

Evaluating Potential Geochemical Effects of Dissolved CO₂ on Glacial Aquifer Materials at the Illinois Basin – Decatur Project (IBDP), Decatur, IL, USA

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Introduction

The Illinois Basin – Decatur Project (IBDP) is a large-scale carbon capture and storage (CCS) demonstration which completed injection of one million metric tons of carbon dioxide (CO₂), captured from an ethanol production facility, into a deep saline reservoir over a period of three years. An extensive Monitoring, Verification, and Accounting (MVA) program was developed to characterize and monitor near-surface and subsurface site conditions. Since March 2009, seventeen shallow monitoring wells ranging in depth from 20 to 300 feet have been used to monitor groundwater levels and chemistry near the project site. Objectives of the shallow groundwater monitoring network included establishing pre-injection conditions and monitoring for anomalous geochemical signals that could indicate CO₂-related changes. If leakage occurred, CO₂ could potentially migrate into shallow groundwater aquifers and lower the pH of the groundwater, which could mobilize trace metals that naturally occur in aquifer materials. In this work, batch experiments were conducted with sediment samples collected from the shallow Tiskilwa glacial outwash aquifer at the IBDP site to evaluate the potential impact of CO₂ leakage on shallow groundwater quality. This study has helped determine which major and trace metal concentrations would potentially be altered in the presence of a CO₂ leak in the shallow subsurface as well as given a better understanding as to which reactions are expected to control the shallow aqueous geochemistry.

Methods

- Archived sediments from the well G104 borehole (Figure 1) were analyzed from the Tiskilwa sand and gravel aquifer (<2 mm grain size) by total digestion and X-ray Diffraction (XRD).
- 100 g of aquifer sediment was placed in two Erlenmeyer flasks (Figure 2) with 300 mL of groundwater collected from well 04S (Figure 1), an adjacent well monitoring the Tiskilwa aquifer. The groundwater was in contact with the sediment in a sealed, unmixed flask for 48 hours before gas infusion. A 10 mL “zero point” sample was collected before gas infusion.
- CO₂ was bubbled continuously in the flask at a rate of 0.2 L/min for 2 weeks. The same experiment with N₂ instead of CO₂ was conducted as a control.
- Samples were collected from each batch 8 hours, 24 hours, 48 hours, 1 week, and 2 weeks after gas infusion began. Source water was added to each batch immediately following sampling to maintain a 3:1 water-rock ratio.
- 5 mL of the unfiltered sample was used to determine pH and 5 mL was then forced through a 0.45 μm syringe filter (Figure 3) and acidified with nitric acid for ICP-MS analysis.
- “Zero point” chemistry and mineralogical data were used in Geochemist’s Workbench™ to obtain a model of major cations and iron reactions with the mineral phases.

Acknowledgements

ISGS contributors: Chris Korose, Randy Locke, Abbas Iranmanesh

References

- Gemini, V. et al., 2015. Geochemical consequences in shallow aquifers from the long-term presence of CO₂ in a natural field: The case of Florina Basin, W. Macedonia, Greece. *Greenhouse Gases Science and Technology* 6, pp. 450–469.
- Little, M. et al., 2010. Potential impacts of leakage from deep CO₂ geosequestration on overlying freshwater aquifers. *Environmental Science and Technology* 44, pp. 9,225–9,232.
- Shao, H. et al., 2015. Couple geochemical impacts of leaking CO₂ and contaminants from subsurface storage reservoirs on groundwater quality. *Environmental Science and Technology* 49, pp. 8,202–8,209.



Figure 1. Illinois Basin - Decatur Project site map. Tiskilwa aquifer materials from well G104 and groundwater from well 04S were used for the batch experiment.



Figure 2. The batch set-up involved a water-rock ratio of 3:1. Both N₂ and CO₂ flowed through separate flasks of deionized water to saturate each gas with water and prevent evaporation.



Figure 3. Samples were collected periodically by syringe, filtered, and acidified prior to analysis.

	Illite	Kaolinite	Chlorite	Quartz	K-spar	P-spar	Pyrite	Calcite	Dolomite	Siderite
Solid sample	49.6%	16.7%	32.9%	61.0%	5.0%	5.3%	1.6%	6.5%	16.3%	1.6%
	Clay minerals 2.7% total sample					Bulk mineral 97.3% total sample				

Table 1. Mineralogy of Tiskilwa aquifer analyzed by XRD. Clay minerals make up 2.7% of the total sample and their percentages reflect composition of clay minerals only.

