

# **Carbon Dioxide Injection into Shallow Sedimentary Aquifer Systems to Assess Potential Degradation of Groundwater Quality at Geological Carbon Sequestration Sites**

**(Project No. 4265)**

**Periodic Report No. 2, Period covered: Nov 1 2010 – Jan 31, 2011**

**Principal Investigator: Bridget Scanlon  
Co-Principal Investigator: Changbing Yang**

Bureau of Economic Geology, University of Texas at Austin

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Participating Utilities: Mr. Broussard, Lafayette Utilities, Louisiana; Mr. Coleman, City of College Station, Texas; Mr. Hovsepian, City of Houston, Texas; Mr. Hunsinger, East Bay Municipal Utility District, CA; Ms. Owen, Tampa Bay Water, Florida.

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Project Objectives of this study are to (1) assess impacts of CO<sub>2</sub> leakage on groundwater quality using field studies based on push-pull tests in shallow sedimentary aquifers at a geological carbon sequestration site in the Gulf Coast, (2) conduct laboratory batch experiments to determine impacts of CO<sub>2</sub> on major and trace elements, (3) simulate test results to assess mechanisms dominating mobilization of major and trace elements in the event of a CO<sub>2</sub> leak, (4) evaluate which geochemical parameters are most diagnostic of CO<sub>2</sub> leakage into underground sources of drinking water (USDWs), and (5) communicate study results to water utilities and regulators.

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## **II. Status Summary**

### ***II. 1. Summary of Work Tasks Completed and Accomplishments***

Task 1 focusing on the batch experiments of water-rock-CO<sub>2</sub> interactions was completed during the reporting period. Three sets of batch experiments were conducted: one batch experiment for aquifer sediments taken from the Helena site in Texas, one for the aquifer sediments and one for the aquitard sediments taken from the Cranfield site in Mississippi. For the three batch experiments, groundwater taken from the two sites were used in the lab and reacted with CO<sub>2</sub> and sediments, instead of distill water used in the batch experiments reported by Lu et al.,(2010) and Little and Jackson (2010). To our knowledge, this is the first time to use directly groundwater to react with sediments and CO<sub>2</sub> in batch experiments for evaluating impact of CO<sub>2</sub> leakage on shallow groundwater quality. In addition, we also concern about how the aquitard functions when CO<sub>2</sub> leaks into shallow aquifer

Before conducting batch experiments, sediment samples were characterized using XRD. Mineralogy data show that sediment samples of the Cranfield site contain poorly carbonates while sediment samples of the Helena contain 2-5% carbonates. Surface area of sediment samples which is a very important parameter for geochemical modeling was also analyzed with the SA 3100 Surface Area and Pore Size Analyzer. For the Helena sediment samples, SEM and XRD were also used for comparing mineralogy composition and surface features before and after sediments reacted with groundwater and CO<sub>2</sub>. However, no significant changes in mineralogy composition and surface features of the Helena sediment samples have been observed before and after the batch experiment. This may be due to the fact that very little amount of mineral dissolution can not be observed with SEM and XRD.

Total 86 water samples were taken for chemical analysis with ICP method for cations and IC method for anions. In addition, alkalinity was measured for 13 water samples using a titration method.

Once CO<sub>2</sub> was introduced into groundwater, groundwater pH will be lowered, however, depending on buffer capacity of sediments, namely, content of carbonate minerals. For the batch experiments with the aquifer sediments taken from the Helena site, groundwater pH decreased from 8.07 to 5.7 while for the batch experiment with aquifer sediments taken from

the Cranfield site, groundwater pH decreased from 7.9 to 4.8\*, then gradually increased to 5.11 after CO<sub>2</sub> was introduced. Release of major ions from was mainly dominated by dissolution of carbonates and silicate minerals. Release of the trace and metal elements from the sediments was mainly dominated by desorption (see Section III.3).

Modeling design of field push-pull tests of Task 2 already started. In this reporting period, a scoping calculation using the numerical tool, CORE2D 4 (Yang, 2006; YANG et al., 2007a) were carried out to understand how to best conduct push-pull tests. However, most of parameters used in the numerical model were taken from the literature. In this quarterly report, the model setup is presented in Section III.3. The detail results will be reported in the next quarterly report.

The baseline characterization of regional groundwater chemistry for Task 3 at the Cranfield shallow aquifer has been completed. Regional groundwater chemistry is mainly dominated by silicate mineral weathering which is also confirmed by XRD mineralogy analysis of aquifer sediments taken from wells drilled at this site. At this site, groundwater is barely used. Only few water wells are using for domestic supply.

## ***II.2. Assessment of actual versus planned progress for each task***

Table 1 lists the research status of this project. Conducting lab experiments in Task 1 has been finished. Progress on this task is behind the scheduled progress because 1) The new postdoc who is working on this project was hired in September 2010 and 2) In addition to the batch experiment of aquifer sediments from the Cranfield site, we conducted another two sets of batch experiments: one set of batch experiment was conducted with the rock samples taken from the aquitard sediments just right above the aquifer at the Cranfield site and one set of batch experiment with aquifer sediments taken from the Helena site. Task 2 on modeling design of the push-pull tests was scheduled to be finished in the third reporting period. But it is behind the schedule because some model parameters are needed from the results of batch experiments. Currently, Task 3 on conducting push-pull tests is on the right track. Currently geochemical characterization of the regional groundwater quality has been finished. However, the field work of push-pull test may be rescheduled at the reporting period 5.

**Table 1** Research status of project 4265

Tasks		Past		Current	Ongoing								
		05/2010-07/2010	08/2010-10/2010	11/2010-01/2011	02/2011-04/2011	05/2011-07/2011	08/2011-10/2011	11/2011-01/2012	02/2012-04/2012	05/2012-09/2012	10/2012-04/2013		
		Reporting Period 1	Reporting Period 2	Reporting Period 3	Reporting Period 4	Reporting Period 5	Reporting Period 6	Reporting Period 7	Draft Report	Final Report	Project end		
Task 1	Conduct Lab experiments	Scheduled	[Grey bar]		[Red arrow from start of Reporting Period 1 to start of Reporting Period 4]								
		Progressing	[Cyan bar]										
Task 2	Model the design of field push-pull tests	Scheduled		[Grey bar]	[Red arrow from start of Reporting Period 3 to start of Reporting Period 4]								
		Progressing			[Cyan bar]								
Task 3	Conduct push-pull tests	Scheduled		[Grey bar]									
		Progressing			[Cyan bar]	[Red arrow from start of Reporting Period 3 to start of Reporting Period 6]							
Task 4	Simulate results of push-pull tests	Scheduled		[Grey bar]									
		Progressing				[Cyan bar]	[Red arrow from start of Reporting Period 5 to start of Reporting Period 7]						
Task 5	Communication	Scheduled											
		Progressing				[Cyan bar]	[Red arrow from start of Reporting Period 4 to start of Reporting Period 7]						

## ***II.2. Tasks proposed to be finished in the coming period***

In the coming period, complete data analysis and geochemical modeling of batch experiments in Task 1 will be finished. Task 2 about modeling design of push-pull tests will be finished. Preparation of field push-pull tests will be initialized.

## ***II.2. Problems encountered***

Currently, we haven't encountered serious problems.

## ***II.3. Rational for proposed changes (if any) to the scoped of work***

There is no significant change currently to the scope of work. However, two sets of batch experiments (one of for the aquifer sediments taken from the Helena site, TX and one for the aquitard sediments from the Cranfield site were conducted which were not described in the scope of work. We think the two additional batch experiments can provide very valuable information for understanding impact of CO<sub>2</sub> leakage on shallow groundwater quality.

## ***II.4. Presentations, papers, reports***

Currently, we haven't presented or published any results related to this project.



### III. Technical Summary

#### III.1 Response to Comments

1. Although this was the status report, the project team is encouraged to provide greater information in future reports including additional detail (for example, what is the nature of the findings / proposed approach for saturating CO<sub>2</sub> in water based on the work at Columbia?), observations, identification of potential problem areas, and anticipated activities for the next reporting period.

[Reply] Several small-scale CO<sub>2</sub> injection tests in mafic and metasedimentary rocks using a single-well-pull test strategy were reported for understanding water-rock reactions and dissolution rates of Ca, Mg silicate bearing rocks by (Assayag et al., 2009; Matter et al., 2007). The injection experiments were conducted at the Lamont–Doherty Earth Observatory test site in Palisades, New York, USA. In one of the experiments, about 1,300 L of an aqueous solution was pumped into a hydraulically isolated interval at 232–240 m depth (the contact zone) over a time period of 3 h. The injected solution was prepared in a polyethylene tank at the wellhead and consisted of formation water pumped from the contact zone (called background water, BW), spiked with oxygen-18 isotopes (30 ml, H<sub>2</sub><sup>18</sup>O enrichment: 98.2%) and sodium chloride (210 g), both used as conservative tracers. Then about 1,300 L of the same solution equilibrated with 1.10<sup>5</sup> Pa CO<sub>2</sub> partial pressure (PCO<sub>2</sub>) were injected over the same interval for the same time period. The incubation period for both tests lasted for three weeks. After the incubation period, the injected solution/background water mixtures were pumped back using a submersible pump and passed through a measurement cell in which electrical conductivity, temperature, and pH were continuously measured. The elapsed pumping time and the extracted fluid volume were recorded automatically, and samples were collected at incremental periods from the discharge stream (from one sample per half-hour to one sample twice a day). The authors reported that in a natural and heterogeneous system, these field results confirm that several geochemical processes lead to the neutralization of the injected CO<sub>2</sub>. The dominant process was determined to be carbonate mineral dissolution followed by cation exchange reactions and/or Ca–Mg

silicate mineral dissolution in the host formations; however, it is difficult to identify the relative contribution in this setting because of the limited precision and accuracy of dissolved inorganic carbon as well as the spatial and temporal variability of the background water compositions. Contribution of ionic exchange also remains to be quantified. Although the studies presented by Assayag et al. (2009) and Matter et al. (2007) focused on chemical processes of geological CO<sub>2</sub> sequestration at a basal aquifer, we are interested in how a single well push-pull test can be conducted in a much shallower aquifer and what we can learn from these experiments.

Assayag N., Matter J., Ader M., Goldberg D., Agrinier P. 2009. Water-rock interactions during a CO<sub>2</sub> injection field-test: Implications on host rock dissolution and alteration effects. *Chemical Geology*, 265:227-235.

Matter J.M., Takahashi T., Goldberg D. 2007. Experimental evaluation of in situ CO<sub>2</sub>-water-rock reactions during CO<sub>2</sub> injection in basaltic rocks: Implications for geological CO<sub>2</sub> sequestration. *Geochem. Geophys. Geosyst.*, 8.

2. We still have not received any useful water quality analysis for the water used in the laboratory experiments or the groundwater at the field site. The piper diagrams provided are not sufficient, we need to see the general minerals and trace constituents for these waters.

[Reply] A detail table of chemistry analysis of water samples taken at the Cranfield shallow aquifer is attached as an appendix in this report.

3. It would be helpful to understand more about the promised project website and how access will be provided to the PAC.

[Reply] We are in the process of developing a secure website and it will be blind except to those authorized to access it.

#### Task 1: Laboratory Batch Experiments

4. The report indicates that a total of five gallons of groundwater were pumped from the well and shipped to the Bureau's lab. This doesn't seem to be adequate to assure that representative samples were obtained for batch testing.

[Reply] It is unclear what this comment relates to. The target well was purged for about 4 hours. During purging, groundwater temperature, electric conductivity, and pH were measured. After these parameters reached steady state, groundwater was sampled and stored at plastic bottles. Groundwater was not filtered on site and not preserved.

5. Please provide a summary of the test protocol and test conditions for the batch tests.

[Reply] The following section under Task 1 includes details of the batch experiments.

6. The laboratory testing still lacks enough specifics to provide a basis for commenting at this time. For example, although no experimental results have been provided for the lab tests, it's still unclear what the exact test conditions will be, what controls are being provided, and what data will be provided (particularly, how alkalinity will be tracked).

[Reply] All these questions are addressed in this quarterly report.

7. Modeling of selected water quality parameters over time for lab tests for a previous project were provided, but insufficient data about the test conditions are provided. It would be helpful to have copies of the report that was used to generate the plots provided.

[Reply] Yes, we included a paper published in Environmental Earth Sciences and the revised version to International Journal of Greenhouse Control. However, the later one is still under review and may be not distributed to the public.

Task 2: Modeling Design of Field Push-Pull Tests

8. Please provide copies of the complied groundwater chemistry data.

[Reply] See reply 2.

Task 3: Conduction of Push-Pull Tests in the Field

9. Please provide a summary of progress on this task, including how ongoing push-pull test protocols are influencing design of the tests for this project. In particular, what has been learned from the Columbia University experience with dissolving carbon dioxide into the injection water?

[Reply] Regarding this comment and the next comment, we are still working on how to design the push-pull tests which may depend on results of the batch experiments. Once we have data from the batch experiments, we can apply modeling techniques for testing different procedures for a push-pull test, including amount of water to be injected over what time period, incubation period, and pumping rate. The results from the Lamont Dougherty field tests are not directly applicable to the proposed tests in our study because the wells were much deeper and the geology and chemical processes are quite different; however, we did obtain insights from this group.

10. The procedures for the field push-pull tests are still unclear, although they may still be under development.

[Reply] The design of the push-pull is still under development. It is true that we may not be able to decide which procedures could be since it is just first half year of the two-year project, but we are making progresses.

Task 4: Modeling of Field Experiments

11. Please indicate the reporting period when this task expected to begin.

[Reply] The modeling work of field experiments was schedule to start at the 7<sup>th</sup> month to 9<sup>th</sup> month of the second year. The results will be reported at the beginning of 9<sup>th</sup> month in the second year.

