

MONITORING DISSOLVED GASES AND IONS IN GROUNDWATER USING AN *IN SITU*
TECHNIQUE

BY

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THESIS

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ABSTRACT

We tested an *in situ* method for monitoring the concentrations of aqueous chemical species and dissolved gases in groundwater. We deployed *in situ* samplers in 8 wells completed in the glacial Glasford formation and underlying Banner formation of the Mahomet aquifer, a regional water supply in east-central Illinois. We distributed and retrieved samplers 25 times over 35 weeks. At one point in this interval, we pumped each well to retrieve a sample for standard analysis, for comparison to results obtained by the *in situ* technique. The *in situ* method relies on the diffusion of analytes through a permeable membrane integral to our samplers. The samplers can be deployed and retrieved from a well without the necessity of pumping groundwater. Since no pumping is required, the method allowed the samplers to be monitored from all of the wells within a few hours. SO_4^{2-} concentrations ranged among the wells from below detection (0.01 mM) to 0.84 mM, and Cl^- ranged from 0.01 to 3.08 mM. These results correspond closely to concentrations measured from pumped samples. Over the first 21 weeks, H_2 , CO_2 , and CH_4 averaged 42.5 nM, 0.012 atm, and 0.009 atm, respectively. At 21 weeks, about the time we pumped the wells, we observed that H_2 increased by a factor of 5, and CH_4 by a factor of 3, in two wells screened in the Glasford formation and three wells screened in the Banner formation. Measurements conducted in the remaining three wells changed little. The concentration of CO_2 in each well remained constant throughout the sampling period. The *in situ* method may provide a useful technique for frequently testing groundwater chemistry over extended periods of time.

To Family and Friends

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CHAPTER 1

INTRODUCTION

In monitoring groundwater chemistry, hydrologists find it necessary to sample wells at short time intervals (Barrez and Mania 2009, Barrez, et al. 2007, Browne 2004, Geesey and Mitchell 2008). Sampling can be time consuming because it requires pumping groundwater to the surface (Madrid and Zayas 2007, Sevee, et al. 2000). Before a representative sample of groundwater can be obtained, the well must be pumped until parameters like DO, pH, and temperature in the effluent stabilize, about 3-5 well volumes (Kwon, et al. 2008). This assures that formation water uncontaminated by the water column overlying the screen is sampled.

In contrast to pumping groundwater to obtain a representative sample, passive sampling offers a means to monitor groundwater chemistry *in situ*. By obtaining samples *in situ*, passive sampling is less time consuming and we avoid perturbing the natural flow regime near the well (Chapelle, et al. 1997, Grossman, et al. 1989, Powell and Puls 1993). The passive, *in situ* method requires a relatively short time period in the field (minutes per well) compared to pumped sampling (hours per well) but a longer time to equilibrate to analytes at the screened interval (~4 days). Therefore, passive, *in situ* sampling is potentially valuable for wells that require frequent monitoring of dissolved gases and aqueous chemical species in groundwater. In wells with multiple screens or thick screened intervals, furthermore, passive sampling affords the possibility of observing groundwater chemistry as a function of position within the well (Metcalf and Robbins 2007, Powell and Puls 1993, Ronen, et al. 1987).

Passive sampling relies on the diffusion of analytes through a permeable membrane. *In situ* methods are available to monitor dissolved gases and aqueous chemical compositions in

groundwater (Bopp, et al. 2007, Hesslein 1976, Petruzzi and Silliman 2006, Seethapathy, et al. 2008). Sanford et al. (1996) developed and Spalding and Watson (2006) refined a dissolved gas sampler for application in groundwater studies. At the screened level of the well, the dissolved gas sampler introduces a fixed volume of inert gas in a closed vessel attached to a gas permeable membrane. Dissolved gases in groundwater diffuse through the permeable membrane reaching equilibrium with their gaseous phase in the sampler in less than a day (McLeish, et al. 2007, Spalding and Watson 2006, Vrobley, et al. 2007). By combining the fraction of the gas in the sampler with a measure of total pressure, it is possible to calculate each gases partial pressure and their dissolved concentrations in the aquifer (Manning, et al. 2003, Sheldon, et al. 2003, Van Der Hoven 2005).

Passive sampling of aqueous chemical species in groundwater has been conducted using diffusion bags (Mayer 1976), dialysis cells (Carignan 1984), and other diffusion based samplers (Seethapathy et al. 2008). The passive sampler generates a chemical potential difference between the ultra-pure water in the sampler and the groundwater at the screen. Ionic species diffuse through the dialysis membrane, integral to the sampler, reaching equilibrium with the groundwater chemistry after a period of time. Using these principles of diffusion, we developed a new aqueous chemical sampler for application in this study. The modified sampler allows for the extraction of large sample sizes for more accurate chemical measurements, is able to fit down a 2 inch monitoring well, and can be deployed jointly with the dissolved gas sampler.

The purpose of this study is to employ passive sampling as a monitor for chemical changes in groundwater at frequent time intervals in a municipal well field. We compared the results of passive, *in situ* sampling to those of pumped sampling as a reference to validate our method. In addition, where most groundwater studies monitor for either aqueous chemical

species or gaseous species, we quantify both parameters for a more comprehensive measure of groundwater geochemistry.

