Groundwater reservoirs as a source for greenhouse gas emissions to the atmosphere

BIOS 35502: Practicum in Environmental Field Biology

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Abstract

Previous studies established that lakes are sources of CO_2 to the atmosphere. Many of these studies predict that a majority of these inputs come from exogenously produced carbon transported to lakes through groundwater. However, direct measurements have not been taken. To directly measure the amount of dissolved organic carbon in groundwater, wells were drilled and sampled around two seepage kettle lakes in the upper peninsula of Michigan. Other measurements like pH, dissolved oxygen content, water level, and temperature were taken to determine potential factors that affect groundwater DIC concentrations. The DIC concentrations in groundwater match estimates made in previous studies, vary spatially and temporally, and are correlated with pH, temperature, and water level. By determining the carbon stored in groundwater, accurate estimates can be made to determine groundwater's role in the global carbon cycle.

Introduction

Inland waters play a significant role in the global and regional carbon cycle (Tranvik et al. 2009). These waters are extremely active sites of transport, transformation, and storage of available carbon, i.e. carbon cycling. Particularly in temperate regions, lakes are typically sources of greenhouse gases (e.g. CO_2 and CH_4) to the atmosphere. The carbon transformed, released, and stored in lakes can come from aquatic or terrestrial sources and can be inorganic or organic in form. Recent work has focused on the impact of terrestrial organic carbon on aquatic carbon cycling (Cole et al. 2007; Tranvik et al. 2009) while less research has been done on the impact of terrestrial inorganic carbon. Lakes can receive dissolved inorganic carbon (DIC) in groundwater inflow from soil respiration and carbonate weathering; however, the degree to which groundwater contributes to the carbon emitted from lakes is unknown.

Previous studies have focused on the source of carbon dioxide (CO_2) and methane (CH_4) emitted from lakes to the atmosphere (McDonald et al. 2013; Wilkinson et al. 2016). Lakes can act as reactors or vents. As reactors, they mineralize terrestrial organic carbon within the lake and release it to the atmosphere. As vents, they receive inorganic terrestrial carbon (DIC) from groundwater and release it to the atmosphere. Humans can also influence whether a lake acts as a reactor or vent. Due to urbanization, the amount of available potable surface water is decreasing. This increases human's reliance on groundwater reservoirs as a primary

source of freshwater which allows degassing to occur more frequently (Macpherson 2009). Consequently, it has become imperative to explore groundwater's role within the carbon cycle.

At the University of Notre Dame Environmental Research Center (UNDERC) located in the Upper Peninsula of Michigan, it has been reported that the majority of lakes on site contain excess CO_2 (Cole et al. 1994) and are sources of greenhouse gases (GHG) to the atmosphere. The CO_2 comes from two potential sources: within the lake or endogenous organic sources, and adjective, exogenous inputs from processes like soil respiration (Wilkinson et al. 2016). The contribution of groundwater to CO_2 emissions from UNDERC lakes has been estimated to be substantial (Wilkinson et al. 2016); however, without direct measurements of groundwater CO_2, it is unclear if these estimates are valid. This study aims to determine 1) the mean GHG concentrations found in the groundwater and variability over time and 2) determine if the GHG concentrations from groundwater are uniformly distributed across the watershed and broader landscape.

Methods

To assess and take direct measurements of the groundwater GHG concentrations spatially and temporally, wells were installed near Peter and Paul Lakes on the UNDERC property. Six of the wells are positioned along transects that extend from the near the top of the watershed to the shoreline of Paul and Peter Lakes (Figure 1). An additional three wells were distributed along the shoreline of Paul Lake in each cardinal direction (north, east, south, and west; Figure 1). Sampled together, all of these wells measured the spatial variability of groundwater GHG concentrations, or the differences of these concentrations near and around Peter and Paul Lakes.

Each of the wells were constructed using a 3-meter long 2" inner diameter polyvinyl chloride (PVC) pipe. At the end of the 3-meter long pipe, 6 holes were drilled around the pipe every inch up to 36 inches. These holes were then covered with a jersey "sock" to filter out unwanted sediment and silt. The well pipes were inserted into a hole excavated by a 3" soil

auger. Wells were drilled into the ground until the auger could no longer pick up consolidated sediment and water infiltration of the hole was observed. The depth of the wells ranged from 1.0 meter deep to 2.5 meters deep. Once the wells were installed, they were left undisturbed to ensure full infiltration occurred; each of the wells required a few hours to completely fill with water. To keep out unwanted organisms and direct rainwater, the wells were capped following installation.