Task 5: Communication

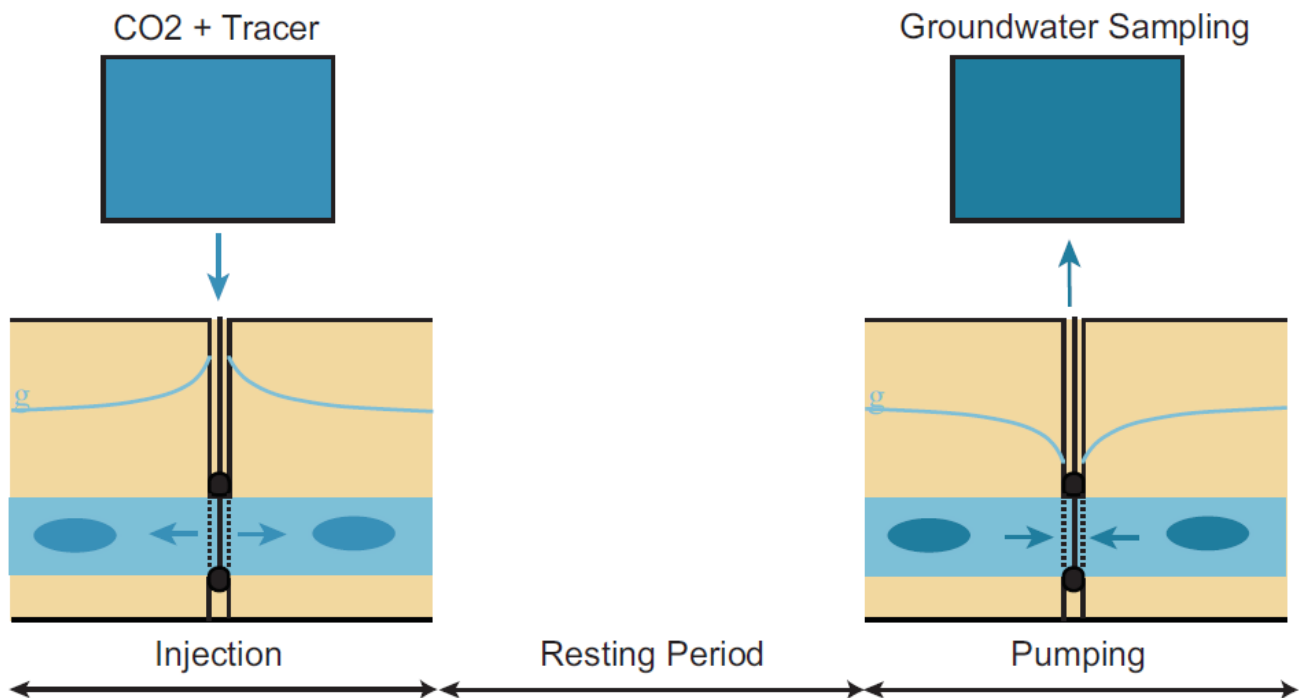
12. The status report indicates that once preliminary results are developed, the team will post them on the “web site.” Please indicate the location of the website, the link and password, and who has access. Note that project data are generally not publically available until released by the Foundation.

[Reply] We are in the process of putting material together for a web site and the site will be secure with access limited to AWWA people.

### ***III.2 Methods and materials***

Impacts of CO<sub>2</sub> leakage on groundwater quality will be evaluated using single-well push-pull tests (PPTs) (Figure 1) in a sedimentary aquifer on the Gulf Coast. These controlled field tests allow isolation of impacts of CO<sub>2</sub> leakage into an aquifer without the confounding issues associated with upward migration of brines with CO<sub>2</sub> that can occur when natural systems (e.g. Keating et al., 2009) are evaluated. Methods of this project are generally subdivided into four tasks: laboratory batch experiments, modeling design of field push-pull tests, conduction of push-pull tests in the field, modeling of field experiments and communication. In this quarterly report, the detailed description of batch experiments was described in the following.

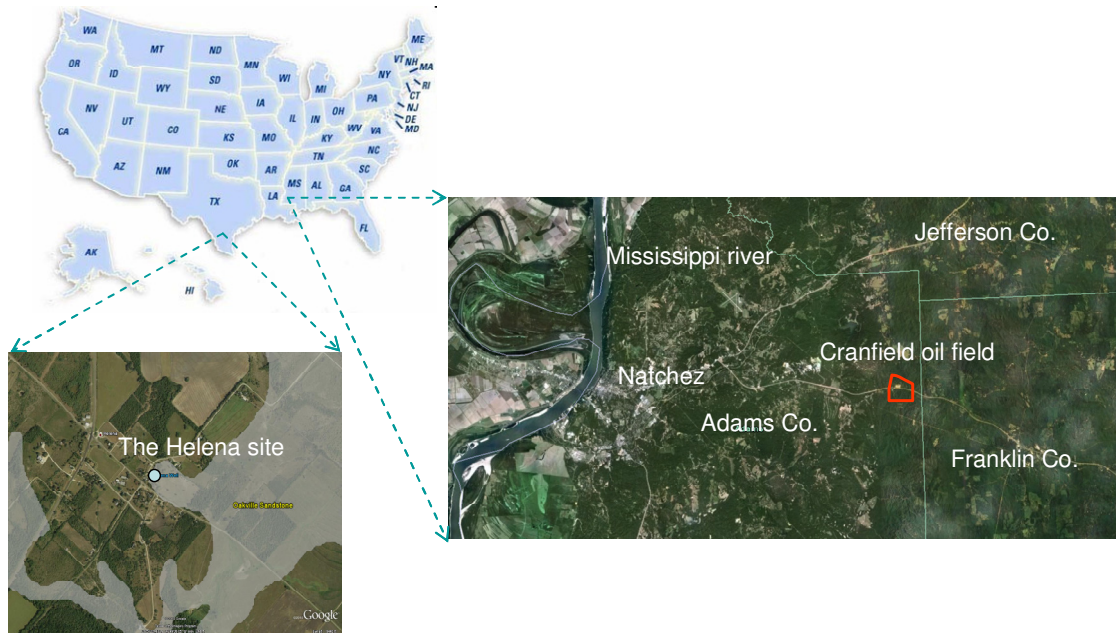
Description of methods for other tasks has been briefly described in the proposal and will be given in detail in rest quarterly reports.



**Figure 1** Schematic of push-pull tests, including an injection phase in which CO<sub>2</sub> and a conservative tracer are injected into the aquifer, a resting period for reactions to take place, and a pull phase in which groundwater is pumped out of the system.

### 1. Batch experiment for the Helena aquifer

Aquifer sediments were taken from two different sites of the Gulf Coast area. The Helena site is located at Karnes County, Texas (Figure 2). The water well was drilled to 75 feet in Oakville sandstone, screened from 60 feet down (a confining clay unit was found at 50-60 feet). Depth to water is 44 feet. The aquifer unit is comprised of unconsolidated coarse to fine sediment. Sediments taken from the depths between 60 ft to 62.5 feet below surface were placed on an aluminum plate and dried in the oven at 90<sup>0</sup>C overnight. Total weight of dry sediment sample is 290 gram. Sediments about 15 grams was taken for the surface area analysis with a Coulter SA 3100 apparatus. Total 180 grams of sediments were manually “pulverized”, thoroughly mixed in a clean and dry glass beaker, and then divided into 9 Erlenmeyer flasks, each having 20 grams. For each flask, total 200 ml of groundwater taken from the well at the Helena site was added to each flask. Water sample with 20 ml was taken for chemical analysis (time = -1 listed in Tables of Appendix 1). A flask with adding 200 ml groundwater and no sediments was also included. All 10 flasks were connected to a gas purging system as shown in the Figure 3.



**Figure 2** Locations of the two sites (the Helena site and the Cranfield site, the push-pull test will be conducted at the Cranfield site)



**Figure 3** Photo of laboratory set up of the batch experiment for the Helena site.

The inlet and outlet of the system shown in Figure 3 were controlled by a data logger which was set to purge gas for 1 minute every 20 minutes. The flasks were purged with high purity Ar gas for 5 days and then 20 ml of water were taken for chemical analysis (time =0 given in tables of Appendix 1). Then Ar tank was replaced with a CO<sub>2</sub> tank and CO<sub>2</sub> gas was bubbled into the system with same frequency for the Argon gas bubbling. It is worth noting that nine flasks were used with same sediments and groundwater in our experiment, different than

those reported in (Lu et al., 2010) and (Little and Jackson, 2010) because with nine flasks, water samples could be taken from one or two of the 9 flasks to minimize change in water volume in a flask and avoid taking too much water from one flask which may affect water-rock-CO<sub>2</sub> interactions in the flask. After CO<sub>2</sub> was bubbled into the system, water samples about 5 ml for each were taken from the nine flasks at different time according to the procedure listed in Table 2. Value of pH was measured immediately after sampling using an Orion 3 pH-meter. The electrode was calibrated daily with buffer solutions at pH of 4, 7 and 10. Alkalinity was measured by titration of a sample aliquot with 0.16 or 1.6 N H<sub>2</sub>SO<sub>4</sub>.

**Table 2** Sampling procedure of water samples from the 9 flasks at different time (noted that the numbers in the column of flasked sample are flask number)

Time (hours)	Flask sampled
1	1, 2
2	2, 3
4	3, 4
7	4, 5
12	5, 6
25	6, 7
56	7, 8
72	8, 9
168	9, 1, 10
264	2, 3

All the water samples were filtered with a 45 micron filter. 5 ml of each sample were separated and acidified with 2% HNO<sub>3</sub> (0.140 ml of conc. HNO<sub>3</sub> were added to 5 ml sample) for ICP analysis. Samples are kept in the refrigerator. After sampling the flasks were stirred and CO<sub>2</sub> was purged for another 5 minutes. One of the sediment samples was dried at the end of the experiment for SEM and XRD analysis to compare change in mineralogy and surface morphology of the sediments before and after reactions among water, sediments and CO<sub>2</sub>.

## 2. Batch experiment for the Cranfield shallow aquifer

Cranfield site is located near the town of Natchez in Adams County, Mississippi, ~15 mi east of the Mississippi River (Figure 2). A well was drilled to a depth of 73 m below surface in Nov. 2008 and screened at depth from 66 m to 73 m below surface for monitoring groundwater quality. Sediments were cored and preserved from surface to 73 m below surface. A shallow

aquifer with mainly fine sands is located at depths from 66 m to 73 m below surface, confined by a clay layer with about 38 m in thickness. Aquifer sediments with 300 grams taken at the depth from 69.5 m to 70 m below surface and the aquitard sediments (the clay layer) with 200 grams taken at the depth from 61 m to 63 m below surface were placed in an aluminum plate and dried in the oven at 90<sup>0</sup>C overnight. In addition, each of 15 gram aquifer and aquitard sediments was taken for surface area analysis and XRD and SEM analysis. The 300 g aquifer sediments were manually “pulverized”, thoroughly mixed in a clean and dry glass beaker, and then divided into three flasks. The 200 g aquitard sediments were also manually “pulverized”, mixed and divided into two flasks. The five flasks were then added 400 ml of groundwater taken from the well at the Cranfield site. About 20 ml water were preserved for chemical analysis. A flask without adding sediments was also added 400 ml groundwater from the Cranfield site for comparison.

All 6 flasks were connected to a gas purging system which is similar to the setup of the Helena site shown in Figure 3. The inlet and outlet of the system were controlled by a data logger which was set to purge gas for 1 minute every 20 minutes. The flasks were purged with high purity Ar gas for a week and then CO<sub>2</sub> was bubbled into the system. Before CO<sub>2</sub> gas was bubbled, 2 ml of water were taken for chemical analysis. Water samples with 2 ml were taken from the flasks at different time. All the water samples were filtered with a 45 micron filter. About half ml of each sample was diluted by adding 4.5 ml 2% HNO<sub>3</sub> (by weight) and then kept in the refrigerator later for ICP-MS analysis.

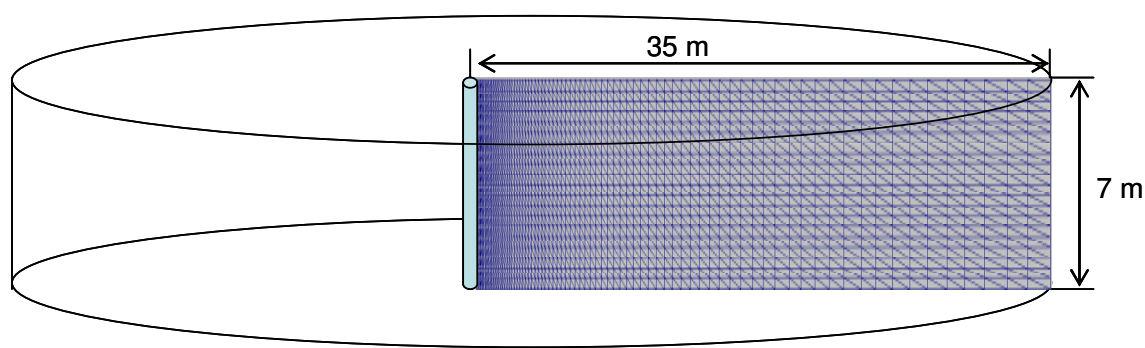
### **3. Modeling design of push-pull tests**

A numerical model was set up for simulating push-pull tests which will be conducted at the Cranfield shallow confined aquifer. Model domain is 3-D axis-symmetric (Figure 4) which was represented by a vertical 2-D cross section. The testing well for push-pull tests is located at the center of the domain with 7 m in thickness for the confined aquifer. The outer boundary to the vertical axis of the well is 35 meters. Since simulated domain was confined at the top and bottom boundaries, no flux boundary conditions were imposed upon the top and bottom boundaries. Since a small amount of water is going to be injected into the well, we assume water head at the outer boundary, 35 m from the well, not to be disturbed. Then a prescribed water head boundary condition, equal to the initial water head is imposed upon the outer boundary. For the inner boundary, a flux boundary condition is imposed upon. The amount of the water was uniformly distributed along the screening section of the well.