CHAPTER 2

METHODOLOGY

2.1 Geologic Setting

We deployed passive, *in situ* samplers in 8 monitoring wells completed in the glacial Glasford and underlying Banner formations (Figure 1). Confined aquifers in the formations of pre-Illinoian and Illinoian age, respectively; they produce much of the potable water for east-central Illinois (Warner 2001). In the study area, the aquifers in the Glasford and Banner formations range in depth from ~150-224 ft and ~225-350 ft, respectively, and are comprised of sands and gravels inter-bedded with layers of glacial till (Herzog, et al. 2003, Panno, et al. 1994).

2.2 Monitoring Wells

The field site is located in the American Illinois Water Company municipal well field in northwest Champaign, IL. The monitoring wells are located at distances varying from ~30 ft to ~4.5 miles from municipal production wells (Figure 1). The monitoring wells at Parkland are closest to a production well while the monitoring well at the Illinois Department of Transportation (IDOT) is the farthest from one and is therefore under the least amount of influence.

2.3 Description of Samplers

2.3.1 Dissolved Gas Sampler

Following the design of Vroblesky et al. (2007), the dissolved gas sampler is composed of an approximately one inch piece of gas-permeable, silicone tubing stopped at one end and

connected to a one-way stopcock (Cole-Parmer) and a 3 mL disposable high-density polyethylene (HDPE) syringe (BD) (Figure 2). We filled the dissolved gas sampler with high-purity N₂ gas, attached the silicone tubing and lowered to the screened interval of the monitoring well with the stopcock in the open position (Figure 2). In the open position, internal gases equilibrate with dissolved gases in the groundwater through the silicone tubing.

2.3.2 Aqueous Chemical Sampler

Developed in our lab, the aqueous chemical sampler is composed of a 5 mL disposable HDPE syringe with two windows (~1 cm x 3.5 cm each) cut into opposite sides and attached to a one-way stopcock. The windows are covered with a reduced-cellulose, dialysis membrane with a pore size of 6-8,000 Daltons and cemented to the chamber of the syringe using a silicone sealant (Figure 3). We filled the aqueous chemical sampler with ultra-pure water (MilliQ) and deployed to the screened interval with the stopcock in the closed position. Ions diffuse through the dialysis membrane and into the sampler.

We conducted a laboratory study to determine the equilibration time between our aqueous chemical sampler and anions in groundwater. We generated a nominal groundwater environment by filling a 150 L carboy with 0.3 mM Cl⁻, F⁻, SO₄²⁻, NO₃⁻, and PO₄³⁻ solution. In the carboy, we positioned 14 aqueous chemical samplers filled with ultra-pure water (MilliQ). Over seven days, we retrieved two samplers and a sample of the groundwater for analysis each day.

2.4 *In Situ* Sampling

We deployed and retrieved the samplers 25 times over 35 weeks. The dissolved gas sampler and the aqueous chemical sampler are attached, in triplicate, to a weighted support line and lowered to the middle of the 3 m (10 ft) long screened interval of the well. Retrieving and redeploying the samplers at a well takes ten to fifteen minutes per well.

Spalding and Watson (2006) showed that the dissolved gas samplers equilibrated with dissolved gases in the groundwater within two days. We left the samplers at the screened interval for at least one week before returning the samplers to the surface for sampling. At the surface, the stopcock is promptly closed and the silicone tubing removed and replaced with a needle. The contents of each syringe are then injected into a capped, He purged, 20 mL serum bottle with a butyl rubber stopper. The dissolved gas sampler is refilled with high-purity N₂ and redeployed to the screened interval. We returned the serum bottle to the lab and analyzed by gas chromatography.

The aqueous chemical samplers are left in the well for at least one week before returning to the surface for sampling. At the surface, the stopcock is opened and the contents of each syringe injected into a polystyrene vial (Falcon tube). After sampling, we refilled the chamber with ultra-pure water and redeployed. The polystyrene vial (Falcon tube) is returned to the lab for analysis by ion chromatography.

2.5 Analytical Techniques

We used an SRI model 8610C gas chromatograph coupled to a sequential thermal conductivity detector (TCD) discharging into a SRI model 810C reductive gas detector (RGD) to measure concentrations of H₂, N₂, CO₂, and CH₄ in a sample. H₂ concentrations are converted from a gas phase concentration to an aqueous molar concentration using an equation from

Löffler and Sanford (2005). An ion chromatograph from Metrohm AG quantified for Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , and F^- concentrations in samples obtained by the aqueous chemical samplers.

CHAPTER 3

RESULTS

3.1 Lab Calibration

3.1.1 Equilibration Time of Aqueous Chemical Sampler

Figure 4 shows how the anion concentrations within the sampler equilibrate to the concentration in the bulk fluid with time. A comparison of the anion concentrations within the equilibrated sampler to the concentration in the bulk fluid showed that they had equilibrated. According to Figure 4, the samplers equilibrated with the water chemistry within four days. In the bulk fluid, nitrate, chloride, and fluoride equilibrated within one day while sulfate and phosphate equilibrated after four days. As shown in Figure 4, the results from duplicate samples taken each day of sampling agreed well with each other. Figure 5 shows the relationship after the sampler equilibrated to the bulk fluid.

3.2 Field Study

3.2.1 *In Situ* Sampling

Figures 6 - 9 show the concentrations of the major anions and gases detected from the passive sampling technique over the 35 week sampling period including sulfate, chloride, H₂, CH₄, and CO₂. Nitrate, phosphate, and fluoride are found below detection (0.01 mM).

3.2.2 Aqueous Chemistry

Chloride concentrations measured from our passive samplers in the study area ranged from 0.01 to 3.12 mM (Figure 6). The IDOT well contained the highest chloride concentration

and the Card A well the lowest. Concentrations in the And A, And B, Card B, Park A, and RR wells remained near 0.045, 0.052, 0.0427, 0.09 and 0.06 mM, respectively, throughout the sampling period. The chloride concentration in the Park B well experienced a change from 3.12 to 0.04 mM over the course of sampling.

