

# **Impacts of Elevated Dissolved CO<sub>2</sub> on a Shallow Groundwater System: Reactive Transport Modeling of a Controlled-Release Field Test**

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## **Abstract**

One of the risks that CO<sub>2</sub> geological sequestration imposes on the environment is the impact of potential CO<sub>2</sub>/brine leakage on shallow groundwater. The reliability of reactive transport models predicting the response of groundwater to CO<sub>2</sub> leakage depends on a thorough understanding of the relevant chemical processes and key parameters affecting dissolved CO<sub>2</sub> transport and reaction. Such understanding can be provided by targeted field tests integrated with reactive transport modeling. A controlled-release field experiment was conducted in Mississippi to study the CO<sub>2</sub>-induced geochemical changes in a shallow sandy aquifer at about 50m depth. The field test involved a dipole system in which the groundwater was pumped from one well, saturated with CO<sub>2</sub> at the pressure corresponding to the hydraulic pressure of the aquifer, and then re-injected into the same aquifer using a second well. Groundwater samples were collected for chemical analyses from four monitoring wells before, during and after the dissolved CO<sub>2</sub> was injected. In

27 this paper, we present reactive transport models used to interpret the observed changes in  
28 metal concentrations in these groundwater samples. A reasonable agreement between  
29 simulated and measured concentrations indicates that the chemical response in the aquifer  
30 can be interpreted using a conceptual model that encompasses two main features: (a) a  
31 fast-reacting but limited pool of reactive minerals that responds quickly to changes in pH  
32 and causes a pulse-like concentration change, and (b) a slow-reacting but essentially  
33 unlimited mineral pool that yields rising metal concentrations upon decreased  
34 groundwater velocities after pumping and injection stopped. During the injection, calcite  
35 dissolution and Ca-driven cation exchange reactions contribute to a sharp pulse in  
36 concentrations of Ca, Ba, Mg, Mn, K, Li, Na and Sr, whereas desorption reactions control  
37 a similar increase in Fe concentrations. After the injection and pumping stops and the  
38 groundwater flow rate decreases, the dissolution of relatively slow reacting minerals such  
39 as plagioclase drives the rising concentrations of alkali and alkaline earth metals observed  
40 at later stages of the test, whereas the dissolution of amorphous iron sulfide causes slowly  
41 increasing Fe concentrations.

42

## 43 1. Introduction

44

45 Ever since the concept of CO<sub>2</sub> geologic storage was proposed about two decades ago,  
46 many studies have been undertaken to assess hydrological, geochemical and mechanical  
47 processes affecting deep injection and containment of CO<sub>2</sub> in storage reservoirs.  
48 Meanwhile, as part of environmental risk assessments for CO<sub>2</sub> storage sites, studies have  
49 also been undertaken to assess the impacts of potential CO<sub>2</sub> leaks from deep storage

50 reservoirs, on the quality of overlying fresh water aquifers (see review papers by  
51 Lemieux, 2011 and Harvey et al., 2012, and references therein). Numerical modeling has  
52 been an important tool to address this issue.

53 Reactive transport models were first used to evaluate the potential impacts of CO<sub>2</sub>  
54 leakage on the water quality of shallow, overlying aquifers (Wang and Jaffe, 2004;  
55 Carroll et al., 2009; Zheng et al., 2009; Apps et al., 2010; Wilkin and Digiulio, 2010), and  
56 to identify potential issues such as the leaching out of organics such as BETX, PAH,  
57 from source rocks (Zheng et al., 2013; Zhong et al., 2014). Later on, they were used to  
58 interpret data from laboratory experiments (e.g. Viswanathan et al., 2012; Zheng et al.,  
59 2016) and field tests (e.g. Zheng et al., 2012; Trautz et al., 2013 and Zheng et al., 2015)  
60 in order to understand key physical and chemical processes that control the response of  
61 aquifers to CO<sub>2</sub> leakage. Most recently, reactive transport models have been used to  
62 predict potential long-term change in aquifer in response to CO<sub>2</sub>/brine leakage (Bacon et  
63 al., 2016), to conduct uncertainty quantifications (Hou et al., 2014) to lay the foundation  
64 for risk assessment studies, and to provide guidance for risk management and mitigation.

65 Laboratory experiments provide useful information on the type and quantity of  
66 trace elements that may be mobilized in response to CO<sub>2</sub> intrusion into potable  
67 groundwater, forming the basis for further modeling analyses. Such experiments (Smyth  
68 et al., 2009; Lu et al., 2010; Little and Jackson, 2010, Wei et al., 2011; Viswanathan et al.,  
69 2012; Humez et al., 2013; Varadharajana et al., 2013; Wunsch et al., 2014; Kirsch et al.,  
70 2014; Lawter et al., 2016) were typically conducted in batch or column mode, where CO<sub>2</sub>  
71 was released into a pre-equilibrated water-rock environment and the geochemical  
72 changes in the aqueous phases were monitored subsequently. Modest to strong increases

73 in concentrations of major and trace elements have typically been reported in these  
74 laboratory experiments, although in terms of the changes of one particular element,  
75 different experiments have led to different results. For example, increases in Fe  
76 concentration has been reported in Smyth et al. (2009) and Lu et al. (2010), whereas  
77 Humez et al. (2013) observed declining Fe concentrations after initial CO<sub>2</sub> influx. The  
78 increase or decrease in metal concentrations also varies significantly from one  
79 experiment to another, likely due to differences in experimental conditions, types of  
80 sediments, mineralogical compositions, etc. However, despite these differences, one  
81 common observation is a concentration increase for alkali and alkaline earth metals and  
82 Si.

83 Laboratory experiments have some inherent limitations such as (1) failing to  
84 preserve the *in situ* water-rock environment as a result of pre-equilibration of sediments  
85 with a synthetic solution (e.g., Smyth et al., 2009) or DI water (Lu et al., 2010), (2)  
86 unwanted oxidation of sediments samples during the experiment (e.g., Little and Jackson,  
87 2010), or (3) the failure to include transport of groundwater and CO<sub>2</sub>. Several field tests  
88 have been conducted to further enhance our understanding of potential impacts of CO<sub>2</sub>  
89 leakage on shallow groundwater. The ZERT (Zero Emissions Research and Technology)  
90 field test in Montana, USA (Kharaka et al., 2010; Spangler et al., 2010) was probably the  
91 first controlled-release experiment in this regard, with food-grade CO<sub>2</sub> injected over a 30  
92 day period into a horizontal perforated pipe a few feet below the water table of a shallow  
93 aquifer. Cahill and Jakobsen (2013) and Cahill et al. (2014) reported a field scale pilot  
94 test in which CO<sub>2</sub> gas was injected at 5-10 m depth into an unconfined aquifer in  
95 Denmark for two days, and water geochemistry changes were monitored for more than

96 100 days. As reported in Peter et al. (2012), CO<sub>2</sub> was injected through 3 wells for a  
97 period of 10 days into an aquifer at 18 m depth in Northeast Germany. All these tests  
98 involved an injection of CO<sub>2</sub> or CO<sub>2</sub>-bearing water into the aquifer, and the monitoring of  
99 changes in water composition via monitoring wells downstream of the injection point. In  
100 general, observations made in field tests are largely consistent with those from laboratory  
101 tests in terms of concentration increases for major and trace elements, but there are two  
102 noticeable differences: first, the level of concentration changes observed in the field is  
103 typically much lower than in the laboratory. For example, an increase in major and trace  
104 element concentrations of 1 to 3 orders of magnitude has been observed in the laboratory  
105 compared to field tests, which never show an increase greater than one order of  
106 magnitude (i.e., 20% to 700%). Secondly, concentration increases in trace elements,  
107 especially for elements of environmental concern such as As, Pb, Ba, Cd, are more  
108 frequently observed in laboratory than in field tests.

109 A thorough understanding of key physical and chemical processes and related parameters  
110 is critical for building a reliable model to predict long term changes in aquifer response to  
111 CO<sub>2</sub>/brine leakage. Researchers have postulated based on laboratory-scale experimental  
112 results (e.g. Lu et al., 2010), the simulation of laboratory-scale data (e.g. Humez et al.,  
113 2011; Viswanathan et al., 2012; Zheng et al., 2015b) or field tests (e.g. Zheng et al.,  
114 2012; Trautz et al., 2013) that a number of chemical processes are potentially responsible  
115 for the mobilization of trace elements. These include the dissolution of carbonates (e.g.,  
116 Kharakha et al., 2006; McGrath et al., 2007; Lu et al., 2010), sulfides (e.g., Wang and  
117 Jaffe, 2004; Zheng et al., 2009; Apps et al., 2010) and iron oxyhydroxide minerals (e.g.,  
118 Kharaka et al., 2006, 2009), as well as surface reactions such as adsorption/desorption

119 (Viswanathan et al., 2012) and ion exchange (Kharaka et al., 2006, 2009; Zheng et al.,  
120 2009; Apps et al., 2010; Zheng et al., 2012; Cahill et al., 2014). The degree to which  
121 these reactions contribute to water quality impacts depends on the specific aqueous  
122 chemistry and aquifer mineralogy for a given system. Field testing integrated with  
123 reactive transport modeling provides an effective and reliable way to identify reactions  
124 and parameters that are needed to build reliable simulation tools for risk assessments of  
125 CO<sub>2</sub> sequestration.

126 A comprehensive longer-term field study involving the controlled release of  
127 groundwater containing dissolved CO<sub>2</sub> was initiated in 2011 to investigate potential  
128 groundwater impacts in Mississippi, USA (Trautz et al., 2013). Injection of dissolved  
129 CO<sub>2</sub> lasted approximately 5 months followed by an extended phase of post-injection  
130 groundwater monitoring. The experiment involved extensive laboratory and field  
131 characterization of groundwater and sediments, an innovative fluid-delivery system,  
132 hydrologic monitoring, and geophysical monitoring for remote detection of dissolved  
133 CO<sub>2</sub>. Trautz et al. (2013) presented the data from this test at one of the monitoring wells,  
134 including preliminary results of reactive transport simulations, and Varadharajan et al.  
135 (2013) reported laboratory test results for aquifer sediments collected while drilling wells  
136 for this test. In this paper, we present reactive transport simulations conducted to  
137 interpret groundwater monitoring data at the site over a significantly longer time frame  
138 than initially reported by Trautz et al. (2013), with the goal to elucidate key chemical  
139 processes and parameters that could affect observed changes in long-term dissolved metal  
140 concentrations in groundwater at this test site.