Three material zones are considered in the simulated domain: a zone for the well bore within the casing, a zone between the casing and the well bore where sand was filled and a zone for the aquifer. The aquifer in the simulated domain is assumed to be homogeneous. Mineralogy data of the aquifer sediments considered in the numerical model is taken from the XRD analysis of the sediment samples. Water injected is assumed to have same chemical composition from the target aquifer and is equilibrated with CO<sub>2</sub> gas at a pressure of 1.10325 bar (1 atm). Potential water-rock-CO<sub>2</sub> interactions are considered to be same as those in the batch experiments. The amount of water volume to be injected and the injection rate during the push phase, the time duration for the resting phase and the pumping rate during the pull phase are the key model parameters.

A 2-D grid with gradually increasing size from the inner boundary to the outer boundary is used in the numerical model (Figure 4).



**Figure 4. A 3-D simulated domain which was represented using a 2-D grid**

CORE2D is used for simulating the synthetic push-pull tests. CORE2D is a model tool for simulating variably flow, heat and solute transport coupled with biogeochemical processes in porous and fractured media (YANG et al., 2007a; Yang and Samper, 2009; Yang et al., 2008; Yang et al., 2007b).

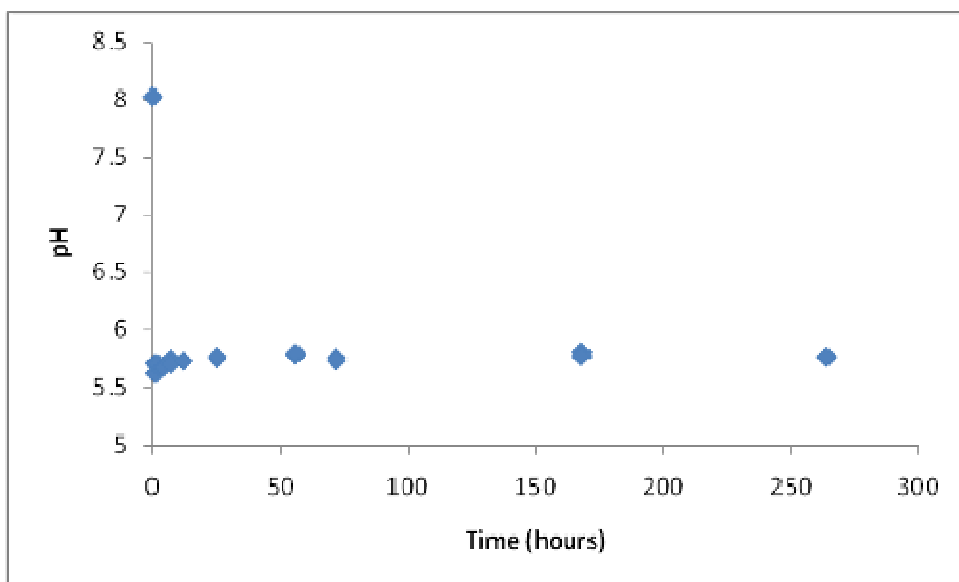
### ***III.3 Data and analysis***

#### **1. Batch experiment for the Helena aquifer**

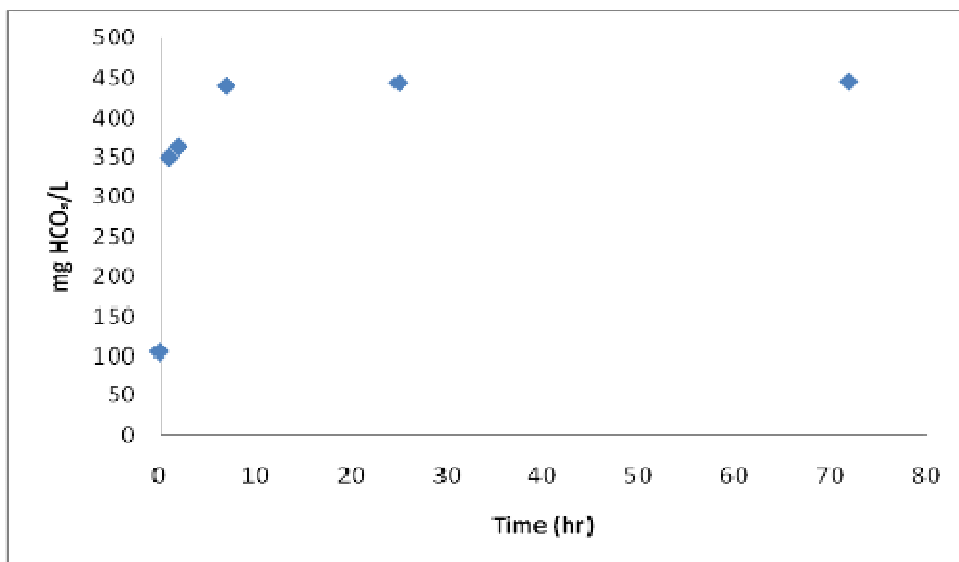
XRD analysis of the sediments taken from the Helena aquifer indicates that the aquifer sediments consist mainly of quartz (64.3%), microcline (24.8% in weight), illite 5.1%, and albite

5.9%. It is also found trace amount of calcite contained in the sediments (~0.04%). The BET surface areas of the Helena aquifer sediment is  $14.42 \text{ m}^2\text{g}^{-1}$ .

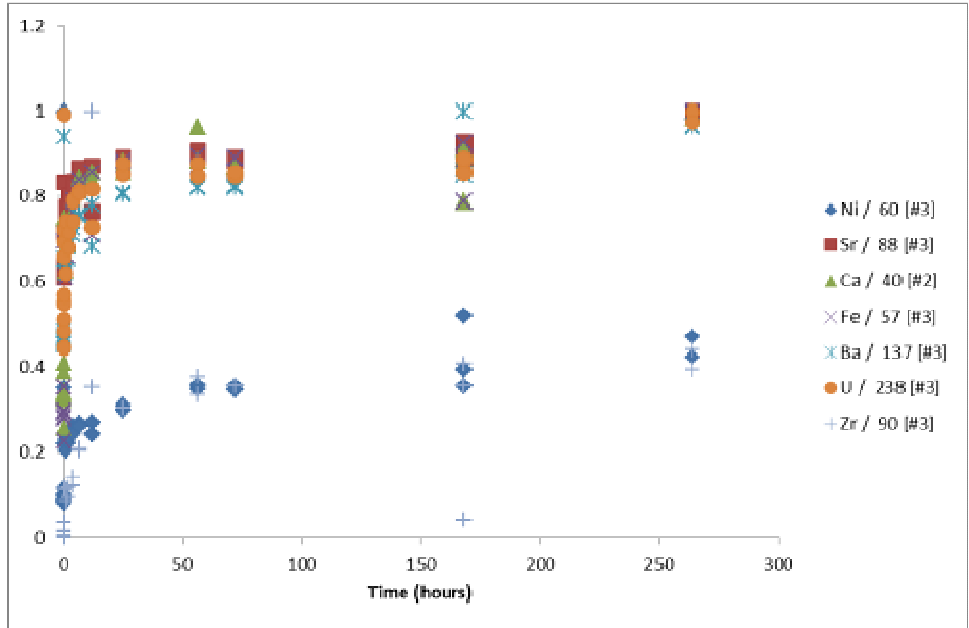
Water chemistry data of this batch experiment is given in Tables A.1.1 and A.1.2. Values of pH show a significant drop after  $\text{CO}_2$  was bubbled into the water-rock system and then gradually increased with time (Figure 5). Groundwater alkalinity measured shows an increasing trend from 100 mg  $\text{HCO}_3/\text{L}$  to 450 mg/L and eventually reaches to a steady state (Figure 6). Normalized concentrations of major ions and trace elements versus with time are shown in Figures 7-10. Detailed chemical data analysis and geochemical modeling will be presented in the next quarterly report.



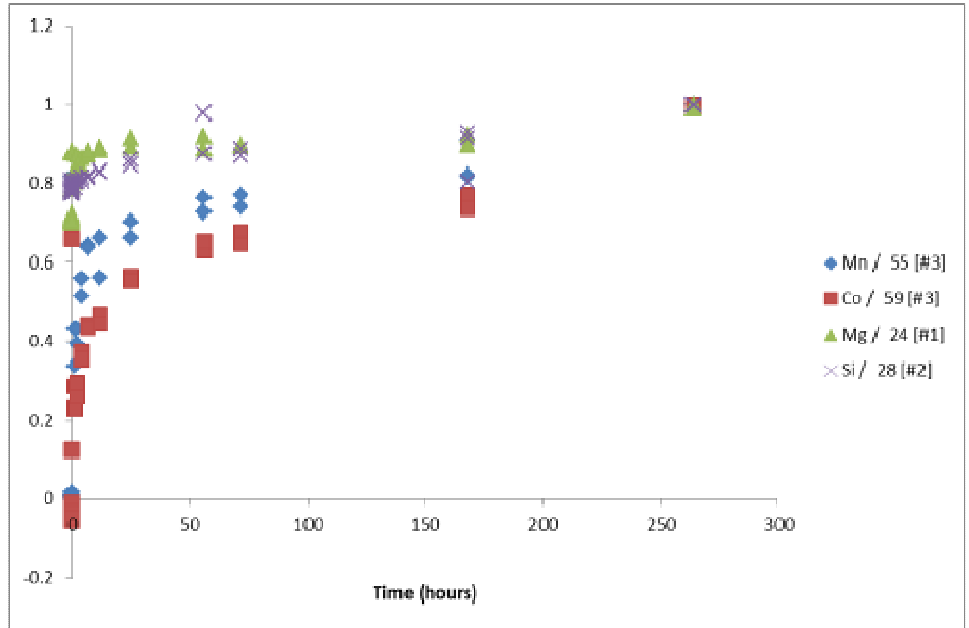
**Figure 5** Time evolution of pH values measured for the batch experiment of the Helena aquifer sediments



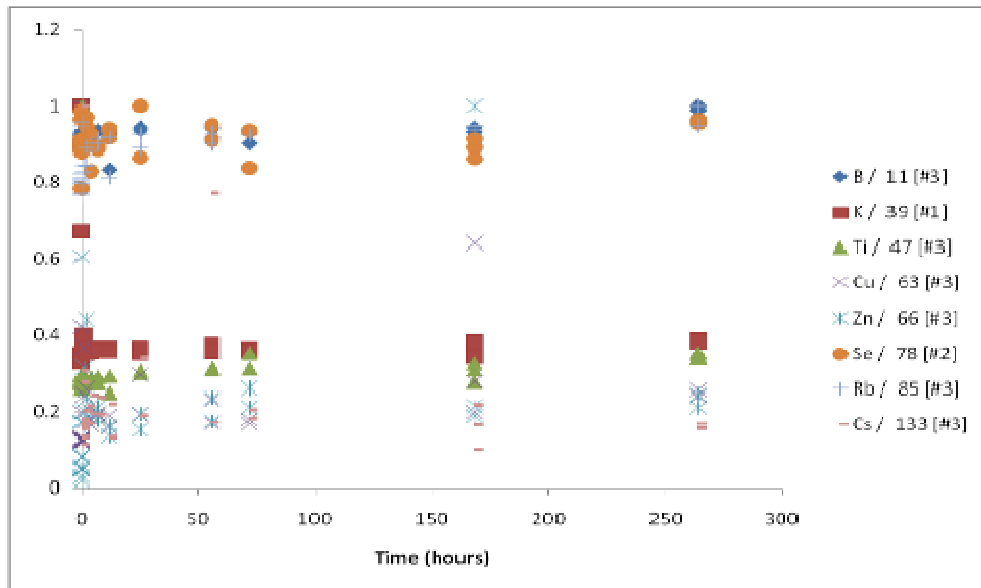
**Figure 6** Time evolution of alkalinity measured for the batch experiment of the Helena aquifer sediments



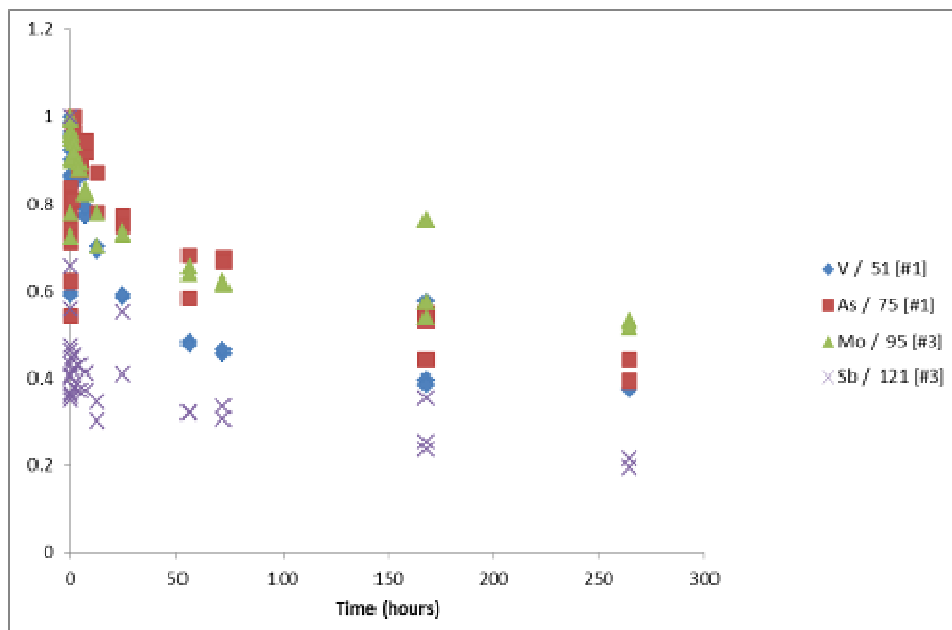
**Figure 7** Normalized concentrations of Ni, Sr, Ca, Fe, Ba, U and Zr to their initial concentrations versus time for the batch experiment of the Helena aquifer sediments



**Figure 8** Normalized concentrations of Mn, Co, Mg, and Si to their initial concentrations (time=-1 in the Tables A.1.1 and A.1.2) versus time for the batch experiment of the Helena aquifer sediments



**Figure 9** Normalized concentrations of B, K, Ti, Cu, Zn, Se, Rb, and Cs to their initial concentrations (time=-1 in the Tables A.1.1 and A.1.2) versus time for the batch experiment of the Helena aquifer sediments



**Figure 10** Normalized concentrations of V, As, Mo, and Sb to their initial concentrations (time=-1 in the Tables A.1.1 and A.1.2) versus time for the batch experiment of the Helena aquifer sediments

## 2. Batch experiment for the Cranfield aquifer

XRD analysis of the sediments taken from the Cranfield site indicates that the aquifer sediments consist mainly of quartz (56.3% in weight), microcline (16.5%), illite (6.0%), kaolinite

(19.5%) and albite (1.8%) and the aquitard sediments mainly consist of quartz (38.8%), microcline (17.5%), illite (19.7%), kaolinite (20.9%) and albite (3.1%). The BET surface areas of the Helena aquifer sediment is XXXXXXXX.