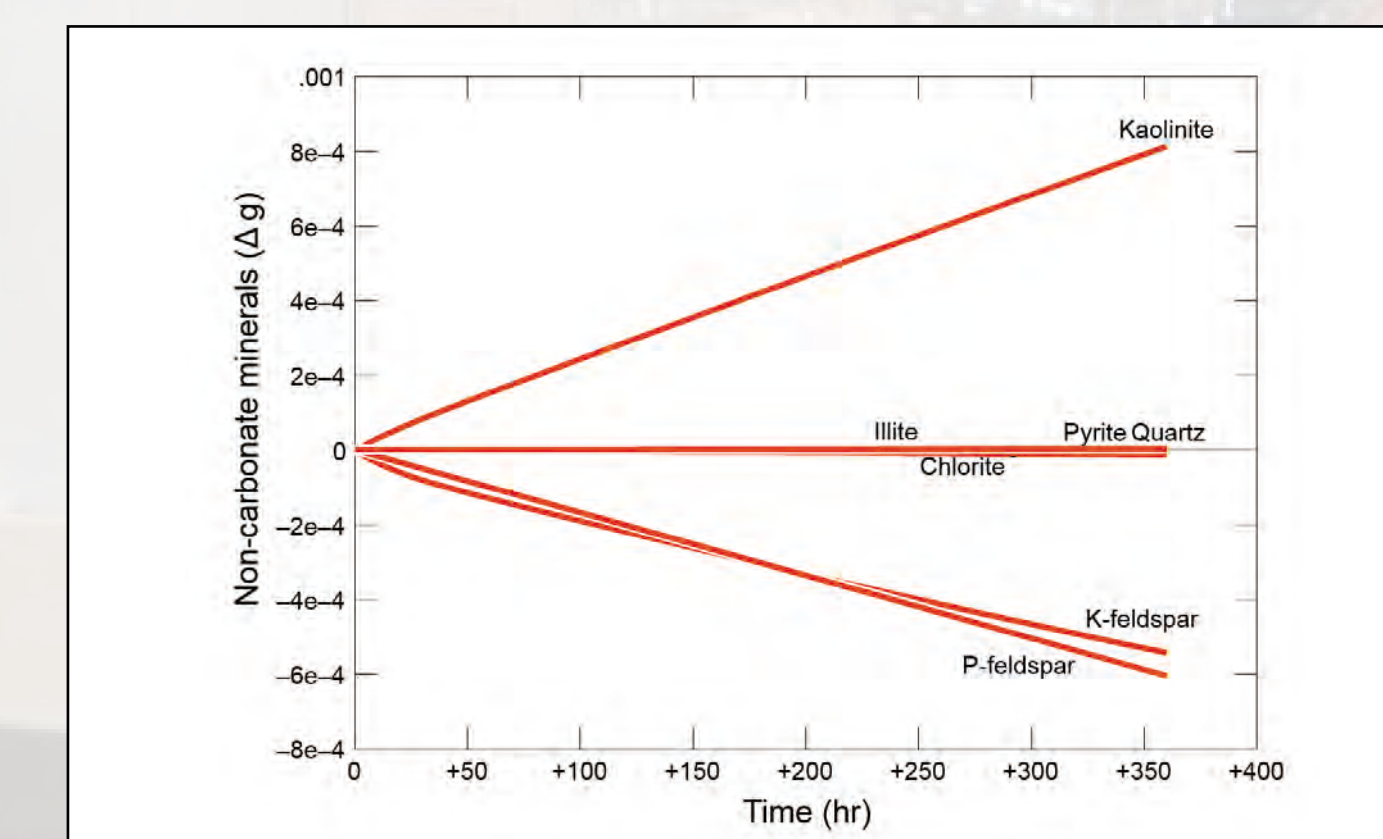


Figure 4. Modeled predictions of non-carbonate Tiskilwa minerals in CO₂-saturated environment.

