Comparison of CO_2 detection methods tested in shallow groundwater monitoring wells at a geological sequestration site

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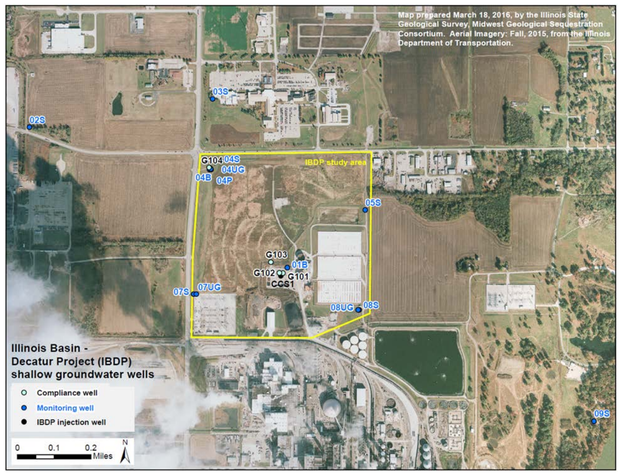
The geological storage of anthropogenic carbon dioxide (CO_2) is one method of reducing the amount of CO_2 released into the atmosphere. Monitoring programs typically determine baseline conditions in surface and near-surface environments before, during, and after CO_2 injection to evaluate if impacts related to injection have occurred. Because CO_2 concentrations in groundwater fluctuate naturally due to complex geochemical and geomicrobiological interactions, a clear understanding of the baseline behavior of CO_2 in groundwater near injection sites is important. Numerous ways of measuring aqueous CO_2 in the field and lab are currently used, but most methods have significant shortcomings (e.g., are tedious, lengthy, have interferences, or have significant lag time before a result is determined). In this study, we examined the effectiveness of two novel CO_2 detection methods and their ability to rapidly detect CO_2 in shallow groundwater monitoring wells associated with the Illinois Basin – Decatur Project geological sequestration site.

The CarboQC beverage carbonation meter was used to measure the concentration of CO_2 in water by monitoring temperature and pressure changes and calculating the P_{CO2} from the ideal gas law. Additionally, a non-dispersive infrared (NDIR) CO_2 sensor enclosed in a gas-permeable, water-impermeable membrane measured CO_2 by determining an equilibrium concentration. Results showed that the CarboQC method provided rapid (< 3 min) and repeatable results under field conditions within a measured concentration range of 15 – 125 mg/L CO_2. The NDIR sensor results correlated well (r^2 = 0.93) with the CarboQC data, but CO_2 equilibration required at least 15 minutes, making the method somewhat less desirable under field conditions. In contrast, NDIR-based sensors have a greater potential for long-term deployment. Both systems are adaptable to in-line groundwater sampling methods. Other specific advantages and disadvantages associated with the two approaches, and anomalies associated with specific samples, are discussed in greater detail in this poster.

CarboQC Carbonation meter

The CarboQC carbonation meter is used by the beer and soft drink industry to measure CO_2 in carbonated beverages and has been shown to be readily adaptable to measurement of freshwaters elevated in CO_2 in our labs. The measuring chamber is filled with sample, the volume of the chamber is expanded, liquid/gas equilibrium is reached and the pressure and temperature are measured. The sample volume is expanded a second time, equilibrium is reached and the pressure and temperature are measured again. The two sets of pressure and temperature are then used to determine CO_2 concentration and dissolved air compensation. Total analysis time is less than 3 minutes.

The Midwest Geological Sequestration Consortium is conducting the Illinois Basin – Decatur Project (IBDP), a large-scale carbon capture and storage (CCS) demonstration project in Decatur, Illinois, USA . The project is evaluating the ability of the Mt. Simon Sandstone, a deep saline formation, to store one million tonnes of carbon dioxide (CO_2) from an ethanol production facility operated by the Archer Daniels Midland Company. Injection began in November 2011 and successfully concluded in November 2014 with a total mass of 999,215 tonnes of CO_2 injected. An extensive Monitoring, Verification and Accounting (MVA) program has been implemented for the IBDP and is focused on the 0.65 km^2 (0.25 mi^2) study site. The IBDP MVA program includes groundwater monitoring from the shallow subsurface to the reservoir. Seventeen shallow groundwater monitoring wells ranging in depth from 6 to 90 meters (20 to 300 feet) have been installed and monitored for groundwater levels and chemistry since March 2009. Groundwater and other environmental monitoring will continue during the post-injection phase of the project. The IBDP site is an active sequestration site, and thus a highly valuable location to demonstrate and test the performance of emerging and established CCS-related monitoring and measurement technologies.

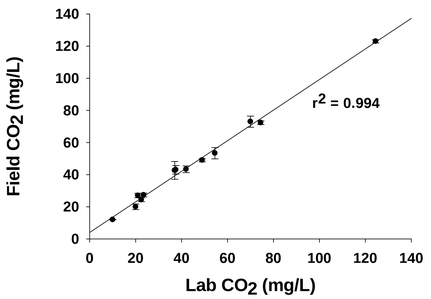


Field and lab analysis of dissolved CO_2 and dissolved inorganic carbon (DIC) using the CarboQC meter

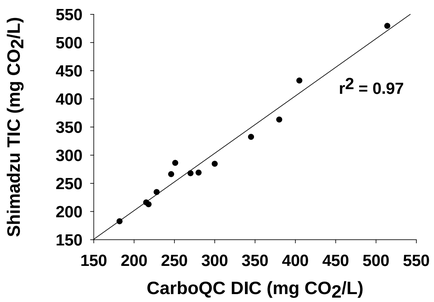
Samples can be analyzed by direct syringe injection in the field or with an attached "pressurized filling device" that measures CO_2 in the lab in water collected in soda bottles (above). The latter method avoids potential CO_2 degassing from samples during analysis. However, field and lab analyses of the IBDP samples (left) pumped from monitoring wells showed that measured CO_2 values were identical using each approach. This is consistent with samples with CO_2 concentrations lower than that at which degassing occurs under normal atmospheric pressure.