Water chemistry data of the batch experiments are given in Tables A.1.3 to A.1.8. Values of pH show a significant drop after CO<sub>2</sub> was bubbled into the water-rock system and then gradually and slowly increased with time (Figure 11). Groundwater alkalinity measured shows an increasing trend for aquifer sediments. Only two data points were measured for the batch experiment with aquitard sediments and no data points were measured for the batch experiment without sediments (Figure 12). Concentrations of major ions and trace elements versus with time are shown in Figures 13-18. Detailed chemical data analysis and geochemical modeling will be presented in the next quarterly report.

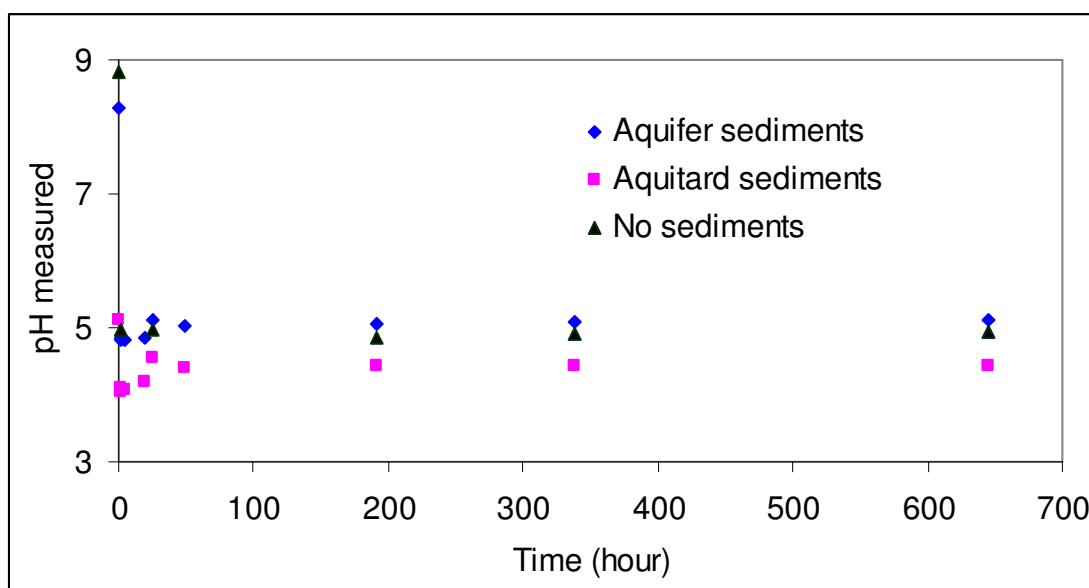


Figure 11 Comparison of pH values measured for the batch experiments of the Cranfield site with the aquifer sediments, aquitard sediments and no sediments.

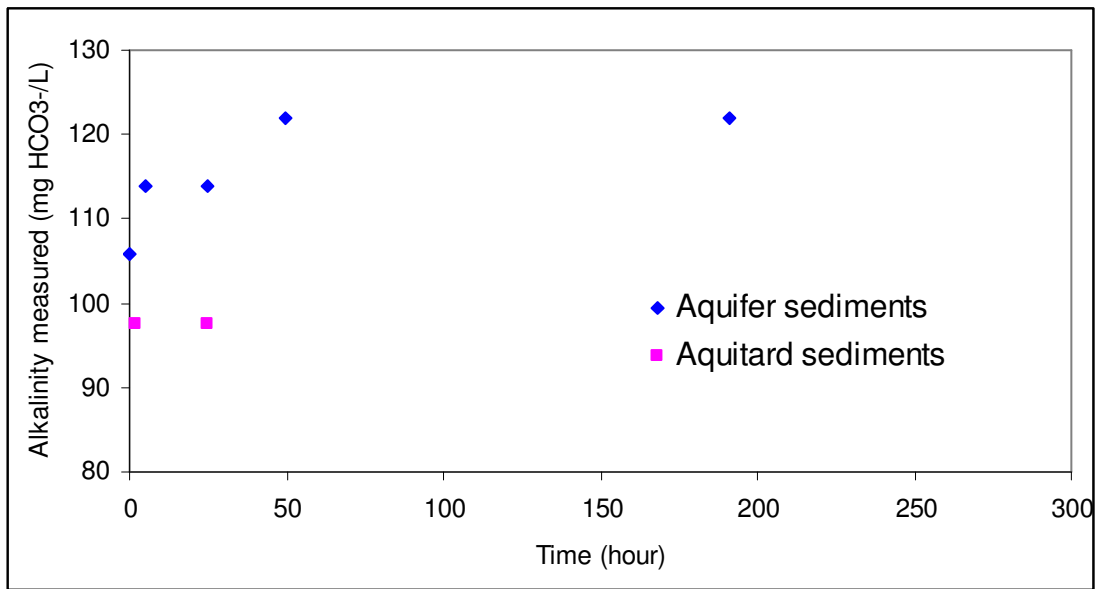


Figure 12 Comparison of alkalinity measured for the batch experiments of the Cranfield site with the aquifer sediments, and aquitard sediments

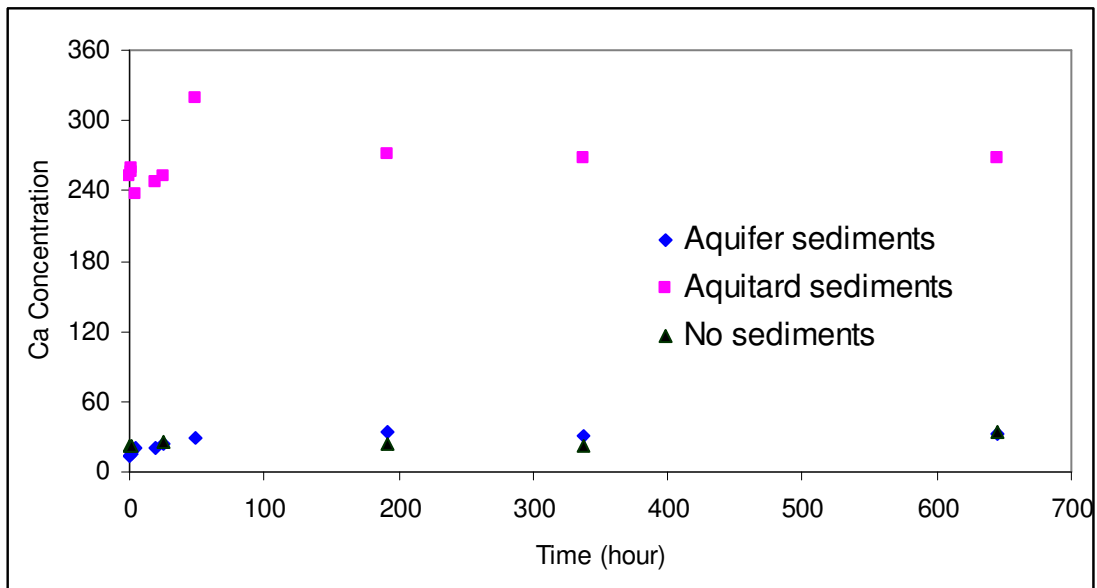


Figure 13 Comparison of Ca concentrations measured for the batch experiments of the Cranfield site with the aquifer sediments, aquitard sediments and no sediments (unit ppm)

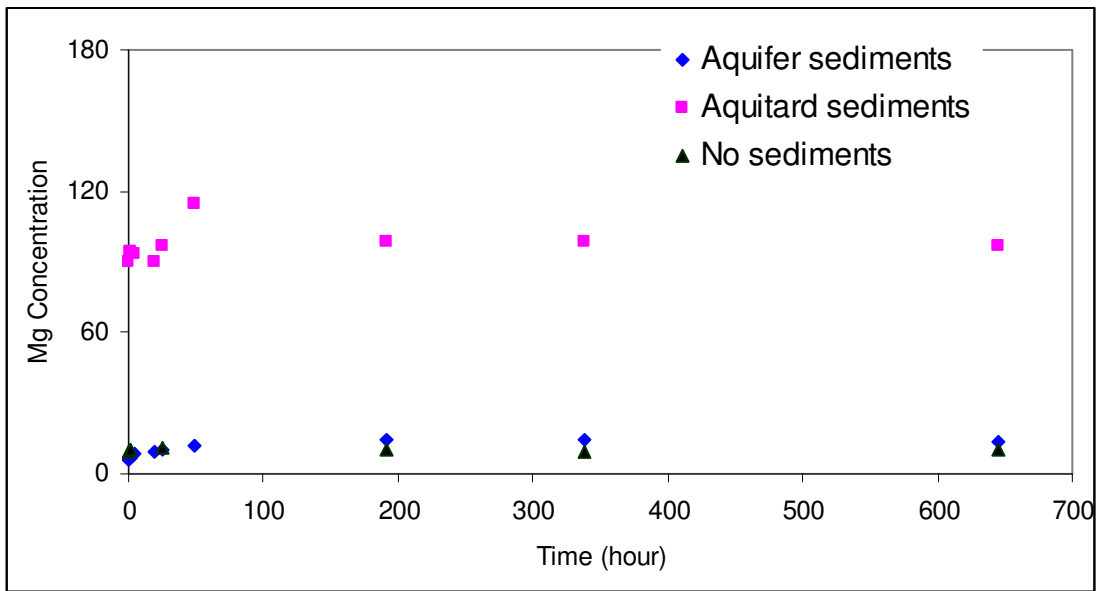


Figure 14 Comparison of Mg concentrations measured for the batch experiments of the Cranfield site with the aquifer sediments, aquitard sediments and no sediments (unit ppm)

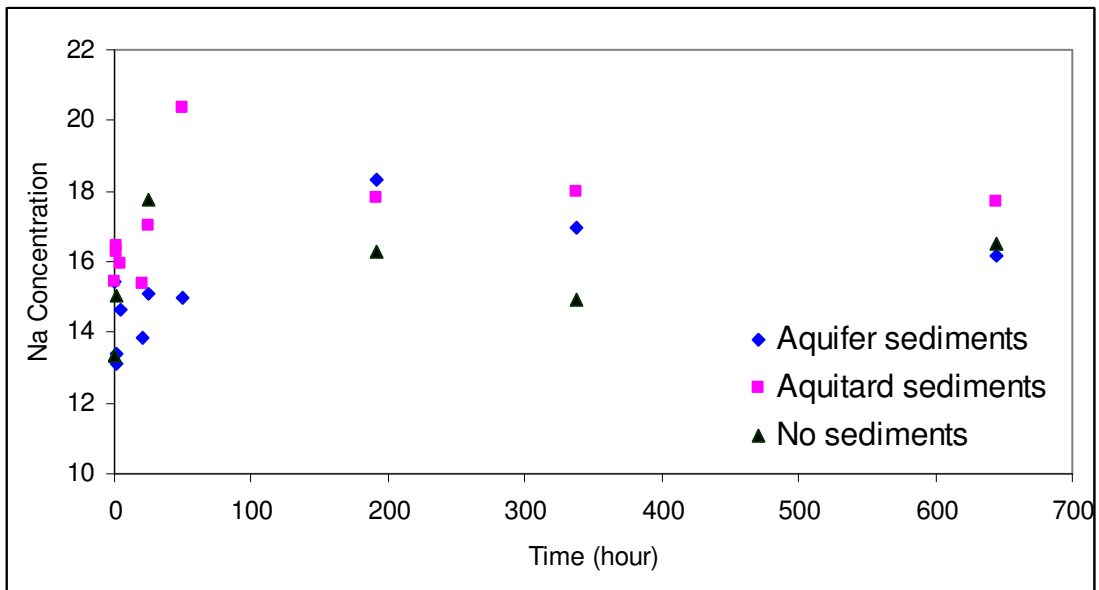


Figure 15 Comparison of Na concentrations measured for the batch experiments of the Cranfield site with the aquifer sediments, aquitard sediments and no sediments (unit ppm)

