Litt and Jackson\textsuperscript{1} report the results of experiments, where CO\textsubscript{2} gas is passed through heat-sterilized natural sediments in small laboratory vessels filled with water. One of the stated objectives is to “understand how CO\textsubscript{2} leaks from deep geosequestration may affect water quality in overlying shallow drinking water aquifers”. In this discussion, we critically examine the choice of aquifers, experimental design, reporting of results, and inappropriate analogy to CO\textsubscript{2} leakage from engineered sites. We conclude that, although CO\textsubscript{2} does certainly acidify water and can cause mineral reactions in sediments, these particular experiments are unreliable and inappropriate as a metaphor for unplanned CO\textsubscript{2} leakage from storage sites.

1. The experiment performed simply does not scale up from the laboratory to the real world. CO\textsubscript{2} gas was bubbled through a small amount of mixed up sediment for almost a year. Unsurprisingly, chemical reactions occurred. However, the flow rate of CO\textsubscript{2} was 0.2 L per minute, which equates to 0.21 metric tons of CO\textsubscript{2} per year. This large quantity of CO\textsubscript{2} was injected into just 400 g of disaggregated sediment, some 525 times more CO\textsubscript{2} by mass than sediment. It is well-known that CO\textsubscript{2} dissolves into water to make an acidic solution, which is normally buffered by dissolution of carbonate minerals within the aquifers.\textsuperscript{2} However, in the open system created by Litt and Jackson,\textsuperscript{1} with the imposition of an effectively infinite flux of CO\textsubscript{2} through it, then that overwhelms the chemical buffering available from minerals. If the experiment was continued, then most of the minerals, except quartz, would dissolve.

2. The authors deliberately chose aquifers that were already high in the undesirable trace metals and elements. It is unsurprising, then, that these aquifers contain minerals that are likely to be extremely reactive to the imposition of large amounts of acidic water. The authors report significant increases in concentrations of alkali and alkaline earths and manganese, cobalt, nickel, and iron. However, it should be clearly explained to the reader that samples of natural groundwater from three (Virginia Beach, Mahomet, and Ogallala) of the four aquifers exceed the EPA National Secondary Drinking Water Regulation\textsuperscript{3} (NSDWR) concentration for Mn and two (Virginia Beach and Ogallala) exceed the NSDWR for Fe and Al (Supporting Information of refs 1 and 4). Natural groundwater samples from the Mahomet and Ogallala aquifers also exceed the EPA Maximum Contaminant Limit (MCL) for As, Se, and Cd. One sample from Ogallala also exceeds the MCL for Cr. Given the high levels of these containments in the natural groundwater, it is difficult to attribute the rise in concentrations observed in the +CO\textsubscript{2} experiments to be anything other than the result of equilibration of the purified waters with the contaminant rich sediments.

3. The use of disaggregated sediment samples will always result in maximum chemical reaction because of the disruption of the natural fabric of the sediment. All of the rock minerals will have reached equilibrium with their surrounding groundwater during the past million years or more. By taking the samples into laboratory glassware, the whole content of the sediment is exposed for chemical reaction, old grain surfaces, new grain surfaces, and especially, new clay matrixes, which are the most reactive. It is well-known that, in these type of experiments, reaction rates tend to be orders of magnitude higher than those in field conditions,\textsuperscript{2} yet this is never explained to the reader.

4. The control experiments are not representative of the conditions that the +CO\textsubscript{2} experiments were subjected to. The bottles were only agitated after water samples were collected for analysis. The control bottles were only sampled five times, whereas the +CO\textsubscript{2} bottles were sampled 12–14 times. Hence, +CO\textsubscript{2} bottles were agitated over twice as many times as the control samples. This agitation will increase the amount of water exposed to the sediment and hence increase the chemical reaction rate. Additionally, +CO\textsubscript{2} samples were constantly subjected to CO\textsubscript{2} bubbling, meaning the sediment and water were constantly being perturbed. This constant perturbation will also have increased the amount of water to sediment contact, again increasing chemical reaction rate. The control samples were not subjected to any gas flow and hence much less perturbation of the water will have occurred, resulting in a lower chemical reaction rate.

5. This article reports a large number of water analyses. But there is no reporting or interpretation of the chemical reactions that have occurred. Hence, there is no communication of the context or process understanding to the reader. Its clear that elements have changed in water concentrations and that the control samples often differ from the CO\textsubscript{2} samples. However, the authors only provide acidity (pH) as an indication of reaction. We do not even know the other crucial reaction parameter of oxidation state, Eh. It is quite possible that some of these grains are interacting with each other, and that some grains can dissolve to form strong acids (for example chalcopyrite, and any other sulphides). The experimental vessels were described as “oxidizing”. However the subsurface is usually “reducing”.\textsuperscript{2} This can also enhance acidity, with CO\textsubscript{2} acting as a catalytic effect.\textsuperscript{5}

6. There are a number of misleading statements in the text which highlight the most negative aspects of the results. For example, “Concentrations of some transition metals, including Mn, Fe, Co, Ni and Zn, were higher by more than 1000% in +CO\textsubscript{2} experiments relative to control treatments across all aquifers\textsuperscript{7}”. Figures 1a and 2a show that, in samples from the Mahomet aquifer, measured Mn and Fe +CO\textsubscript{2} concentrations throughout the entire experiment are well