On a weekly basis throughout June and early July of 2016, the wells were sampled to establish temporal variability, or the variabilities of groundwater GHG concentrations through the sampling period of 6 weeks. To parse out potential random variability, the wells were sampled at the same time each sampling day, approximately 11:00 in the morning. In addition to sampling at the same time every day, it was important that fresh groundwater was sampled for GHG concentrations and not the stagnant water in the well; stagnant water has had time to equilibrate with the atmosphere and is not representative of the actual groundwater. To obtain fresh groundwater, the well was purged (i.e. removed all of the stagnant water in the pipe) with a constructed bailer bucket and was left alone to refill with enough fresh groundwater to fill two 250 mL sample bottles (U.S. EPA 1996). Complete infiltration typically took between 2 and 10 minutes depending on the depth of well and the proximity to the lake.

A typical sampling event consisted of measuring the water level in the well, taking the groundwater temperature, and collecting approximately 500 mL of groundwater from the well to analyze immediately in the laboratory. Water level was read at each sample site before purging the well with a water level meter. Following purging and subsequent infiltration, groundwater temperature was recorded with a thermometer in the field. In addition, at each well site, we filled two gas tight plastic bottles with fresh groundwater ensuring that the bottle was overflowing before fastening the cap in order to minimize gas exchange.

Immediately following field data collection, the groundwater was analyzed for concentrations. I measured pH, dissolved oxygen concentration with a YSI ProODO

multiparameter handheld meter (YSI Incorporated, Yellow Springs, Ohio, USA), and dissolved inorganic carbon concentration (DIC) measured on a gas chromatograph (Janagir et al. 2012). To measure DIC, 10 mL of groundwater from each site was acidified with 200 µL of H_2SO_4 and equilibrated with 20 mL of inert gas (He) through vigorous shaking in a capped syringe. 10 mL of the helium headspace was injected into a Shimadzu GC-8A gas chromatograph with a 2 m column, packed with Porapak-Q, and connected to a thermal conductivity detector (Wilkinson et al. 2016). The acid catalyst converted all inorganic carbon species to headspace equilibrated CO_2 so that the gas chromatograph could measure the dissolved inorganic carbon concentration found in the groundwater samples. DIC values were calculated from the absorbance peaks measured by the gas chromatograph (Wilkinson et al. 2016). As the concentration of CO_2, or the partial pressure of CO_2 (pCO_2) was not directly measured, we calculated this value using the acid neutralizing capacity (ANC). ANC can be calculated from DIC measurements, pH, and temperature following the equations presented in Wilkinson et al. (2016). This method of calculation has been shown to have a strong correlation with actual sampled values of pCO_2 since pCO_2 is dependent on pH and DIC concentration (Wilkinson et al. 2016).

To determine the relationship between time and CO_2 concentration as well as spatial variability and CO_2 concentration, linear regression analyses were performed in R (R Core Team 2016). Some of the factors that were studied included normal groundwater quality checks (pH, color, dissolved oxygen concentration, and temperature). In addition, multiple simple linear regression analyses were used to determine if DIC and pCO_2 were negatively or positively correlated with pH, dissolved oxygen content, water depth, and groundwater temperature. Independent T-tests were performed to determine the difference of DIC or pCO_2 in groundwater between the two lakes. Since we were concerned with variability, I calculated the coefficient of variation for the DIC and pCO_2 of each groundwater well through time. This is an indicator of how the wells changed over time. Differences in DIC concentration were quantified and

compared using an analysis of variance (ANOVA) and subsequent Tukey's HSD tests. ANOVAs were performed to compare the wells located along the transects, which are a measure of distance from the lake.

Results

In the groundwater wells located on a transect on Paul Lake, the DIC concentration generally increased over time, with the bottom and middle wells having a higher DIC concentration than the well located at the top of the watershed (Figure 2, Figure 3, ANOVA, $F_{2,28}$= 5.24, p = 0.01). In the wells along Peter Lake, DIC concentration remained consistent through time, with the bottom well containing the higher DIC concentration and the top well containing a lower DIC concentration (Figure 2, Figure 4, ANOVA, $F_{2,25}$ = 5.94, p = 0.008). When comparing the two lakes, the Peter Lake wells had lower DIC concentrations than the Paul Lake wells (T-Test, t_{57} = -8.22, p < 0.001).

In the cardinal wells located on Paul Lake, the western well increased in DIC; while the other three wells (south, north, and east) remained consistent over the two weeks that DIC was measured (Figure 4). In addition, the west well had the highest mean DIC concentration, while the east well had the lowest; the other two wells, south and north, had DIC concentrations that were slightly higher than the east well (ANOVA, $F_{3,12}$ = 132.8, p < 0.01).

Not only did the wells contain different concentrations of DIC, but they also differed in variability. The coefficient of variation was calculated for each of the wells and plotted for each well and lake over time (Figure 5). In general, as time progressed, the DIC concentration in the wells became more variable, with the Paul Lake wells being more variable than the Peter Lake wells. Furthermore, the wells located at the bottom of the watershed and at the top of the watershed were more variable than the middle well on both Peter Lake and Paul Lake (Figure 5).