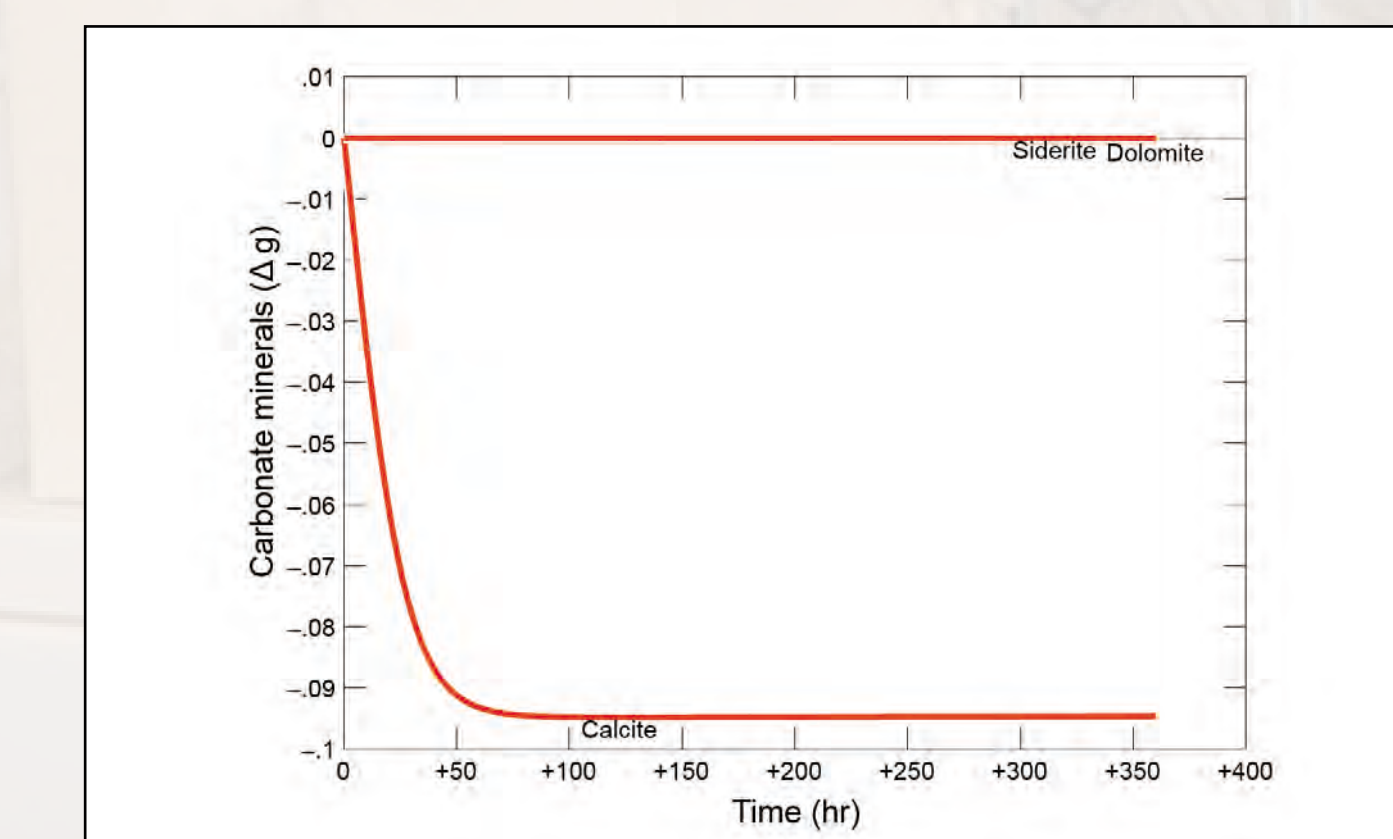


Figure 5. Modeled predictions of carbonate Tiskilwa minerals in CO₂-saturated environment.

