



Working paper SCCS 2010-7 Scottish Carbon Capture and Storage

Working Paper SCCS 2010-07 www.geos.ed.ac.uk/sccs/publications.html

Brief comments on

17 Nov 2010

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

Environmental Science and Technology, November 2010

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Comment

This is a Jacuzzi experiment which (incorrectly) appears to slay all hope of storing CO₂ below ground and retaining our drinking waters. But we need to read exactly what was undertaken to come to a judgment. When we read what was completed, the experiment just does not scale up from the laboratory to the real world. And the results are inconsistent – some controls change in metal ion content; some CO₂ affected samples change up and down in metal ion content. Its not well understood.

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Version 22 December 2010

Clarifying the Impacts of Sparkling Water: Comments on Potential Impacts of Leakage from Deep CO₂ Geosequestration on Overlying Freshwater Aquifers

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Abstract

The potential impacts of CO₂ on freshwater aquifers outlined by Little and Jackson, 2010 appear, incorrectly, to slay all hope of storing CO₂ below ground and retaining safe drinking waters. Without doubt the effects of CO₂ addition to drinking water aquifers deserve careful investigation. However, the experiments performed by Little and Jackson are fatally flawed and there are a number of misleading and incorrect statements in the text. The authors collected sediment samples from aquifers which were already high in undesirable trace metals and elements, so much so that the natural groundwater measured in three of the four exceeds the EPA recommended concentration limit for Manganese and two exceed the limit for Iron, Aluminium, Selenium, Arsenic and Cadmium. They then mixed these sediments with purified water and sealed one set of samples and bubbled CO₂ through the other set. The amount of CO₂ used is unreasonably large and concentrated and was performed on very small amounts of powdered sediment samples. This method will always produce the maximum chemical reaction result, as the natural fabric of the sediment has been disrupted and a much greater proportion of reactive surfaces are exposed to the CO₂. Many natural CO₂ springs exist in the USA and Europe, where the sparkling waters are drunk and bathed in for their health benefits. Some of these do have elevated cations and even metals in their analyses but not to harmful amounts. If CO₂ bubbling through rock was this dangerous, then humans wouldn't be able to drink sparkling water with such impunity.

Introduction

The article of Little and Jackson reports 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 (in)appropriate 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) Unrealistic CO₂ flux

The experiment performed by Little and Jackson 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 aquifers (Lu et al, 2010). However, in the open system created by Little and Jackson, 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. Hence, we have to be extremely careful in calculating how representative this is.

Part of the expressed purpose of his article is to assess some of the environmental risks which may derive from engineered CO₂ storage. To do this, the authors make comparisons with localised leakage from an engineered site storing CO₂ from a power plant. The key question is how valid is that comparison?

The authors state the CO₂ flow rate to be to be 0.005% of the emissions from a 500MW coal fired power plant (presumably per year) but it is not explained as to how that calculation is made. The flux of CO₂ bubbled through each of the flasks is 0.21 tonnes per year, through a bottle area of 0.03m² (assuming a 1 litre conical flask). If that is scaled up to an imagined CO₂ leak at a storage site along a fault of 1,000m long x 500m wide, then that same flow rate is equivalent to a leak of 3.5 Million tonnes of CO₂ per year.

In order to put this in perspective we compare the experiment rate to the leakage actually conceivable from an engineered storage site. For example, we consider a reservoir containing 50 Million tonnes of CO₂. The worst case leakage scenario is typically represented by assumptions that the reservoir could leak 1% of its CO₂ over 1,000 years (IPCC, 2005) (ie 0.001% per year). This would equate to 500 tonnes per year, meaning that the experimental rate used by Little and Jackson is 7,000 times too large to represent even a very bad unplanned CO₂ leak.

2) The choice of aquifers

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 Regulation (NSDWR) concentration for Mn and two (Virginia Beach and Ogallala) exceed the NSDWR for Fe and Al (Table 1 from Little and Jackson Supporting Information and Smith and Harlow, 2001).

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. Groundwater from Virginia Beach may also exceed the MCL for other trace elements, as only measurements of Mg, Ca, Mn and Fe are provided (Table 1).

Given the high levels of these containments in the natural groundwater, it is difficult to attribute the rise in concentrations observed in the +CO₂ samples to be anything more than the result of equilibration of the purified waters with the contaminant rich sediments (Figures 1 and 2).

3) The use of disaggregated sediment samples and pure water

The authors acquired disaggregated sediment samples of sand and mud from shallow aquifers across the USA, and mixed this with nanopure water at a large water to rock ratio of 3 to 1.