In order to correlate DIC and pCO$_2$ with other explanatory abiotic factors, several regressions were performed (Table 1). Dissolved oxygen concentration was found to be

significantly negatively correlated with DIC concentration and pCO$_2$ (Table 1, Figure 6). In addition, on Peter and Paul Lakes, as pH increased, DIC and pCO$_2$ significantly decreased (Figure 7, and Table 1). Furthermore, as samples were taken deeper in the water table on Peter, or as water was taken from deeper wells, DIC and pCO$_2$ was significantly negatively correlated. However, this relationship was not observed for the Paul wells (Table 1, Figure 7).

Discussion

The groundwater surrounding Peter and Paul Lakes was supersaturated with CO_2 (the concentration in groundwater was greater than the atmosphere). Previous studies have found that lakes, including Peter and Paul, are supersaturated with CO_2 and are a net source of CO_2 to the atmosphere. This means that lakes are either decomposing terrestrial material or receiving CO_2 from groundwater (Cole et al. 1994). Given the inflowing supersaturated CO_2 in the ground water of Peter and Paul Lakes, a portion of the CO_2 emitted from these lakes is likely from ground water. Other studies have estimated a majority of carbon input to lakes come from groundwater (Striegl and Michmerhuizen et al. 1998, McDonald et al. 2013). In order to maintain supersaturated pCO$_2$ concentrations that seepage kettle lake like Peter and Paul emit (Cole et al. 1993, McDonald et al. 2013), incoming groundwater must have pCO$_2$ concentrations of 1000 µmol/L, or about 22,000 ppm[v] (Wilkinson et al. 2016). In this study, the direct measurements of the groundwater found the DIC concentration in groundwater inputs to be 1464.79 +/- 64.05 µmol/L on average with a pCO$_2$ of 23,430.49 +/-1188.23 ppm[v], a number that validates previous estimates (Wilkinson et al. 2016). Our direct measurements confirm assumptions that the consumption and production of CO_2 in groundwater play a major role in the global carbon cycle (Tranvik et al. 2009). These shallow water inputs from groundwater are an integral part of surface hydrology, providing base flow to rivers, streams and some lakes (Macpherson et al. 2009). Shallow groundwater inputs that pass though biologically active, and organic rich sediments and soils like those found at UNDERC, leads to CO_2 enrichment that can be the source for this excess gas (Crawford et al. 2014).

Dissolved oxygen and pH

The nature and carbon storage capacity of groundwater was studied to determine how groundwater contributes to the carbon cycle in these lake systems. Groundwater generally contains little to no dissolved oxygen due to the lack of available photosynthetic light; instead, it acts like the hypolimnion of a eutrophic lake system in that nearly all of the inorganic carbon located in the water is due to respiration. Since aerobic respiration consumes one mole of oxygen for every mole of carbon dioxide (Mattson and Likens 1993), oxygen consumption is only equal to the carbon dioxide production if there are no external organic matter or groundwater inputs. Any deviation above this 1:1 line can be assumed to be due to anaerobic respiration, methanogenesis, sulfate reduction, denitrification, or any combination of the four (Crawford et al. 2013, Wilkinson et al. 2016) and groundwater input rich in CO_2. All of the groundwater DIC and dissolved oxygen concentrations were above this 1:1 line suggesting that the exogenous inputs typically found in Peter and Paul Lake match observed groundwater inputs (Figure 6).

Besides under-saturation in dissolved oxygen correlating with higher DIC concentrations, pH was negatively correlated with DIC concentration. As pH decreases, the most abundant species of DIC is CO_2. Due to the low pH in the groundwater surrounding Peter and Paul, the measured DIC was dominated by CO_2. The pCO_2 found at this low pH are most likely due to mineralization, the transformation of organic carbon to mineral, or inorganic carbon (Stumm 2003). This is also consistent with our results that show samples taken nearer to the surface had greater pCO_2 values as the pH was also more acidic closer to the lake (Table 1). Other studies have also found that the plant root respiration and oxidation of organic carbon in unsaturated zone of the soil can explain why most of the groundwater carbon dioxide is found near the top of the water table (Macpherson et al. 2009).

Temporal variability of Paul Lake and Peter Lake wells

Over time, DIC concentrations increased for all of the transect wells near Paul Lake. This trend can be attributed to changing temperatures in groundwater. DIC was measured in the summer months or, the peak "season" of DIC production, when lakes are producing the greatest amount of DIC (Wilkinson et al. 2016). Concurrently, a slight increase in well temperatures (from 11.3 +/-0.37 °C to 13.4 +/- 0.57 °C) were observed over time on the Paul Lake transect wells (SLR, t_{23} = 3.3, R^2 = 0.26, p < 0.01); this increase in temperature on Paul Lake wells is weakly correlated with increased DIC concentrations (Table 1). This suggests that increased well temperatures facilitated more microbial production of DIC and influenced the general increase in DIC production over the 6-week period the wells were sampled. For the cardinal wells on Paul, only the west well experienced increasing DIC concentrations over the short sampling period; the remaining cardinal wells did not increase (Figure 4). Increased temperatures may also play a role in causing higher DIC concentrations over time since greater temperatures were observed for the Paul Lake west well (Table 2).