Sulfate concentrations ranged among the wells from below detection (0.01 mM) to 0.84 mM (Figure 7). The highest sulfate concentration existed at the IDOT well and the lowest average concentration at the RR well. The sulfate concentration in the remaining six wells varied from below detection to 0.06 mM over the course of the study.

3.2.3 Dissolved Gas Analysis

Over the 35 week sampling period, hydrogen concentrations among all the wells varied from 4.1 nM to 353.5 nM (Figure 8). The Park B well contained the lowest amount of hydrogen (4.1 nM) while the Card B well had the highest (353.5 nM). The IDOT and RR wells maintained a concentration of about 26 and 41 nM throughout sampling. The results for hydrogen concentrations in the And A, And B, Card A, and Park A wells showed increases before and after the time we pumped each well.

Methane concentrations varied from below detection to 78.1 atm in the study area (Figure 8). The IDOT well maintained methane concentrations below detection for the entire study. In contrast, the And B well showed the highest methane concentration after we pumped the well. We detected 0.107 atm CH₄ in the And A well and 0.142 atm in the RR well before pumping. After pumping, the concentration of methane in And A dropped to 0.066 atm and RR 0.063 atm. In the Card A and Card B wells, we found an average of 0.021 atm and 0.22 atm CH₄ throughout

the sampling interval. The methane concentration in Park A ranged from 0.011 atm to 0.487 atm and in the Park B well, below detection to 0.165 atm.

The concentration of CO₂ in each well changed little throughout the sampling period with only slight variation from their average concentrations (Figure 9). In the IDOT, Card A, Card B, and Park B wells, we detected CO₂ concentrations of approximately 0.0088 atm ± 0.0006. CO₂ concentrations in the And A, RR, and Park A wells remained near 0.0059 atm ± 0.0002. Throughout sampling, And B maintained the highest average CO₂ concentration of 0.0253 atm. Among the monitoring wells, pH varied from 7.14 in the And B well to 7.69 in the Card B well.

3.2.4 Comparison of Passive and Pumped Sampling Methods

We compared results from the passive samplers before we pumped the well to those of the pumped samples. The direct comparisons showed close correspondence (Figure 6 and 7). Gas concentrations could not be compared between the two sampling methods as submersible pumps electrolytically produce H₂ (Chapelle et al. 1997).

Chloride concentrations in six of the eight wells diverged from pumped samples by no more than 0.19 mM to measurements (Figure 6). The other two wells (IDOT and Park A), chloride concentrations differed between the passive and pumped samples by greater than 0.19 mM. In the IDOT well, chloride concentrations are higher in the passive samplers than in the pumped sample. The opposite is true for the Park A well, higher chloride concentrations were measured in the single pumped sample than in the passive samplers.

Across all eight wells, sulfate concentrations from our passive samplers differed by no greater than 0.04 mM to samples obtained by pumping (Figure 7). In general, sulfate

concentrations in the pumped samples are slightly higher, an average of $0.022 \text{ mM} \pm 0.015$, than concentrations in the passive samples.

CHAPTER 4

DISCUSSION

4.1 Comparison of Passive and Pumped Sampling Methods

We observed a close correspondence between chloride and sulfate concentrations in the passive samplers to those obtained using a pump (Figure 6 and 7). In six of the eight wells (exceptions IDOT and Park A), chloride concentrations in the pumped samples varied from those in the passive samples by less than 0.19 mM. Chloride concentrations from passive sampling in the IDOT well contained a higher concentration than the pumped samples by 1.0 mM (Figure 6). Differences in chloride concentration between techniques in the IDOT well may be due to its proximity to a large salt storage facility ~100 ft from the well. When returning the samplers to the surface for sampling, we would place the samplers on the ground and incidentally coat the samplers with salt before redeploying to the screened interval. However, after we pumped the well for the first time (Day 66 of sampling) and noticed the discrepancy in chloride concentrations, we placed a plastic tarp on the ground and washed the samplers before redeployment. After pumping the second time (Day 146), we observed, again, a difference in the pumped sample and the passive samples. Chloride concentrations in the Park A well measured from the passive samples showed a concentration lower than the pumped samples by 0.6 mM. Differences in how the two methods obtain a sample may attribute for the discrepancy between chloride concentrations in the pumped samples to those in the passive samples at the Park A well. In pumping the well, we extract water from the formation near the screen. This includes groundwater from the sand pack along with groundwater above and below the outside of the screened interval. The averaging of groundwater from different areas outside the screened

interval can lead to mixing of waters with different chloride concentrations. Passive sampling, on the other hand, obtains an average measurement over four days from formation water flowing through the screen and over the permeable membranes of the samplers. In the absence of analytical error, we would not necessarily expect to obtain the same chemical measurement between the two sampling techniques but the results can still be illustrative. The chloride concentration difference in the passive and pumped samples in the Park A well may be due to analytical error.

Sulfate concentrations showed the least amount of variability between the pumped samples and the passive samples (Figure 7). Among the eight wells, we determined the difference in sulfate concentration between the pumped samples and the passive samples over the sampling interval. We calculated an average difference of $0.022 \text{ mM} \pm 0.015$ between the results from the pumped and passive samples over the sampling period.

