Project Title: Potential Risks of Freshwater Aquifer Contamination with Geosequestration

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1. Abstract

Substantial leakage of CO_2 from deep geological strata to shallow potable aquifers is likely to be rare, but chemical detection of potential leakage nonetheless remains an integral component of any safe carbon capture and storage system. CO_2 that infiltrates an unconfined freshwater aquifer will have an immediate impact on water chemistry by lowering pH in most cases and by altering the concentration of total dissolved solids. Chemical signatures in affected waters provide an important opportunity for early detection of leaks. In the presence of CO_2, trace elements such as Mn, Fe, and Ca can increase by an order of magnitude or more above control concentrations within 100 days. Therefore, these and other elements should be monitored along with pH as geochemical markers of potential CO_2 leaks. Dissolved inorganic carbon and alkalinity can also be rapidly responsive to CO_2 and are stable indicators of a leak. Importantly, such changes may be detectable long before direct changes in CO_2 are observed. The experimental results also suggest that the relative severity of the impact of leaks on overlying drinking-water aquifers should be considered in the selection of CO_2 sequestration sites. One primary selection criteria should be metal and metalloid availability, such as uranium and arsenic abundance, to carefully monitor chemical species that could trigger changes above maximum contaminant levels (MCLs). Overall, the risks of leakage from underground CO_2 storage are real but appear to be manageable if systems are closely monitored.

II. Table of Contents

Page

III. Executive Summary

Increases in global greenhouse gas emissions are increasing rapidly. To stabilize the atmospheric CO2 concentration between 440 and 485 ppm, global CO_2 emissions must peak between 2010 and 2030 and decrease soon thereafter. One way that fossil fuel use could continue while still constraining greenhouse gas emissions is through the application of geologic carbon capture and storage (CCS). A key opportunity is to capture CO_2 emissions at large industrial point sources, such as power plants, and transport the CO_2 via pipeline to sites where the CO_2 would be injected underground into geologic reservoirs for long-term storage. One public concern about this opportunity is the potential for leaks from the geologic reservoirs that could affect drinking-water aquifers.

Substantial leakage of CO_2 from deep geological strata to shallow potable aquifers is likely to be rare, but chemical detection of potential leakage nonetheless remains an integral component of any safe carbon capture and storage system. CO_2 that infiltrates an unconfined freshwater aquifer will have an immediate impact on water chemistry by lowering pH in most cases and by altering the concentration of total dissolved solids. Chemical signatures in affected waters provide an important opportunity for early detection of leaks.

Two sets of long-term groundwater incubations were performed in the laboratory for five aquifers around the United States where CCS technologies appear to be potentially feasible: Aquia (MD), Virginia Beach (VA), Mahomet (IL), Ogallala (TX), and Central Valley (CA). In the presence of CO_2, trace elements such as Mn, Fe, and Ca were found to increase in some cases by an order of magnitude or more above control concentrations within 100 days. Therefore, these and other elements should be monitored along with pH as geochemical markers of potential CO_2 leaks. Dissolved inorganic carbon and alkalinity can also be rapidly responsive to CO_2 and are stable indicators of a leak. Importantly, such changes may be detectable long before direct changes in CO_2 are observed in the ground water.

The experimental results also show that the chemical impact of a CO_2 leak may differ within the same aquifer because of inter-aquifer mineralogical heterogeneities. For example, wide variations in Virginia Beach experimental pH and the behavior of Co and Ni, two elements which can be mobilized as a result of desorption from Fe and Mn oxyhydroxides, suggest a heterogeneous lithology. Co/Ni values were similar among all Mahomet groundwater experiments but varied among the Virginia Beach samples. Therefore, groundwater produced from lithologically different strata in aquifers above geosequestration sites should be regularly monitored to increase the probability of an advanced detection of CO_2 leaks.