DIC concentrations in the Peter Lake wells remained consistent, but still fluctuated over time (Figure 3). The temporal trends on Peter may be explained by changes in water level, or how deep the samples were drilled, rather than temperature. As time progressed, samples were taken from deeper in the ground because the depth to groundwater level increased (SLR, R^2 = 0.26, t_{30} = 3.2, p < 0.01), which is weakly but significantly correlated with lower DIC concentrations (Table 1). This factor, which decreases DIC, may have caused the dissimilar pattern of increasing DIC over time with wells located on Peter Lake compared with the wells located on Paul Lake, which did not have this relationship.

Besides DIC concentration changing over the course of the sampling period, variability of DIC in the transect wells increased over time and was generally higher in Paul Lake wells than in to Peter Lake wells. These temporal groundwater variabilities may be the source of variabilities in CO_2 efflux found in these lakes over the course of the summer, consistent with predictions made in other studies (Wilkinson et al. 2016). This result is also consistent with

another study that supports that lakes with the highest reported CO_2 concentrations were in

areas of highest groundwater discharge (Kodovska et al. 2016, Sadat-Noori et al. 2016).

Therefore, groundwater may be a driving factor of the supersaturation of primarily groundwater

fed lakes.

Spatial variability of groundwater DIC

Besides changing DIC levels over time, groundwater DIC levels also varied spatially

from well to well. Paul and Peter wells located closest to the water's edge had the highest DIC

concentrations, relative to each respective lake, while the top wells had the lowest DIC

concentrations (Figure 4). This suggests that as groundwater flows along the hydraulic gradient,

the water picks up DIC from soil respiration. The spatial trend of increasing DIC with increasing

proximity to the lake is similar to the pattern in other systems (Crawford et al. 2014). Overall,

Paul Lake had higher DIC concentrations than Peter wells. This may be due to variability in

groundwater and surface water flow among the lakes as Paul flows into Peter and may receive

more carbon inputs. This hypothesis is supported by the significant differences in DIC

concentration among the cardinal wells on Paul Lake (ANOVA, $F_{3,12} = 132.8$, $p < 0.01$). The

west well, located at the main transect on Paul, had the highest DIC concentration, while the

east well had the lowest concentration which could reflect the regional groundwater flow path.

This data suggests that DIC inputs are variable around the lake. In general, the wells located

nearest the water table and farthest from the water table have the most variable DIC. Typically,

shallow wells (less than 10m deep) have the most variable DIC concentrations spatially

(Macpherson et al. 2009, Sadat-Noori et al. 2016) and are typically irregularly dispersed

(Kodovska et al. 2016). Variability can prove problematic for those trying to estimate the global

impacts of $p$$CO_2$ to the atmosphere based on groundwater inputs.

This study validates previous estimates that lakes at UNDERC act like vents, releasing

groundwater CO_2 inputs to the atmosphere. In addition, temperature and groundwater level

described much of the spatial and temporal variability in the measurements of DIC. In the future,

with increasing storm events and warmer conditions, DIC delivered to lakes from groundwater could increase, making lakes an even stronger source of CO_2 to the atmosphere. Warmer climates can also result in more terrestrial production and potential for degassing of groundwater from the soils as an additional source of CO_2 to the atmosphere (Schindler et al. 1997, Tranvik et al. 2009). It is important to study groundwater as a source of CO_2 to the atmosphere. Groundwater plays an important, yet understudied, role in the global carbon cycle that is integral to predicting our future global carbon budget. While this study only provided an initial look into the abiotic factors that govern the carbon storage capacity of groundwater and its substantial input into lakes, it is clear from the spatial and temporal heterogeneity observed in this one small region that groundwater dynamics play an important role in the regional carbon cycle.

Acknowledgements

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Tables and Figures

	Slope	R^2	t-statistic	p-value	Slope	R^2	t-statistic	p-value
dO	-0.14,	0.41	t_{55}=-6.17	>0.001	-0.16	0.41	t_{49}=-5.936	>0.001
				Peter Lake				
pH	-0.66	0.38	t_{23}=-3.94	>0.001	-1.05	0.55	t_{23}=-5.461	>0.001
Temperature	0.01	0.01	t_{26}=0.36	0.73	0.04	0.03	t_{23}=0.87	0.40
Water level	-0.69	0.38	t_{26}=-4.16	>0.001	-0.94	0.36	t_{23}=-3.853	>0.001
				Paul Lake				
pH	-0.57	0.16	t_{26}=-2.471	0.02	-1.01	0.37	t_{26}=-4.06	>0.001
Temperature	0.09	0.23	t_{29}=3.178	>0.01	0.12	0.28	t_{26}= 3.36	>0.01
Water level	-0.10	0.01	t_{29}=-0.662	0.51	-0.17	0.03	t_{26}=-0.88	0.39

Table 1. DIC concentrations (µmol/L) in terms of abiotic factors sampled. At each transect well (located on Peter and Paul Lake), dissolved oxygen, pH, temperature, and the water level was taken. Multiple simple linear regressions were performed correlating these abiotic factors with DIC concentrations.