141

142 **2. Field test**

143 **2.1. Test description**

144 The study site is located in Jackson County Mississippi and lies in the Pascagoula River  
145 Drainage Basin in the Gulf Coastal Plain physiographic province, which is  
146 topographically gently rolling to flat with local salt marshes. The stratigraphic interval  
147 into which carbonated water was injected is composed of fine silty sand with minor clay  
148 interbedding at depths between 46.9 and 54.6 m (Figure 1, right). An innovative closed  
149 loop groundwater delivery system was used to pump groundwater from the confined  
150 shallow aquifer through a carbonation unit to infuse it with CO<sub>2</sub> before injecting the  
151 carbonated groundwater back into the same shallow aquifer. The test configuration is  
152 shown in Figure 1: groundwater is injected through well IW-1 and pumped out from well  
153 PW-1. Groundwater samples were collected from the five monitoring wells over three  
154 test periods (Table 1): (1) for 13 months prior to pumping and injection (background), (2)  
155 for five months during pumping and injection, and (3) for 10 months after pumping and  
156 injection ended. Groundwater samples were analyzed in the laboratory to evaluate trends  
157 in major and minor cations, anions, trace elements, organic carbon, and dissolved gases.  
158 In addition, geophysical monitoring using complex electrical tomography allowed  
159 changes in electrical resistivity of the groundwater to be observed, and the position of the  
160 dissolved CO<sub>2</sub> plume as it migrated between wells to be tracked (Dafflon et al., 2013).

161 Table 1. Test period durations

Test Period	Start Date	End Date	Approx. Duration	Wells Sampled

			(months)	
Pre-CO <sub>2</sub> injection baseline	2-Sep-2010	18-Oct-2011	13	All wells
Pre-pumping (static baseline)	2-Sep-2010	12-Aug-2011	11	All wells
Pumping (dynamic baseline)	12-Aug-2011	18-Oct-2011	2	MW, BG wells
CO <sub>2</sub> injection (pumping continues)	18-Oct-2011	23-Mar-2012	5	MW, BG wells
Post-CO <sub>2</sub> injection	23-Mar-2012	15-Jan-2013	10	MW, BG wells

162

163       A decrease in groundwater pH by 1.5–3 units was observed at nearby monitoring

164       wells as the dissolved CO<sub>2</sub> plume migrated through the sandy aquifer. In general, four

165       groups of metals exhibiting different trends in metal/solute concentration changes (with

166       limited exceptions) were observed during the test: (1) solutes below

167       detection/background concentration levels (Type I: Al, Sb, As, Be, Cd, Cu, Pb, Hg, Ag,

168       Tl, Zn, P, Se, Br<sup>−</sup>, Cl<sup>−</sup>, NO<sub>2</sub><sup>−</sup>, NO<sub>3</sub><sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, HS<sup>−</sup>), (2) metals potentially leaching out of

169       geophysical probes employed in the field experiment (Type II: Cr, Co Ni), (3) metals

170       displaying an apparent concentration increase upon injection of CO<sub>2</sub> (Type III: Ba, Ca, Fe,

171       Li, Mg, Mn, K, Si, Na, and Sr) and (4) those showing a concentration decrease (Type IV:

172       Mo and F) after exposure to dissolved CO<sub>2</sub>. It should be noted that none of the metal

173       concentrations measured during the controlled release experiment exceeded primary

174       drinking water standards (i.e., maximum contaminant levels) established by the U.S.

175       Environmental Protection Agency under the Clean Water Act.

176

177      **2.2. Trend analyses of observed metal concentrations**

178            In previous work, we reported on the early-time groundwater composition trends  
179    observed during the first few months after injection of carbonated water started (Trautz et  
180    al., 2013). For several metals (Ba, Ca, Fe, Li, Mg, Mn, K, Si, Na, Sr), the concentration  
181    data exhibited a clear “pulse”-like response (see Figure 2 for Sr as example) upon arrival  
182    of carbonated groundwater at the monitoring well closest to the injection point (MW-3).  
183    This response was attributed to Ca-driven exchange reactions triggered by the dissolution  
184    of a very small, finite amount of calcite in the sediments. As groundwater quality data  
185    continued to be collected over a longer time frame, it became evident that the  
186    concentration of some metals (e.g., Ca, Ba, Fe) started to slowly increase once pumping  
187    and injection ended and the groundwater velocities returned to ambient conditions  
188    (Zheng et al., 2015). This later increase (superposed on an initial fast, exchange-driven  
189    pulse) was attributed to slow mineral dissolution, noticeable only under conditions of  
190    increased groundwater residence time once the pump was turned off (Zheng et al., 2015).

191            Here, we further evaluate the groundwater quality response to carbonation using  
192    the *full* set of analytical data collected *before* (13 months), *during* (5 months), and *after*  
193    the release of CO<sub>2</sub> (10 months after turning off the injection pump). Accordingly, the  
194    monitoring data were classified into three groups: *pre*-, *during*, and *post*-injection, with  
195    the ‘*pre*-injection’ data defined as analyses before the arrival of the carbonated plume at  
196    specific wells, measured as the start of the pH decrease at these wells. Thus, these data  
197    may include samples that were technically sampled during the injection period but prior  
198    to plume arrival.

199 Using these three sets of data together, elemental correlation plots (Figure 3) and  
200 Principal Component Analyses (PCA; Figure 4; Numerical Dynamics, 2014), including  
201 multivariate regression were performed to further distinguish trends and possible  
202 differences in responses to carbonation. Metal concentration data collected prior to  
203 injection ('pre' in Figure 3) show a narrow variability with regards to a correlation to Ca  
204 concentrations. During CO<sub>2</sub> injection, the strongest correlation between Ca and other  
205 released metals is observed for Ba, Mg, Sr, and Mn (Figure 3). These metals were shown  
206 to have significantly higher concentrations in pH-5 sequential leachates of sediments  
207 collected from the field site (Varadharajan et al., 2013). Post-pumping data for these  
208 elements exhibit more scattered and possibly different correlation trends (Figure 3),  
209 which would support the hypothesis of the two distinct release mechanisms (during and  
210 post-pumping, respectively) postulated by Zheng et al. (2015). Similar analyses also  
211 show some correlation of Ca with Fe, Na, and alkalinity, as well as a good correlation  
212 between Fe and Mn. A weaker correlation of Si with Ca (Figure 3) (and also Na, not  
213 shown) although quite more scattered, also lends support to the hypothesis of Zheng et al.  
214 (2015) suggesting that the slow dissolution of plagioclase may contribute to the long-term  
215 concentration trends of these elements.

216 Plots of PCA loadings allow for an evaluation of the similarity or dissimilarity of  
217 measured dissolved metal concentrations. Points located in close proximity have a  
218 common denominator, thus in our case, possibly a similar metal source and/or release  
219 mechanism. The PCA loadings for individual elements (Figure 4) show three groups of  
220 metal correlations. First, elements falling in the upper left quadrant of Figure 4 (Ba, Ca,  
221 Co, Li, Mg, Mn, Na, Si, and Sr) include seven of the top ten loadings contributors; these

222 correspond to metals that were shown to yield high concentrations in acid leachates of  
223 site sediments (Varadharajan et al., 2013). The consistent grouping of these elements in  
224 both the field and laboratory studies confirms that these elements form a distinct group of  
225 released metals. Second, Fe, Cr, and Ni appear to form their own group (lower left  
226 quadrant in Figure 4), suggesting another source and/or release mechanism for these  
227 elements in the field study. No release was observed for these metals in leaching  
228 experiments (Varadharajan et al., 2013). One possible explanation is a contamination of  
229 groundwater samples with corrosion products from stainless steel geophysical electrodes  
230 that were deployed in the field but not present in lab-scale experiments. Third, alkalinity,  
231 chloride, and dissolved organic matter also fall within the top 10 contributors, but in this  
232 case because of their individual variability, or lack thereof.

### 233 **2.3. Postulated metal release mechanisms**

234 The release of trace elements from sediments due to reaction with dissolved CO<sub>2</sub>  
235 has been explained by various mechanisms including: (1) the dissolution of calcite with  
236 trace amounts of impurities of other elements (Lu et al., 2010), (2) metal desorption from  
237 mineral surfaces (Viswanathan et al., 2012; Zheng et al., 2012), (3) the dissolution of  
238 silicate minerals (Yang et al., 2013), and/or (4) cation exchange reactions, which are  
239 triggered by an increase in Ca<sup>+</sup><sup>2</sup> concentrations after calcite dissolution (Zheng et al.,  
240 2012). To date, metal concentration trends observed in most tests reported in the  
241 literature have been monotonic increases, mainly because laboratory tests were typically  
242 performed in batch experiments—without any transport component—and most field tests  
243 were conducted over fairly short time periods (Kharaka et al., 2010). One exception is a  
244 field test in which CO<sub>2</sub> gas was injected into a shallow aquifer at 5-10 m depth for 72

245 days, followed by post-injection monitoring of the groundwater composition (Cahill et al.,  
246 2014). During this test, concentrations of major and trace elements increased first upon  
247 arrival of the carbonated groundwater, but then decreased during the remaining CO<sub>2</sub>  
248 injection period, and continued to decrease over the post injection time-period. In contrast,  
249 during the field test conducted for the present study, a rapid pulse-like release of  
250 dissolved cations upon the arrival of carbonated groundwater was observed, followed by  
251 slowly-rising cation concentrations almost immediately after the injection was stopped.

252 This latter behavior can be explained by a conceptual model that includes two  
253 contaminant release source terms (Zheng et al., 2015): (a) a fast-reacting but limited pool  
254 of reactive minerals that responds quickly to changes in pH, and (b) a slow-reacting but  
255 essentially unlimited mineral pool that yields slowly rising concentrations upon decreased  
256 groundwater velocities (increased residence time) after pumping and injection stopped.  
257 The fast-reacting and slow-reacting pools, and the associated release processes, are  
258 believed to differ for different elements, as summarized in Table 2 and discussed in  
259 further detail below. The geochemical models developed in this study were set up to  
260 simulate the minerals (pools) and processes postulated in this table.