Finally, the experimental results also suggest that the relative severity of the impact of leaks on overlying drinking-water aquifers should be considered in the selection of CO_2 sequestration sites. One primary selection criteria should be metal and metalloid availability, such as uranium and arsenic abundance, to carefully monitor chemical species that could trigger changes in drinking-water quality above maximum contaminant levels (MCLs). Overall, the risks of leakage from underground CO_2 storage are real but appear to be manageable if systems are closely monitored.

IV. Report Details

Experimental Methods

We performed two sets of incubations as part of this project. In the first set, we established and analyzed 1.5-year-long laboratory incubations of CO_2 infiltration of four overlying drinking-water aquifers, measuring changes in pH and chemistry. We developed methods to select sequestration sites to minimize potential human health risks, and identified geochemical signatures for early leak detection.

Aquifer sediment from 17 distinct locations within the Aquia (MD), Virginia Beach (VA), Mahomet (IL), and Ogallala (TX) aquifers was acquired from the Illinois State Geological Survey, the United States Geological Survey, the Virginia Department of Environmental Quality, and the Maryland Geological Survey. Additional samples were then obtain for the Central Valley Aquifer of CA. Sediment samples from the Mahomet (IL), Ogallala (TX), and unconfined Atlantic coast aquifer systems (VA and MD) were incubated in water with CO_2 for 500 days. For the initial characterization, all aquifer sediment samples were oven-dried for 36 h at 110 °C in order to minimize microbial activity over the long-duration experiment. Dry samples were divided as follows: two ~400 g subsamples were set aside for the groundwater experiment; one ~5 g aliquot was powdered on a stainless steel mill for mass spectrometry; and ~1 g was epoxy mounted for microprobe analysis, the latter performed on 6 samples. The 17 pairs of 400-g samples were weighed precisely and placed into bottles with 18.6MΩ/cm nanopure makeup water at a water-to-rock ratio of 3 to 1, were maintained at approximately 20 °C. One set of 17 bottles was sealed and placed in an opaque box to serve as the control, and the other set of 17 bottles was prepared for exposure to CO_2, or "+CO_2", as follows. A stream of 99.8% pure CO_2 was piped at atmospheric pressure to each bottle through 17 individually flow-regulated channels at a constant flow rate of 0.2 L/min for 320 to 344 days. This flow rate is roughly equivalent to 0.005% of the CO_2 emissions at a typical 500-megawatt coal-fired power plant (Metz et al. 2005*).* Each channel was fed into the bottles through a 2-hole rubber stopper and delivered the CO_2 into the bottles via a plastic bubble diffuser that was completely inundated and ~1 cm above the surface of the aquifer sediment. The other hole in the stopper was connected to an exhaust tube leading from the headspace of each incubation bottle. Each bottle had an independent CO_2 delivery and exit system and is covered in aluminum foil to minimize photosynthesis.

At intervals of a week to a month (initially for a maximum of 344 days for the Mahomet and Ogallala samples, 320 days for Virginia Beach, and 334 days for Aquia; Little and Jackson 2010; out to ~500 days for the completed first incubation), ~3mL aliquots were removed from each bottle and tested for pH within 10 s to minimize the effect of degassing. A second aliquot was removed and forced through a syringe with 2-μm filter paper to produce 2 mL of filtered experimental groundwater from each bottle. The 2-mL aliquots were diluted to 10 mL with quartz distilled 18 MΩ/cm water for ICP-MS analysis. After each sampling, nanopure water was added to the bottles to maintain the 3:1 water-to-rock ratio. Sampling and evaporation accounted for water losses in the range of 5 to 20% for a 30-day sampling interval; thus the maximum effect of these losses was an artificial element concentration increase of 20%. Bottles were gently agitated for ~10 s after each sampling and at no other time during the experiment.