Groundwater well	Mean temperature (°C)	Standard error
West	14.75	0.25
East	11.38	0.38
North	11.72	0.13
South	10.94	0.54

Table 2. Mean temperatures (+/- the standard error) of the cardinal wells located around Paul Lake. The west well had the highest temperature compared to the other three wells (ANOVA, $F_{3,12}$ = 23.26, $p < 0.001$).
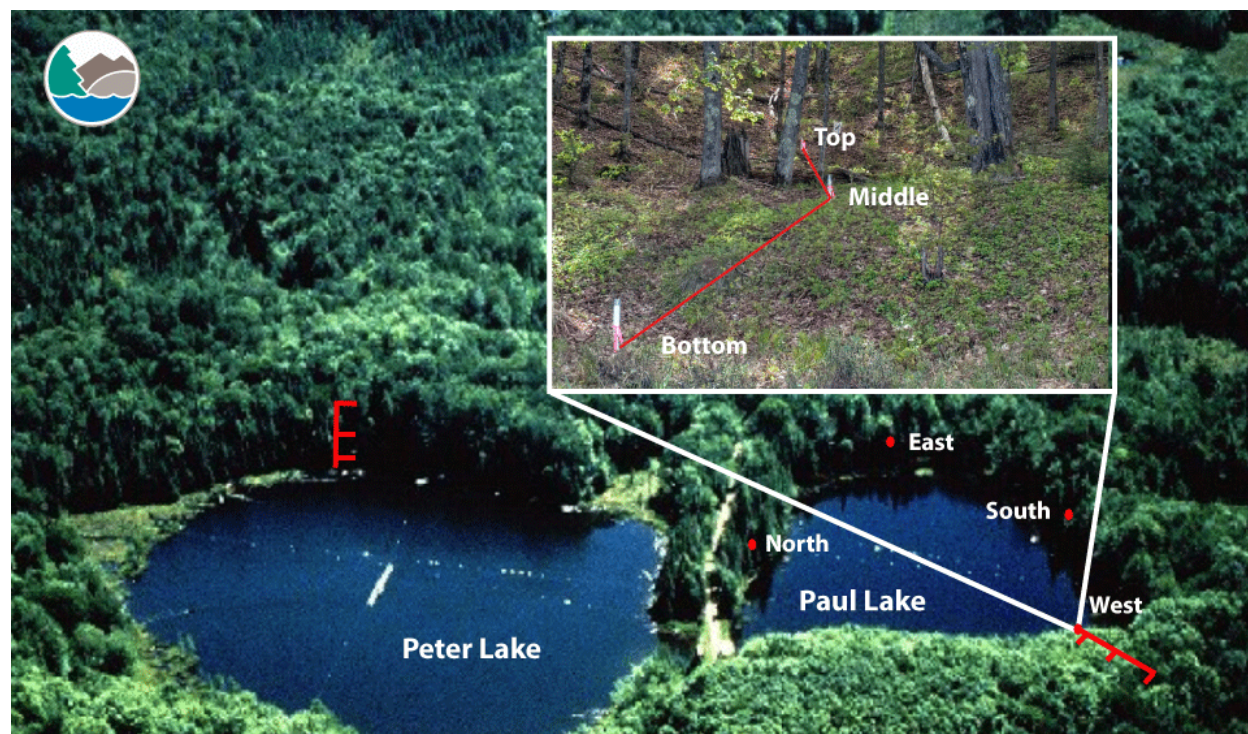
Figure 1. Map of groundwater wells located on Peter and Paul Lakes. Two transects extend from Peter and Paul Lake containing three wells each. Three additional wells were drilled in each cardinal direction on Paul Lake. The transect wells on Peter are positioned at 3.4, 10.7, and 14.9 meters from shore respectively. The transect wells on Paul are located at 2.0, 10.5, and 24 meters from shore respectively. The cardinal wells are located 2.2, 1.3, and 1.5 meters from the shore (north, south, and east).
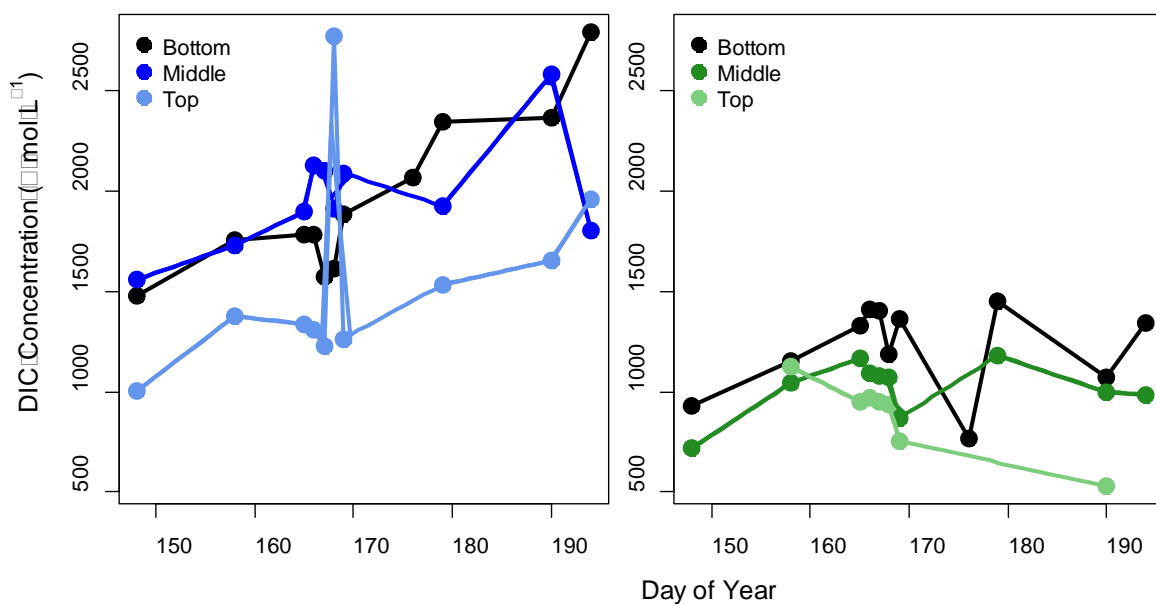