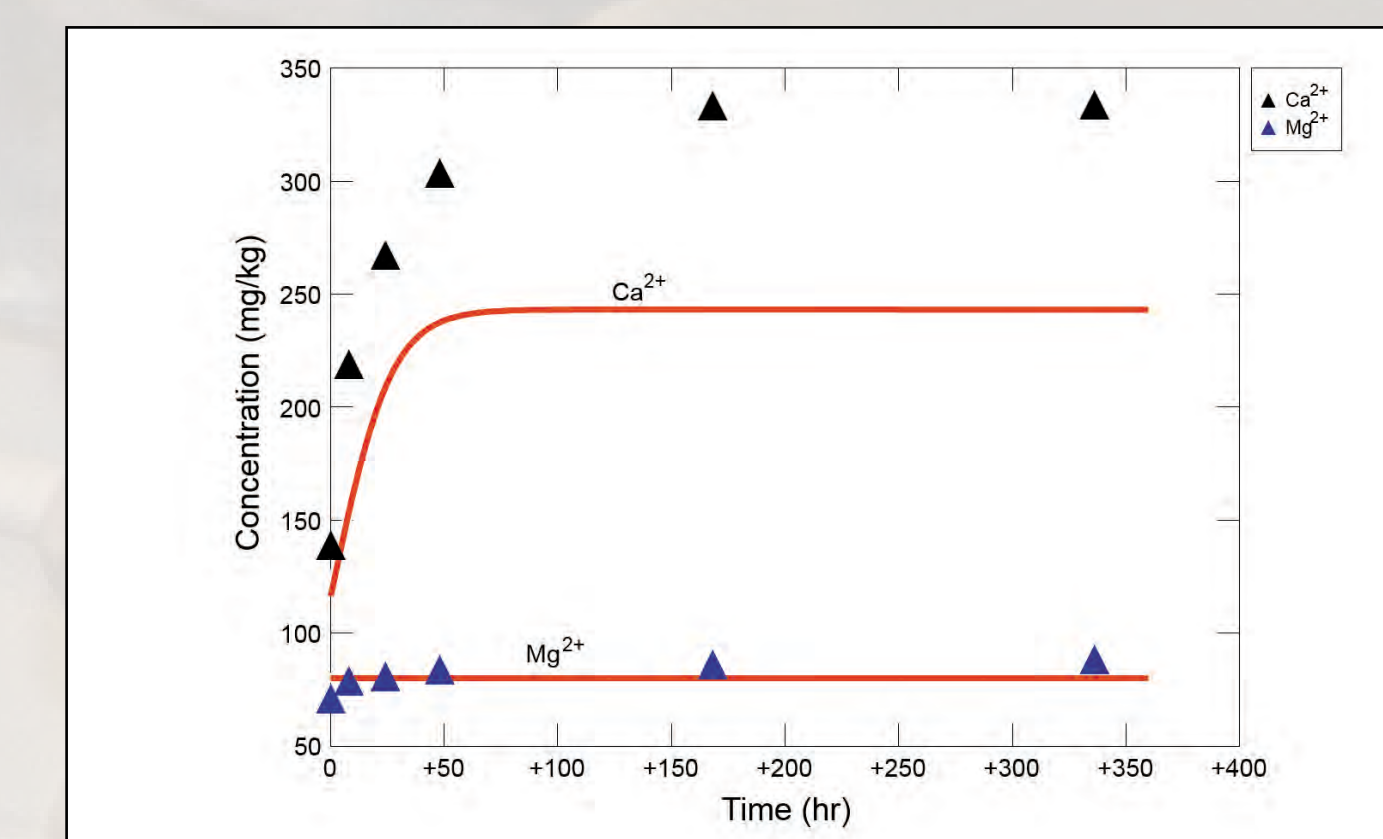


Figure 6. Modeled predictions of calcium and magnesium concentrations (red lines) vs. experimental data (triangles).