Total DIC can also be determined by acidifying collected water samples, which drives bicarbonate alkalinity to CO_2. Comparison of this approach with a Shimadzu TIC analyzer (lower left) and conventional determination of total alkalinity by pH titration with H_2SO_4 (below) showed that these methods were highly correlated for the IBDP groundwater samples as well.

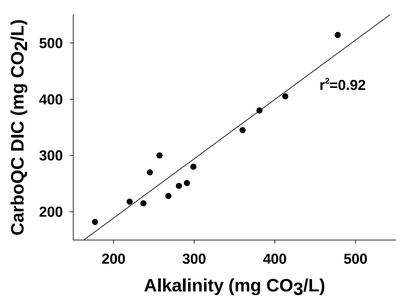
Comparison of Field- and Lab-Measured Dissolved CO_2 using CarboQC



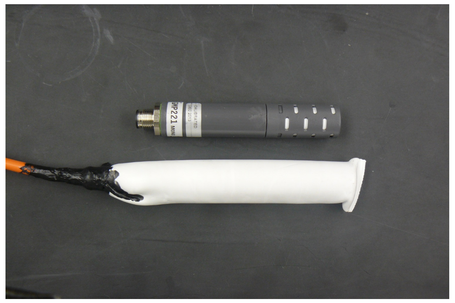
CarboQC vs Shimadzu Total Inorganic Carbon

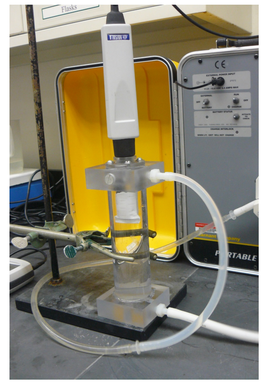


pH alkalinity vs CarboQC DIC



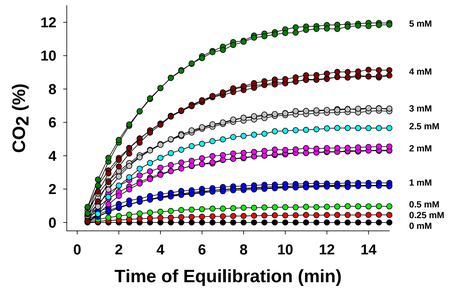
NDIR Sensor





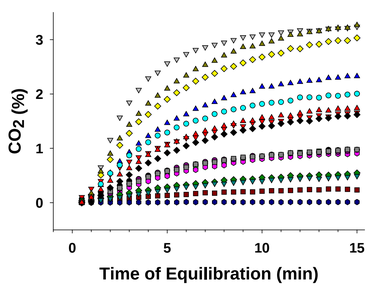
Infrared gas analyzers were used that are designed to measure CO_2 concentrations up to 20% in humid air using a single-beam dual-wavelength non-dispersive infrared (NDIR) light source and a silicon-based sensor (left; Vaisala, Finland). A waterproof poly-tetrafluoroethylene (PTFE) sleeve highly-permeable to CO_2 covers the sensor and is sealed to the meter cable (left). The sensor was placed in a flow-through cell (right) to allow dissolved CO_2 in pumped or recirculated water to reach equilibrium with the atmosphere inside the gas permeable membrane. Unlike the CarboQC approach, the NDIR sensor has the potential to provide continuous monitoring of CO_2 at depth underground.

Bicarbonate calibration of NDIR sensor

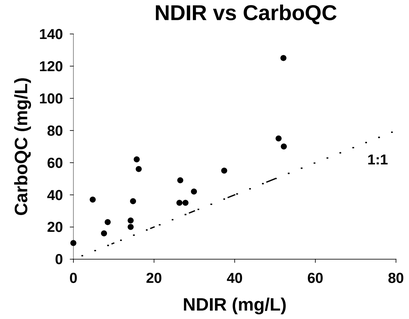


CO_2 standards were created by acidifying sodium bicarbonate solutions between 0 – 5 mM. A linear response between the initial concentration and the sensor was observed (left), but equilibration time for CO_2 across the gas-permeable membrane took up to 15 minutes. Field samples (below left) had a similar response and may require an even longer time for full equilibration due to dissolved constituents in the water. Comparison of calculated dissolved CO_2 by the CarboQC and NDIR methods (below) showed that the NDIR approach consistently underestimated that measured by the CarboQC. Some unusually high readings for the CarboQC may be indicative of interferences due to specific water quality variables, and relevant factors are currently being investigated.

Vaisala Sensor - Decatur Samples



NDIR vs CarboQC



Conclusions

- The CarboQC carbonation meter rapidly and effectively analyzed CO_2 and dissolved inorganic carbon in standard solutions and pumped groundwater samples at a geological CO_2 sequestration site.
- The NDIR sensor approach correlated well with dissolved CO_2 concentrations in the lab and field, but required extended time for gas equilibration across the sensor membrane.
- CO_2 equilibration time across the NDIR gas permeable appeared to vary depending on the water sample, and may be related to variations in water quality.