Figure 2. DIC temporal variation on Paul (left) and Peter (right). The DIC concentration (µmol/L) increased over the sampling period (6 weeks) while Peter remained more consistent over the same amount of time.
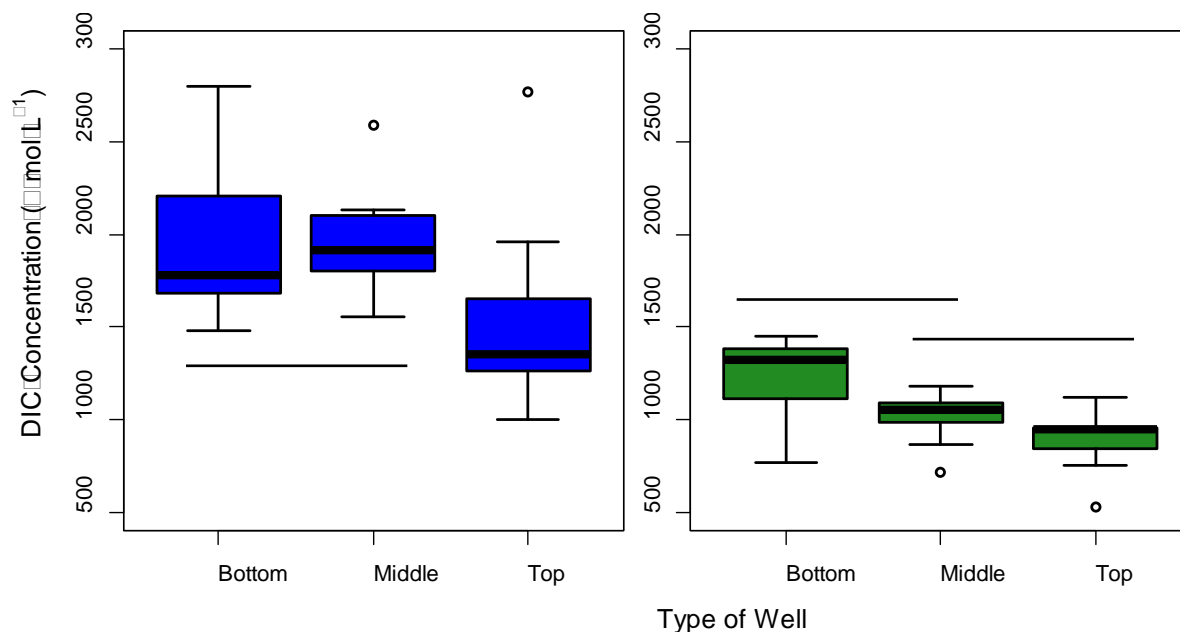
Figure 3. Groundwater DIC concentration (μmol/L) in the transect wells on Paul Lake (left) and Peter Lake (right). Lines represent data that is not significantly different from each other. In the wells on Paul Lake, the bottom and middle wells are both significantly different form each other (ANOVA, $F_{2,28}$= 5.24, p = 0.01, Tukey HSD, p= 0.02). In the wells along Peter Lake, DIC concentration remained consistent through time, with the bottom well containing the higher DIC concentration and the top well containing a lower DIC concentration (ANOVA, $F_{2,25}$ = 5.94, p = 0.008, Tukey HSD, p < 0.01). When comparing the two lakes, the Peter Lake wells had lower DIC concentrations than the Paul Lake wells (T-Test, t_{57} = -8.22, p < 0.001).
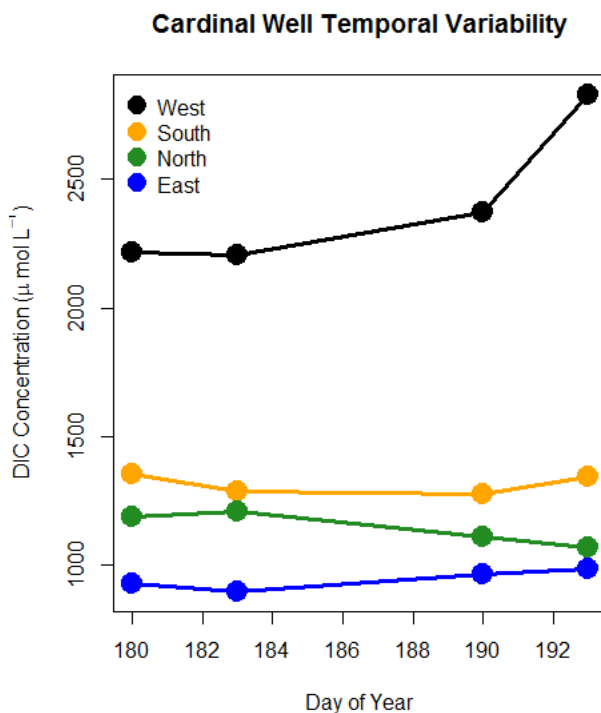
Cardinal Well Temporal Variability