4.2 Dissolved Gaseous Species

One of the interesting aspects of this study is that we obtained a time-series of groundwater chemistry in each of the wells. Over the 35 week sampling interval, we detected significant variation in biologically sensitive parameters (CH_4 and H_2) present in the groundwater (Figure 8). Changes in these two analytes occurred near the time we pumped each well, (Day 155-158). Fermentative microorganisms are the typical producers of H_2 in an anoxic aquifer and other microorganisms consume H_2 as part of their metabolisms (Conrad 1996, Logan, et al. 2002, Lovley, et al. 1994). Dissolved methane can be produced in groundwater through either hydrogentrophic methanogenesis:



or acetoclastic methanogenesis:



H₂ and CH₄ concentrations in the And B well increased prior to and after pumping the well. The process of pumping the well is known to affect the chemistry of water in the well (Chapelle et al. 1997, Powell and Puls 1993). Various factors might explain this phenomenon. Physical features include disturbing the aquifer matrix and sand pack and microbiological features include stimulating growth of methanogens through the reaction pathways described in equation (1) and (2) (Grossman et al. 1989, Kwon et al. 2008). Our pumping of the wells at 6 L min⁻¹ may have caused the disruption in the aquifer matrix or the sand pack surrounding the well bore contributing to the release of H₂ and enabling microorganisms to produce CH₄ according to reaction (1). In the Park A and Park B wells, CH₄ partial pressures began to increase in the passive samples before the pumping event. We suspect that this increase, therefore, is a result of changes in production well activity rather than pumping of the monitoring well itself. The activity of large production wells (>1 MGD⁻¹) in the study area can induce changes in groundwater flow directions at the screened interval. Changes in production well activity may vary the direction groundwater is flowing through the screen. Local carbon sources outside the screen in the formation can produce both H₂ and CH₄ observed in the passive samples (McMahon and Chapelle 1991). These carbon sources developed in lenses in the Glasford and Banner formations due to glacial erosion of the land surface and subsequent deposition of organic material (Panno et al. 1994, Warner 2001). The Park A and Park B wells are especially susceptible to groundwater flow changes because they lie within 30 ft of a 2.1 MGD⁻¹ production well screened in the Banner formation (Figure 1). Partial pressures of CH₄ in And A and RR decreased after pumping and stabilized near 0.06 and 0.07 atm, respectively, possibly due to a

groundwater flow changes from varying production well activities. In the IDOT, Card A, and Card B wells, CH₄ partial pressures changed little over the sampling period (Figure 8).

In Card A, Card B, Park A, and Park B wells, H₂ concentration increased after pumping the well and decreased for the remainder of the study (Figure 8). Similar to the mechanism for CH₄ increases, our pumping rate may have been high enough to perturb the surrounding aquifer matrix or sand pack causing the release of H₂. Concentrations of H₂ in the IDOT well experienced little change throughout the sampling interval. Since the IDOT well is ~7 miles from the nearest production well, we suspect that these large production wells contribute the most to changes in H₂ and CH₄ concentrations detected from the passive samples.

Among the eight wells, CO₂ partial pressure remains roughly invariant (Figure 9). The partial pressure of CO₂ responds to the free concentration of H₂ and CH₃COOH according to equations (1) and (2). Since this amount of H₂ and CH₃COOH in the study area are known to be small, CO₂ is probably unaffected by microbial activity over the course of the study. The And B well contained a higher partial pressure of CO₂ by 0.015 atm than in any of the other wells and this could be attributed to increased organic matter oxidation occurring in an organic lens near the well (McMahon and Chapelle 1991, Park, et al. 2009).

CHAPTER 5

CONCLUSIONS

Passive and pump sampling techniques provide a means for characterizing groundwater geochemistry. The comparisons of the results from pump sampling to those of passive sampling indicate a close association. Although both sampling techniques could obtain similar concentrations of chloride and sulfate, passive sampling was by far the easiest to employ. Among the eight wells, pumping to obtain a representative groundwater sample required three days of field work whereas passive sampling required only ~3 hours. The time difference spent in the field results from the ease of the passive sampling technique. When we deploy the passive samplers, we allow the four day equilibration period to pass before returning to the field to sample again. In the field, all that is needed for the passive sampling method are needles, sample bottles, and bottles of the receiving phase (N_2 (g) and ultra-pure water) for refilling the two types of passive samplers. This is a small burden and does not require specialized transport where field supplies for pump sampling include a pump, a generator, a filter system, sample bottles, and the use of a large vehicle. In addition, the passive sampling technique allowed for a time-series of gaseous analytes in groundwater important in microbial processes. H_2 and CH_4 changes over the course of the sampling interval would have been lost employing the pump sampling technique. We show that passive sampling offers a time-effective option for frequently sampling groundwater chemistry.

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FIGURES



Figure 1: A map of the Mahomet Aquifer indicating locations of monitoring (orange and blue balloons) and production wells (open red circles).



Figure 2: Dissolved Gas Sampler (As described by Vroblesky et al. 2007).



Figure 3: Aqueous chemical sampler ready for deployment.