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Figure 1. Mn concentrations in ppb plotted against time for the three main aquifers in the study. (a) Mahomet Mn concentrations plotted against time for the Mahomet aquifer. While the Mn concentrations in +CO$_2$ samples show an increase over the control samples, at no point in the experiment do the Mn concentrations exceed those measured in the natural groundwater. (b) Virginia Beach Mn concentrations plotted against time for the Virginia Beach aquifer. The +CO$_2$ sample (VB4) that shows the largest Mn increase also shows a significant increase in its corresponding control. At the end of the experiment the highest Mn concentration is measured in the VB3 control sample. (c) Ogallala Mn concentrations plotted against time for the Ogallala aquifer. A wide range of Mn concentrations can be observed throughout the experiment. There is a very large spike in several samples at day 315. Mn concentrations then fall so the majority of the +CO$_2$ samples approach the natural groundwater concentrations.
Figure 2. Fe concentrations in ppb plotted against time for the three main aquifers in the study. (a) Mahomet Fe concentrations plotted against time for the Mahomet aquifer. While the Fe concentrations in $+\text{CO}_2$ samples show an increase over the control samples, at no point in the experiment do the Fe concentrations exceed those measured in the natural groundwater. (b) Virginia Beach Fe concentrations plotted against time for the Virginia Beach aquifer. Only one $+\text{CO}_2$ sample (VB3) exhibits a large Fe increase over the range measured in the natural groundwater. By the end of the study all $+\text{CO}_2$ samples are below the Fe concentrations measured in natural groundwater. (c) Ogallala Fe concentrations plotted against time for the Ogallala aquifer. Two $+\text{CO}_2$ samples exhibit significant increases in Fe concentrations, but these decrease over the course of the experiments. At the end of the study all $+\text{CO}_2$ samples have similar Fe concentrations of $\sim750$ ppb.
below the natural groundwater concentrations. Within the Virginia Beach aquifer, only one $+\text{CO}_2$ sample (VB4) exhibits a large increase in Mn concentrations and this is mirrored by the corresponding control sample. Figure 1b illustrates that by the end of the experiment two out of the four $+\text{CO}_2$ samples and two of the four control samples exhibit Mn concentrations slightly above the natural groundwater levels. Indeed, the highest Mn concentration at the end of the study is measured in a control sample (VB3). Figure 2b shows that for Fe, only two $+\text{CO}_2$ samples show a significant increase above the natural groundwater concentrations during the experiment. At the end of the study all samples exhibit concentrations below those of the natural groundwater.

It is only the Ogallala aquifer that shows significantly increased Mn and Fe concentrations over and above the natural groundwater levels. Figure 1c illustrates that Mn concentrations vary considerably throughout the experiment, and there is a strange correlated peak in several samples on day 315. The majority of the $+\text{CO}_2$ samples approach the natural groundwater level toward the end of the experiment. Figure 2c clearly shows that only two out of the seven samples exhibit large Fe concentration increases.

7. Lastly, there is a large amount of evidence that these effects from metal pollution are uncommon. Many natural CO$_2$ springs exist in the U.S.A. and Europe. Many of these are located in spa towns, where the naturally carbonated waters are drunk and bathed in for health benefits. Some of these do indeed have elevated cations and even metals in their analyses, but these are not present in harmful concentrations. It is widely documented that the slightly acidic waters caused by dissolution of injected CO$_2$ may sometimes leach metals and dissolved organic carbon from the surrounding rocks. But the quantities are small. This is because of factors, such as the intact fabric of the rock, which has already experienced hundreds of thousands of years of interaction with porewater and come to equilibrium. It is also because of the much smaller flow rates of natural CO$_2$, which produces lesser concentrations of the noxious metals, and those metal rich waters are diluted into the much larger volumes of underground water, to become an imperceptible rise in aquifer chemistry readings. If CO$_2$ and water migrating through rock was always this dangerous, then we would not be able to drink sparkling water with such impunity.

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■ REFERENCES

G\text{ood 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,\textsuperscript{1} we presented experimental results to help understand the potential consequences of CO\textsubscript{2} 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 Jackson \textsuperscript{1} 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 Gillfillan and Haszeldine \textsuperscript{4} in the order in which they were given:

1. Large quantities of CO\textsubscript{2} 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 CO\textsubscript{2} that bubbled into the water alone, not through the sediments. The samples are sandy in texture and are naturally “disaggregated”. The amount of CO\textsubscript{2} 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 CO\textsubscript{2}, 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 CO\textsubscript{2} provides insight into why some systems (and landowners) 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 CO\textsubscript{2} because we ran +CO\textsubscript{2} 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 +CO\textsubscript{2} experiments were subjected to. Both +CO\textsubscript{2} 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 CO\textsubscript{2}, 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 +CO\textsubscript{2} 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 CO\textsubscript{2} 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 CO\textsubscript{2} 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 CO\textsubscript{2} 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 CO\textsubscript{2} 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,\textsuperscript{5} with reducing conditions being controlled by many factors such as microbes and organic matter in addition to apparent isolation from O\textsubscript{2} 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 statements 8 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 study 1 and on the work of other groups around the world to improve the efficacy of CCS.

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■ REFERENCES