Figure 4. DIC temporal variability for the cardinal wells on Paul Lake. The west well had the highest mean DIC concentration, while the east well had the lowest; the other two wells, south and north, had DIC concentrations that were slightly higher than the east well (ANOVA, $F_{3,12}$ = 132.8, $p < 0.01$, Tukey HSD, $p < 0.05$).
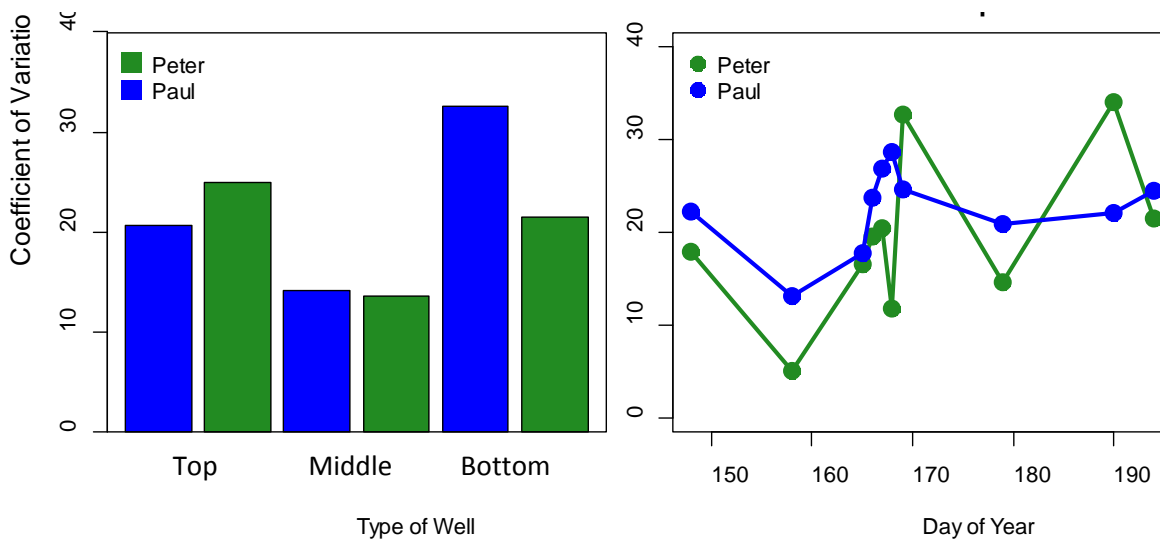