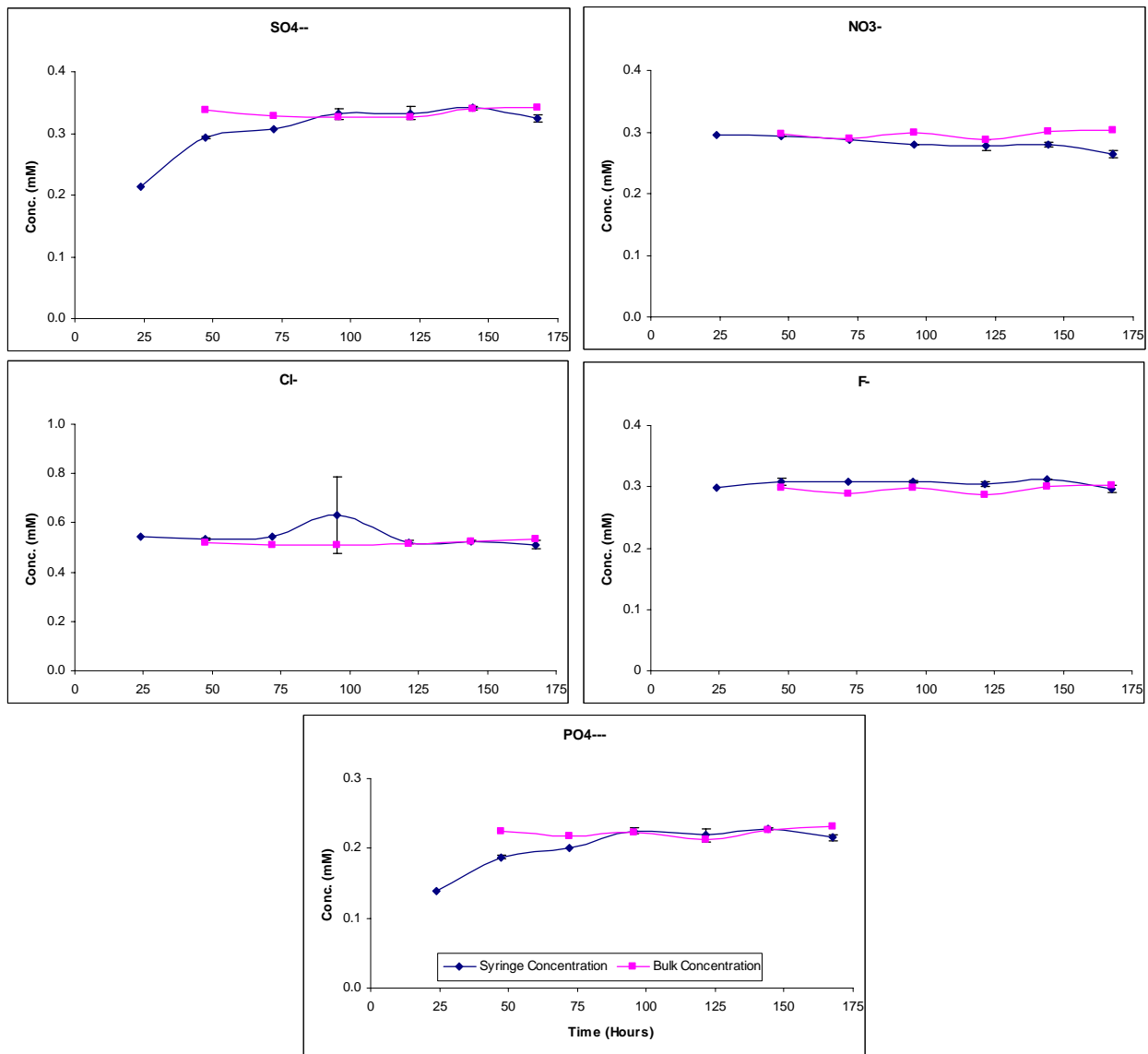


Figure 4: Equilibration of SO₄²⁻, NO₃⁻, Cl⁻, F⁻, and PO₄³⁻ concentrations in the aqueous chemical sampler to the bulk fluid