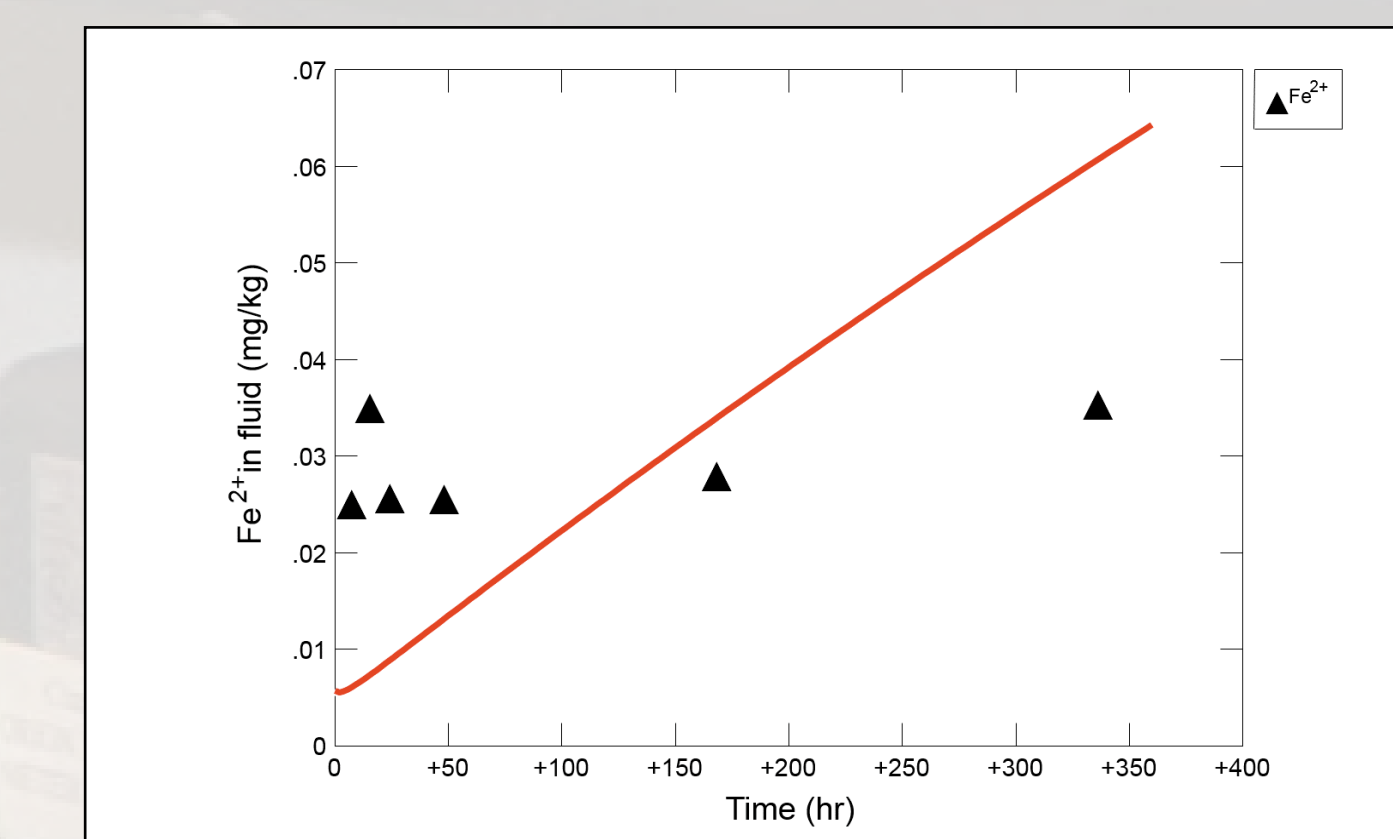


Figure 7. Modeled prediction of iron concentration (red line) vs. experimental data (triangles).