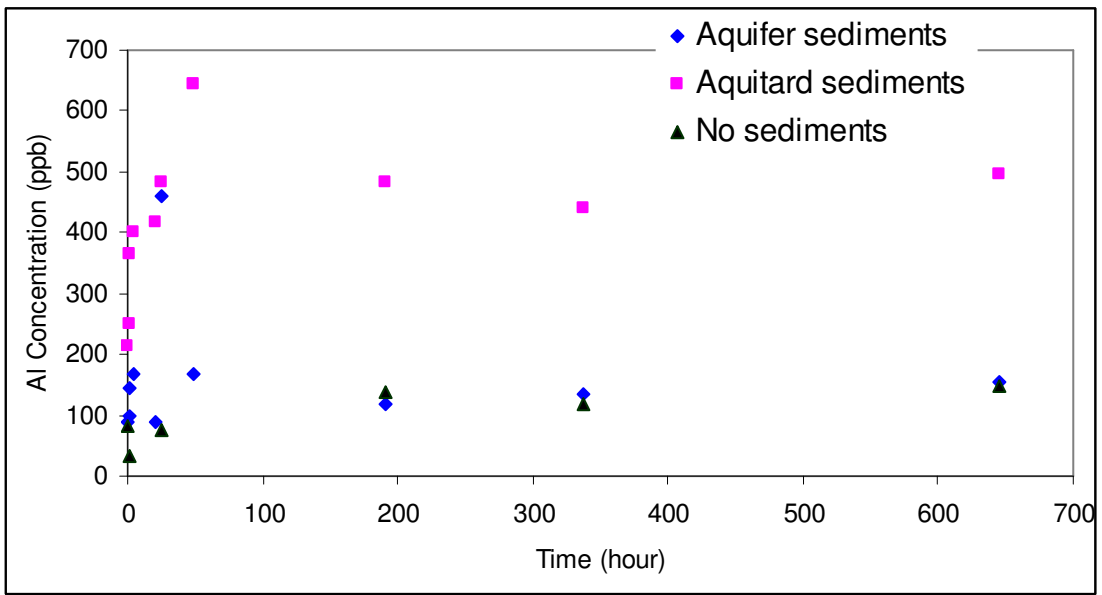


Figure 16 Comparison of Al concentrations measured for the batch experiments of the Cranfield site with the aquifer sediments, aquitard sediments and no sediments (unit ppb)

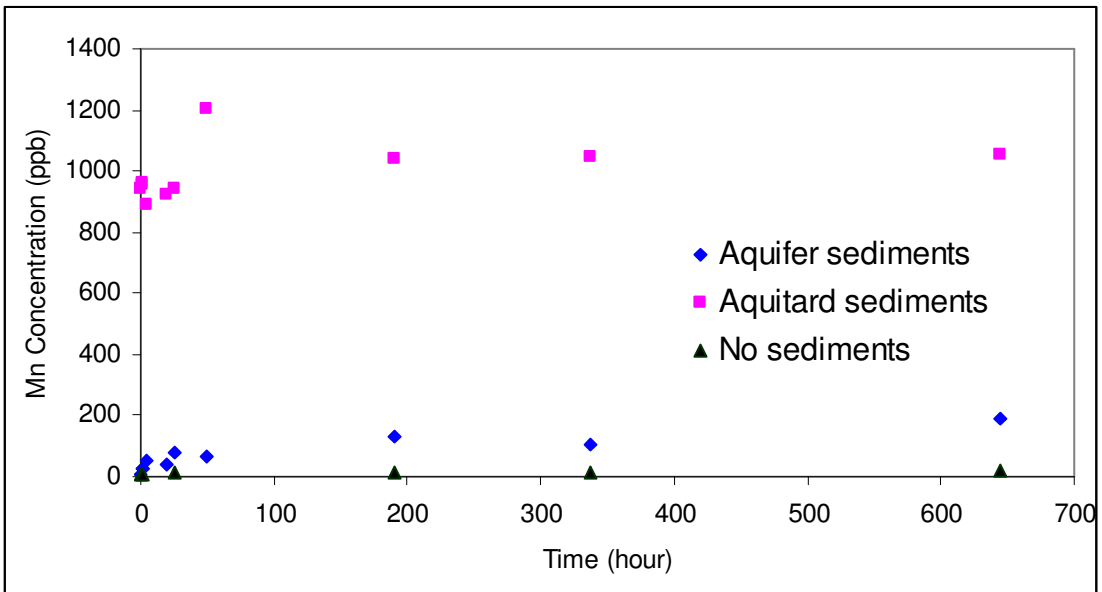


Figure 17 Comparison of Mn concentrations measured for the batch experiments of the Cranfield site with the aquifer sediments, aquitard sediments and no sediments (unit ppb)



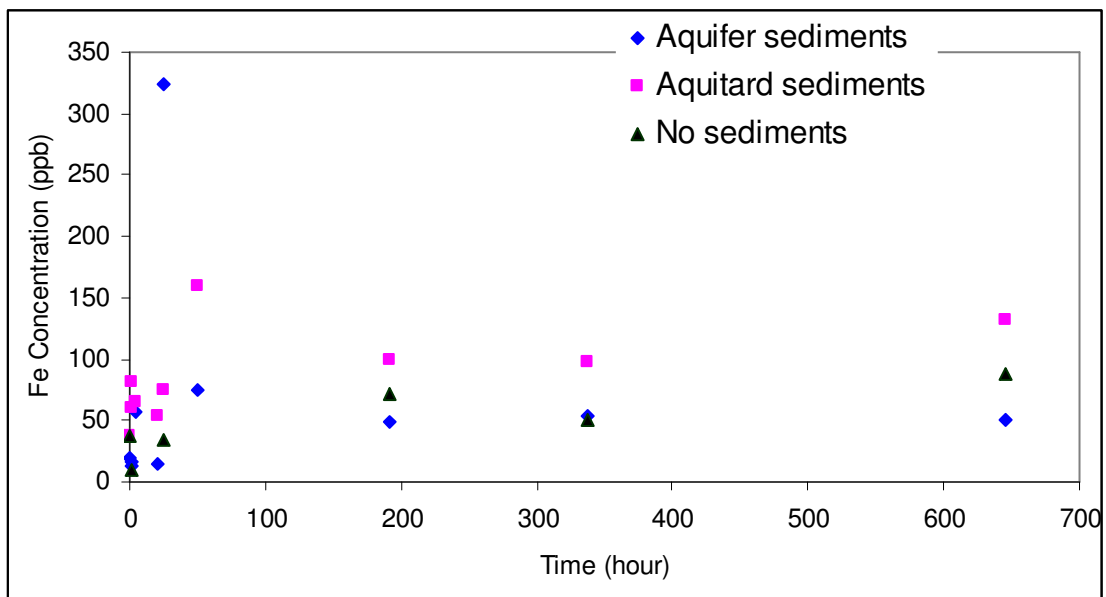


Figure 18 Comparison of Fe concentrations measured for the batch experiments of the Cranfield site with the aquifer sediments, aquitard sediments and no sediments (unit ppb)

### 3. Modeling design of push-pull tests in Task 3

Results of the modeling excises will be reported in the next quarterly report.

### 4. Conducting push-pull tests in Task 3

At current reporting period, geochemical characterization of regional groundwater has been completed. Groundwater samples were taken from 9 wells at the Cranfield site and shipped to Mississippi State University for chemical analysis (Figure 19). Those wells were drilled down to depths from 300 ft to 400 below surface. Water chemistry data are listed in tables of Appendix 2.

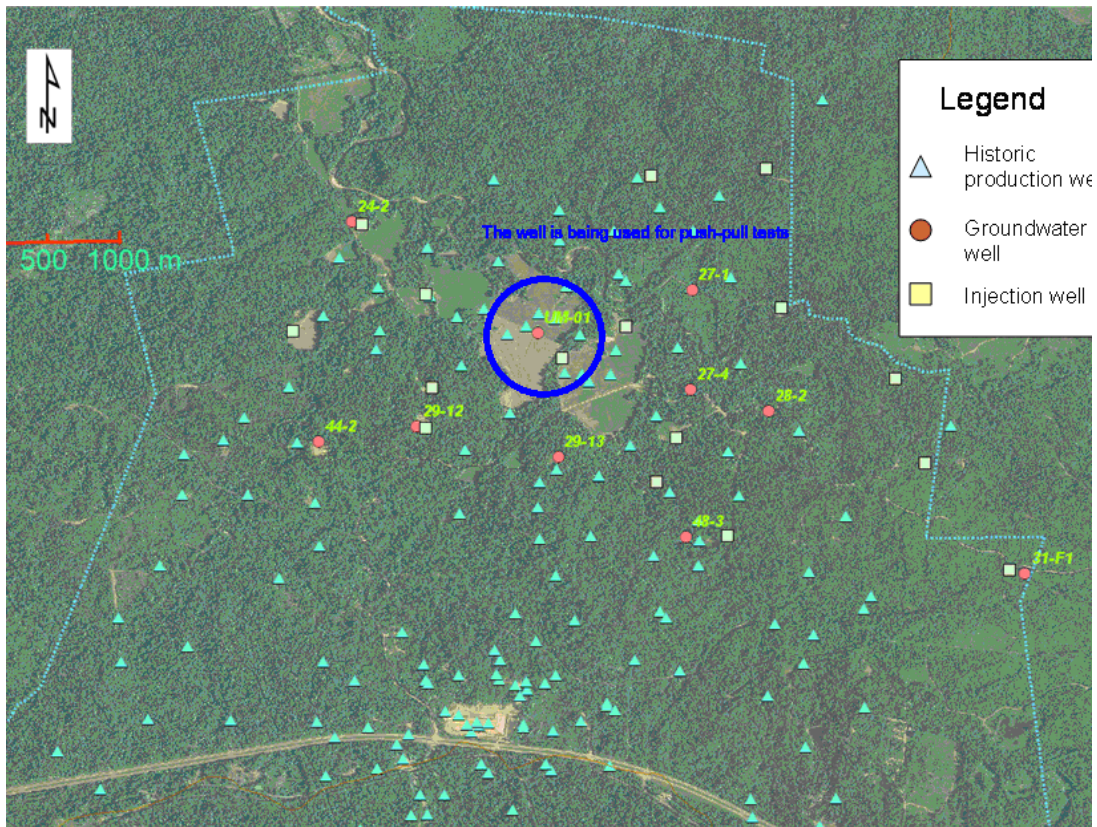


Figure 19 Locations of shallow groundwater wells at the Cranfield site (the well marked with blue circle is going to be conducted for push-pull tests)

Sturation indices of carbonate minerals were calculated based on the water chemistry data in Table A.2.1. (Figure 20). Saturation indices of calcite for all water samples are smaller than -0.6 and saturation indices of dolomite are smaller than -1.1 and therefore calcite and dolomite are under-saturated with the groundwater in the Cranfield shallow aquifer. This is consistent with the XRD results that aquifer sediments are free of carbonate minerals.

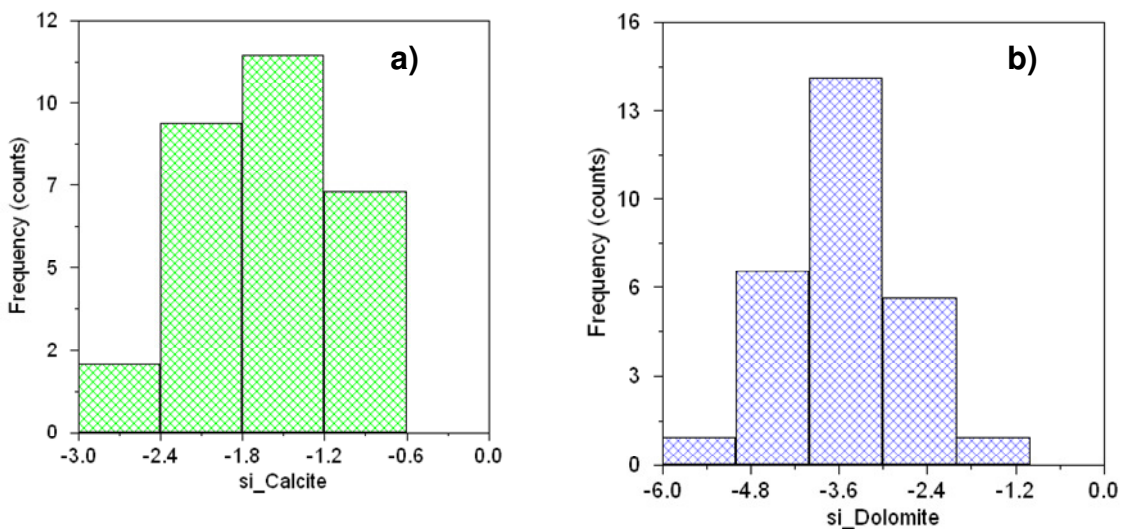
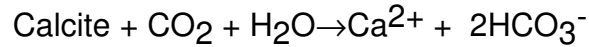
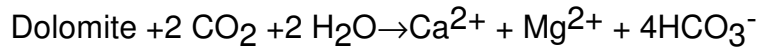


Figure 20 Saturation indices of calcite (a) and dolomite (b) for the groundwater samples collected at the Cranfield shallow aquifer

Dissolution of one mole dolomite will lead to a molar ratio of 4:1 among  $\text{HCO}_3^-$  and Ca in groundwater while dissolution of one mole calcite may lead to a molar ratio of 2:1 among  $\text{HCO}_3^-$  and Ca. Ca and  $\text{HCO}_3^-$  data from the water samples don't show obvious correlation between Ca and  $\text{HCO}_3^-$  (Figure 21a).



Molar ratio of  $\text{HCO}_3^-$  versus Si from the water chemistry data may provide valuable information of sources of ions in water. If ratio of  $\text{HCO}_3^-$  to Si is greater than 10, groundwater chemistry is mainly dominated by carbonate mineral weathering. If ratio of  $\text{HCO}_3^-$  to Si is smaller than 5, groundwater chemistry is dominated by silicate mineral weathering. If ratio of  $\text{HCO}_3^-$  to Si is between 5 and 10, groundwater chemistry may be dominated by both carbonate and silicate minerals weathering. Ratios of  $\text{HCO}_3^-$  to Si in most water samples are close to the line of silicate mineral weathering (Figure 21b) suggesting that groundwater chemistry of the Cranfield shallow aquifer is dominated by silicate mineral weathering.

The PHREEQC model tool (Parkhurst and Appelo, 1999) was used to calculate partial pressure of  $\text{CO}_2$  in the shallow aquifer. As  $\text{CO}_2$  partial pressure increases,  $\text{HCO}_3^-$  increases (Figure 22a). Groundwater pH shows a good linear correlation with partial pressure of  $\text{CO}_2$  (Figure 22b). This may suggest that  $\text{CO}_2$  from microbial processes may dominate groundwater pH and carbonate parameters at the Cranfield shallow aquifers.