Inorganic elemental concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS) on a VG PlasmaQuad 3 at the Duke University Division of Earth and Ocean Sciences. For the whole-rock samples, Li, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Mo,

Ba, and U were analyzed; for the experimental groundwater, Li, B, Mg, Al, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Ba, and U were analyzed. Instrument calibration standards were prepared from serial dilutions of certified water standard NIST1643e. Samples and standards were diluted to the same proportions with an internal standard solution in 2% HNO3 containing 10 parts per billion (ppb) In, Tm, and Bi to monitor and correct for instrument drift. All dilutions were carried out with solutions prepared from deionized-quartz-distilled H2O and quartz-distilled HNO_3. Instrument drift was also monitored and corrected for each element analyzed by analysis of the calibration standards at regular intervals between analysis of samples and standards. To allow for determination of U and Th concentrations, NIST1643e was spiked with plasmagrade single-element solutions of U and Th prior to serial dilution. External precision for most elements was typically 4% or less, based on replicate analysis of samples and standards.

The microprobe analysis employed an energy dispersive spectrometry on a Cameca Camebax electron microprobe for a qualitative identification of mineral grain cross sections. The microprobe was operated at 15 kV accelerated potential and 15 μ Amp beam current on polished samples. Data were reduced using 4Pi Revolution software.

A second set of incubations began in the summer of 2011 and ran to 2013. For these incubations, we implemented a new experimental design intended to promote more reducing (hypoxic) conditions typical of some aquifers. We also added six new samples representing the Central Valley of CA. The analytical methods for this study were similar to the original study (see above). A control group was maintained without introduction of CO_2, and waters were sampled for the same anions, cations, and metals. New to the second study was the measurement of oxygen reduction potential (ORP) during sampling intervals; ORP is measure of the tendency of a chemical species to acquire electrons and thereby be reduced. As with the first study, incubations were initially left to equilibrate with degassed ultra-pure water for one week prior to the first baseline sampling event and the introduction of CO_2. During this study we modified our sampling protocol to incorporate the addition of ultra-pure water to within 0.1 g of the initial water weight before sampling. Prior incubations added the ultra-pure water after taking samples. This new procedure provided more accurate pH measurements regardless of the frequency of sampling. Furthermore, we recorded the amount of water taken per sampling event. These measurements were used in mass balance calculations of the total amount of trace elements sampled from each incubation. To support ORP measurements, we measured concentrations of As(V) and As(III) as an indication of the redox conditions in each incubation. To do this we modified a procedure for speciating As(III) from groundwater using an anion exchange resin (Bednar et al., 2002). Once the As(V) had been stripped from sample waters, the waters were analyzed for trace elements using ICP-MS. The resulting value provided the fraction of As(III) relative to the total As indicated by ICP-MS analyses of untreated incubation waters.

Beginning in the second quarter of 2012, we took three additional steps to promote reducing conditions within the CO_2-added incubations. First, we plumbed an inert gas flow of 99.998% He into the incubations and sparged for one hour at daily intervals for one month. Second, we installed a chemical O_2 trap onto the CO_2 gas line to prevent oxygen contamination of incubation waters. Third, we began sampling incubations by drawing waters through tubing using a syringe. This approach limited exposure of incubation waters to atmospheric O_2. Along with the second set of experiments, we took steps to incorporate modeling into the study. Aqueous geochemical and reactive transport models can provide complementary findings to laboratory-based studies. The USGS aqueous geochemical model,

PHREEQC was used to model chemical species abundances in incubation waters. We also explored the feasibility of using PHREEQC and PHAST to predict the spatiotemporal properties of a CO_2 leaks into shallow aquifers of various geochemical characteristics.

Results and Discussion

The chemical composition of our groundwater experiments was significantly affected by the addition of CO_2. All $+CO_2$ groundwater experiments produced a pH below EPA's minimum MCL of 6.5 units. Most alkali and alkaline metal concentrations (Li, Mg, Ca, Rb, Sr) in the $+CO_2$ experiments were >30% higher than in the control. For instance, Li showed a significant, time-dependent increasing trend. Decreases of Mg concentrations in MH4, VB3, VB4, and VB5 and decreases of Ca in VB4 were the only exceptions to the enhanced dissolution of the earth metals in response to the addition of CO_2.