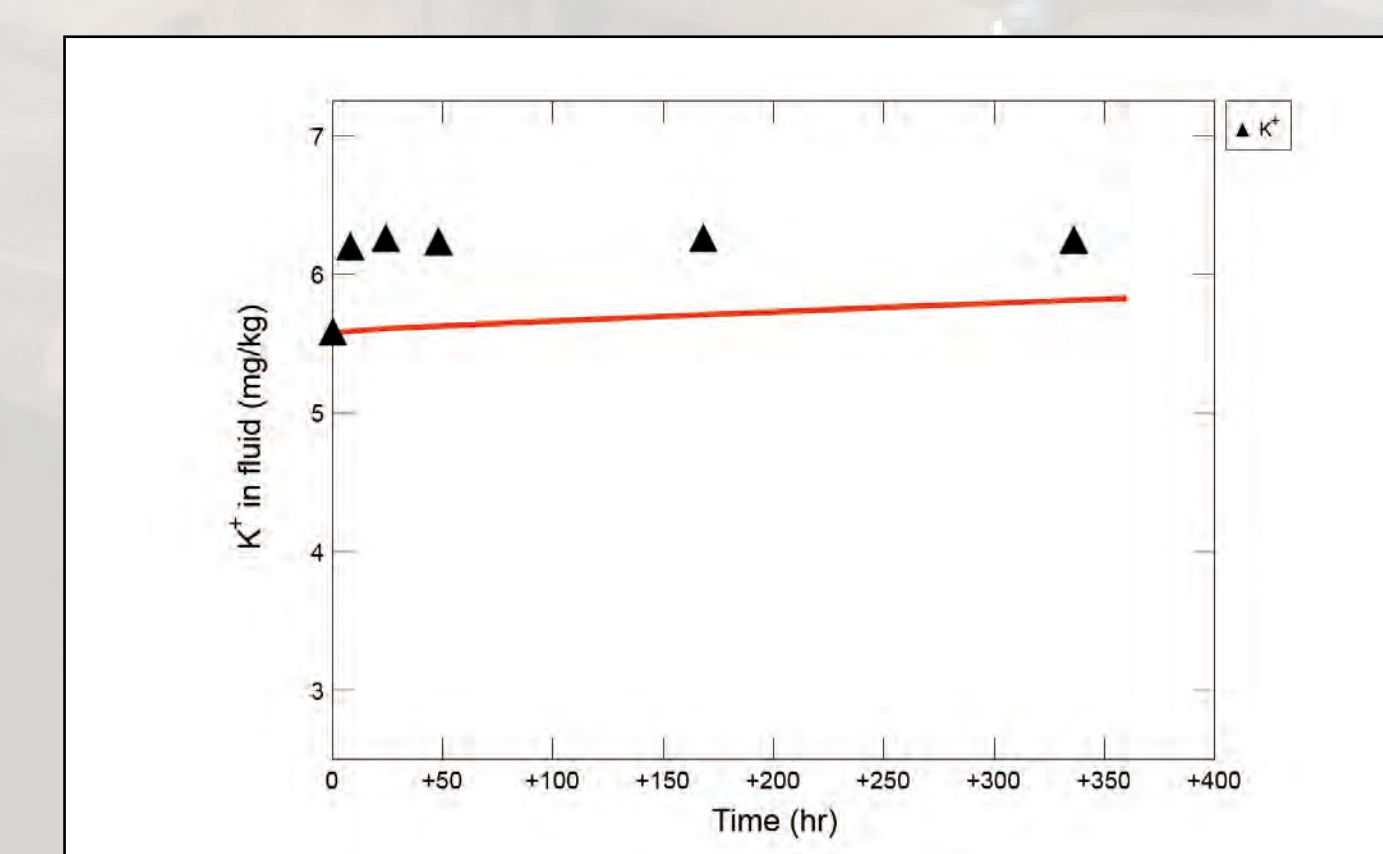


Figure 8. Modeled prediction of potassium concentration (red line) vs. experimental data (triangles).