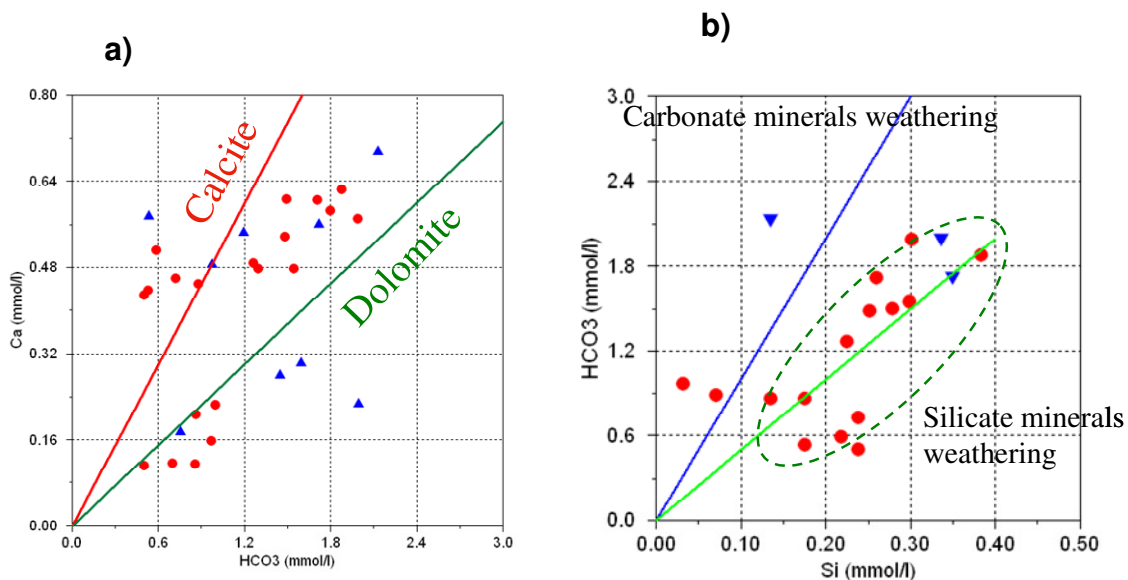


Figure 21 a)  $\text{HCO}_3^-$  versus Ca and b)  $\text{HCO}_3^-$  versus Si measured for the water samples collected at the Cranfield shallow aquifer

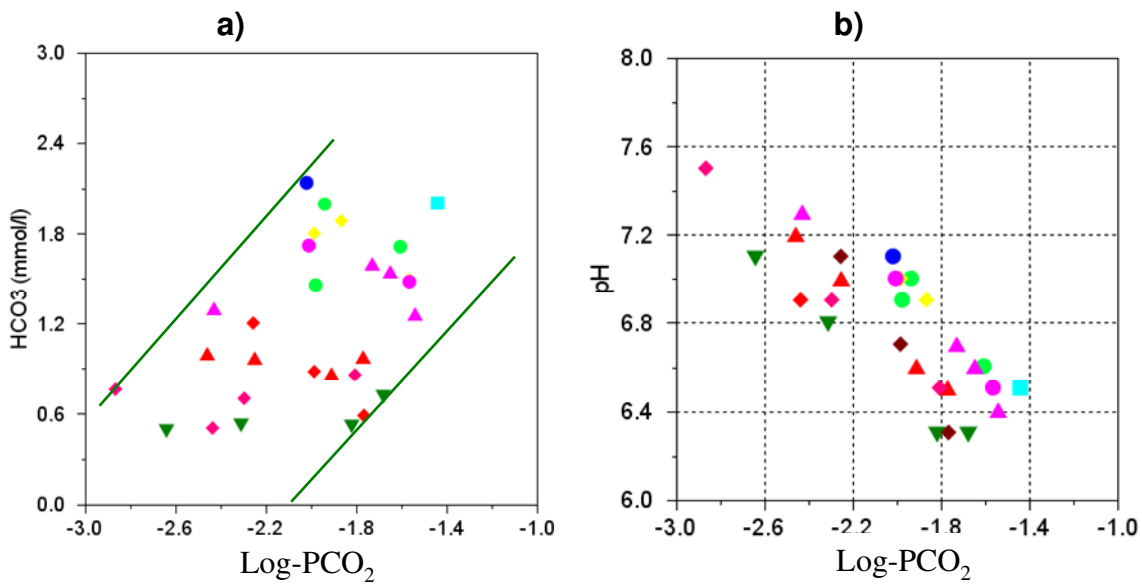


Figure 22 a)  $\text{HCO}_3^-$  versus  $\log\text{-PCO}_2$  and b) pH versus  $\log\text{-PCO}_2$  for the water samples collected at the Cranfield shallow aquifer

Ratio of stable carbon isotope,  $\delta^{13}\text{C}$  could be used to trace carbon sources.  $\delta^{13}\text{C}$  of dissolved inorganic carbon versus bicarbonate and  $\log\text{-PCO}_2$  are shown in Figure 23. It can be seen that  $\delta^{13}\text{C}$  ranges from -14 to -26. Since the aquifer sediments are free of carbonate minerals,  $\delta^{13}\text{C}$  may be dominated by  $\text{CO}_2$  from microbial processes.

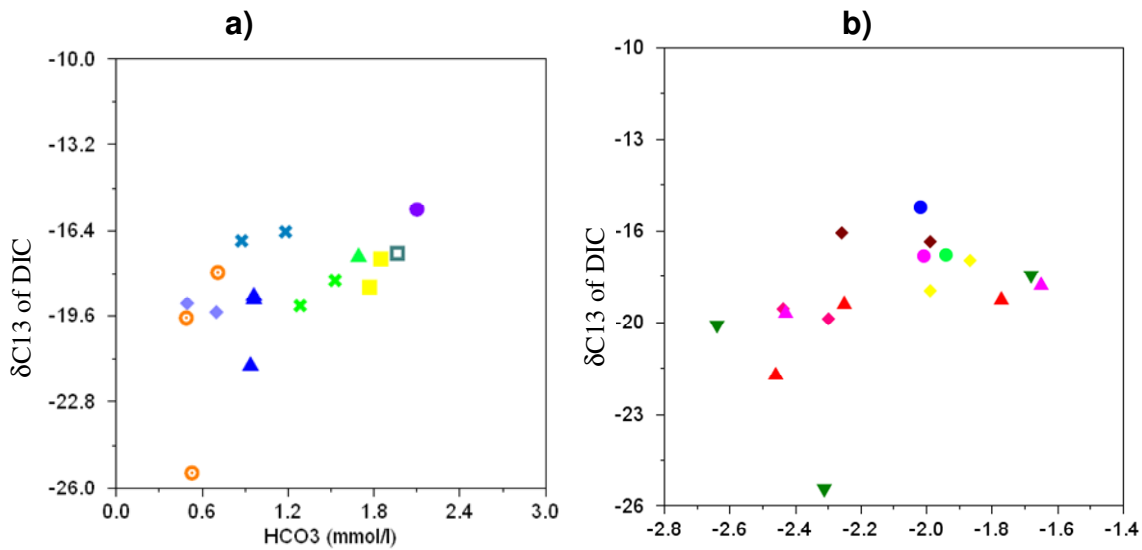


Figure 23 a)  $\delta^{13}\text{C}$  of DIC versus  $\text{HCO}_3^-$  and b)  $\delta^{13}\text{C}$  of DIC versus  $\log\text{-PCO}_2$  for the water samples collected at the Cranfield shallow aquifer

## **IV. Website update**

Water Research Foundation Project 4265 — “Carbon Dioxide Injection into Shallow Sedimentary Aquifer Systems to Assess Potential Degradation of Groundwater Quality at Geological Carbon Sequestration Sites”

Principal Investigator: Bridget Scanlon

Co-Principal Investigator: Changbing Yang

Bureau of Economic Geology, University of Texas at Austin

Periodic Report No. 2, Period covered: Nov 1 2010 – Jan 31, 2011

### **Activities and Progress since Last Update**

Batch experiments of water-rock-CO<sub>2</sub> interactions have been completed and preliminary model for designing push-pull tests was initialized.

### **Findings of Significance to Foundation Subscribers and Other Stakeholders**

### **Statement of How Overall Project Results Benefit Foundation Subscribers and Drinking Water Community**

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Yang, C., Samper, J., Molinero, J., Bonilla, M., 2007b. Modelling geochemical and microbial consumption of dissolved oxygen after backfilling a high level radioactive waste repository. *Journal of Contaminant Hydrology*

## Appendix 1 Water compositions of the batch experiments

Table A.1.1 Concentrations of Major ions measured for the Helena batch experiment at different time (unit: ppm)

Time (hr)	Cations					pH	Anions							
	Na	Mg	Si	K	Ca		F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	HCO <sub>3</sub> <sup>-</sup>
-1 <sup>1</sup>	295.35	52.37	18.33	41.47	163.94	7.82	13.19	6251.71	2.85	1514.07	20.19	150.45	0.00	427.12
0 <sup>2</sup>	309.78	43.60	18.18	15.35	74.16	8.03	1.34	637.71	5.63	152.49	2.78	1.29	2.27	105.76
1	313.98	48.70	18.42	15.84	143.25	5.69	1.36	638.61	9.08	154.49	3.23	6.49	0.00	349.83
2	315.53	50.37	18.68	14.94	151.17	5.68	1.31	649.59	9.62	157.88	3.86	11.77	0.00	362.85
4	307.02	50.62	18.75	14.90	170.30	5.73	1.39	660.20	6.43	160.41	2.99	13.03	0.00	
7	308.90	52.02	18.86	15.00	182.17	5.73	1.37	654.47	6.59	159.26	2.75	13.14	0.00	439.32
12	308.12	52.66	19.16	15.02	185.24	5.76	1.36	651.83	8.48	161.10	3.34	13.34	0.00	
25	307.39	53.60	19.72	14.90	190.28	5.79	1.21	630.29	3.57	152.57	2.23	12.34	0.00	443.39
56	305.52	53.63	21.38	15.19	202.05	5.75	1.22	636.23	0.00	154.50	2.27	12.85	0.00	
72	301.47	53.18	20.28	14.96	190.07	5.79	1.09	593.43	0.00	143.56	2.15	12.41	0.00	445.02
168	302.53	53.79	20.42	15.00	188.73	5.77	1.29	637.25	0.00	156.65	2.28	17.57	0.00	
264	325.12	59.02	23.06	15.98	216.85	5.67								

<sup>1</sup> Groundwater taken from the Helena site before any treatment

<sup>2</sup> Groundwater in the batch after Ar bubbling for 5 days and right before CO<sub>2</sub> gas was bubbled into the flasks



Table A.1.2 Concentrations of trace element measured for the Helena batch experiment at different time (unit: ppb)

Time (hr.)	B	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Rb	Zr	Mo	Ag	Sb	Cs	Ba	Pb	U	Sr
-1 <sup>1</sup>	763.03	29.76	4.24	11.10	0.98	691.85	28.24	1.36	7.61	27.29	49.57	10.41	6.83	11.20	0.30	10.67	18.73	0.38	0.07	325.11	37.28	25.17	2236.63
0 <sup>2</sup>	787.74	27.10	5.28	16.68	0.24	6.41	5.57	-0.05	4.26	4.46	6.28	12.64	6.32	9.49	0.03	13.84	1.16	0.33	0.06	167.59	0.13	14.55	1701.62
1	795.89	46.19	4.31	16.24	0.44	324.62	2.19	0.53	4.71	8.34	21.01	14.88	6.37	9.79	0.26	14.00	4.77	0.29	0.05	219.93	0.32	17.23	2041.87
2	795.55	32.44	4.18	16.64	0.35	348.16	2.98	0.57	4.93	5.91	27.55	16.39	6.77	10.16	0.28	13.69	2.03	0.28	0.05	231.38	0.63	17.65	2144.03
4	792.30	32.96	4.26	16.10	0.34	453.25	1.88	0.75	5.47	4.74	16.85	14.87	6.21	10.42	0.35	13.03	1.94	0.27	0.06	248.58	0.31	19.42	2232.22
7	799.98	26.40	4.22	14.51	0.34	539.90	1.40	0.91	5.76	5.25	15.79	15.56	6.29	10.61	0.54	12.15	2.74	0.27	0.05	261.81	0.37	20.55	2326.18
12	754.25	30.56	4.04	12.95	0.41	516.95	8.33	0.94	5.55	4.75	12.29	13.78	6.56	10.11	1.78	10.91	3.86	0.22	0.04	253.64	0.28	19.57	2198.83
25	804.95	26.75	4.54	10.95	0.31	576.28	2.86	1.16	6.62	6.65	14.12	12.73	6.59	10.62	0.80	10.77	4.30	0.33	0.07	278.90	0.15	21.93	2387.07
56	794.66	29.02	4.66	8.94	0.21	628.59	7.55	1.32	7.64	5.45	16.73	10.57	6.57	10.70	0.94	9.54	4.90	0.22	0.12	284.15	0.66	21.84	2415.34
72	783.10	30.19	4.99	8.55	0.10	637.22	13.00	1.37	7.60	4.73	19.31	11.24	6.26	10.80	0.93	9.10	4.27	0.22	0.05	284.46	0.21	21.61	2382.81
168	801.41	14.78	4.55	8.42	0.21	717.02	4.40	1.56	9.19	10.15	38.24	8.50	6.28	11.04	0.70	9.21	2.76	0.19	0.04	313.10	0.40	21.97	2433.19
264	851.67	16.31	5.20	7.00	0.27	842.84	4.43	2.06	9.71	6.77	18.59	7.01	6.78	11.40	1.10	7.72	0.16	0.14	0.04	334.20	0.63	25.02	2684.82

<sup>1</sup> Groundwater taken from the Helena site before any treatment

<sup>2</sup> Groundwater in the batch after Ar bubbling for 5 days and right before CO<sub>2</sub> gas was bubbled into the system