261  
262 Table 2. Fast-reacting, limited and slow-reacting, unlimited pools proposed for  
263 the release of Type III metals.

Element	Fast-reacting limited pool	Slow-reacting unlimited pool
Ca	Calcite dissolution	Plagioclase (Ab80An20) dissolution

Ba, Mg, Mn, K, Li, Na, Sr	Cation exchange with Ca	No specific minerals. However, Ca from the slow-reacting Ca pool (plagioclase) triggers further cation exchange with these metals.
Fe	Desorption	Iron sulfide (FeS_m) dissolution
Si	Desorption	Plagioclase (Ab80An20) dissolution

264

265

266 **3. Groundwater Flow and Geochemical Model Development**

267 The reactive transport models in this paper focus on the Type (III) metals/metalloids  
 268 discussed earlier, because the increasing dissolved concentration of these metals upon  
 269 exposure to CO<sub>2</sub>-saturated water is obviously of more potential concern than the  
 270 decreasing or un-detectable concentrations of the other metals. The simulations were  
 271 conducted with TOUGHREACT V2 (Xu et al., 2011), a numerical model that was  
 272 developed by introducing reactive chemistry into the existing framework of a non-  
 273 isothermal multi-phase multi-component fluid and heat flow simulator, TOUGH (Pruess  
 274 et al., 1999).

275

276 **3.1. Model domain and discretization**

277 Because the aquifer was found to be fairly homogeneous in the vertical direction,  
 278 a 2-D planar (X-Y) model was employed. The spatial domain of the groundwater flow  
 279 covers an area of about 500 m × 500 m. An area of 40 m × 100 m was finely discretized  
 280 with a 1-m grid size. Areas of 20 m × 40 m surrounding the injection well and monitoring  
 281 wells have even finer gridding with a 0.5-m grid size (Figure 5). A honeycomb mesh  
 282 structure was used to minimize numerical errors resulting from the radial groundwater

283 flow pattern around injection and monitoring wells, and other cases of flow vector  
284 orientations deviating significantly from a direction perpendicular to interfaces between  
285 model grid blocks.

286 **3.2. Hydrological parameters**

287 Hydrodynamic parameters used in the model are listed in Table 3. Two pumping  
288 tests were conducted to measure the hydraulic conductivity. Drawdown data from a 39-  
289 hour pumping test were used to calculate an average hydraulic conductivity of 41 ft/day  
290 (12.5 m/day or  $1.45 \times 10^{-4}$  m/s) and a storativity of 0.00017 for the transmissive  
291 stratigraphic interval in which the test was conducted. Data from another 18-hour  
292 pumping test yielded close agreement with a hydraulic conductivity of 47 ft/day (14.3  
293 m/day or  $1.65 \times 10^{-4}$  m/s) and a storativity of 0.00029. The hydraulic conductivity used in  
294 the model is the average of values from these two pumping tests (13.4 m/day),  
295 corresponding to a permeability of  $1.55 \times 10^{-11}$  m<sup>2</sup>. The storativity used in the model was  
296 taken as 0.00023, which was converted to a pore compressibility of  $3.8 \times 10^{-9}$  Pa<sup>-1</sup>  
297 assuming zero water expansivity.

298 In TOUGHREACT, hydrodynamic dispersion is not computed. The effect of  
299 dispersion is approximated by numerical dispersion, which is roughly equal to half the  
300 spacing of grid blocks and in the present case corresponds to dispersivity values between  
301 0.25 m close to the injection well and 0.5 m further away.

302

303 Table 3. Hydrodynamic parameters used in the model

Parameter	Aquifer
Porosity $\phi$	0.3

Permeability [m <sup>2</sup> ]	1.55×10-11
Hydraulic conductivity (m/day)	13.4
Pore compressibility (Pa <sup>-1</sup> )	3.8×10-9
Average molecular diffusion coefficient (m <sup>2</sup> /s) for all aqueous species	1×10-9
Dispersivity	0.25 m (numerical)
Tortuosity	0.67*

304 \* Based on the Millington and Quirk (1961) equation

305

306 **3.3. Geochemical parameters**

307 Table 4 lists the chemical composition of initial (ambient) pore water and injected  
 308 water in the model. The initial composition of the modeled water was based on average  
 309 concentrations measured over a 20-month pre-injection baseline period. Detection limits  
 310 were used for the concentration of species for which concentrations were below the  
 311 detection limit. The pH and carbonate composition of the injected water were computed  
 312 by assuming equilibration of the initial water with a partial CO<sub>2</sub> pressure ( $P_{CO_2}$ ) of 3.8 bar,  
 313 corresponding to full saturation of the water with CO<sub>2</sub> gas at the prevailing local  
 314 hydrostatic pressure. The pH value obtained in this manner (4.97) is consistent with  
 315 measured pH values in the field (~5) after injection started. The injected water has  
 316 essentially the same composition as the initial water except for its lower pH and higher  
 317 total dissolved carbonate concentration (0.133 moles/kg). The initial water is slightly

318 under-saturated with respect to calcite, with a saturation index of -0.5; in contrast, the  
319 calcite saturation index in the injected water is much lower (-3.3) due to the lower pH  
320 induced by carbonation.

321

322 Table 4. Composition of initial water used in the model. The unit of concentration of  
323 chemical species is molality (moles per kg water)

Species	Concentration	Species	Concentration	Species	concentration
pH	7.91	K	$7.10 \times 10^{-5}$	Zn	$2.14 \times 10^{-7}$
Al	$4.45 \times 10^{-6}$	Li	$6.97 \times 10^{-6}$	S(-2)	$3.70 \times 10^{-5}$
Ba	$4.07 \times 10^{-7}$	Mg	$5.35 \times 10^{-5}$	Cr	$4.81 \times 10^{-8}$
Br	$8.27 \times 10^{-7}$	Mn	$1.16 \times 10^{-6}$	Se	$7.00 \times 10^{-9}$
Ca	$7.34 \times 10^{-5}$	Mo	$4.41 \times 10^{-8}$	As	$9.22 \times 10^{-9}$
Cd	$8.45 \times 10^{-10}$	Na	$6.70 \times 10^{-3}$	N(+5)	$1.67 \times 10^{-4}$
Cl	$7.31 \times 10^{-4}$	Ni	$3.41 \times 10^{-8}$	Acetic acid (aq)	$5.31 \times 10^{-5}$
Co	$9.67 \times 10^{-9}$	Pb	$9.65 \times 10^{-10}$	Methane(aq)	$9.87 \times 10^{-6}$
Cu	$1.73 \times 10^{-8}$	S(+6)	$1.02 \times 10^{-5}$	Ethane(aq)	$2.51 \times 10^{-5}$
F	$2.40 \times 10^{-5}$	Sb	$1.33 \times 10^{-8}$	Hg	$3.49 \times 10^{-10}$
Fe(II)	$4.00 \times 10^{-6}$	Si	$1.75 \times 10^{-4}$	Fe(III)	$3.46 \times 10^{-6}$
C(+4)	$6.22 \times 10^{-3}$	Sr	$1.13 \times 10^{-6}$	O <sub>2</sub> (aq) <sup>#</sup>	$1.08 \times 10^{-74}$
P	$3.18 \times 10^{-6}$	Na	$6.70 \times 10^{-3}$		

324 <sup>#</sup>Computed from redox couple HS<sup>-</sup>/SO<sub>4</sub><sup>-2</sup>

325 Chemical reactions considered in the model are aqueous complexation, surface  
326 complexation (using a double diffuse layer model), cation exchange (using the Gaines-  
327 Thomas convention) and mineral precipitation/dissolution under kinetic constraints  
328 (using published rate laws). Aqueous complexes considered in the model are listed in  
329 Table A1 in the Appendix. The cation exchange and surface complexation reactions are  
330 listed in Table A2 and A3 in the Appendix, respectively. In the current geochemical  
331 model, it is assumed that ferrihydrite (as Fe(OH)<sub>3</sub>(s)) is the adsorbent. The reaction  
332 constants for surface complexation of H<sup>+</sup> and chromium are taken from Dzombak and

333 Morel (1990), for surface complexation reactions of iron and carbonate from Appelo et al.  
334 (2002), and for surface complexation on silicate from Jordan et al. (2007).

335 Based on the mineralogical characterization of the sediment, the model  
336 considered illite, smectite,  $\text{Fe(OH)}_3(s)$  and amorphous iron sulfide (mackinawite,  $\text{FeS}_m$ ),  
337 in addition to major aquifer minerals such as quartz, K-feldspar and plagioclase (Table 4).

338 The amount of iron sulfide ( $\text{FeS}_m$ ) was estimated from selective extractions (~0.02  
339 vol%), and the amount of  $\text{Fe(OH)}_3(s)$  from calibration of sediment acid titration  
340 simulations (~0.135 vol%) as discussed later. Carbonates were not detected using x-ray  
341 diffraction (XRD) and solid total inorganic carbon-total organic carbon (TIC-TOC)  
342 analysis. However, calcite was found by micro-X ray spectroscopy (Varadharajan et al.,  
343 2013). Therefore, trace amounts of calcite were included in the simulations, with an  
344 amount calibrated to yield best agreement between simulated and observed metal  
345 concentration trends. The amounts of illite, smectite, quartz, and K-feldspar were roughly  
346 estimated based on XRD characterization of sediment cores and thin sections (Table 5).

347 Equilibrium constants for these minerals and other secondary phases allowed to form are  
348 given in Table 5. These data, as well as dissociation constants for all considered aqueous  
349 species (Table A1) were taken from the *Data0.dat.YMPv4.0* EQ3/6 thermodynamic  
350 database (Wolery, 2007; SNL 2007). Details on the implemented rate laws and kinetic  
351 data for mineral dissolution are given in Appendix A.

352

353 Table 5. Equilibrium constants ( $\log(K)$ ) and initial volume fraction of minerals  
354 in the sediment (on a dry basis).  $\log(K)$  values are for dissolution reactions that  
355 are written with the primary species listed in the first column of Table A1.