The use of disaggregated sediment samples will always result in maximum chemical reaction. This is because the natural fabric of the sediment has been disrupted. No longer is CO₂ and water in contact just with sandgrains and thin clay films that line the microscopic pores. All of these minerals will have reached equilibrium with their surrounding groundwater during the past million years or more – a lot longer than CO₂ geosequestration is needed (Haszeldine, 2009). 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.

The use of nanopure water adds to this effect. This water is completely out of equilibrium with the minerals contained in the sediment and contains none of trace elements that would normally buffer the acidic waters induced by the addition of CO₂. This is always going to produce the most rapid and reactions with greatest adverse environmental impact. It is well known that in these type of experiments reaction rates tend to be orders of magnitude higher than those in field conditions (Lu et al., 2010), yet this is never explained to the reader.

4) The experimental design and ‘control’ experiments

The control experiments are not representative of the conditions which the +CO₂ sediment samples were subjected to. These bottles were only agitated after water samples were collected for analysis. Thus control bottles were only sampled five times, whereas the +CO₂ samples were sampled twelve to fourteen times during the course of the study. Hence, the +CO₂ samples 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 in the +CO₂ experiments compared to those in the control bottles.

More importantly the +CO₂ samples were constantly subjected to CO₂ bubbling through them, 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 the rate of chemical reaction. However, 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. To make the control samples more representative, samples should have been taken at the same frequency as the +CO₂ samples and an inert gas such as Ar should have been bubbled through the bottles so both +CO₂ and control water samples were subject to the same amount of perturbation.

5) The chemistry

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" (Lu et al, 2010). This can also enhance acidity, with CO₂ acting as a catalytic effect (Apps et al, 2010).

6) Ambiguous statements in the text

There are a number of misleading statements in the text which highlight the most negative aspects of the results. These often use the most extreme values without providing the reader a balanced representation of the range of measured concentrations of contaminants. We outline the most misleading statements below.

i) Statement in results; "*All +CO₂ groundwater experiments produced a pH below EPA's minimum MCL of 6.5 units*"

This is incorrect; the EPA does not specify a MCL for pH (USEPA, 2010). It does state a non-enforceable guideline called a National Secondary Drinking Water Regulation (NSDWR) that the recommended pH range is 6.5 – 8.5, but does not require water systems to comply with this (USEPA, 2010).

ii) Statement in results; "*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*"

This is an extremely misleading statement. For Mn, whilst the average concentration range measured in the +CO₂ experiments were higher than the control by an excess of 1000% in a couple of cases, three of the control samples had higher average Mn concentrations than the +CO₂ samples. Additionally, five of the control samples were above the NSDWR by the end of the experiment, one by 2278%. For Fe, again whilst some +CO₂ samples were in excess of 1000% higher than the corresponding control samples, two average Fe control concentrations end up above the +CO₂ concentrations.

When we examine the results in detail using the data provided by Little and Jackson in their supporting information we can see exactly how misleading this statement is. Figure 1 and 2 show the Mn and Fe concentrations, respectively, from the +CO₂ and control experiments plotted with the natural groundwater concentrations from the three main aquifers in the study.

Figures 1(a) and 2(a) clearly 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. This is more surprising when the exaggeration of the chemical reaction rate caused by the experimental procedures is considered.

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 and all +CO₂ samples reach a similar concentration of Fe of around 750 ppb at the end of the study.

When we examine the concentration results for the other metal ions we find similar discrepancies. For Co and Ni, the control concentrations measured in VB3 are higher than the +CO₂ values. However, it is for Zn where the statement is most misleading. Only two of the +CO₂ samples exhibit Zn increases above 1000%. Six out of seventeen of the control values have higher average Zn concentrations than the +CO₂ samples (Table 3, Little and Jackson, 2010).

iii) Statement in discussion; “Our results showed that increased Al, Mn, Fe, Zn, Cd, Se, Ba, Tl and U concentrations approached or exceeded their MCL under such conditions”

Again, this is an extremely misleading statement. As with pH the EPA do not specify a MCL for Al, Mn, Fe or Zn, only a secondary recommendation, a NSDWR (USEPA, 2010).

Only Fe and Mn exceeded NSDWR in the majority of the +CO₂ samples. However, as mentioned in point 2, so does the natural groundwater in the majority of the aquifers.