Concentrations of some transition metals, including Mn, Fe, Co, Ni, and Zn, were higher by more than 1000% in $+CO_2$ experiments relative to the control treatments across all aquifers. In general, the high concentrations observed in the $+CO_2$ experiments were apparent within 2 weeks of exposure and did not continue to increase over the remainder of the experiment. However, Co in M1, M2, and M3 did exhibit a significant, logarithmic time-dependent increase over the entire experiment. The remaining transition metals did not behave the same across all aquifers. Cd in the $+CO_2$ Aquia, Virginia Beach, and Mahomet experiments was higher than the control treatments by as much as 1000%. Yet, Cd in the $+CO_2$ Ogallala experiments produced lower or roughly equivalent concentrations than the control. Al, V, and Cr in $+CO_2$ Virginia Beach samples were elevated relative to the control; however, Al, V, and Cr in $+CO_2$ Aquia, Mahomet, and Ogallala experiments were lower relative to the control. Cu was generally higher in the Aquia and Ogallala $+CO_2$ experiments but lower in MH2, MH3, VB1, VB3, and OG2 $+CO_2$ experiments relative to the control treatments. $+CO_2$ Mo was lower than the control by 1 to 2 orders of magnitude in all aquifers and produced a significant, time-dependent logarithmic decrease in Mahomet samples.

In response to exposure to CO_2, B, Ba, Tl, and U values were typically higher and As, Se, and Sb values were lower in the Aquia, Mahomet, and Ogallala samples relative to the control treatments. Ba and U in some Ogallala and Mahomet $+CO_2$ experiments produced a significant, time-dependent logarithmic increase, while As in some Ogallala $+CO_2$ experiments produced a time-dependent decrease. In the Virginia Beach $+CO_2$ experiments, B and Ba were higher than in the control, whereas As was lower relative to the control. Se, Sb, Tl, and U increased in some $+CO_2$ VB samples and decreased in others relative to the control.

Concentrations that exceeded their primary or secondary U.S. EPA MCL health standard and concentrations that exhibited a significant, time-dependent increase were of concern because the ultimate long-term equilibrium concentration may exceed the MCL. Mn and Fe exceeded the MCL in most samples, while Al exceeded its MCL only in VB1, VB2, and VB3. Zn concentrations in VB3 reached ~50% of the secondary MCL (2500 ppb) and Cd concentrations in VB3 and AQ1 exceeded 50% of the primary MCL (>2.5 ppb), but neither element exhibited a significant, long-term increasing trend. Cr and Cu concentrations were ~3 orders below MCL in all samples. Although As concentrations in some control Ogallala experiments exceeded the 10 ppb MCL, consistent with natural field measurements (Scanlon et al. 2009), the addition of CO2 caused a decrease in As concentrations. In some Ogallala and Mahomet samples, Ba displayed a significant, time-dependent increase, reaching 25 to 50% of the MCL. Se, Sb, and Tl did not show a significant increasing trend; however, Se=22 ppb in

VB3 (selenium MCL=50 ppb) and Tl > 0.15 ppb in VB3, MH2, and MH4 (thallium MCL=0.5 ppb). In both + CO_2 and control VB5 samples, U exceeded the 30 ppb MCL. Uranium in the + CO_2 OG3 experiment also exceeded the MCL, and other Ogallala samples exhibited a time-dependent increasing trend without exceeding the MCL. The continued time-dependent increase of Ba and U over >300 days of exposure to CO_2 justified the need for even longer laboratory experiments and monitoring, extending out to ~500 days.

The carbonate-poor experiment samples (AQ1, VB1, VB2, VB3, and VB4) produced the lowest pH values and the lowest Ca concentrations among + CO_2 and control experiments. The low pH/low Ca composition may have resulted from mixing of nanopure water with carbonate poor
sediment and, in the case of the Virginia Beach samples which contain chalcopyrite, from the formation of sulfuric acid. These samples, and particularly VB3, also produced the highest concentrations of Al, Cr, Co, Ni, Zn, Cd, As, and Se.