Primary Mineral	Volume fraction (%)	logK(25 °C)	Potential Secondary Minerals allowed to form	logK(25°C, 1 bar)
Quartz	94.4	-3.75	Dolomite	2.52
Calcite	0.0086	1.85	Siderite	-0.25
FeS_m	0.01	-3.5	Witherite	1.77
K-feldspar	2	-22.39	Rhodochrosite	0.252
Smectite-Na	0.5	-38.32	Strontianite	-0.31
Illite	1	-42.69	Dawsonite	-17.9
Fe(OH) <sub>3</sub> (s)	0.135	-5.66		
Ab80An20	2	-14.8		

356

357 **3.4. pH Buffering Capacity**

358 Sediment titrations were conducted to evaluate the pH buffering capacity of the aquifer  
 359 (Varadharajan et al., 2013). A mixture of 1 g sediment and 5 ml deionized water was  
 360 titrated with a 0.01M HCl solution. Simulations of these sediment acid titrations were  
 361 used to constrain pH buffering reactions implemented in the reactive transport model.  
 362 These reactions were assumed to consist primarily of surface protonation/deprotonation  
 363 reactions, as well as the dissolution of carbonate minerals (calcite). However, the  
 364 simulations showed that the calcite amount in the sediments (Table 5) was too small to  
 365 significantly buffer pH upon acid titration. This implies that, for these sediments, the pH  
 366 buffering behavior was dominated by H<sup>+</sup> adsorption. To model such adsorption,  
 367 protonation/deprotonation reaction equilibrium constants and sorption site densities were  
 368 taken from Dzombak and Morel (1990), assuming that H<sup>+</sup> adsorption occurs dominantly  
 369 onto ferric iron (oxy)hydroxides (here modeled as ferrihydrite in the form of Fe(OH)<sub>3</sub>(s) ).  
 370 Using these data, the volume fraction of Fe(OH)<sub>3</sub>(s) in the sediment was then calibrated  
 371 (0.135%) to best reproduce the titration curve obtained for sample PW-1-160 that is

372 representative of the aquifer sandy sediment (Figure A1 in electronic supplementary  
373 information (ESI)).

374

375 **4. Modeling results**

376 Results of various simulations are presented below and organized as follows. First, results  
377 of a “base case” model are presented. This model implements the metal release reactions  
378 postulated in Table 2, with focus on simulated trends of pH, alkalinity, and  
379 concentrations of alkali and alkaline earth metals, Ba, Fe, Si and Cr. In a second part, we  
380 then evaluate the sensitivity of modeling results to a variety of key parameters and  
381 processes such as surface protonation, calcite dissolution, and cation exchange capacity  
382 (CEC). Finally, we also explore conceptual model variations to help explain some of the  
383 discrepancies between observed metal concentration trends and the base-case model  
384 results.

385

386 **4.1. Base-Case Model**

387 *pH and Alkalinity*

388 Groundwater pumped out from PW-1 is saturated with CO<sub>2</sub> at the surface and then  
389 injected through IW-1. The dissolved CO<sub>2</sub> dissociates into bicarbonate and protons (CO<sub>2</sub>  
390 + H<sub>2</sub>O ⇌ HCO<sub>3</sub><sup>-</sup> + H<sup>+</sup>), which increases the total dissolved inorganic carbon content (DIC)  
391 and decreases pH in the impacted groundwater. This carbonated water displaces the  
392 groundwater in the aquifer, spreads out from IW-1 towards PW-1, and forms a plume of  
393 elliptic shape that is high in DIC and low in pH, as illustrated by the simulated spatial  
394 distribution of pH at several time points (Figure 6a and b). The center of the plume has a

395 pH of around 5; the edge of the plume a pH between 5 and 8 caused by dispersion and  
396 buffering of the acidic plume by chemical reactions. Low-pH groundwater arrives first at  
397 MW-3, then at MW-2 and MW-1. At the end of the injection/pumping period (i.e., 156  
398 days after the injection and pumping started), low-pH groundwater arrives at MW-4  
399 (Figure 6c). Once injection/pumping ends, because of the stagnant regional groundwater  
400 flow, the plume remains at the same location, however, the pH value at the center of the  
401 plume increases gradually.

402 Modeling results for groundwater pH match measured data reasonably well, but  
403 some discrepancies are observed (Figure 6c). For example, the pH at MW-4 started to  
404 drop earlier in the model compared to what was observed in the field. Furthermore, at  
405 other well locations the modeled pH does not rebound fast enough to match the recovery  
406 exhibited in the field. A change in dissolved  $\text{CO}_2$  concentration is just one of many  
407 processes that can affect groundwater pH. Other processes include the dissolution of  
408 calcite and plagioclase, and surface complexation. Sensitivity analyses reported later in  
409 this paper illustrate how these processes affect the simulated spatial and temporal  
410 evolution of pH.

411 Figure 7a and b show the modeled spatial distribution of alkalinity at two time-points.  
412 Given the high-DIC concentrations during injection and the simulated pH conditions of  
413 the plume, bicarbonate ( $\text{HCO}_3^-$ ) is the dominant component of total alkalinity, with much  
414 lower concentrations of carbonate ( $\text{CO}_3^{2-}$ ). Hence, the simulated alkalinity values are  
415 taken as the sum of the predicted concentrations of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . Unlike the plume of  
416 DIC and pH, the plume of bicarbonate is shaped like a donut—higher concentrations at

417 the moving edge of the plume but very low concentration in the center, which is caused  
418 by the dominance of carbonic acid ( $\text{H}_2\text{CO}_3^0$ ) once the pH drops below about 6.  
419 The modeled alkalinity values are compared with the measured total alkalinity trends in  
420 Figure 7c. As the plume passes the monitoring wells, the temporal evolution of alkalinity  
421 shows a pulse-like shape initially, followed by a slow recovery after  $\text{CO}_2$  injection and  
422 pumping stopped. This trend is clearly observed at MW-1, MW-2 and MW-3, but less  
423 pronounced at MW-4. Computed and measured breakthroughs of alkalinity are similar at  
424 MW-3, but only show qualitative and not quantitative agreements at other wells. The  
425 major discrepancy between model results and field data is that the computed peak heights  
426 of alkalinity breakthrough curves *increase* for wells further away from IW-1, while the  
427 observed peak heights *decrease* with longer distances away from IW-1. This type of  
428 discrepancy persists for breakthrough curves of most dissolved species, as discussed later.

429 Alkali and alkaline earth metals

430 The increase in carbonate content and the drop of pH trigger the dissolution of  
431 two calcium-bearing minerals: calcite and Ab80An20 (a plagioclase with 80% albite and  
432 20% anorthite). The former dissolves much faster than the latter. The current model  
433 calibration indicates that the amount of calcite is fairly small and would be depleted  
434 shortly after the arrival of acidified water. The dissolution of a limited amount of calcite  
435 creates a donut-shape plume of Ca as shown in Figure 8a and b. Regarding the  
436 breakthrough curves of Ca at the four monitoring wells (Figure 8c), two concentration  
437 trends can be observed: (1) a pulse-like temporal change characterized by a rise in Ca  
438 concentrations upon the arrival of acidified water followed by a decrease in

439 concentrations until the end of CO<sub>2</sub> injection (“pulse period”), and (2) a bounce-back of  
440 Ca concentration levels during the post-injection period ( “recovery period”).  
441 This evolution of Ca at MW-3 was interpreted by Zheng et al. (2015) with a model  
442 concept that encompasses (a) a fast-reacting but limited pool of reactive minerals that  
443 respond quickly to changes in pH and can explain the pulse period, and (b) a slow-  
444 reacting but essentially unlimited mineral pool to yield rising concentrations upon  
445 decreased groundwater velocities after pumping and injection stopped in the recovery  
446 period. This conceptualization combines the initial fast pulsing behavior with transport-  
447 limited kinetic dissolution trends (e.g., Johnson et al., 1998) that are strongly dependent  
448 on groundwater residence times. Under these conditions, rising metal concentrations from  
449 the dissolution of minerals are only noticeable when the groundwater velocity is slow  
450 (relative to the reaction rate) or inversely when reaction rates are fast (relative to the  
451 groundwater velocity). For Ca, the fast-reacting but limited pool is the dissolution of a  
452 limited amount of calcite (~0.009% in volume fraction), and the slow-reacting but  
453 essentially unlimited pool is the dissolution of plagioclase. The close match between the  
454 computed and measured breakthrough curves of Ca at MW-3 support this concept. Model  
455 results at other wells, however, fail to quantitatively reproduce the measured data,  
456 although qualitatively they exhibit similar trends. Similarly to alkalinity, the most  
457 noticeable discrepancy between modeled and measured data is that the computed  
458 breakthroughs at the four monitoring well show increasingly higher peaks with distance  
459 from the injection well (IW-1), during the “pulse period”, whereas measured  
460 breakthroughs at these four monitoring wells show increasingly lower peaks as the plume  
461 moves further away from IW-1.

462 The release of Ca into solution triggers a series of cation exchange reactions that lead to  
463 the increase in concentrations of major elements such as Na, K, Mg, Mn, and trace  
464 elements such Ba, Sr, and Li. This explains why the concentrations of these elements  
465 exhibit trends parallel to Ca (e.g. see Figure 9a for barium as example). Because cation  
466 exchange reactions are fast (relative to mineral dissolution), the temporal evolution of  
467 concentrations for these elements (Sr, Li, Na, K, Mg and Mn; Figures A2 to A7 in ESI) is  
468 quite similar to that of Ca. The best fits of measured data with model results are achieved  
469 for Ba, Sr, Li, and Mg, and the matches between measured and computed values are not  
470 as good for Na, K and Mn. The deviations between measured and computed  
471 concentrations of Ca at wells other than MW-3 are similar to deviations observed for Ba,  
472 Sr, Li, Na, K, Mg and Mn.

