6349	0.7287	3.3636
4-6 Eiss2	N4D	5/11/2022	2.6069	0.9292	3.5361
4-6 Eiss2	N4D	6/5/2022	2.7612	1.0540	3.8152
4-6 Eiss2	N4D	6/28/2022	2.7923	1.0020	3.7943
4-6 Eiss2	N4D	7/29/2022	2.6603	1.1910	3.8513
4-6 Eiss2	N4D	8/18/2022	2.8369	1.0510	3.8879
4-6 Eiss2	N4D	9/15/2022	3.0499	1.4430	4.4929
4-6 Eiss2	N4D	10/6/2022	3.1681	1.8370	5.0051
4-6 Eiss2	N4D	10/31/2022	3.1266	3.9660	7.0926
4-6 Eiss2	N4D	12/2/2022	3.0664	2.0440	5.1104
1-1 Stream	N4D	3/27/2022	2.7590	0.1155	2.8745

Site	Watershed	Date	Dissolved CO_2	Aqueous CO_2	Soil CO_2
1-1 Stream	N4D	4/16/2022	2.8007	0.1289	2.9296
1-1 Stream	N4D	5/11/2022	2.8147	0.0946	2.9093
1-1 Stream	N4D	6/5/2022	2.8023	0.0868	2.8891
1-1 Stream	N4D	6/28/2022	2.8520	0.1465	2.9985
1-1 Stream	N4D	7/29/2022	2.7817	0.1361	2.9178
3-1 Stream	N4D	11/28/2021	3.3527	0.2398	3.5925
3-1 Stream	N4D	12/21/2021	3.5863	0.2621	3.8484
3-1 Stream	N4D	1/13/2022	3.4748	0.1726	3.6474
3-1 Stream	N4D	1/30/2022	3.4704	0.4994	3.9698
3-1 Stream	N4D	3/2/2022	3.6198	0.3325	3.9523
3-1 Stream	N4D	3/27/2022	2.7853	0.1084	2.8937
3-1 Stream	N4D	4/16/2022	2.9751	0.1078	3.0829
3-1 Stream	N4D	5/11/2022	2.8682	0.1079	2.9761
3-1 Stream	N4D	6/5/2022	2.9718	0.1352	3.1070
3-1 Stream	N4D	6/28/2022	2.9062	0.1753	3.0815
3-1 Stream	N4D	7/29/2022	3.0069	0.2050	3.2119
3-1 Stream	N4D	8/18/2022	3.0325	0.1220	3.1545
3-1 Stream	N4D	9/15/2022	2.7775	0.1427	2.9202
3-1 Stream	N4D	10/6/2022	3.4730	0.1292	3.6022
3-1 Stream	N4D	10/31/2022	3.6130	0.2946	3.9076
3-1 Stream	N4D	12/2/2022	3.4437	0.4283	3.8720
4-1 Stream	N4D	11/28/2021	3.4294	0.6471	4.0765
4-1 Stream	N4D	12/21/2021	3.5956	0.6845	4.2801
4-1 Stream	N4D	1/13/2022	3.7572	0.0000	3.7572
4-1 Stream	N4D	1/30/2022	3.5305	0.3542	3.8847
4-1 Stream	N4D	3/2/2022	3.2645	0.4439	3.7084
4-1 Stream	N4D	3/27/2022	2.8712	0.1671	3.0383
4-1 Stream	N4D	4/16/2022	2.9266	0.1713	3.0979

Site	Watershed	Date	Dissolved CO_2	Aqueous CO_2	Soil CO_2
4-1 Stream	N4D	5/11/2022	2.9056	0.1625	3.0681
4-1 Stream	N4D	6/5/2022	2.8585	0.1723	3.0308
4-1 Stream	N4D	7/29/2022	3.0446	0.2885	3.3331
4-1 Stream	N4D	8/18/2022	2.9877	0.2153	3.2030
4-1 Stream	N4D	9/15/2022	3.5393	0.4378	3.9771
4-1 Stream	N4D	10/6/2022	3.2590	1.0120	4.2710
4-1 Stream	N4D	10/31/2022	2.9466	0.8226	3.7692
4-1 Stream	N4D	12/2/2022	3.2978	0.2491	3.5469

Appendix E - Groundwater Ages: CFCs and SF_6

Table 7 Supersaturated indicates there are additional non-atmospheric source(s) of the CFC and SF_6 making a valid age determination impossible. Current and historic ages provided below as well as calculated ages found in the table were provided/calculated by the Tritium Laboratory at the University of Miami.