For Al only three +CO₂ samples exceeded the recommended lower limit of the NSDWR over the course of the experiments, and only one exceeded the recommended upper limit. One control value also exceeded and one was within 90% of the lower recommendation. The control concentration measured in sample VB3 exceeded the upper recommendation and recorded the highest overall Al concentration. 12 of the 17 control samples exceeded the average +CO₂ concentrations.

For Zn, only one of the +CO₂ samples came close to 50% of the NSDWR and 6 of the 17 average control concentrations were higher than the +CO₂ values.

For Cd, only two of the 17 +CO₂ concentrations exceed 50% of the MCL, one of the control values exceeds the +CO₂ concentration and two control values are not provided.

For Se, one +CO₂ concentration reaches 38% of the MCL, the rest are much lower and 10 of the control samples exceed the +CO₂ concentrations, one of which is 46% of the MCL concentration.

For Ba, whilst all +CO₂ samples are higher than the control values, only two of the +CO₂ concentrations exceed 50% of the MCL.

For Tl, again the all of concentrations of +CO₂ samples are higher than the control values. However, the highest +CO₂ concentration is only 40% of the MCL.

Lastly for U, only two of the +CO₂ samples exceeded the MCL, one of which exhibited a corresponding control concentration which also exceeds the MCL.

iv) Statement in discussion; “Additionally Li, Co, U, and Ba concentrations continued to rise after >300 days of exposure to CO₂.”

Unsurprisingly, this statement is also misleading. Li can be seen to still be rising in only one of the Ogallala samples, OG3. The remainder in Ogallala and the other samples have levelled off within the error margins of the data. Hence, this statement is based on a single +CO₂ sample.

For Co, a consistent increase throughout the +CO₂ experiment is only shown in two samples, MH2 and VB2.

For U, only one sample OG2, shows any sign of increasing concentrations, and that is tenuous at best. The remainder of +CO₂ samples in all aquifers, if anything, show a slight decrease in U concentrations.

For Ba, both Ogallala and Mahomet are illustrated but again only one sample (OG10) shows a clear increase in Ba concentrations. The remainder have levelled off.

Hence, this statement appears to the reader to have been based on single samples from single aquifers. From the data and graphs presented it is impossible to come to any other conclusion than the authors 'cherry picked' the data to show the negative effect they wanted.

7) Natural waters and dilution

And lastly, there is a large amount of evidence that these effects from metal pollution are uncommon (Barroso et al., 2009). 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. However, these are not present in harmful concentrations.

It is also worth highlighting that the majority of commercially bottled sparkling waters available are not naturally carbonated, but have the CO₂ added to natural spring water during production (www.finewaters.com). This was invented in 1767 by Joseph Priestly in England and published in 1772 as "Pyrmont Water" (Prestly, 1772). Modern examples include Perrier, San Pellegrino, and Highland Spring. Consequently, analytical comparisons such as Barroso et al., 2009 must be treated with caution, to disentangle natural sources from commercial designs.

Examples of natural carbonated waters sourced from geologically recent volcanism and artesian flow regions include Gerolsteiner (www.gerolsteiner.de) – from recent volcanism and ancient dolomite in the German Eifel, with analysis of 2,527 mg/l TDS; Badoit (www.badoit.com) from French granite and sediments; geothermal 73°C spa waters from Vidago and Chaves in Portuguese granite. Other examples include Chateldon, Saint Geron, Vichy Celestins and Vichy St Yorre, (Auvergne, France); La Salvetat, Quezac and Wattwiller-Jouvence (Alsace, France); Borsec (Carpathians, Romania); Cabreiroá (Galicia, Spain) Caldes de Malavella (Pyrenees, Spain); Rogaška Slatina (Slovenia); Borjomi (Georgia), ULIVETO (Tuscany, Italy), Ferrarelle (Vesuvius, Italy) and Pedras Salgadas (Portugal),

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 rocks (Kharakha et al. 2010). 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, much, 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 readings (Apps et al., 2010). If CO₂ and water migrating through rock was always this dangerous, then we wouldn't be able to drink sparkling water with such impunity.

References

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United States Environmental Protection Agency, Drinking Water Contaminants. <http://water.epa.gov/drink/contaminants/index.cfm#Secondary> accessed on November 16th 2010.

Table 1. Natural Groundwater compositions for the aquifers Little and Jackson, 2010 obtained sediment from.