Table A.1.3 Concentrations of major ions measured for the Cranfield batch experiment of aquifer sediments at different time (unit: ppm)

time (hr)	Cations (ppm)					pH	Anions (ppm)							
	Na	Mg	Si	K	Ca		F-	Cl-	NO2-	SO4--	Br-	NO3-	PO4---	HCO3-
-1 <sup>1</sup>	15.13	9.47	16.67	2.56	21.78	7.85								87.05
0 <sup>2</sup>	15.42	5.75	9.33	6.44	14.01	8.29	0.77	41.47	0.00	6.43	0.00	868.95	0.00	105.76
1.25	13.41	6.66	8.92	5.51	14.65	4.84	0.28	41.82	0.00	5.58	0.17	839.65	0.00	
2.17	13.11	6.97	9.45	6.10	16.21	4.83	0.00	41.94	0.00	5.56	0.09	773.78	0.00	
5	14.63	8.30	10.75	7.21	20.30	4.81	0.42	42.69	0.00	6.30	0.00	747.26	0.00	113.90
20	13.85	9.04	13.43	9.84	20.66	4.85	0.00	44.57	0.00	5.56	0.00	0.00	0.00	
25	15.08	10.44	16.10	7.26	23.66	5.11	0.00	41.03	0.00	6.09	0.00	701.70	0.00	113.90
49.5	14.96	12.18	22.58	8.03	28.47	5.03	0.00	42.09	0.00	5.64	0.00	0.00	0.00	122.03
191	18.34	14.68	27.62	9.66	33.96	5.05	0.00	43.92	0.00	6.72	0.09	584.82	0.00	122.03
337.5	16.97	14.16	28.10	8.58	31.16	5.08								
645	16.16	13.84	28.05	8.29	31.92	5.11								

<sup>1</sup> Groundwater taken from the Helena site before any treatment

<sup>2</sup> Groundwater in the batch after Ar bubbling for one week and right before CO<sub>2</sub> gas was bubbled into the system

Table A.1.4. Concentrations of trace elements measured for the Cranfield batch experiment of aquifer sediments at different time  
(unit: ppb)

time (hr)	B	Al	P	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Rb	Sr	Zr	Mo	Ag	Cd	Cs	Ba	Pb	Bi	U
-1 <sup>1</sup>	362.08	411.06	62.35	11.59	0.66	1.96	6.72	161.09	1.64	9.02	43.18	115.4 4	- 0.02	0.6 2	4.42	90.99	3.54	0.21	7.05	0.76	0.14	261.3 8	14.0 6	0.5 4	0.09
0 <sup>2</sup>	28.03	88.32	24.47	3.46	3.27	0.61	5.33	20.20	0.93	3.75	17.99	164.2 6	3.40	0.4 9	1.28	40.01	1.08	8.94	0.18	0.01	0.05	43.62	0.24	0.1 1	0.14
1.25	21.71	145.80	23.10	2.97	0.31	0.24	28.46	15.71	16.13	7.66	19.50	115.3 7	3.27	0.6 1	1.18	42.71	1.02	0.04	0.08	0.13	0.01	66.57	0.32	0.2 9	0.28
2.17	28.95	98.06	19.53	3.04	0.35	0.34	26.46	13.24	15.71	8.62	13.26	235.1 4	1.43	0.4 7	1.25	47.27	1.04	0.11	0.10	0.27	0.03	76.68	0.33	0.0 6	0.35
5	32.68	167.56	20.95	4.73	0.45	0.40	50.65	57.64	26.04	11.1 8	22.62	182.6 0	3.06	0.5 4	1.54	92.62	1.51	0.05	0.16	0.61	0.03	91.52	2.26	0.1 0	0.39
20	30.07	89.23	13.15	4.15	0.25	0.28	41.96	14.82	24.29	12.8 5	10.31	240.6 6	1.23	0.2 9	1.47	62.79	1.37	0.01	0.08	0.29	0.02	103.6 8	0.60	0.1 2	0.54
25	70.62	460.92	21.53	8.41	2.44	0.78	76.29	323.69	42.88	22.9 4	16.95	310.6 6	3.85	0.3 1	3.42	71.81	5.10	0.33	0.53	0.57	0.31	120.2 7	3.27	0.9 1	0.97
49.5	144.06	167.99	18.39	6.95	0.46	1.02	67.24	75.55	35.21	24.3 8	20.14	668.9 3	0.42	0.1 0	1.94	87.95	11.89	0.12	0.43	1.28	0.04	141.5 4	6.28	4.6 0	0.58
191	184.38	119.18	17.09	7.89	0.48	0.58	132.7 3	49.08	63.10	32.6 6	32.62	316.4 0	1.90	0.2 5	2.14	119.89	2.86	0.06	0.16	1.13	0.02	168.6 1	2.63	0.5 3	0.63
337.5	308.86	135.66	15.66	7.98	0.49	0.68	104.8 6	53.39	48.33	27.8 8	14.38	184.9 7	1.10	0.0 2	1.90	102.72	3.27	0.00	0.07	1.14	0.02	156.9 4	3.96	0.4 2	0.60
645	311.97	153.81	10.15	7.53	0.67	0.46	189.8 8	50.55	73.12	35.3 1	8.54	331.5 9	0.87	0.0 3	1.90	98.77	3.30	0.04	0.05	1.04	0.02	189.9 8	2.26	0.3 7	0.58

<sup>1</sup> Groundwater taken from the Helena site before any treatment

<sup>2</sup> Groundwater in the batch after Ar bubbling for one week and right before CO<sub>2</sub> gas was bubbled into the system

Table A.1.5. Concentrations of major ions measured for the Cranfield batch experiment of aquitard sediments at different time (unit: ppm)

time (hr)	Cations (ppm)					pH	Anions (ppm)							
	Na	Mg	Si	K	Ca		F-	Cl-	NO2-	SO4--	Br-	NO3-	PO4---	HCO3-
-1 <sup>1</sup>	15.13	9.47	16.67	2.56	21.78	7.85								
0 <sup>2</sup>	15.42	89.82	25.45	11.87	251.98	5.12	0.00	39.46	0.00	1054.30	0.00	62.88	0.00	
1.25	16.44	94.37	25.89	12.31	259.70	4.05	0.00	39.69	0.00	1081.80	0.00	69.05	0.00	
2.17	16.28	94.48	25.57	12.29	256.00	4.10	0.33	40.09	0.00	1090.32	0.00	84.53	0.00	97.63
5	15.94	93.15	24.06	12.04	237.99	4.08	0.28	39.87	0.00	1090.67	0.00	898.79	0.00	
20	15.36	90.36	25.75	11.87	247.61	4.19	0.98	39.39	0.00	1074.48	0.00	869.37	0.00	
25	17.00	96.99	26.55	13.11	252.66	4.55	0.26	40.96	0.00	1117.37	0.00	825.54	0.00	97.63
49.5	20.37	114.54	36.03	15.28	319.84	4.40	0.88	40.80	0.00	1123.67	0.00	882.47	4.63	
191	17.79	98.33	31.54	13.75	271.33	4.43	0.00	41.74	0.00	1126.01	0.00	775.49	0.00	
337.5	17.97	98.84	31.53	13.45	267.06	4.44								
645	17.69	96.89	31.78	13.14	267.02	4.42								

<sup>1</sup> Water taken from the Helena site before any treatment

<sup>2</sup> Water in the batch after Ar bubbling for one week and right before CO<sub>2</sub> gas was bubbled into the system

Table A.1.6. Concentrations of trace elements measured for the Cranfield batch experiment of aquitard sediments at different time (unit: ppb)

time (hr)	B	Al	P	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Rb	Sr	Zr	Mo	Ag	Cd	Cs	Ba	Pb	Bi	U
-1 <sup>1</sup>	362.08	411.06	62.35	11.59	0.66	1.96	6.72	161.09	1.64	9.02	43.18	115.44	-0.02	0.62	4.42	90.99	3.54	0.21	7.05	0.76	0.14	261.38	14.06	0.54	0.09
0 <sup>2</sup>	31.48	213.65	14.22	10.15	0.13	1.09	942.75	37.09	3141.14	5468.25	9.91	4015.70	1.21	76.08	6.14	2057.78	1.25	0.03	0.19	21.06	0.04	30.60	1.59	0.05	0.11
1.25	33.21	248.97	8.29	6.30	0.09	0.59	964.28	60.56	3258.23	5650.80	11.15	4140.24	1.60	78.48	6.30	2127.87	1.04	0.00	0.07	22.00	0.03	31.23	3.11	0.01	0.25
2.17	58.42	366.11	6.65	6.50	0.10	5.67	954.55	81.98	3194.69	5565.10	12.68	4155.83	1.58	79.16	6.38	2085.52	1.22	0.35	0.45	22.25	0.07	31.30	3.84	0.26	0.39
5	42.32	401.84	4.90	6.10	0.08	0.78	892.27	65.02	2995.97	5225.38	12.98	3879.91	1.88	73.03	5.85	1951.49	1.49	0.02	0.13	20.89	0.02	32.90	3.80	0.29	0.36
20	40.03	416.55	-1.53	6.29	0.11	0.79	922.78	53.61	3114.71	5427.53	17.20	4093.10	1.81	75.62	5.97	2005.74	1.46	0.01	0.08	22.32	0.02	109.77	3.72	0.29	0.37
25	63.37	483.00	3.67	6.90	0.21	1.54	940.55	74.63	3168.84	5560.11	18.07	4296.81	1.89	74.28	6.31	2036.82	2.17	0.08	0.11	23.32	0.03	30.72	3.91	0.90	0.37
49.5	156.24	645.12	30.36	11.69	0.44	1.84	1205.83	159.07	4087.94	7188.65	31.99	5699.75	2.51	98.07	7.86	2615.15	3.84	0.10	0.17	31.36	0.06	41.05	9.73	1.37	0.42
191	179.16	484.01	7.98	8.94	0.30	1.42	1042.16	99.61	3558.93	6261.04	31.86	4845.17	1.44	82.41	6.78	2370.93	4.58	0.05	0.17	27.71	0.03	44.85	6.59	1.24	0.33
337.5	334.40	441.81	-7.18	8.44	0.22	1.14	1046.89	96.89	3500.03	6160.53	20.13	4705.96	1.44	86.71	6.70	2174.30	3.95	0.01	0.15	28.05	0.04	28.28	5.92	1.10	0.31
645	313.17	497.70	-4.49	8.46	0.28	1.02	1053.70	132.50	3557.88	6344.47	16.79	4690.54	2.23	82.66	6.67	2188.38	3.45	0.02	0.07	22.04	0.03	30.13	4.83	0.35	0.29

<sup>1</sup> Groundwater taken from the Helena site before any treatment

<sup>2</sup> Groundwater in the batch after Ar bubbling for one week and right before CO<sub>2</sub> gas was bubbled into the system

Table A.1.7. Concentrations of major ions measured for the batch experiment of groundwater taken from the Cranfield shallow aquifer without adding sediments (unit: ppm)

time (hr)	Cations (ppm)					pH	Anions (ppm)							
	Na	Mg	Si	K	Ca		F-	Cl-	NO <sub>2</sub> -	SO <sub>4</sub> --	Br-	NO <sub>3</sub> -	PO <sub>4</sub> ---	HCO <sub>3</sub> -
-1 <sup>1</sup>	15.13	9.47	16.67	2.56	21.78	7.85								
0 <sup>2</sup>	13.32	9.07	16.70	1.86	22.23	8.83	0.00	37.94	2.18	3.10	0.00	732.58	0.00	
1.25	15.04	9.81	16.55	1.77	22.83	4.96	0.30	39.27	2.24	3.29	0.00	648.80	0.00	
25	17.77	10.90	18.42	2.91	25.58	4.96	0.00	40.54	2.25	3.11	0.09	753.57	0.00	
191	16.26	10.14	17.25	2.90	23.87	4.84	0.00	42.59	2.07	3.67	0.00	0.00	0.00	
337.5	14.95	9.59	16.38	1.86	22.44	4.91								
645	16.50	10.19	25.36	2.11	34.31	4.94								

<sup>1</sup> Water taken from the Helena site before any treatment

<sup>2</sup> Water in the batch after Ar bubbling for one week and right before CO<sub>2</sub> gas was bubbled into the system

Table A.1.8. Concentrations of trace elements measured for the batch experiment of groundwater taken from the Cranfield shallow aquifer without adding sediments

time (hr)	B	Al	P	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Rb	Sr	Zr	Mo	Ag	Cd	Cs	Ba	Pb	Bi	U
-1 <sup>1</sup>	362.08	411.06	62.35	11.59	0.66	1.96	6.72	161.09	1.64	9.02	43.18	115.44	-0.02	0.62	4.42	90.99	3.54	0.21	7.05	0.76	0.14	261.38	14.06	0.54	0.09
0 <sup>2</sup>	20.92	80.87	16.25	5.59	0.32	0.90	6.79	36.66	0.24	3.72	5.57	136.85	0.03	0.33	3.58	83.54	1.05	0.12	0.76	0.13	0.07	79.41	0.14	0.13	0.27
1.25	24.26	34.45	13.61	4.59	0.38	0.24	8.06	10.50	1.12	5.14	9.59	244.47	-0.10	0.17	3.81	93.66	1.05	0.16	0.11	0.41	0.07	88.59	0.27	0.18	0.20
25	60.88	73.99	16.19	5.64	0.36	0.63	10.07	33.58	1.70	9.71	26.34	939.92	0.07	0.53	5.21	106.55	2.15	0.15	0.11	1.74	0.09	99.91	4.80	4.05	0.17
191	181.81	138.42	10.64	5.77	0.44	0.78	10.25	72.39	1.75	7.75	13.97	301.11	-0.02	0.37	4.22	111.95	3.49	0.12	0.08	1.12	0.09	92.15	3.16	1.24	0.16
337.5	258.83	118.78	8.23	5.08	0.44	0.66	11.05	51.01	1.58	7.47	13.12	247.74	-0.10	0.45	4.02	95.51	2.91	0.10	0.06	0.88	0.08	87.83	2.42	0.83	0.16
645	322.61	146.59	10.66	5.28	0.55	0.80	22.54	87.71	1.98	9.24	18.66	300.77	-0.13	0.37	4.44	103.53	3.41	0.14	0.07	0.93	0.09	96.21	2.79	0.36	0.18