Current maximum value of SF_6 is roughly 11.0 pmol/mol.

Current value of CFC-12 is 498 pmol/mol, max was 546 pmol/mol in 2003

Current value of CFC-11 is 228 pmol/mol, max was 268 pmol/mol in 1994

Current value of CFC-113 is 69 pmol/mol, max was 85 pmol/mol in 1994

*indicates supersaturated

Site	Watershed	Date	Recharge Temp (°C)	SF_6 (Yrs)	CFC12 (Yrs)	CFC11 (Yrs)	CFC113 (Yrs)
3-5-1 Mor	N4D	3/2/2022	1.5	36	57	64	52
3-5-1 Mor	N4D	3/2/2022	1.5	37	57	63	52
3-5-1 Mor	N4D	6/5/2022	1.5	33	56	62	52
3-5-1 Mor	N4D	6/5/2022	1.5	36	57	65	54
3-5-1 Mor	N4D	6/5/2022	1.5	35	56	62	53
3-5-1 Mor	N4D	7/29/2022	1.5	29	56	62	52
3-5-1 Mor	N4D	7/29/2022	1.5	24	45	51	41
3-5-1 Mor	N4D	10/30/2022	1.5	27	57	65	53
3-5-1 Mor	N4D	10/30/2022	1.5	18	50	55	45
3-5-1 Mor	N4D	10/30/2022	1.5	27	57	62	53
4-6 Eiss2	N4D	3/2/2022	1.5	17	46	49	40
4-6 Eiss2	N4D	3/2/2022	1.5	*	46	49	41
4-6 Eiss2	N4D	3/2/2022	1.5	9	46	49	40
4-6 Eiss2	N4D	6/5/2022	1.5	18	47	50	39
4-6 Eiss2	N4D	6/5/2022	1.5	18	47	50	39
4-6 Eiss2	N4D	6/5/2022	1.5	21	47	50	40
4-6 Eiss2	N4D	7/29/2022	1.5	21	46	49	39
4-6 Eiss2	N4D	7/29/2022	1.5	22	46	49	39

Site	Watershed	Date	Recharge Temp (°C)	SF_6 (Yrs)	CFC12 (Yrs)	CFC11 (Yrs)	CFC113 (Yrs)
4-6 Eiss2	N4D	10/30/2022	1.5	10	48	51	41
4-6 Eiss2	N4D	10/30/2022	1.5	15	48	51	42
4-6 Eiss2	N4D	10/30/2022	1.5	13	48	51	41
4-6 Mor	N4D	3/2/2022	1.5	14	41	46	39
4-6 Mor	N4D	3/2/2022	1.5	11	41	46	39
4-6 Mor	N4D	3/2/2022	1.5	10	42	46	39
4-6 Mor	N4D	6/5/2022	1.5	14	47	50	40
4-6 Mor	N4D	6/5/2022	1.5	18	47	50	40
4-6 Mor	N4D	6/5/2022	1.5	17	47	50	40
4-6 Mor	N4D	7/29/2022	1.5	27	48	52	38
4-6 Mor	N4D	7/29/2022	1.5	25	48	52	41
4-6 Mor	N4D	10/30/2022	1.5	16	48	52	43
4-6 Mor	N4D	10/30/2022	1.5	16	49	52	43
4-6 Mor	N4D	10/30/2022	1.5	19	49	52	43
1-1 Mor	N1B	2/27/2022	1.5	4	47	50	41
1-1 Mor	N1B	2/27/2022	1.5	15	47	50	41
1-1 Mor	N1B	2/27/2022	1.5	*	47	50	41
1-1 Mor	N1B	6/6/2022	1.5	22	47	50	40
1-1 Mor	N1B	6/6/2022	1.5	21	47	50	40
1-1 Mor	N1B	7/29/2022	1.5	14	46	50	40
1-1 Mor	N1B	7/29/2022	1.5	17	47	50	40
1-1 Mor	N1B	7/29/2022	1.5	16	47	50	40
1-1 Mor	N1B	10/30/2022	1.5	21	47	50	41
1-1 Mor	N1B	10/30/2022	1.5	23	47	50	41
1-1 Mor	N1B	10/30/2022	1.5	15	47	50	41
3-5-1 Mor	N4D	3/2/2022	13.7	30	52	60	48
3-5-1 Mor	N4D	3/2/2022	13.7	31	52	59	48
3-5-1 Mor	N4D	6/5/2022	13.7	26	51	59	48