Trace element and anion analyses for the second set of CO_2-added incubations were completed through day 510. These incubations exhibited greater than twofold increases with of alkalinity, SO_4, PO_4, Ca, Mg, Sr, Ba, Li, B, Mg, Rb, Sr, Ba, Pb, and U, and greater than tenfold increases for Mn, Be, Al, Fe, Co, Ni, Zn, Cd, and Tl. . Analyses within the last 200 days of the experiment showed some of these increases have tapered off. Similarly, some elements, such as Ba, Ca, Mg, and Sr, increased rapidly through day 60, but either remained steady or slightly declined toward the end of the study. The toxic metals Tl and Ba, increased steadily through course of the experiment. Some trace metal concentrations decreased with the addition of CO_2. For example, V, As, Mo, and Sb all decreased following the addition of CO_2 and remained low through the course of the experiment. The decline of As was most likely from adsorption caused by the decrease in pH.

As with the prior experiment, the pH declined in all CO_2 added waters. During the first two weeks of the experiment, pH declined by about 1 unit in all of the incubations. Afterward, values remained relatively stable. The pH of control group waters has shown little change during the 510 experiment days, with a few samples showing slight increases of 0.5 units or less. As of day 510, the pH of Central Valley incubations is 1.5 units lower than the control group, Ogallala incubations are 0.8 units lower than the control, and the Virginia Beach incubation is 4.1 units lower than control. The large pH decline in the Virginia Beach incubation compared with the significantly smaller drop in Ogallala and Central Valley incubations can be attributed to the lack of carbonate buffers in the Virginia Beach aquifer sediments, which are mainly quartz sands.

The ORP of incubation waters did not systematically decrease as expected, however values varied significantly through the course of the experiment. Overall the ORP in incubation waters were 68% higher relative to the control group. By day 159 the ORP of incubation and control waters were about equal. At day 300, the ORP was 32% lower in the incubations, with negative values (i.e. reducing conditions) in Ogallala 4 and 9. Presently, Ogallala 9 exhibited the most reducing waters, with ORP values measuring below -100 mV. The Woodland sample from the Central Valley showed a steady decline through day 300, but since has slightly increased. The Blum, Johnson Ranch, and Sutter samples are almost unchanged, which suggests redox buffered conditions. Overall, these observations suggest that incubation redox conditions are dependent on aquifer sediment mineralogy.

Analyses on aquifer sediments provide more insight on redox conditions within both the incubation and control waters. Arsenic has been shown to be a reliable indicator of redox conditions (Rüde and Wohnlich, 2000), and were used to supplement ORP measurements

during the third quarter of 2012. These measurements of the As redox-couple indicated As (III) to be the stable phase in all of the incubation waters except for one Blum and Sutter. At the low-pH conditions in the CO_2-added incubations, As (III) is expected to be dominant when ORP is slightly positive (i.e. >200 mV). With the exception of the Johnson Ranch samples, dissolved As of the control group waters is in the As(V) coordination, suggesting more oxidizing conditions, which is expected at the higher pH and ORP values. These results showed excellent agreement with calculation of dominant As species using PHREEQC.

Compared with the previous incubations, in which waters were more oxidizing, the newer incubations showed some significant differences. Alkali earth elemental concentrations were lower in the hypoxic waters, particularly in the Virginia Beach incubation. On the contrary, some transition metals (Al, Mn, Fe, Co, Ni, Zn, Mo) were enriched in the hypoxic experiment waters relative to the oxidizing experiment. In addition, we found Cr to be most abundant in the Virginia Beach incubation. This is likely the result of the oxidized Cr (IV) being more difficult to sorb and precipitate than Cr(III). Thus Cr(III) is often retarded in more reducing ground waters (Stollenwerk and Grove, 1985) comparable to the other incubations.

The first paper of the project was published in the October issue of Environmental Science and Technology (Little and Jackson 2010 Potential impacts of leakage from deep CO_2 geosequestration on overlying freshwater aquifers. Environmental Science and Technology 44:9225–9232). A second short response paper (Little and Jackson 2011 Environmental Science and Technology 35:3175-3176) was also published in the spring of 2011. A new manuscript, discussing a second incubation experiment, is currently in the final stages of preparation.