473 Iron

474 Measured total Fe concentrations (essentially all Fe(II) within the observed pH range)  
475 exhibit similar spatial and temporal distributions as Ca. However, for Fe, the fast-reacting  
476 (limited) pool is modeled as the desorption of Fe(II) from the surface of  $\text{Fe(OH)}_3(s)$ , and  
477 the slow-reacting (unlimited) pool as the dissolution of iron sulfide. This concept leads to  
478 a fair fit between measured and computed data at MW-3 (Figure 9b). However, the initial  
479 modeled pulse is much narrower than observed, and with a higher peak than the  
480 measured data. This discrepancy may be the result of assuming equilibrium surface  
481 complexation reactions. Surface complexation reactions are typically quite fast, ranging  
482 from days to weeks, such that these reactions can often be treated as an equilibrium  
483 process for the simulation of subsurface systems over the long term. However, in the  
484 present case, this assumption may yield a Fe pulse at MW-3 that is too short in time

485 (lasting only a few weeks). As soon as the injection/pumping stops, the simulated  
486 concentration of Fe increases, which is modeled here with reasonable results (Figure 9b)  
487 by the dissolution of iron sulfide. The pH decrease resulting from the introduction of  
488 CO<sub>2</sub> in the subsurface could also induce a greater rate of microbial Fe(III) reduction (Kirk,  
489 2011; Kirk et al., 2013). This could not be ruled out as another mechanism leading to  
490 increased Fe(II) concentrations in groundwater, also it would not be expected to be the  
491 cause of the initial short-lived Fe(II) pulse observed in the field. It should also be noted  
492 that the modeled and measured Fe breakthrough curves at MW-1, MW-2 and MW-4 only  
493 match qualitatively but not quantitatively.

494 *Silicon*

495 The spatial and temporal evolution of Si (Figure 9c) is similar to that of Ca and Fe.  
496 Therefore, in the base case model, release mechanisms similar to those proposed for Ca  
497 and Fe are used to explain the behavior of Si: the fast-reacting (limited) pool for Si is  
498 driven by Si desorption from Fe(OH)<sub>3</sub>(s) surfaces, and the slow-reacting (unlimited) pool  
499 is represented by the dissolution of plagioclase (Ab<sub>80</sub>An<sub>20</sub>). This concept explains  
500 qualitatively the first “pulse period” and the following “recovery period” exhibited in the  
501 breakthrough curves of Si at MW-1, MW-2 and MW-3, but results in similar departures  
502 as for other species— moving further away from IW-1, the peaks of the computed  
503 breakthrough curves at the four monitoring wells keep increasing, in contrast to the  
504 measured breakthrough peaks, which continue decreasing.

505 *Chromium*

506 Cr appears to behave slightly differently from other metals. The breakthrough of Cr at  
507 MW-3 is similar to that of other elements, i.e. an initial “pulse period” is followed by a

508 “recovery period” after injection stopped (Figure 9d). But such a trend is not observed for  
509 the Cr breakthrough curves at other wells. Cr breakthrough curves at MW-1 and MW-2  
510 only show an initial rising and falling, but no further concentration increase during the  
511 recovery period. Cr concentrations at MW-4 are below the detection limit. The model  
512 that considers desorption of Cr matches somewhat the measured Cr at MW-3 but not the  
513 observed behavior at other wells.

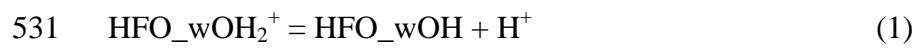
#### 514 **4.2. Sensitivity of model results to input parameters and modeled processes**

515 In this section, we explore the sensitivity of model results to key parameters and reactive  
516 processes, trying to shed light on how these processes affect the modeled concentration  
517 trends of dissolved major and trace elements as a result of the injection of CO<sub>2</sub>-bearing  
518 water. These sensitivity analyses are by no means exhaustive and are only intended to  
519 show the effect of presumed key input parameters (or particular types of reactions) on  
520 model results. To do so, for each sensitivity case, only the model inputs being tested are  
521 varied, while the rest of the parameters and reactions remain the same as in the base-case  
522 model.

523

##### 524 **4.2.1. The impact of surface complexation on modeled pH**

525 Many reactions can affect groundwater pH, including the pH buffering by the dissolution  
526 of calcite (or other carbonate minerals) (e.g. Carroll et al., 2009) and surface protonation  
527 reactions (e.g. Zheng et al., 2009; Zheng et al., 2012; Table A3). Another pH-buffering  
528 surface reaction that was not considered in these earlier studies is the surface  
529 adsorption/desorption of bicarbonate (Appelo et al., 2002). The dominant of these  
530 surface complexation reactions can be written as (Table A3):



533

534 In the base-case model, the volume fraction of calcite was found to be too small for  
535 calcite to buffer pH significantly. Hence, reactions (1) and (2) are the main reactions that  
536 buffer pH. We conducted two sensitivity analyses to illustrate how these two reactions  
537 affect the temporal changes of pH: Model “A” does not consider surface complexation of  
538 bicarbonate and Model “B” considers neither surface protonation nor surface  
539 complexation of bicarbonate. In comparison with the base-case model, Model A leads to  
540 an earlier breakthrough of pH, lower pH values, and slightly higher total dissolved  
541 carbonate concentrations, with increasingly noticeable differences away from MW-1  
542 (Figure 10a and b). Similar but more pronounced differences from the base-case model  
543 are predicted if neither surface protonation nor surface complexation of carbonate is  
544 considered (Model B) (Figure 10c and d). The earlier breakthrough of pH with models A  
545 and B leads to an earlier rise of Ca and trace metals concentrations, which does not fit the  
546 measured data as well as the base-case model. It is however noteworthy to mention that  
547 these observations are based on specific surface complexation reactions and equilibrium  
548 sorption constants (Dzombak and Morel, 1990; Appelo et al., 2002), together with the  
549 assumption that  $\text{Fe(OH)}_3(s)$  is the dominant adsorbent with an amount calibrated based  
550 on sediment titration data (Section 3.4)— Changing any of these model conditions might  
551 change the model results described above.

#### 552 **4.2.2. Sensitivity to calcite volume fraction and dissolution rate**

553 In the geochemical model presented here, the calcite dissolution rate and the abundance  
554 of calcite play the key role in determining the responses of most major and trace elements,  
555 especially during the initial “pulse period” of the breakthrough curve. This is because  
556 alkali and alkaline earth metal are released via cation exchange, which is directly driven

557 by the amount of Ca released by calcite dissolution (in other words, increasing the  
558 amount of calcite in the model enhances the release of Ca and other metals). In this  
559 sensitivity analysis, the calcite effective dissolution rate ( $r$  in Equation A1) was  
560 increased by raising the specific surface area of calcite by two orders of magnitude.  
561 When doing so, the higher calcite dissolution rate has an insignificant impact on pH  
562 (Figure A9 in ESI), but leads to a higher peak value and narrower span of the initial Ca  
563 concentration pulse (Figure 11a and b). The higher dissolution rate also leads to a faster  
564 depletion of calcite. The resulting changes in trace metal (Ba, Mg, Mn, K, Li, Na and Sr)  
565 concentrations (see Figure 11b using Ba as an example) follow the Ca trend, because the  
566 change in Ca concentration is the driving force for the concentration changes in other  
567 trace metals.

568 The current model relies on the dissolution and the subsequent depletion of a limited  
569 amount of calcite to explain the pulse-like behavior in the breakthrough of Ca and some  
570 major and trace elements. In the base case, the volume fraction of calcite was calibrated  
571 yielding a quite a small amount ( $8.6 \times 10^{-5}$ , dimensionless units), which is well below  
572 XRD detection limits. Figure 11c shows model results for a sensitivity analysis with a  
573 calcite volume fraction that is 10 times higher. The higher initial volume fraction of  
574 calcite results in a higher Ca concentration peak, a wider span of the pulse, and also in  
575 higher Ca concentrations during the recovery period. The concentration profiles of alkali  
576 and alkaline earth metals are affected in a similar manner by the increased amount of  
577 calcite because their profiles follow that of Ca (see Figure 11d for Ba as an example).  
578 The higher initial volume fraction of calcite also leads to a much delayed breakthrough of  
579 pH (see Figure A10 in ESI).

580 **4.2.3. Sensitivity to cation exchange capacity (CEC)**

581 The base-case model relies on cation exchange reactions to explain the changes in  
582 concentration of Ba, Mg, Mn, K, Li, Na and Sr. Here we vary the CEC value input in the  
583 model to examine the effect of CEC on the concentration of relevant species. Figure 12a  
584 shows the breakthrough curve of Ca at MW-1 and MW-3 calculated using CEC values  
585 that are either twice as large, or half of the value used in the base-case model. Larger  
586 CEC values result in more Ca residing in exchangeable sites. . . Therefore, the  
587 concentration of Ca in the aqueous phase is lower at larger CEC values (Figure 12a).  
588 Conversely, it is higher at lower CEC values as less Ca is partitioned on exchangeable  
589 sites (Figure 12a). Larger CEC values also mean that exchange sites would retain more  
590 trace metals in the solid phase and therefore lead to lower concentration of trace metals in  
591 aqueous phase, as exemplified with Ba (Figure 12b).

592 **4.2.4. The Effect of Cation Exchange on Iron Concentrations**

593 In the base case, the desorption of Fe from  $\text{Fe(OH)}_3(\text{s})$  surfaces is used to interpret  
594 the initial pulse shown in the breakthrough curve of Fe. One question, however, is  
595 whether Fe could be rather present in exchangeable surface sites, thus whether cation  
596 exchange is rather the process that leads to the increase in Fe concentrations. In order to  
597 test this hypothesis, we conducted a simulation (Model C in Figure 13a) in which Fe(II)  
598 was included as an exchangeable cation and excluded from sorption sites. With this  
599 conceptual model, the release of Fe via cation exchange with Ca is responsible for the  
600 initial pulse of Fe. Figure 13a shows the model results of this simulation, using exchange  
601 equilibrium constants for Fe(II) from Appelo and Postma (1994). In this case, the

602 computed Fe concentrations are much lower than measured concentrations, therefore  
603 suggesting that exchangeable Fe alone does not provide a high enough Fe source.