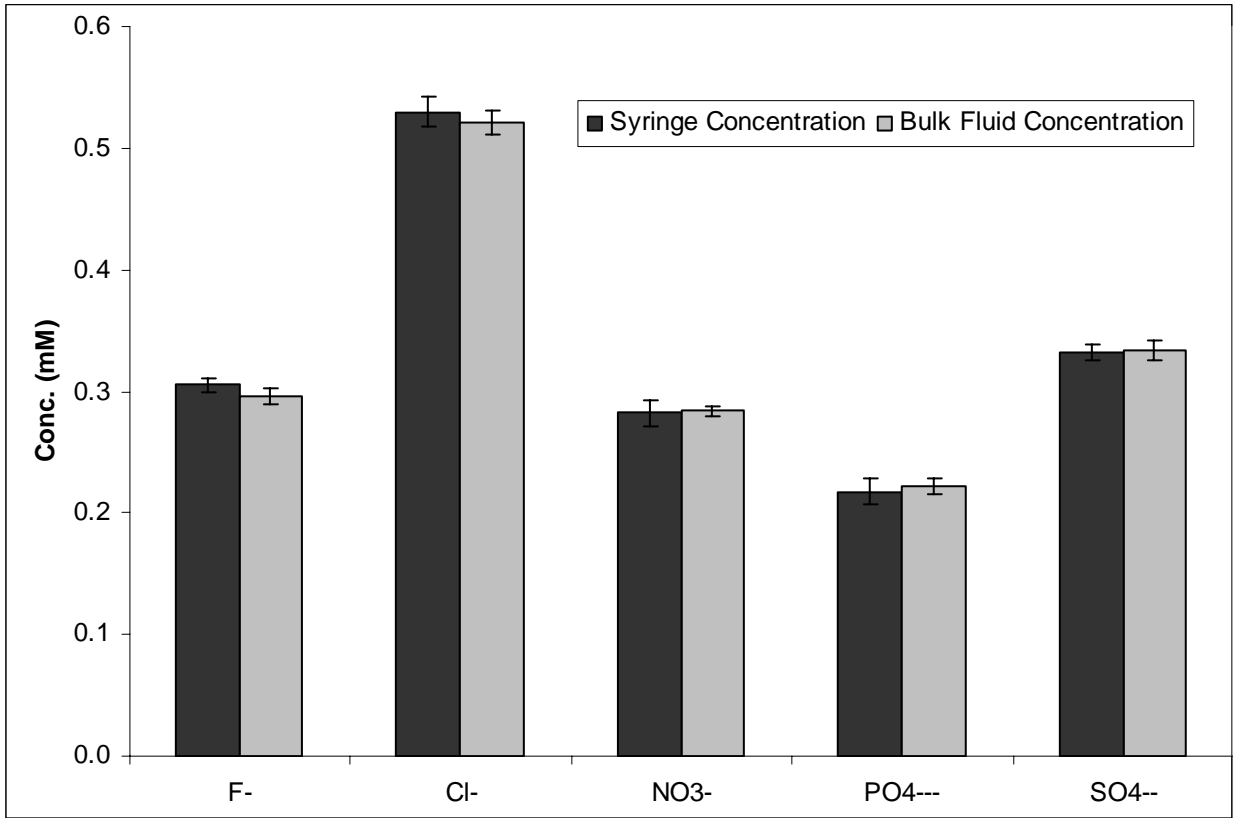


Figure 5: Comparison of equilibrated sampler concentration to F⁻, Cl⁻, SO₄²⁻, PO₄³⁻, and NO₃⁻ concentrations in the bulk fluid.

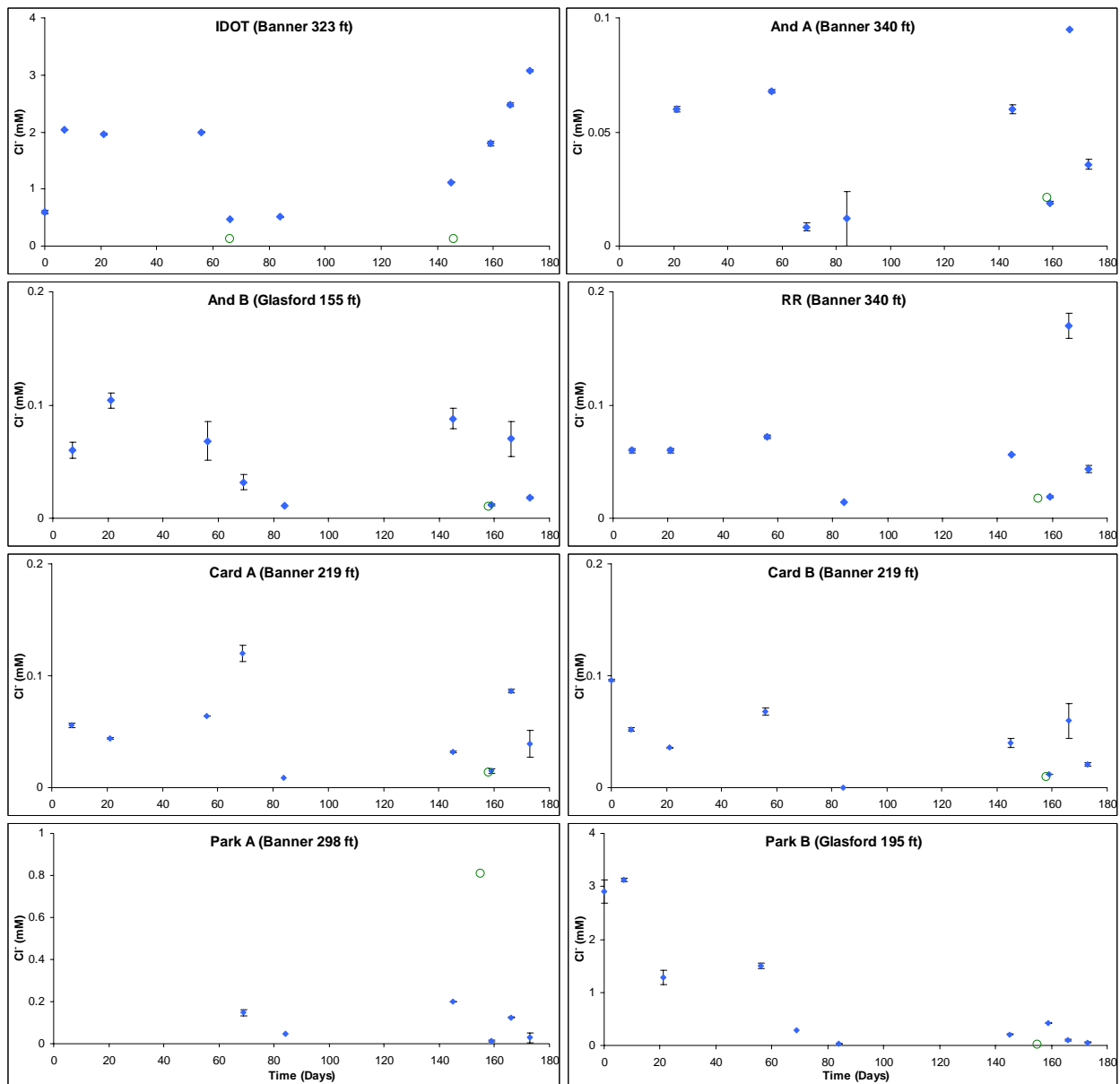


Figure 6: Results of chloride concentrations obtained by the aqueous chemical sampler (blue diamonds) and the pumped method (open green circles) over the 35 week sampling interval. Blue diamonds represent average of triplicate samples and error bars are the standard deviation.