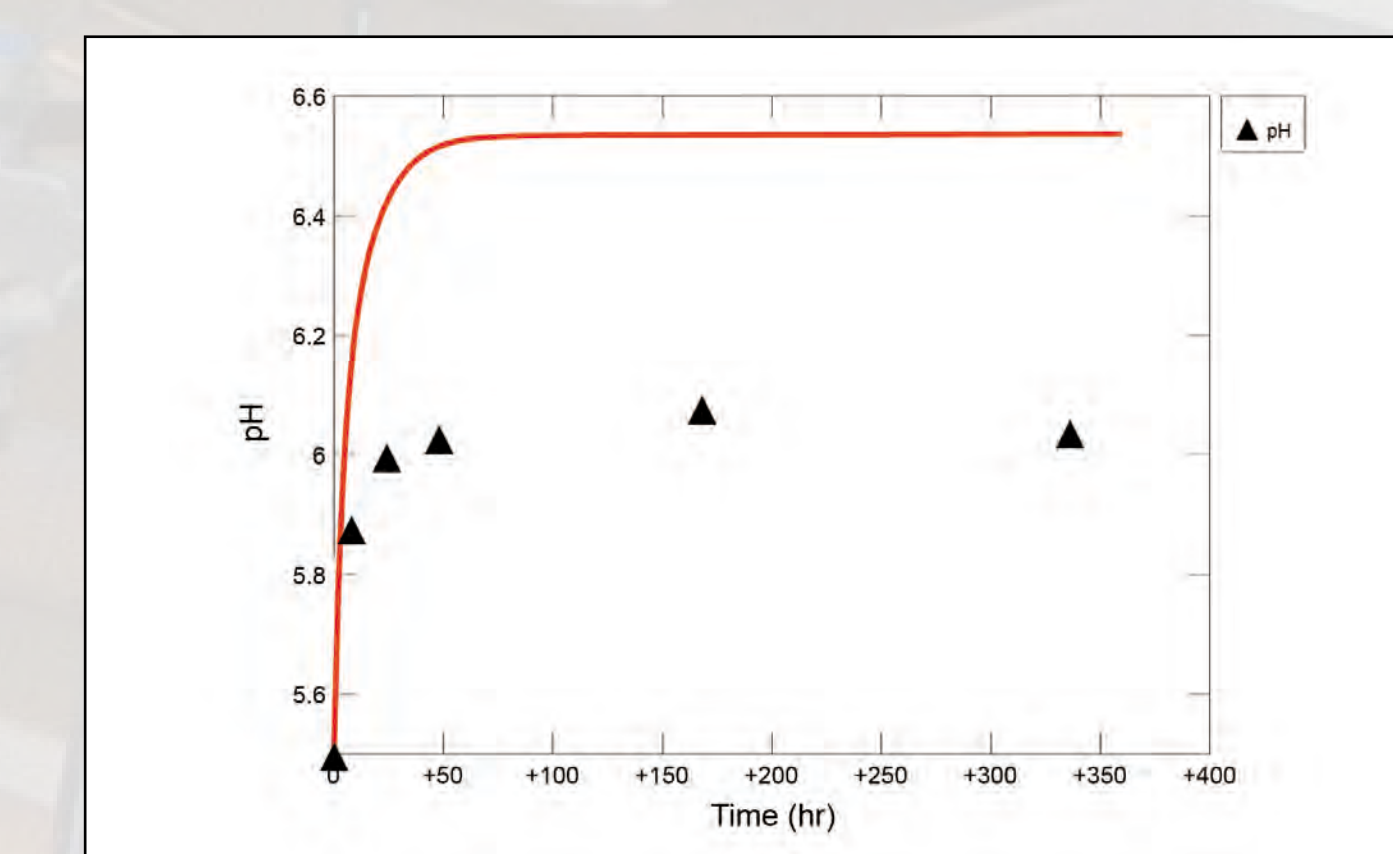


Figure 9. Modeled prediction of pH (red line) vs. experimental data (triangles).

