

Response to Comment on “Potential Impacts of Leakage from Deep CO₂ Geosequestration on Overlying Freshwater Aquifers”

Good science using a range of laboratory, field, and modeling approaches is critical for understanding the benefits, risks, and unforeseen consequences of carbon capture and storage (CCS). As described in Little and Jackson,¹ we presented experimental results to help understand the potential consequences of CO₂ leaks into overlying aquifers. This research, and our previous CCS-related work (e.g., refs 2 and 3), was undertaken to improve the efficacy and safety of CCS technologies worldwide. To this end, we are currently extending the work in Little and Jackson¹ to include more sites and to analyze the impact of a broader range of environmental conditions. We are also working to understand more completely the mechanisms for changes in element concentrations observed in our study and in other research (e.g., dissolution of mineral phases or enhanced desorption). Here, we address the specific comments from Gilfillan and Haszeldine⁴ in the order in which they were given:

1. Large quantities of CO₂ were bubbled through “mixed up” sediment overwhelming the buffering capacity of the samples.

This point is based on a misunderstanding of our methods. The sediment was not directly perturbed by the CO₂, which bubbled into the water alone, not through the sediments. The samples are sandy in texture and are naturally “disaggregated”. The amount of CO₂ represents a very small leak compared to the size of proposed CCS projects. Most of our samples (e.g., Mahomet and Ogallala) were effectively buffered by carbonate minerals. The system was open in respect to CO₂, which escapes freely from the system, not in respect to water. If we had created a system with a continuous flow of nonreacted water through the sediment samples, then the comment about mineral dissolution might be more appropriate.

2. “The authors deliberately chose aquifers that were already high in the undesirable trace metals and elements.”

We were, and remain, interested in the minority of sites for which potential contamination may be a problem. Characterizing both average and extreme responses to CO₂ provides insight into why some systems (and land-owners) might be vulnerable, and how to avoid those situations. Understanding average *and* extreme responses is critical to the successful implementation of CCS.

The observed concentration changes relative to the controls help to explain what could happen if a leak occurred in vulnerable locations. It is not “difficult to attribute” the rise in concentrations to CO₂ because we ran + CO₂ and control experiments on subsamples cut from the same core samples, under the same laboratory conditions. Moreover, nothing in point 2 contradicts anything that we stated clearly in the paper; for example, “To prioritize the potential risks, samples were collected only from those drinking-water aquifers where natural, in situ concentrations of As, U, Ra, Cd, Cr, Cu, Pb, Hg, or Se were greater than 10% of U.S. Environmental Protection Agency’s

primary maximum contaminant level (MCL) for drinking water.” In fact, point 2 cites the published Supporting Information from our own paper. All of the aquifer systems we used are currently exploited for drinking water.

- 3,4. “The use of disaggregated sediment samples will always result in maximum chemical reaction due to the disruption of the natural fabric of the sediment.”

“The control experiments are not representative of the conditions that the +CO₂ experiments were subjected to.” Both +CO₂ and control subsamples came from the same original disaggregated core samples. The sediments are quite porous with a sandy texture, and therefore, the reactions should be extensive regardless of the number of times shaken. Moreover, the sediment was not directly perturbed by the CO₂, which bubbled into the water alone, not through the sediments. No laboratory or field experiment or model can truly replicate an actual field-deployment of CCS, nor did we intend to mimic field conditions perfectly. For these reasons and those discussed above, we compared our +CO₂ experimental results to a control.

5. Criticisms of our interpretation of the chemical reactions and questioning the utility of running experiments under oxidizing conditions.

In our paper, we acknowledge that the impact of CO₂ leakage will be based on metal availability, carbonate buffering capacity, and redox state among other chemical and physical factors. We also address three main goals: “1) to understand how CO₂ leaks from deep geosequestration may affect water quality in overlying shallow drinking-water aquifers; 2) to develop selection criteria for sequestration sites based on inorganic metal contamination caused by CO₂ leaks; and 3) to identify geochemical signatures in affected waters which could be used as early detection criteria.” As we state in our conclusion, studies like ours should be continued and broadened to include a broader range of redox conditions and combined with CO₂ plume experiments and modeling to “provide a robust tool for predicting the areal extent and geochemical impact of leakage.” Our lab is pursuing some of this work, particularly in an effort to better understand the pertinent chemical reactions.

It should be stated that principle groundwater aquifers are often mixed between oxic and reducing conditions to varying degrees,⁵ with reducing conditions being controlled by many factors such as microbes and organic matter in addition to apparent isolation from O₂ in the atmosphere. There is value in running this experiment in oxidizing conditions, particularly when much of the Ogallala is oxic, and there will be value in expanding the work to reducing conditions, as we are doing.

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6. “There are a number of misleading statements in the text which highlight the most negative aspects of the results.” Our statements were not “misleading”. To begin with, we provided all of the individual sample data so that readers could draw their own conclusions. On the basis of our results, Co and Ni concentrations rose 10-fold in one or more samples of every aquifer we tested, in some cases by more than 100 fold (e.g., Table 3, ref 1). Concentrations of Mn rose by >10-fold in samples of three of the four aquifers, and Zn showed a >10-fold increase in one aquifer. We never stated or implied that concentrations increased dramatically in every sample. Furthermore, we compared our results to other laboratory and field experiments, including those of Lu et al.⁶ and Kharaka et al.,⁷ which also showed increases in elements such as Ca, Mn, and Ba.
7. “If CO₂ and water migrating through rock was always this dangerous, then we wouldn’t be able to drink sparkling water with such impunity.” The publication cited in support of these statements⁸ is an analysis of 39 commercially available, sparkling-water samples obtained in supermarkets. The fact that a regulated consumer market can supply safe samples of bubbly water hardly seems relevant.

Overall, our intent was to help predict and understand the minority of cases where problems with CCS and groundwater may occur. We believe that intent is still valid. We look forward to additional research that builds on the results of our study¹ and on the work of other groups around the world to improve the efficacy of CCS.

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