From supporting information <http://pubs.acs.org/doi/suppl/10.1021/es102235w> accessed November 18th, 2010

Highlighted cells indicate natural groundwater concentrations that are above USEPA Maximum Contaminant Levels (MCL) or National Secondary Drinking Water Regulations (NSDWR)

Type	MCL		NSDWR		MCL		NSDWR				NSDWR		MCL		MCL		MCL		MCL	
Level	2000		50-200		100	50	300				1300	5000	10	50			5	2000		30
	Li	B	Mg	Al	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Cd	Ba	U
Conc	ppb	ppb	ppm	ppb	ppm	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
AQ1																				
VB1			61		42			7	665											
VB2			2.4		46			166	434											
VB3			44		27			8	1267											
VB4			10		54			297	4143											
VB5			27		65			43	1774											
MH ⁱ							22	1750						9						
MH ⁱⁱ														46						
MH ⁱⁱⁱ	32.8			75			32	2070					1.3							
MH1	18	425	31	90	50	47	5.8	108	827	13	16	0.79	7.3	36	131	538	22	12	167	
MH2	18	462	32	88	56	47	5.8	34	792	13	14	0.79	7.3	3.6	131	450	22	12	218	
MH3	18	299	28	37	69	47	5.8	58	1094	13	17	0.79	7.3	2.1	131	425	22	12	90	
MH4	18	101	23	37	47	47	5.8	58	962	13	17	0.79	7.3	4.3	131	413	22	12	411	
OG ⁱ			5		3.6															
OG ⁱⁱ			26	50	49	33	20	20	20			1	41	2	50	1200	1	10	99	
OG ⁱⁱⁱ	342	61	4	81	43	19	1	11				3	13	10	19	2600	6.3		43	
OG ^{iv}	91.3	231	41	6	56	37.2	4.9	3.45	60	0.09	0.7	1.4	9.5	6.5	62	1460	4.7	0.22	62.5	6.9
OG ^v			78	50	104	91	2	6	46			8	38	45	92	4200	16	10	100	
OG2	73	179	21	1	35	45	1.2	0.1	10	0.047	0.06	1.3	3.1	7.1	3.5	964	8.3	0.02	72	2.5
OG3	148	250	90	1.3	154	20	0.55	128	15	0.432	2.6	2.3	1.8	3.2	21	4375	5.9	0.07	100	5.795
OG5	148	250	90	1.3	154	20	0.55	128	15	0.432	2.6	2.3	1.8	3.2	21	4375	5.9	0.07	100	5.795
OG6	148	250	90	1.3	154	20	0.55	128	15	0.432	2.6	2.3	1.8	3.2	21	4375	5.9	0.07	100	5.795
OG7	0.18	25	190	13	405	0.85	354	10	0.224	0.04	0.04	0.55	2320	4.0	0.9	1.4	17	0.06	47	0.003
OG8	0.18	25	190	13	405	0.85	354	10	0.224	0.04	0.04	0.55	2320	4.0	0.9	1.4	17	0.06	47	0.003
OG10	0.18	25	190	13	405	0.85	354	10	0.224	0.04	0.04	0.55	2320	4.0	0.9	1.4	17	0.06	47	0.003

MCL [U.S. Environmental Protection Agency (USEPA) (2010). Drinking Water Contaminants. <<http://www.epa.gov/safewater/contaminants/index.html>>]

MHⁱ is a medium value from LIHRBMas1, a well near the Mahomet samples [Thomas, M.A. (2003). Arsenic in midwestern glacial deposits— Occurrence and relation to selected hydrogeologic and geochemical factors. U.S. Geological Survey Water-Resources Investigations Report 03-4228.]

MHⁱⁱ is a set of maximum concentrations in a well near the Mahomet samples [Holm, T.R., W.R. Kelly, S.D. Wilson, G.S. Roadcap, J.L. Talbott, and J.W. Scott. 2004. Arsenic geochemistry and distribution in the Mahomet Aquifer, Illinois. Illinois Waste Management and Research Center Research Report 107. Champaign, Illinois: Illinois Waste Management and Research Center.]

MHⁱⁱⁱ is a well in Champagne County, near the Mahomet samples [Kelly, W.R., T.R. Holm, S.D. Wilson, and G.S. Roadcap (2005). Arsenic in Glacial Aquifers: Sources and Geochemical Controls. Ground Water, 43(4), 500-510.]

OGⁱ is a median concentration from a well near the Ogallala samples [Fahlquist, L (2003). Ground-Water Quality of the Southern High Plains Aquifer, Texas and New Mexico, 2001. U.S. Geological Survey Open File Report 03-345.]