Figure 5. Temporal and spatial variability of DIC on the Peter and Paul transect wells. The coefficient of variation was calculated for each of the transect wells and plotted for each well and lake over time. As time progressed, the DIC concentration in the wells became more variable, with the Paul Lake wells being more variable than the Peter Lake wells. The wells

located at the bottom of the watershed and at the top of the watershed were more variable than the middle well on both Peter Lake and Paul Lake
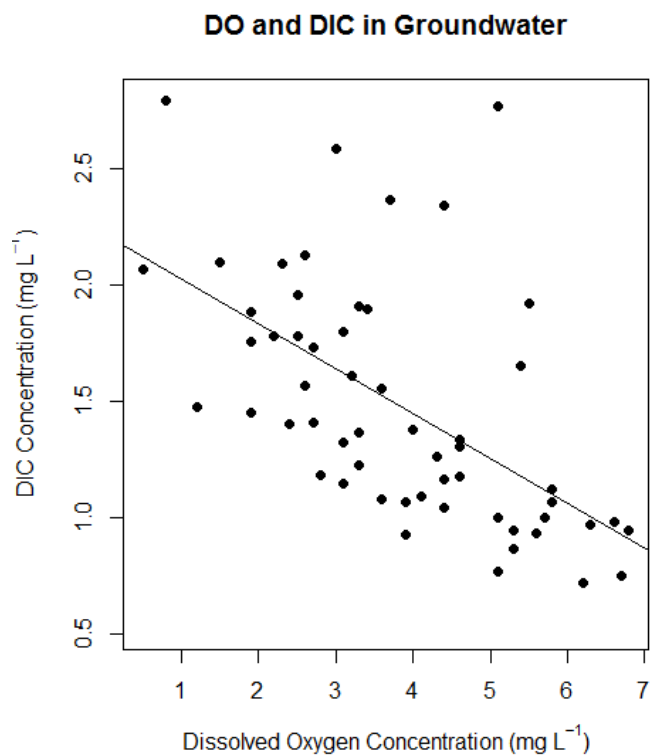
DO and DIC in Groundwater

Figure 6. Dissolved Oxygen concentration (mg/L) as a predictor of groundwater DIC (mg/L). The more dissolved oxygen in the groundwater the less DIC in the groundwater (Simple linear regression, $R^2 = 0.41$, $t_{55} = -6.17$, $p > 0.001$). This indicates that not a lot of respiration occurred in areas of higher dissolved oxygen concentrations.
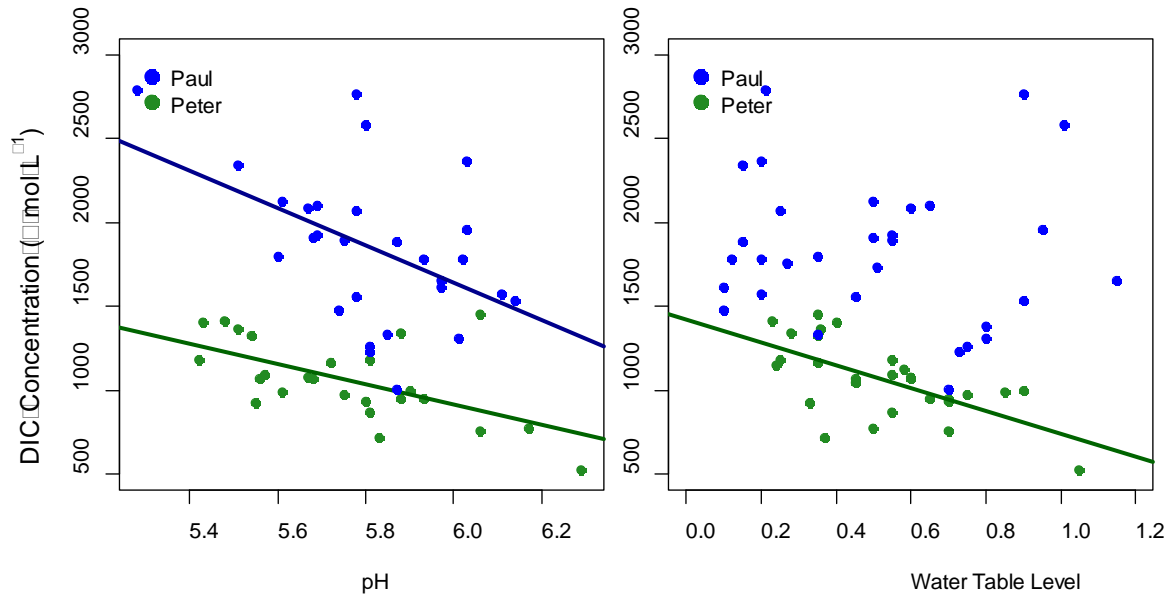
Figure 7. pH as a predictor of groundwater DIC in Peter and Paul wells (left). Water table level explaining groundwater DIC concentrations around Peter and Paul Lakes (right). On Peter and Paul Lakes, as pH increased, DIC significantly decreased (SLR, $R^2 = 0.38$, $t_{23} = -3.94$, p > 0.001). As samples were taken deeper in the water table on Peter Lake, or as water was taken from deeper wells, DIC was significantly negatively correlated (SLR, $R^2 = 0.38$, $t_{26} = -4.16$, p > 0.001). However, this relationship was not observed for the Paul wells (SLR, $R^2 = 0.01$, $t_{23} = -0.66$, p = 0.51).