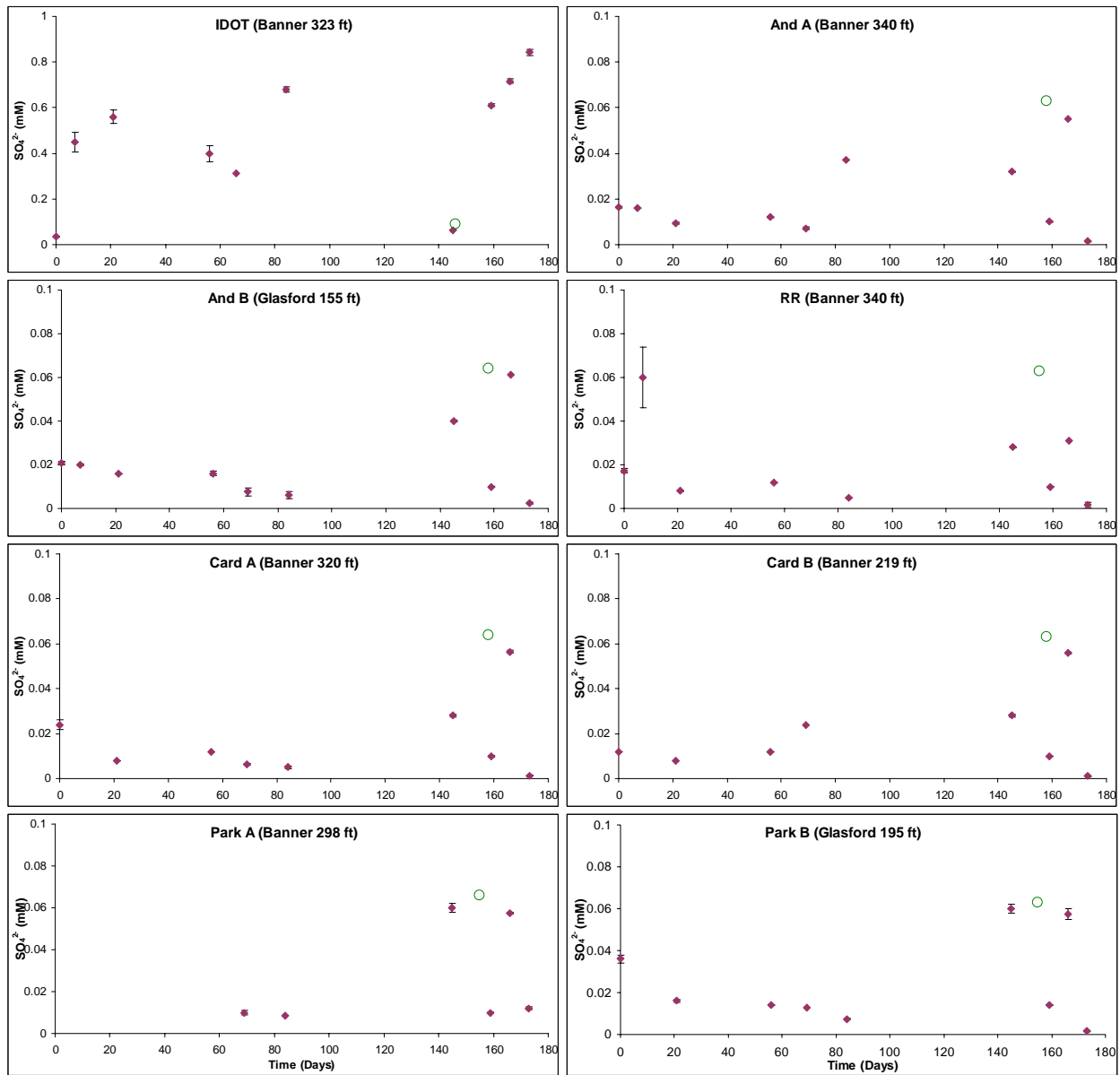


Figure 7: Results of sulfate concentrations obtained by the aqueous chemical sampler (purple diamonds) and the pumped method (open green circles) over the 35 week sampling interval. Purple diamonds represent average of triplicate samples and error bars are the standard deviation.