OGⁱⁱ Nativ 92 (max Lubbock Co.)

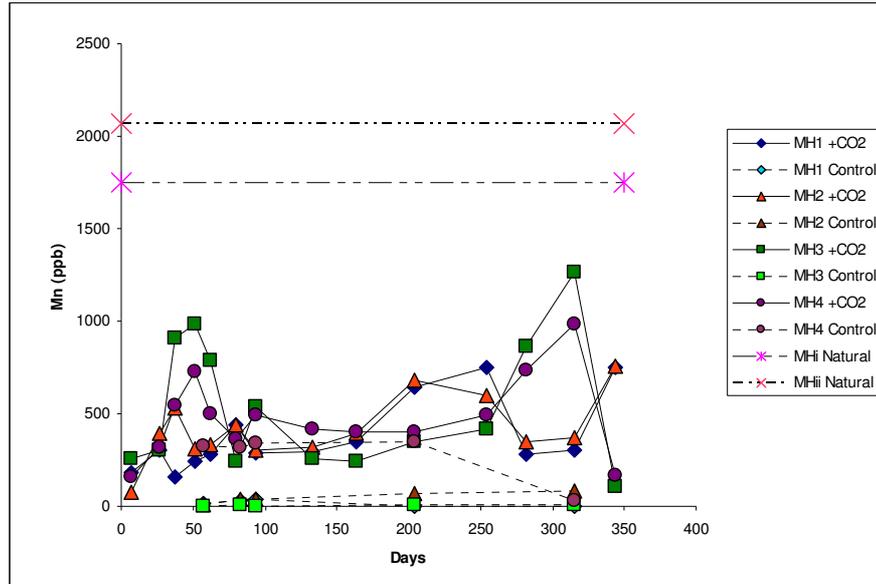
OGⁱⁱⁱ Schriver 98 (“South” which is all, Medium)

OG^{iv} Hopkins 1993 (North) – near our sample OG2

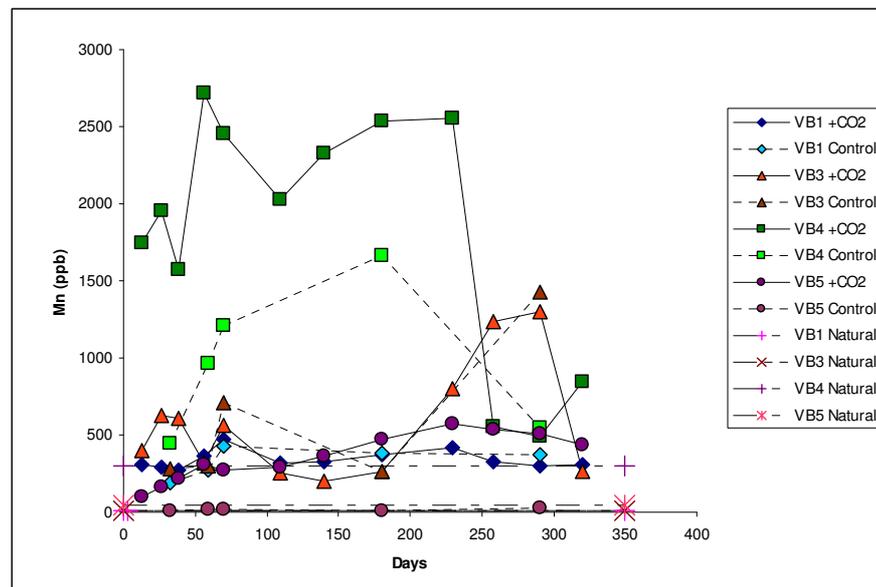
OG^v Hopkins 1993 (South) – near all of our Ogallala samples

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.