604

605 **4.3. Enhancing Metal Release Near the Injection Wells**

606 The base-case model and the sensitivity simulations described above assume that  
607 the source of trace elements resides in the aquifer, with Ca release by calcite dissolution  
608 being the driving force on a series of cation exchange reactions. However, one concept  
609 that cannot be completely ruled out is that the top and bottom clay layers bounding the  
610 injection interval could be the source of released trace elements. Because the injection  
611 well is screened beyond the interval of the sandy aquifer, the injected carbonated water  
612 could infiltrate the top and bottom clay layers near the injection well and sweep off some  
613 trace elements therein and carry them into the aquifer. Another possibility is simply that  
614 the clay content of the aquifer near the injection well could be higher than at other  
615 locations due to local heterogeneity. Without resorting to a 3D model, these cases can be  
616 tested by either increasing the cation exchange capacity near the injection well, or by  
617 increasing the calcite volume fraction in this area, as long as the calcite amount remains  
618 low enough to drive more cation exchange (by Ca dissolution) without significantly  
619 affecting pH. For simplicity we chose the latter (Model D in Figure 13b), and increased  
620 the volume fraction of calcite to  $3.5 \times 10^{-4}$  (dimensionless units) within a 4-meter radius  
621 area around the injection well. Note that the total amount of calcite relative the affected  
622 area in the aquifer is still too small to have a noticeable effect on the magnitude of pH  
623 drop. Because the amount of metals loaded onto exchangeable sites is large enough to  
624 account for the observed released concentrations, the amount of exchangeable Ca

625 produced by calcite dissolution is the main factor limiting the release of these metals.  
626 Therefore, increasing the volume fraction of calcite near the injection well is equivalent  
627 to increasing the source of metals at this location. Figure 13b shows the model results for  
628 Ba when applying this concept (similar results for Ca are shown in Figure A11 in ESI).  
629 In comparison to the base-case model, this case leads to overall better matches of the  
630 measured data at MW-1, MW-2 and MW-4, but to a somewhat worse fit of the data at  
631 MW-3. Although this concept leads to slightly worse fit of pH breakthrough (Figure A12  
632 in ESI), the overall better match between measured and simulated data for this case  
633 suggests that the top and bottom clay formations near the injection well, or a generally  
634 increased amount of exchangeable metals at this location (from heterogeneous  
635 distribution of clay minerals), could explain the observed decreasing pulse intensity of  
636 dissolved metals concentrations away from the injections well.

637 **5. Summary and Conclusions**

638 A controlled release field test was conducted with an extensive water quality  
639 monitoring program during and after the injection of carbonated water, to mimic the  
640 effect of a potential leak of CO<sub>2</sub> from a deep storage site to a shallow aquifer. This field  
641 test provided a great opportunity to evaluate and model potential reactive mechanisms  
642 responsible for the release of metals in groundwater and strengthen our understanding of  
643 the hydrogeological and chemical processes relevant to potential impacts on groundwater  
644 quality at CO<sub>2</sub> geological sequestration sites. Reactive transport models have been  
645 developed to interpret the concentration changes observed at four monitoring wells  
646 during the field test. The breakthrough curves of major and trace elements at these  
647 monitoring wells show a pulse-like change during the carbonated water injection period,

648 followed by slowly increasing concentration levels during the post-injection period. A  
649 reasonable match between model results and field data indicate that this trend can be  
650 interpreted with a conceptual model that considers (a) a fast-reacting but limited pool of  
651 reactive minerals that respond quickly to changes in pH, to explain the pulse-like changes  
652 in metal concentrations, and (b) a slow-reacting but essentially unlimited mineral pool  
653 that yields rising concentrations upon decreased groundwater velocities after pumping  
654 and injection stopped.

655 For Ca, Ba, Mg, Mn, K, Li, Na and Sr, a reasonable agreement of model results with  
656 observed data was obtained when the fast-reacting but limited pool was modeled as  
657 calcite dissolution and Ca-driven cations exchange reactions, and the slow-reacting but  
658 unlimited pool was modeled as the dissolution of plagioclase and longer-term Ca-driven  
659 cation exchange. For Fe, best results were obtained when modeling fast desorption from  
660 iron hydroxides ( $\text{Fe(OH)}_3(s)$ ) together with slow dissolution of amorphous iron sulfide;  
661 similarly, good results for Si were obtained by considering fast desorption of Si from iron  
662 hydroxides concomitant with slow dissolution of plagioclase. In our modeling study,  
663 small finite amounts of fast-dissolving calcite were assumed to be the source of the initial  
664 Ca pulse, although it should be noted that finite amounts of Ca and/or Mg desorbing from  
665 organics or hydroxides would be expected to yield a similar pulse behavior.

666 A series of sensitivity analyses demonstrated that the initial calcite volume  
667 fraction, calcite dissolution rate and CEC value of the sediments are critical parameters to  
668 model the temporal changes in concentrations of Ca, Ba, Mg, Mn, K, Li, Na and Sr. The  
669 regional groundwater flow affects not only the time of breakthrough but also the  
670 concentration levels during the post-injection period. This is because the groundwater

671 residence time, which is inversely proportional to flow rate, has a direct effect on extent  
672 of reaction, thus slow mineral dissolution becomes noticeable only under slow flow rates  
673 (large residence times).

674 The most noticeable discrepancy between modeled and observed breakthrough  
675 curves is that computed breakthroughs at the four monitoring wells show increasing pulse  
676 peak concentrations at wells further away from the injection well (IW-1). In contrast, the  
677 observed breakthrough at four monitoring wells show the reverse behavior, with  
678 decreasing peak heights of breakthrough curves at larger distances away from IW-1. This  
679 discrepancy is reduced when chemical spatial heterogeneity is considered in the model.  
680 Essentially, the observed decreasing pulse peaks away from the injection well can be  
681 reproduced by modeling a larger initial source of Ca and/or trace elements near the  
682 injection well than farther away from it. This source term could result of carbonated water  
683 contacting clays (such as the top and bottom aquitards near the injection well), or simply  
684 a more abundant fast-release source of Ca (calcite, or possibly Ca-adsorbing organic  
685 matter and/or hydroxides) near the injection well. Overall, this study further demonstrates  
686 the importance of thorough field geochemical and hydrological characterization for  
687 environmental risk assessments, covering both the CO<sub>2</sub> injection and post-injection time-  
688 periods at CO<sub>2</sub> sequestration sites, and considering the important effect of groundwater  
689 flow rate (residence time) on the magnitude of released metal concentrations.

