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Comment on Potential Impacts of Leakage from Deep CO₂ Geosequestration on Overlying Freshwater Aquifers

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Little and Jackson¹ report the results of experiments where CO₂ gas is passed through heat-sterilised natural sediments in small laboratory vessels filled with water. One of the stated objectives is to “*understand how CO₂ 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 CO₂ leakage from engineered sites. We conclude that, although CO₂ does certainly acidify water and can cause mineral reactions in sediments, these particular experiments are unreliable and inappropriate as a metaphor for unplanned CO₂ leakage from storage sites.

1. The experiment performed simply does not scale up from the laboratory to the real world. CO₂ gas was bubbled through a small amount of mixed up sediment for almost a year. Unsurprisingly, chemical reactions occurred. However, the flow rate of CO₂ was 0.2 litres per minute which equates to 0.21 tonnes of CO₂ per year. This large quantity of CO₂ was injected into just 400 grams of disaggregated sediment, some 525 times more CO₂ by mass than sediment. It is well known that CO₂ dissolves into water to make an acidic solution, which is normally buffered by dissolution of carbonate minerals within the aquifers². However, in the open system created by Little and Jackson¹, with the imposition of an effectively infinite flux of CO₂ 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 which were already high in the undesirable trace metals and elements. It's unsurprising, then, that these aquifers contain minerals which 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 Regulation³ (NSDWR) concentration for Mn and two (Virginia Beach and Ogallala) exceed the NSDWR for Fe and Al (Supporting Information¹ and⁴). 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 +CO₂ experiments to be anything more 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 due to 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 and new grain surfaces – and especially new clay matrix 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 conditions², yet this is never explained to the reader.

4. The control experiments are not representative of the conditions that the +CO₂ 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 +CO₂ bottles were sampled 12-14 times. Hence, +CO₂ 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 reactions. Additionally, +CO₂ samples were constantly subjected to CO₂ 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. 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. It is clear that elements have changed in water concentrations, and that the control samples often differ from the CO₂ samples. However, the authors only provide acidity (pH) as an indication of reaction. We don't 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”². This can also enhance acidity, with CO₂ acting as a catalytic effect⁵.

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, Co, Ni and Zn, were higher by more than 1000% in +CO₂ experiments relative to control treatments across all aquifers**”.

Figures 1(a) and 2(a) show that in samples from the Mahomet aquifer measured Mn and Fe +CO₂ concentrations throughout the entire experiment are well below the natural groundwater concentrations. Within the Virginia Beach aquifer, only one +CO₂ sample (VB4) exhibits a large increase in Mn concentrations and this is mirrored by the corresponding control sample. Figure 1(b) illustrates that by the end of the experiment two out of the four +CO₂ 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 2(b) shows that for Fe, only two +CO₂ 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 1(c) 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 +CO₂ samples approach the natural groundwater level towards the end of the experiment. Figure 2(c) 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 uncommon⁶. Many natural CO₂ springs exist in the USA 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 CO₂ may sometimes leach metals and Dissolved Organic Carbon from the surrounding rocks⁷. 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 CO₂ 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 readings⁵. If CO₂ and water migrating through rock was always this dangerous, then we wouldn't be able to drink sparkling water with such impunity.