We have published additional papers accompanying the incubation studies. One uses data for key reservoir properties to produce geo-referenced rasters of estimated storage capacity and cost for regions within 15 deep-saline sandstone aquifers in the United States (Eccles et al. 2012). When the cost and corresponding capacity estimates are assembled into a marginal abatement cost curve, we find that 75% of the estimated storage capacity could be available for <\$2/tonne. Furthermore, ~80% of the total estimated storage capacity in the rasters is concentrated within just two of the aquifers – the Frio Formation along the Texas Gulf Coast, and the Mt. Simon Formation in the Michigan Basin, which together make up only ~20% of the areas analyzed. These results, and the work of other research groups, suggest there should be an abundance of low-cost storage for CO_2 in deep saline aquifers, but a majority of this storage is likely to be concentrated within specific regions of a smaller number of these aquifers.

The second additional paper analyzes the potential of waste-to-energy using carbon capture and storage technologies to obtain carbon- negative fuels and was published in the spring of 2012 (Chandel et al. 2012 The potential of waste-to-energy in reducing greenhouse gas emissions. Carbon Management **3**:133–144). For the 5-largest landfill sites in each U.S. state, we estimate that at least 58 and 11 have enough municipal solid waste (MSW) to fuel waste-to- energy plants of >50 MWe and >100 MWe , respectively, half of them directly over or within 20 km of underground saline and other storage reservoirs. Moreover, negative CO_2 emissions could be achieved with carbon capture and sequestration because 66% of the carbon in MSW is typically biogenic. The estimated cost of CO_2 capture associated with negative carbon emissions for MSW is substantially less than for some geo-engineering methods, including capturing CO_2 directly from air.

We published additional papers highlighting the importance of carbon and capture

utilization and storage for negative emissions scenarios, specifically the opportunity to combine biomass energy with carbon capture and storage (BECCS, as it is commonly referred to). Russell et al. (2012) examines BECCS in the framework of geoengineering technologies, highlighting how CCS technologies can form part of a long-term solution to not just mitigating CO_2 rise but actually removing CO_2 from the atmosphere on a net basis. Such negative emissions scenarios feature prominently in all representative concentration pathways. Carbon dioxide removal (CDR) approaches are designed to remove CO2 from the atmosphere and transfer it to long-lived carbon reservoirs. They include land use management to protect or enhance terrestrial carbon sinks and, in the context of this project, using biomass for carbon sequestration as well as (or instead of) a carbon neutral energy source. Ongoing work now includes analysis of biomass vulnerable to loss in fires (Verón et al. 2012) with sites for carbon sequestration.

Finally, postdoctoral associate, Stephen Osborn, obtained a faculty position at Cal Poly Pomona for 2012. His replacement, Josiah Strauss now works full time for the Dolan Integration Group. Former postdoctoral associate and Co-PI Mark Little works for the Frank Hawkins Kenan Institute at the University of North Carolina Chapel Hill. This project trained at least six undergraduate students.

Conclusions

Overall, we find that the risks of leakage from underground CO_2 storage are real but, given the research described here and the research of other investigators, manageable if systems are closely monitored. Given the potential impacts of CO_2 leaks, chemical signatures in affected waters will provide an opportunity for early detection of leaks. In the presence of CO_2, the elements Mn, Fe, and Ca all increased by at least an order of magnitude above control experiment concentrations within 100 days. Therefore, all three elements should be monitored, along with pH, as geochemical markers of CO_2 leaks. Dissolved inorganic carbon and alkalinity are also responsive and stable indicators of a leak. Results from this project on aquifer sediments should also provide greater insight on the role of oxidation-reduction conditions within ground waters.

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Talk presented at the American Geophysical Union Science and Policy Forum, Washington, D.C., June 25, 2013: "Water-energy interactions in the southeastern U.S." – Robert B. Jackson

Talk presented at the National Research Council, Committee on Geoengineering, September 10, 2013: "Carbon Storage on Land" – Robert B. Jackson.