<sup>1</sup> Groundwater taken from the Helena site before any treatment

<sup>2</sup> Groundwater in the batch after Ar bubbling for one week and right before CO<sub>2</sub> gas was bubbled into the system

## Appendix 2. Groundwater chemistry at the Cranfield site

Table A. 2.1. Groundwater chemistry at the Cranfield shallow aquifer

Sampling date	wells	Temperature °C	Conductivity µ S/cm	Al mg/L	Ba mg/L	Ca mg/L	Cd mg/L	Cu mg/L	Fe mg/L	K mg/L	Mg mg/L	Mn mg/L	Na mg/L	Pb mg/L	S mg/L	Si mg/L	Zn mg/L
7/15/2008 <sup>1</sup>	24-2	n.a. <sup>2</sup>	n.a.	<0.021	0.08	19.53	<0.002	0.003	0.04	1.76	7.86	0.006	8.50	n.a.	n.a.	n.a.	0.064
	27-1	n.a.	n.a.	<0.021	0.06	11.31	0.003	<0.002	11.59	1.25	3.69	0.644	22.45	n.a.	n.a.	n.a.	0.014
	29-12	n.a.	n.a.	<0.021	0.09	7.09	<0.002	0.003	1.22	2.10	2.36	0.043	73.40	n.a.	n.a.	n.a.	0.016
	29-13	n.a.	n.a.	<0.021	0.02	12.24	<0.002	0.003	0.02	0.72	4.03	0.003	7.67	n.a.	n.a.	n.a.	0.027
	44-2	n.a.	n.a.	<0.021	0.20	23.06	<0.002	<0.002	0.22	2.91	9.25	0.127	9.74	n.a.	n.a.	n.a.	0.065
3/30/2009	UM-1	20.8	174.50	<0.021	0.20	21.92	<0.002	0.004	0.11	3.30	6.77	0.128	14.14	0.012	n.a.	n.a.	0.968
	24-2	17.6	242.50	<0.021	0.05	8.97	0.003	0.003	11.17	1.69	3.16	0.708	28.31	0.008	n.a.	7.56	0.006
	28-2	19.2		<0.021	0.20	23.42	<0.002	0.004	1.77	2.72	9.11	0.111	8.77	0.009	n.a.	n.a.	0.005
	29-12	19.9	378.40	<0.021	0.03	4.62	<0.002	0.005	0.04	1.76	1.83	0.006	63.09	<0.006	n.a.	n.a.	0.009
	29-13	20.6	183.90	<0.021	0.08	19.13	<0.002	0.004	<0.015	1.62	7.94	<0.002	8.19	<0.006	n.a.	n.a.	0.015
	44-2	18.5	111.60	<0.021	0.01	17.14	<0.002	0.003	<0.015	1.50	5.48	0.018	19.20	0.007	n.a.	n.a.	0.004
5/29/2009	UM-1	20.5	221.40	<0.021	0.13	17.98	<0.002	0.005	0.05	1.53	7.03	0.045	9.31	<0.006	0.79	4.20	0.033
	24-2	20.7	272.00	<0.021	0.02	6.28	<0.002	<0.002	0.09	1.05	2.09	0.526	18.20	<0.006	2.22	1.89	0.019
	27-1	21.1	236.50	<0.021	0.20	22.84	<0.002	0.006	<0.015	2.25	8.75	0.131	8.01	<0.006	1.50	18.12	1.157
	27-4	n.a.	n.a.	<0.021	0.21	27.94	<0.002	0.004	0.02	4.10	8.94	0.216	9.83	0.065	0.89	8.11	1.068
	28-2	21.1	230.00	<0.021	0.22	25.02	<0.002	0.002	1.69	2.66	9.81	0.124	8.73	0.008	1.52	23.00	0.028
	29-12	21.2	295.00	<0.021	0.03	4.44	<0.002	0.003	0.02	1.68	1.76	0.009	74.30	<0.006	1.37	14.27	0.009
	29-13	21.5	185.40	<0.021	0.09	19.09	<0.002	0.003	0.19	1.56	7.93	0.004	7.60	0.008	0.75	17.95	0.026
	44-2	20	236.50	<0.021	0.02	18.35	<0.002	0.003	<0.015	1.53	5.92	0.024	19.75	<0.006	2.87	14.30	0.020
	48-3	20.8	214.20	<0.021	0.15	22.52	<0.002	0.002	0.10	2.17	9.06	0.139	8.81	<0.006	1.54	21.04	1.187
9/23/2009	UM-1	21.5	225.70	<0.021	0.11	20.52	0.002	0.003	<0.015	1.72	8.66	0.022	11.24	<0.006	0.71	13.06	0.037
	31-F1	25.2	329.90	<0.021	0.14	9.17	<0.002	0.010	<0.015	7.78	2.01	0.226	51.85	<0.006	3.49	20.22	0.280
	24-2	20.8	265.80	<0.021	0.05	8.25	0.003	<0.002	6.86	1.59	2.89	0.665	29.73	<0.006	2.96	8.08	0.012
	27-1	n.a.	n.a.	<0.021	0.20	24.21	0.002	<0.002	1.90	2.47	9.76	0.108	8.68	0.009	0.65	15.60	0.022
	28-2	21.6	229.50	<0.021	0.22	24.30	<0.002	<0.002	1.75	2.76	9.68	0.119	9.12	<0.006	1.51	16.68	0.028
	29-12	21.3	391.10	<0.021	0.03	4.56	<0.002	0.007	0.02	1.73	1.82	0.009	65.14	<0.006	1.40	10.53	0.012
	29-13	21.5	187.60	<0.021	0.09	19.48	<0.002	0.004	<0.015	1.61	8.19	0.003	8.13	0.007	0.78	13.55	0.034
	44-2	20.7	235.70	<0.021	0.02	17.52	<0.002	<0.002	<0.015	1.50	5.66	0.023	19.43	<0.006	2.99	10.53	0.028
	48-3	25.8	253.40	<0.021	0.15	21.47	<0.002	0.005	1.03	2.26	9.02	0.122	8.74	0.007	0.60	15.10	0.022
7/21/2010	UM-1	21.7	233.23	<0.021	0.09	20.93	<0.002	0.006	0.00	1.62	8.92	0.006	11.88	<0.006	0.67	12.53	0.018
	31-F1	22.6	315.70	<0.021	0.18	8.59	<0.002	0.003	0.94	8.37	1.88	0.179	57.82	<0.006	3.45	20.05	0.004
	24-2	20.6	266.70	<0.021	0.04	7.88	0.004	0.004	10.31	1.49	2.58	0.648	32.13	<0.006	2.76	8.21	0.006
	29-12	20.9	369.53	<0.021	0.03	4.64	<0.002	0.005	0.03	1.67	1.81	0.007	65.08	<0.006	1.58	10.56	0.003
	29-13	21.5	185.50	<0.021	0.09	20.75	<0.002	0.004	0.00	1.60	8.31	0.001	8.71	<0.006	0.80	13.65	0.016
	44-2	19.7	226.30	<0.021	0.01	17.48	<0.002	0.003	0.02	1.44	5.58	0.017	20.33	<0.006	3.04	10.45	0.008
	48-3	22	201.6	<0.021	0.136	21.13	<0.002	0.002	0.87	2.2	8.975	0.118	9.11	<0.006	1.23	15.44	0.011

Note: <sup>1</sup> Water samples were not filtered with 0.45 µm filters; <sup>2</sup> n.a. means "not measured".



Table 1. Groundwater chemistry at the Cranfield shallow aquifer (continued)

Sampling date	wells	F	Cl	SO4	Br	NO3	PO4	pH		Alkalinity (mg/L of CaCO3)		TOC	TIC	13C	2H	18O
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	Field	Lab	field	lab	mg/L	mg/L	‰	‰
7/15/2008	24-2	1.15	26.77	9.91	<0.01	<0.01	0.48	n.a.	6.50	n.a.	n.a.	60.96	17.80	-18.78	n.a.	n.a.
	27-1	0.12	5.23	4.87	<0.01	<0.01	<0.022	n.a.	6.90	n.a.	72.70	19.11	30.30	n.a.	n.a.	n.a.
	29-12	0.22	124.00	1.78	0.15	<0.01	<0.022	n.a.	7.50	n.a.	38.00	12.44	13.60	n.a.	n.a.	n.a.
	29-13	0.11	6.18	5.27	<0.01	3.53	<0.022	n.a.	6.70	n.a.	80.00	14.50	28.20	n.a.	n.a.	n.a.
	44-2	0.15	10.09	11.01	<0.01	0.10	0.06	n.a.	6.80	n.a.	26.80	10.68	14.60	-25.46	n.a.	n.a.
3/30/2009	UM-1	0.18	20.72	13.67	<0.01	0.02	<0.022	7.11	5.70	75.20	60.00	1.86	34.10	-16.50	n.a.	n.a.
	24-2	0.17	36.94	10.76	<0.01	0.01	0.09	7.47	6.2	n.a.	50	0.52	25.80	-21.3	n.a.	n.a.
	28-2	0.15	95.08	4.70	0.28	1.83	0.40	7.33	6.1	104.1	90	8.11	44.70	-18.56	n.a.	n.a.
	29-12	0.11	6.60	4.56	<0.01	3.16	<0.022	7.01	6	50.6	35	0.51	22.80	-19.51	n.a.	n.a.
	29-13	0.11	50.33	9.82	0.08	0.10	<0.022	6.96	6	77.9	65	0.36	40.90	-19.25	n.a.	n.a.
44-2	0.11	50.3	9.82	0.08	0.1	<0.022	6.83	6	n.a.	25	0.34	22.10	-19.73	n.a.	n.a.	
5/29/2009	UM-1	0.22	16.76	1.06	0.21	1.92	0.78	6.16	6.7		44	0.26	23.23	-16.82	-228.8	-3.99
	24-2	0.23	36.50	13.03	0.04	<0.01	0.45	6.76	7	81.7	48.4	0.46	24.44	-18.92	-25.1	-4.32
	27-1	0.18	4.96	3.41	<0.01	<0.01	0.08	6.65	7	n.a.	99.6	42.90	42.60	-17.28	-23.6	-4.19
	27-4	0.30	2.66	0.39	<0.01	<0.01	0.05	n.a.	7.1	n.a.	106.8	3.88	15.67	-15.63	-23.1	-4.17
	28-2	0.16	4.95	3.72	<0.01	<0.01	<0.022	6.57	6.9	113.4	94	0.39	46.30	-17.48	-23.2	-4.22
	29-12	0.15	91.00	3.40	0.22	1.54	1.55	6.39	6.9	43.6	25	0.40	21.91	-19.17	-22.6	-3.95
	29-13	0.11	6.67	1.73	n.a.	2.38	<0.022	6.31	6.6	n.a.	77.2	0.35	45.01	-18.28	-23	-4.05
	44-2	0.11	47.20	8.27	0.25	0.18	<0.022	6.13	6.3	n.a.	36	0.29	21.25	-17.99	-23.3	-4.15
48-3	0.12	5.65	3.89	<0.01	<0.01	<0.022	6.93	7	n.a.	86	4.35	33.64	-17.13	-25.1	-4.14	
9/23/2009	UM-1	0.15	31.33	1.77	<0.01	3.53	0.37	6.03	6.3	63.4	29.3	0.34	32.20	-18.17	-4.21	-22.9
	31-F1	0.20	6.47	9.13	0.02	0.09	0.24	6.66	6.5	146.4	99.9	2.33	58.70	-14.63	-4.33	-24.9
	24-2	0.21	38.54	8.30	<0.01	<0.01	<0.022	6.66	6.6	70.1	43	0.78	19.20	-19.08	-4.24	-23.9
	27-1	0.38	5.19	0.27	<0.01	<0.01	<0.022	6.67	6.6	115.7	85.5	23.07	43.90	-18.27	-4.11	-23.1
	28-2	0.12	4.98	3.83	<0.01	<0.01	<0.022	6.43	6.5	115.1	74.7	0.41	43.20	-17.57	-4.28	-22.8
	29-12	0.18	95.07	3.68	<0.01	1.33	0.44	6.19	6.5	42.8	42.9	0.53	18.50	-17.85	-4.28	-24.9
	29-13	0.12	6.61	1.82	<0.01	2.22	<0.022	6.12	6.4	88.7	63.1	0.43	39.40	n.a.	-4.39	-24.7
	44-2	0.13	47.14	8.56	<0.01	<0.01	<0.022	6.12	6.3	40.8	26.4	0.50	19.20	-18.43	-4.32	-23.6
48-3	0.77	5.07	0.22	<0.01	<0.01	0.27	6.36	6.5	106	74	21.25	41.90	-17.9	-4.32	-23.8	
7/21/2010	UM-1	0.07	34.50	2.80	0.05	3.54	n.a.	5.42	6.2	60.6	56	0.23	32.70			
	31-F1	0.11	5.36	11.40	0.02	0.00	0.46	5.66	6.4	154.3	138	0.33	58.85			
	24-2	0.15	39.07	8.60	0.04	0.01	n.a.	5.92	6.4	67.4	51.2	0.53	21.34			
	29-12	0.13	88.74	4.80	0.08	1.42	n.a.	5.5	6.2	40.5	38.8	0.27	19.47			
	29-13	0.08	6.92	3.33	0.03	2.35	n.a.	5.56	6.2	87.1	76.4	0.15	37.38			
	44-2	0.09	47.01	10.33	0.07	0.12	n.a.	5.34	6.1	36.1	42.6	0.16	19.21			
48-3	0.10	5.09	3.85	0.02	0.02	n.a.	5.6	6.3	97.8	88	0.35	40.69				

Note: <sup>1</sup> Water samples were not filtered with 0.45 µm filters; <sup>2</sup> n.a means "not measured".