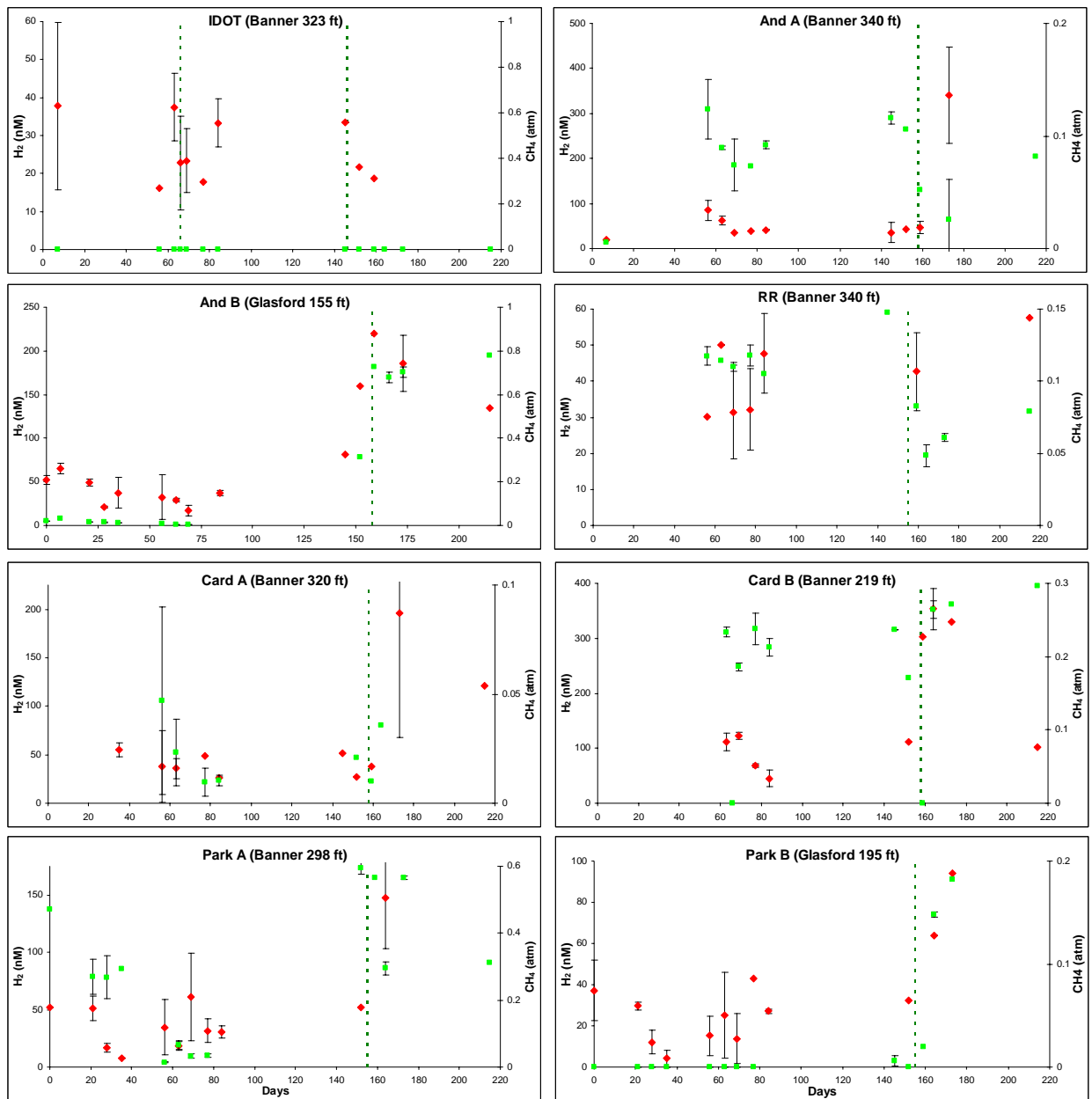


Figure 8: H_2 (nM) (diamonds) and CH_4 (atm) (boxes) concentrations from the dissolved gas sampler over the 35 week sampling interval. Each point represents the average of triplicate samples and error bars the standard deviation. Dashed green line signifies the time the well was pumped.

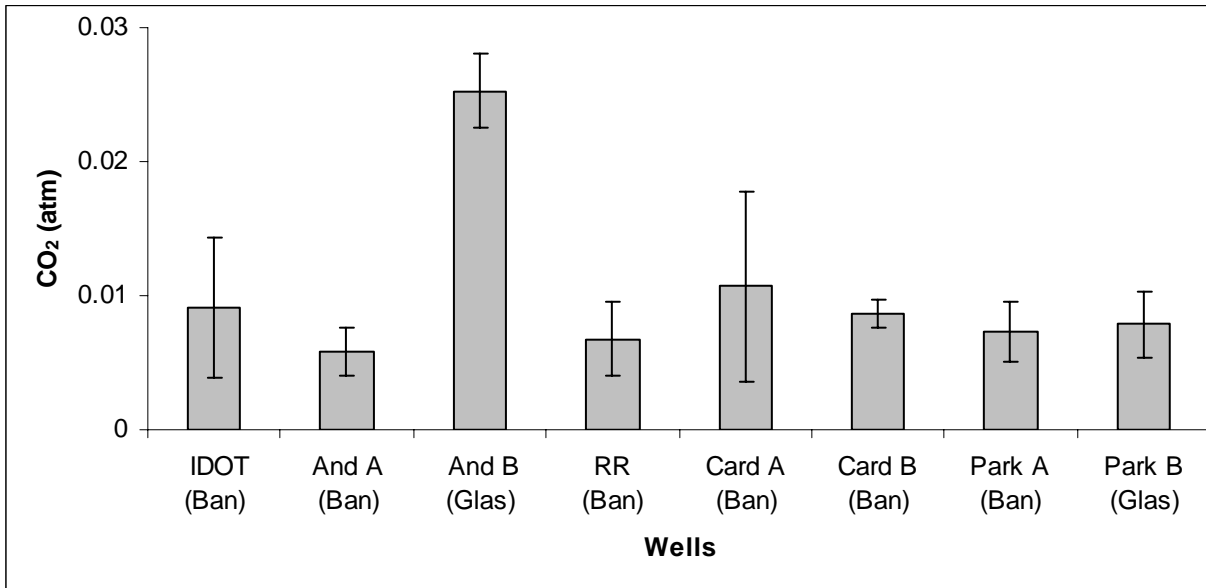


Figure 9: Average CO₂ (atm) concentrations from the dissolved gas sampler over the 35 week sampling interval. Error bars represent the standard deviation.