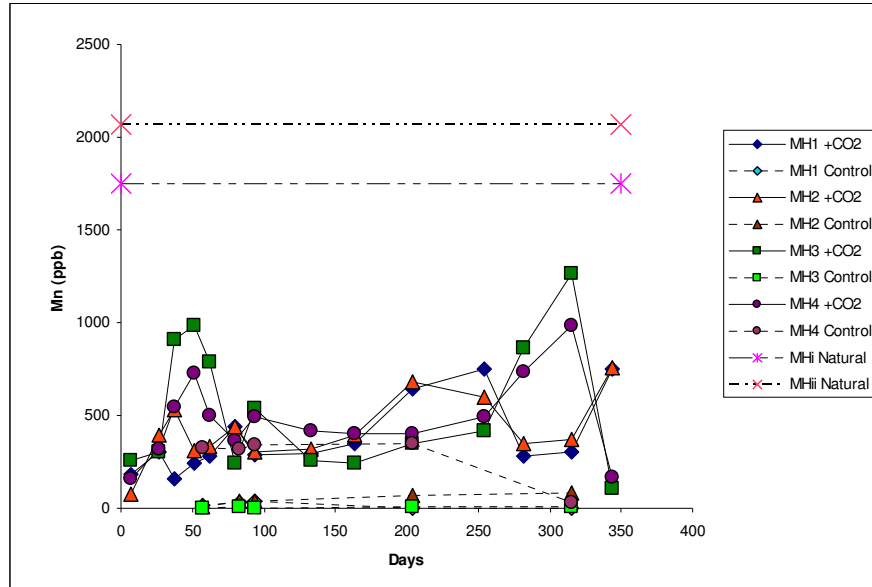
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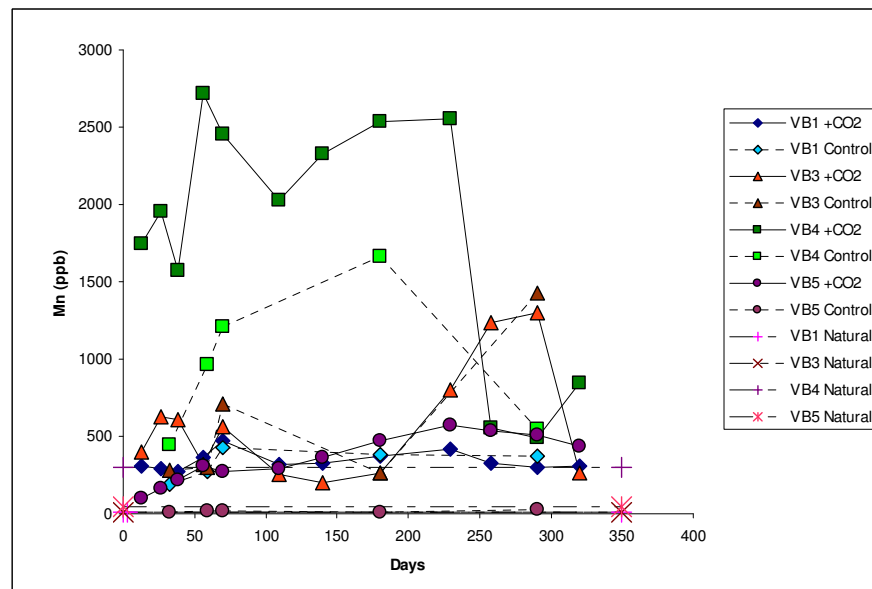
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Figure 1 - Mn concentrations in ppb plotted against time for the three main aquifers in the study

(a) Mahomet
Mn concentrations plotted against time for the Mahomet aquifer. Whilst the Mn concentrations in +CO₂ 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 +CO₂ 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 +CO₂ samples approach the natural groundwater concentrations.