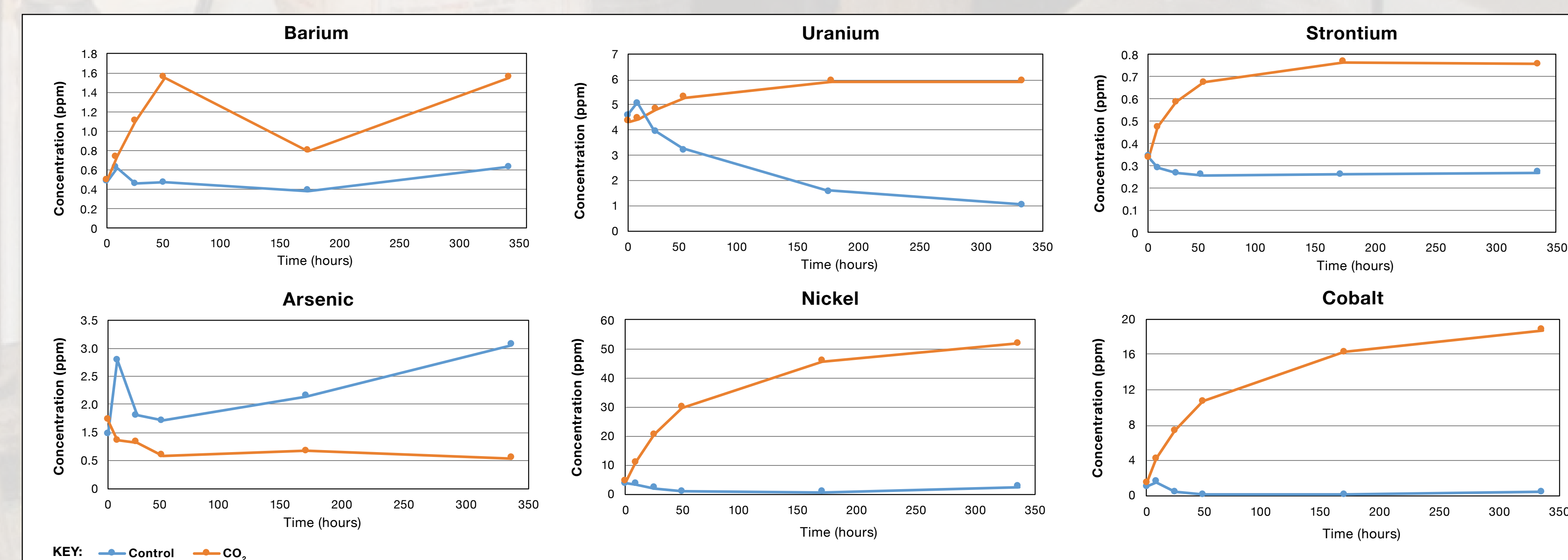


Figure 10. Time series graphs of selected trace metals. Ba and Sr are in ppm. U, Ni, Co, and As are in ppb. The EPA primary Maximum Contaminant Level (MCL) is 2 ppm for Ba, 30 ppb for U, 10 ppb for As, and 100 ppb for Ni. Co and Sr do not have primary or secondary EPA MCLs.

	As	Ba	Co	Ni	Sr	U
Detection limit	0.5	1	0.2	20	0.5	0.1
Solid sample value	3.8	194	2.9	<20	100.3	0.8

Table 2. Trace metal concentrations (in mg/kg) of the sediment sample used for this study determined by total digestion.

Results and Discussion

- Table 1 shows the mineral composition of the Tiskilwa aquifer. Figure 4 predicts the change in mass (Δg) over the course of the batch experiments as a result of being exposed to CO₂-saturated natural groundwater. Illite, chlorite, and quartz are all relatively non-reactive, while pyrite is only reactive in the presence of O₂. The dissolution of P- and K-feldspar could potentially release calcium and potassium into solution while kaolinite mineralization is relatively insignificant to the geochemical environment because feldspar is releasing Al and Si while kaolinite is precipitating both constituents.
- Calcite dissolution shown in Figure 5 along with P-feldspar dissolution (Figure 4) is the cause for the sharp initial increase of calcium as seen in experimental and modeled data in Figure 6. Figure 5 predicts little to no dolomite dissolution as the experimental data in Figure 6 shows a slight initial increase before stabilization.
- Iron experimental data in Figure 7 may show a slight upward trend, and potassium experimental data in Figure 8 show an initial increase before stabilizing. Both constituents roughly followed their modeled predictions.
- The initial pH of CO₂-saturated un-buffered groundwater was 5.5. Figure 9 shows a sharp increase before stabilizing near 6.0 perhaps due to buffering by carbonates.
- The trace metal increases in Figure 10 are likely due to pH change from CO₂ saturation (Figure 9). Ba, Sr, Ni, and Co all increase sharply during the first 48 hours, then stabilize along with pH. Uranium generally shows a slightly increasing trend throughout, while As decreases slightly. The control data for each plot except for As shows either very little change or a slight decrease, likely due to N₂ saturation stripping dissolved CO₂ out of solution to create a slightly basic environment. Results from the As control are inconclusive due to higher variability. Table 2 shows the results from total digestion analysis of solid samples for six trace metals that are important either due to their potential toxicity (Ba, U, As, Ni), or their usefulness in understanding the geochemical environment (Sr, Co).

Conclusions

- The batch experiments performed in this study indicated CO₂ interaction with shallow groundwater would decrease groundwater pH and increase both major and trace element concentrations.
- Dissolution of carbonate minerals in batch experiments, such as calcite/dolomite was rapid.
- The concentrations of trace metals of environmental concern, including Fe, Co, Ni, and U increased as a result of CO₂ introduction. Inconsistencies in the control experiment for As caused difficulties in experimental interpretations.
- Trace metal concentrations observed in the Tiskilwa aquifer are significantly lower than EPA MCLs and metal release from mineral surfaces may be mitigated by carbonates buffering pH changes during CO₂ exposure.
- Modeling results indicated that the system is almost immediately buffered by carbonate minerals while the silicate minerals were much slower to react but could be a long term factor in the system.
- This study developed a site-specific understanding of the types of aquifer responses that may be observed if a CO₂ leak were to occur. Overall, results were consistent with other studies of this type (Little et al., 2010; Shao et al., 2015; Gemini et al., 2015) The results will be further extended to improve the representativeness of the experimental design by conducting a column flow-through study to better reflect in-situ groundwater flow conditions.