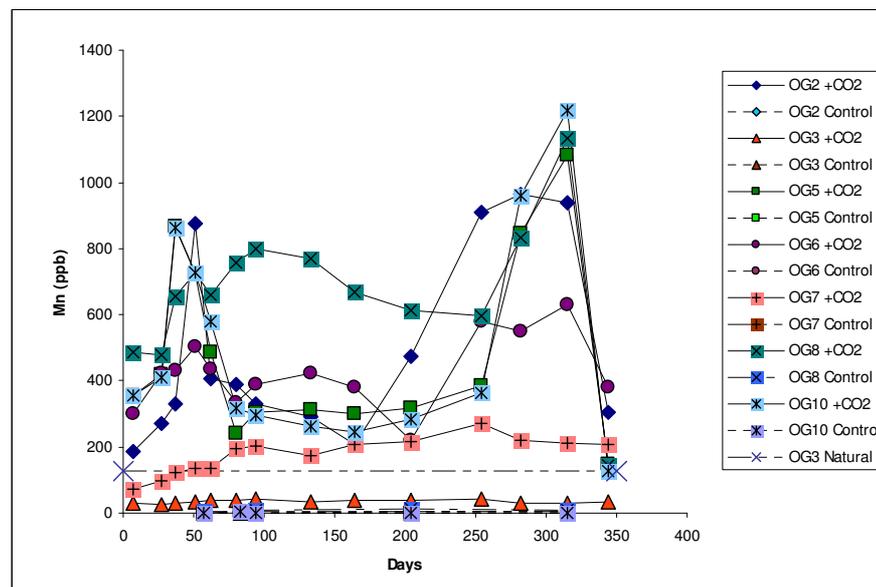
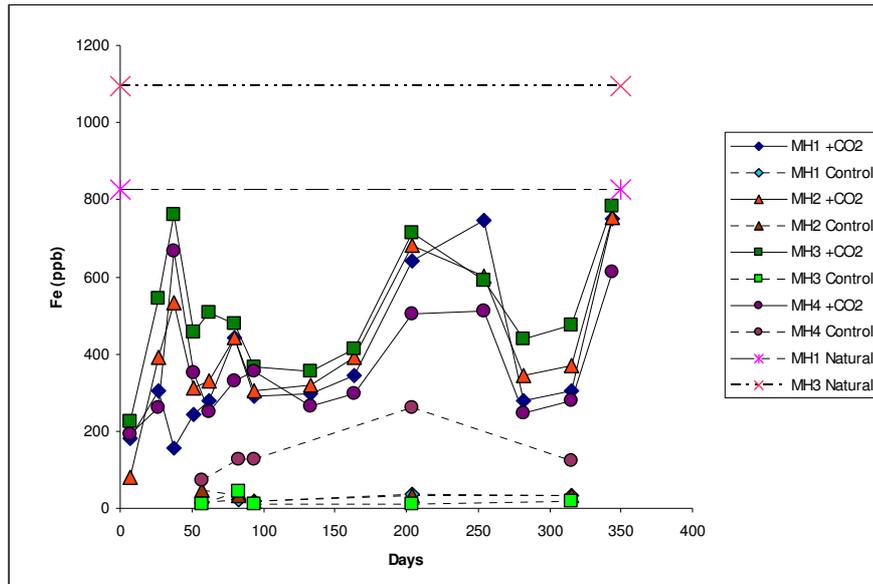


Figure 2 - Fe concentrations in ppb plotted against time for the three main aquifers in the study

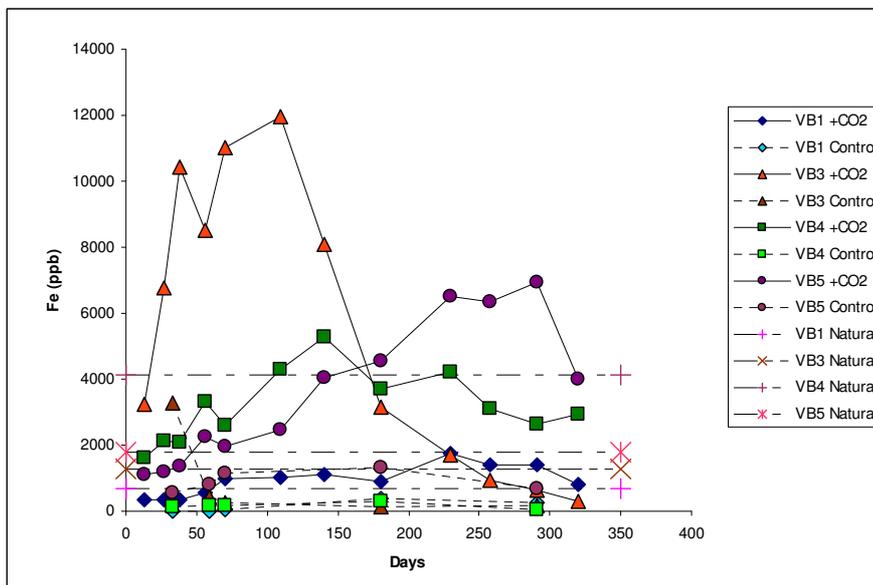
(a) Mahomet

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.