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697

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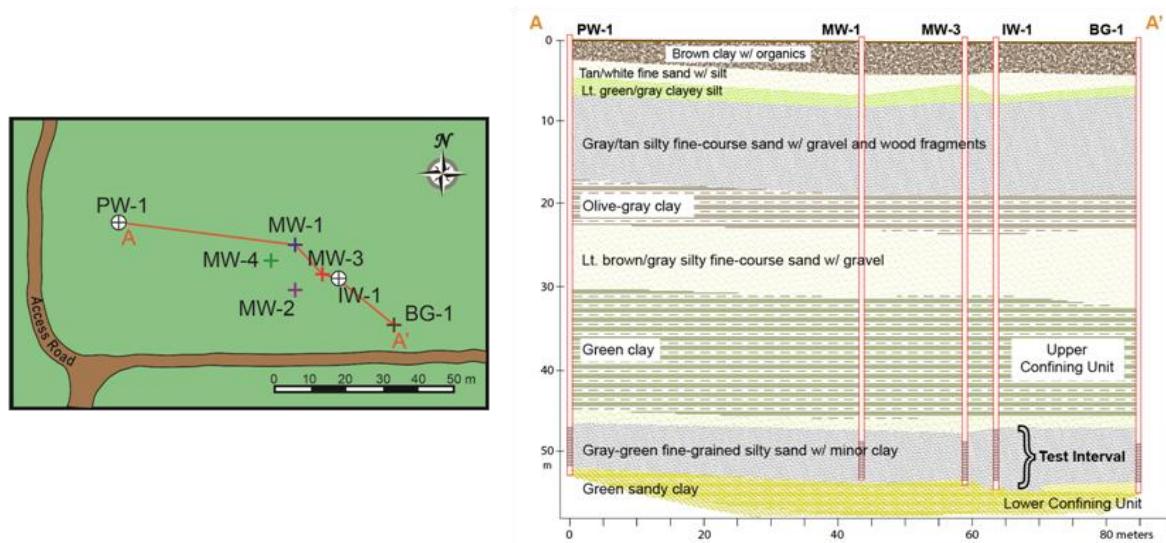
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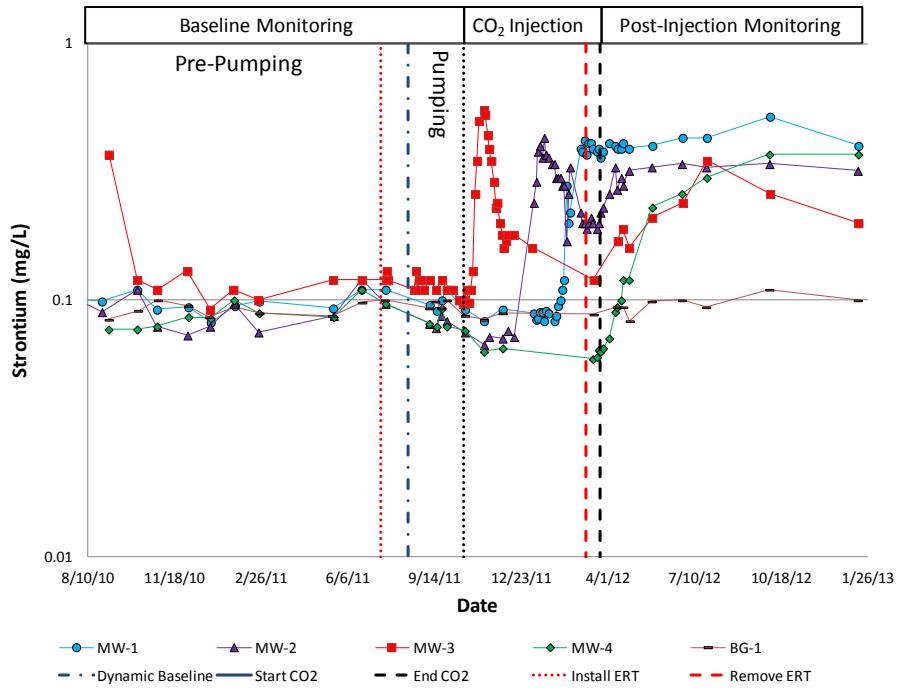
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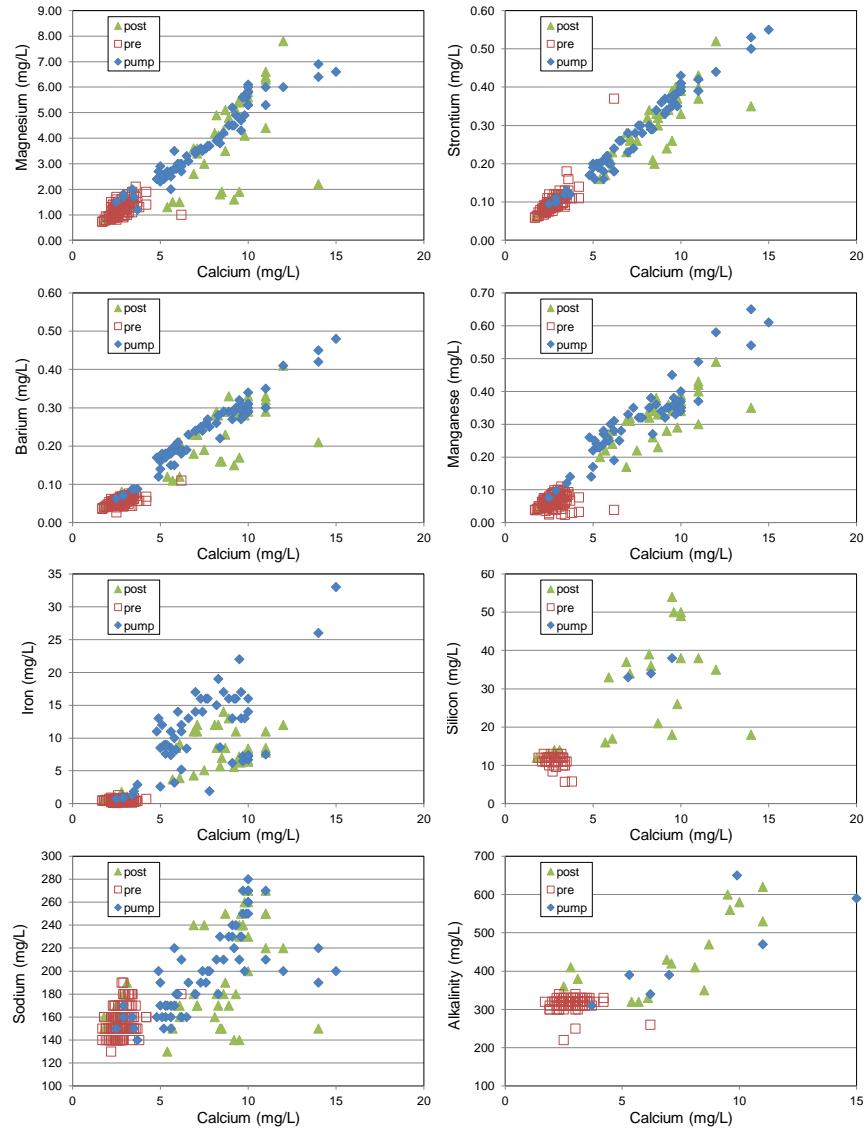
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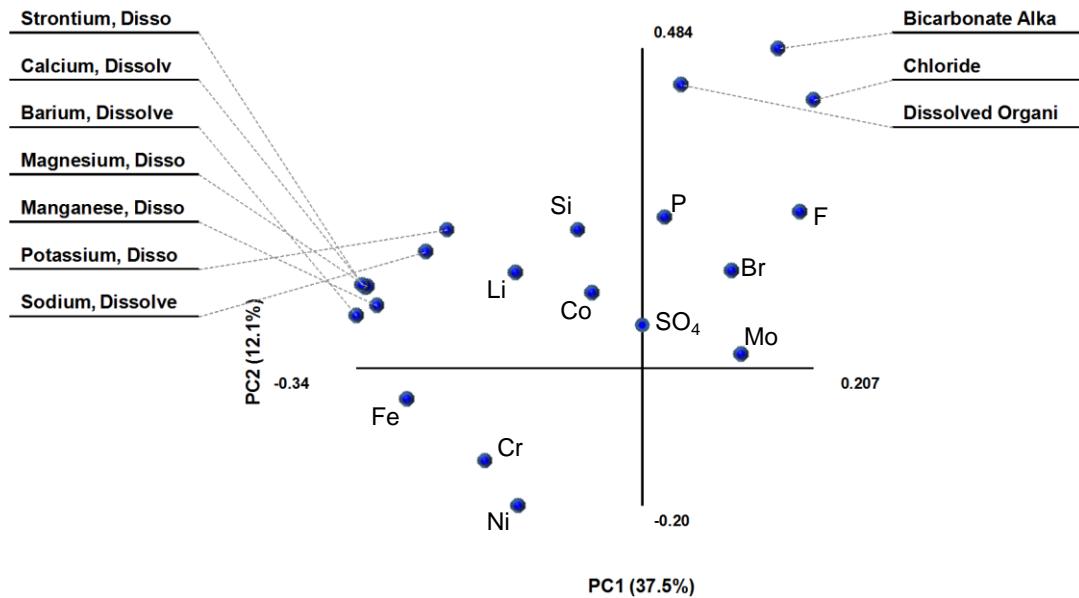
**Figure 1.** Schematic showing plan view of the well field (left) and geologic cross-section A-A' (right). Well abbreviations refer to the pumping well (PW), the injection well (IW), the monitoring wells (MW) and the background well (BG) used to characterize the pristine groundwater composition not affected by CO<sub>2</sub> injection.



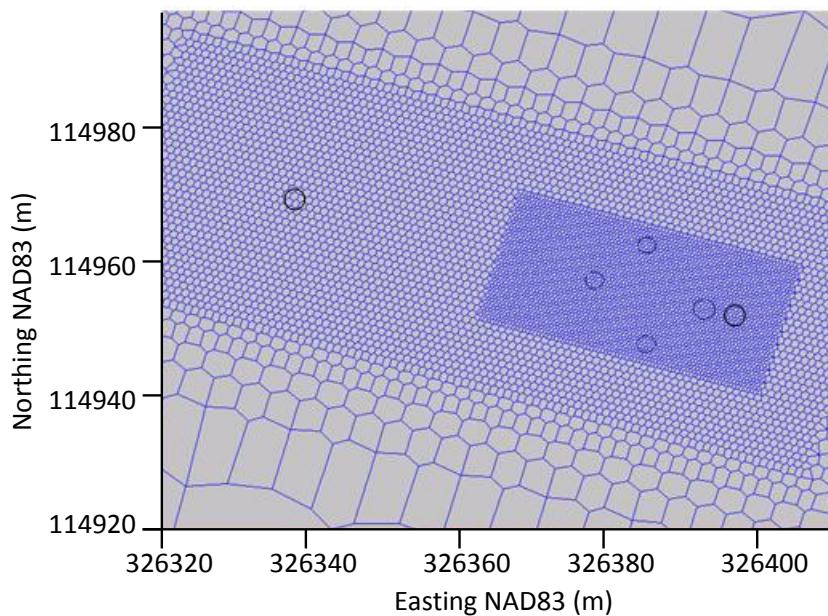
**Figure 2.** Strontium concentrations in groundwater illustrating the trend of Type III metals mobilized by the carbonation of groundwater, with highest peak concentrations observed at MW-3. Trends of pH changes are shown in Figure 6 for all monitoring wells.



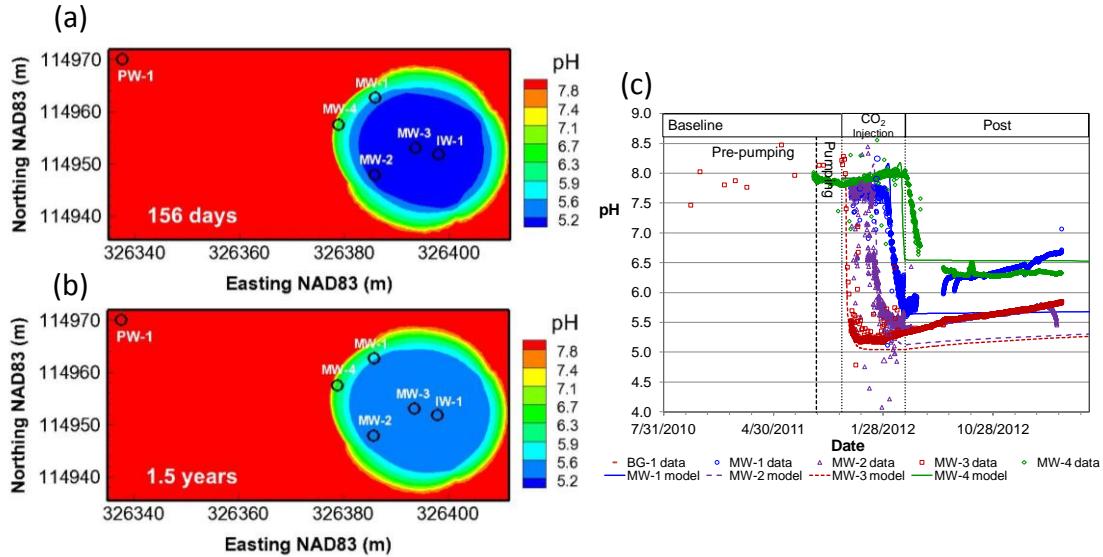
**Figure 3.** Correlation plots between the dissolved concentrations of Ca, other metals, and alkalinity. A clear correlation is seen with the data collected during injection (labeled as “pump”); some of the post-pumping data points (labeled as “post”) appear to show a different trend.