Site	Watershed	Date	Recharge Temp (°C)	SF_6 (Yrs)	CFC12 (Yrs)	CFC11 (Yrs)	CFC113 (Yrs)
3-5-1 Mor	N4D	6/5/2022	13.7	29	52	61	50
3-5-1 Mor	N4D	6/5/2022	13.7	29	51	59	49
3-5-1 Mor	N4D	7/29/2022	13.7	19	51	58	48
3-5-1 Mor	N4D	7/29/2022	13.7	18	40	48	37
3-5-1 Mor	N4D	10/30/2022	13.7	15	52	61	49
3-5-1 Mor	N4D	10/30/2022	13.7	5	42	50	39
3-5-1 Mor	N4D	10/30/2022	13.7	15	52	61	49
4-6 Eiss2	N4D	3/2/2022	13.7	4	34	41	34
4-6 Eiss2	N4D	3/2/2022	13.7	*	35	42	35
4-6 Eiss2	N4D	3/2/2022	13.7	*	34	41	34
4-6 Eiss2	N4D	6/5/2022	13.7	5	35	43	33
4-6 Eiss2	N4D	6/5/2022	13.7	5	35	43	33
4-6 Eiss2	N4D	6/5/2022	13.7	8	36	43	34
4-6 Eiss2	N4D	7/29/2022	13.7	9	34	40	33
4-6 Eiss2	N4D	7/29/2022	13.7	10	35	40	33
4-6 Eiss2	N4D	10/30/2022	13.7	*	37	44	35
4-6 Eiss2	N4D	10/30/2022	13.7	*	38	45	35
4-6 Eiss2	N4D	10/30/2022	13.7	*	38	45	35
4-6 Mor	N4D	3/2/2022	13.7	*	*	28	33
4-6 Mor	N4D	3/2/2022	13.7	*	*	29	33
4-6 Mor	N4D	3/2/2022	13.7	*	*	32	33
4-6 Mor	N4D	6/5/2022	13.7	*	35	42	34
4-6 Mor	N4D	6/5/2022	13.7	5	35	42	34
4-6 Mor	N4D	6/5/2022	13.7	4	35	42	34
4-6 Mor	N4D	7/29/2022	13.7	15	39	47	31 or 15
4-6 Mor	N4D	7/29/2022	13.7	13	39	47	35
4-6 Mor	N4D	10/30/2022	13.7	3	38	46	37
4-6 Mor	N4D	10/30/2022	13.7	3	38	46	37

Site	Watershed	Date	Recharge Temp (°C)	SF_6 (Yrs)	CFC12 (Yrs)	CFC11 (Yrs)	CFC113 (Yrs)
4-6 Mor	N4D	10/30/2022	13.7	6	38	46	37
1-1 Mor	N1B	2/27/2022	13.7	*	35	43	35
1-1 Mor	N1B	2/27/2022	13.7	1	35	43	35
1-1 Mor	N1B	2/27/2022	13.7	*	36	43	35
1-1 Mor	N1B	6/6/2022	13.7	10	36	42	34
1-1 Mor	N1B	6/6/2022	13.7	8	35	42	34
1-1 Mor	N1B	7/29/2022	13.7	*	35	42	34
1-1 Mor	N1B	7/29/2022	13.7	4	35	42	34
1-1 Mor	N1B	7/29/2022	13.7	3	35	42	34
1-1 Mor	N1B	10/30/2022	13.7	8	35	42	35
1-1 Mor	N1B	10/30/2022	13.7	11	35	43	35
1-1 Mor	N1B	10/30/2022	13.7	2	35	43	35