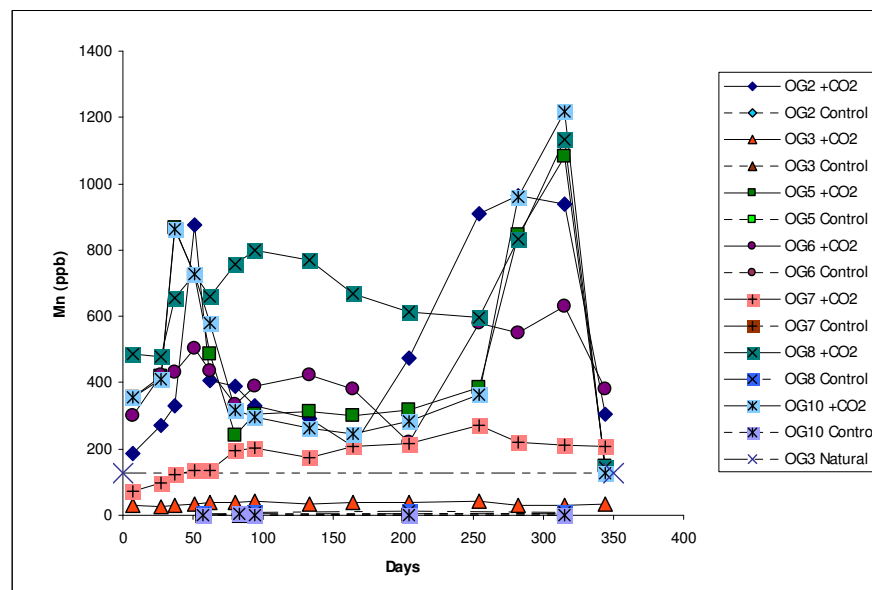
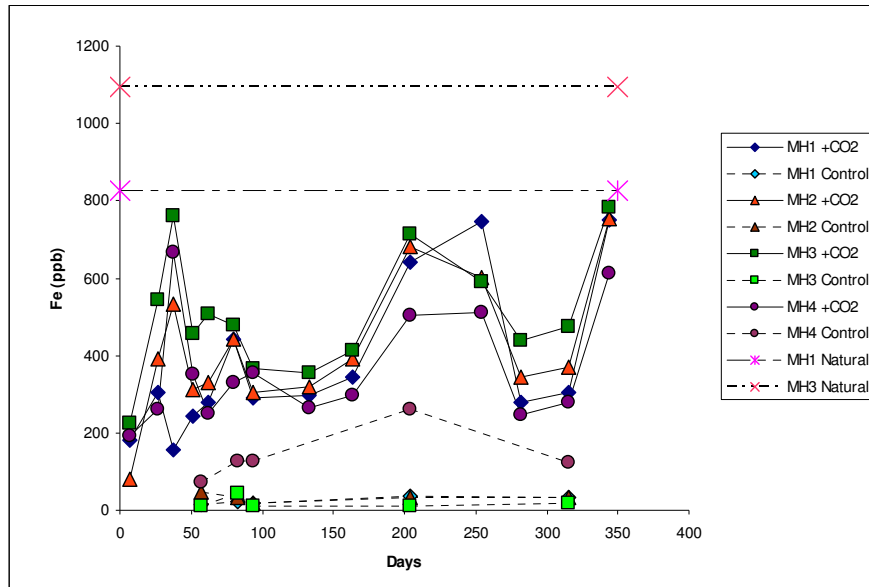


Figure 2 - Fe concentrations in ppb plotted against time for the three main aquifers in the study

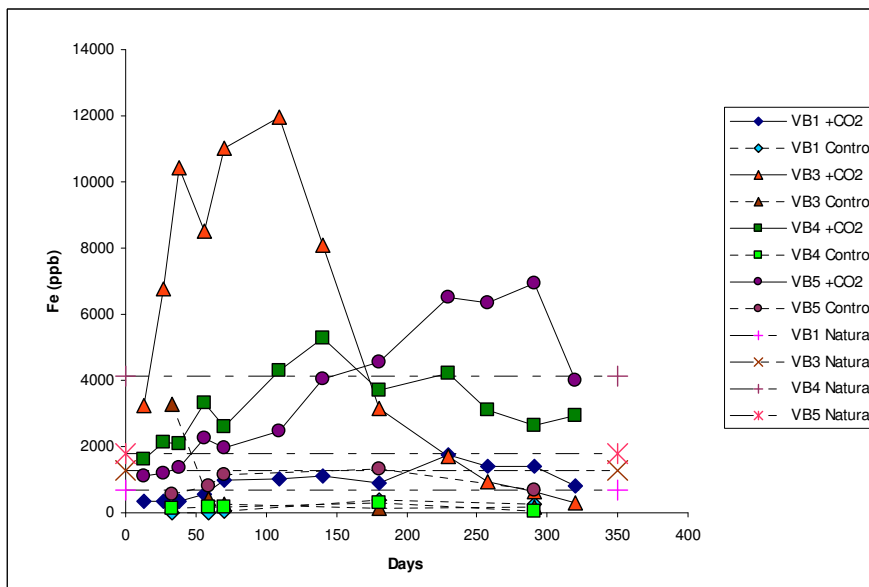
(a) Mahomet

Fe concentrations plotted against time for the Mahomet aquifer. Whilst the Fe concentrations in +CO₂ 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 +CO₂ sample (VB3) exhibits a large Fe increase over the range measured in the natural groundwater. By the end of the study all +CO₂ Fe concentrations are below the Fe concentrations measured in natural groundwater.



(c) Ogallala

Fe concentrations plotted against time for the Ogallala aquifer. Two +CO₂ samples exhibit significant increases in Fe concentrations, but these decrease over the course of the experiments. At the end of the study all +CO₂ samples have similar Fe concentrations of ~750 ppb.