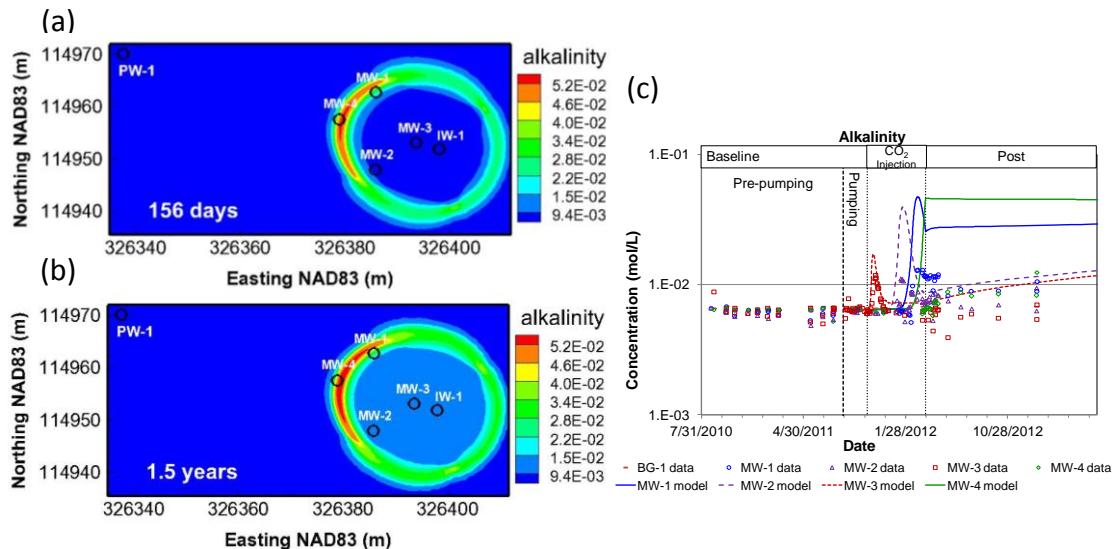
**Figure 4.** Principal Component Analyses plot of loadings for different elements (variables). The 10 top variables are underlined. Points sitting together have common denominators, hence possibly a similar source term and/or release mechanism.



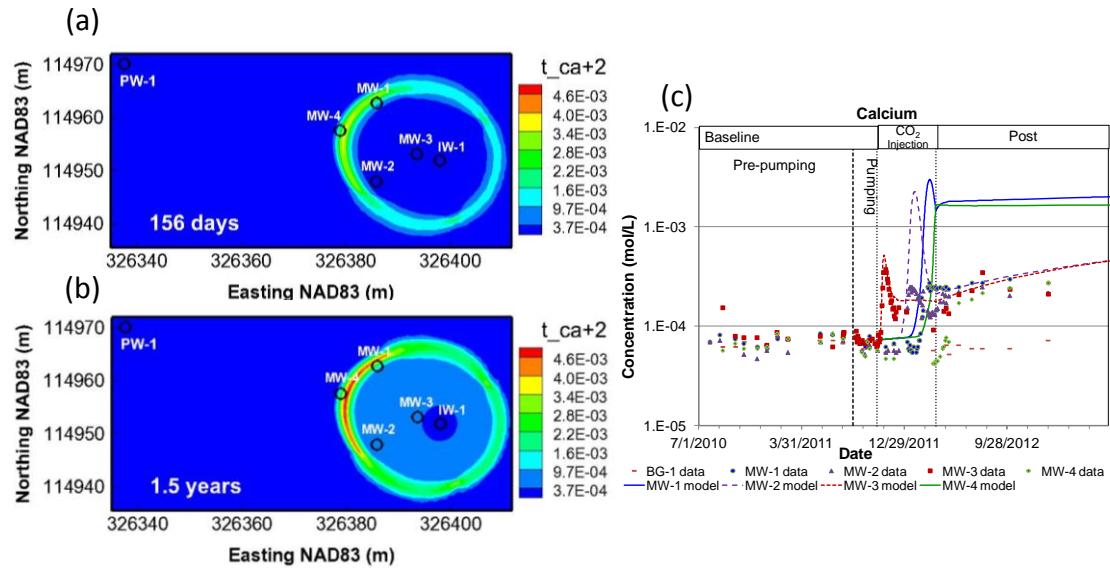
**Figure 5.** Close-up view of the model discretization in the area of interest. The centers of the circles correspond to the positions of wells.



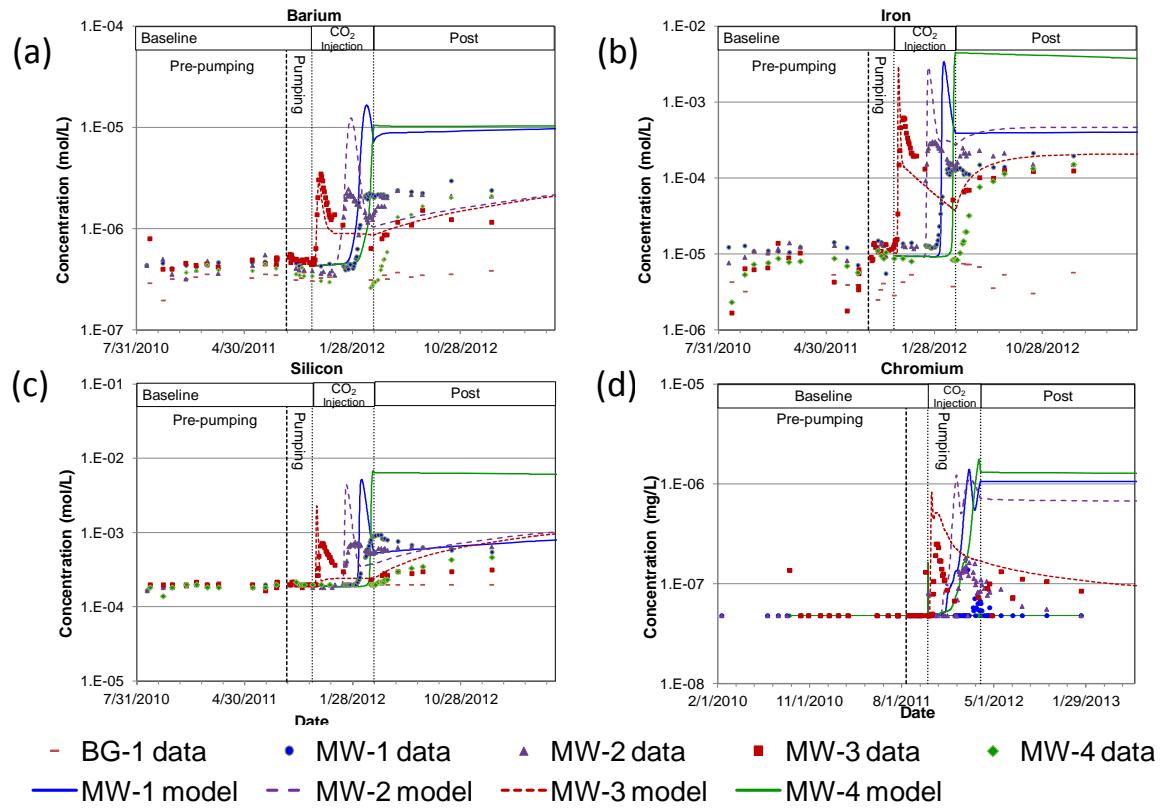
**Figure 6.** Simulated spatial distributions of pH at 156 days (a) and 1.5 years (b) , and Simulated and observed breakthrough curves of pH (c) at monitoring wells MW-1, MW-2, MW-3, and MW-4.



**Figure 7.** Simulated spatial distributions of alkalinity at 156 days (a) and 1.5 years (b) , and simulated and observed breakthrough curves of alkalinity (c) at monitoring wells MW-1, MW-2, MW-3, and MW-4.

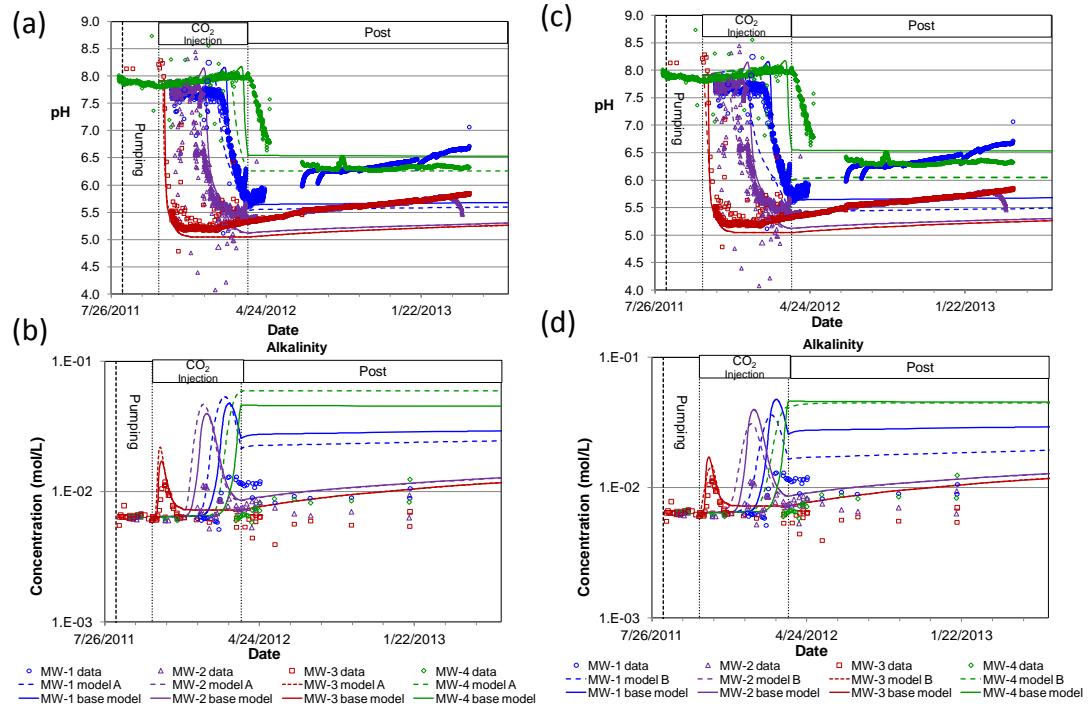


**Figure 8.** Simulated spatial distributions of total dissolved Ca (“t\_ca+2”) at 156 days (a) and 1.5 years (b) after the beginning of CO<sub>2</sub> injection, and Ca breakthrough curves (c) at monitoring wells MW-1, MW-2, MW-3, and MW-4.

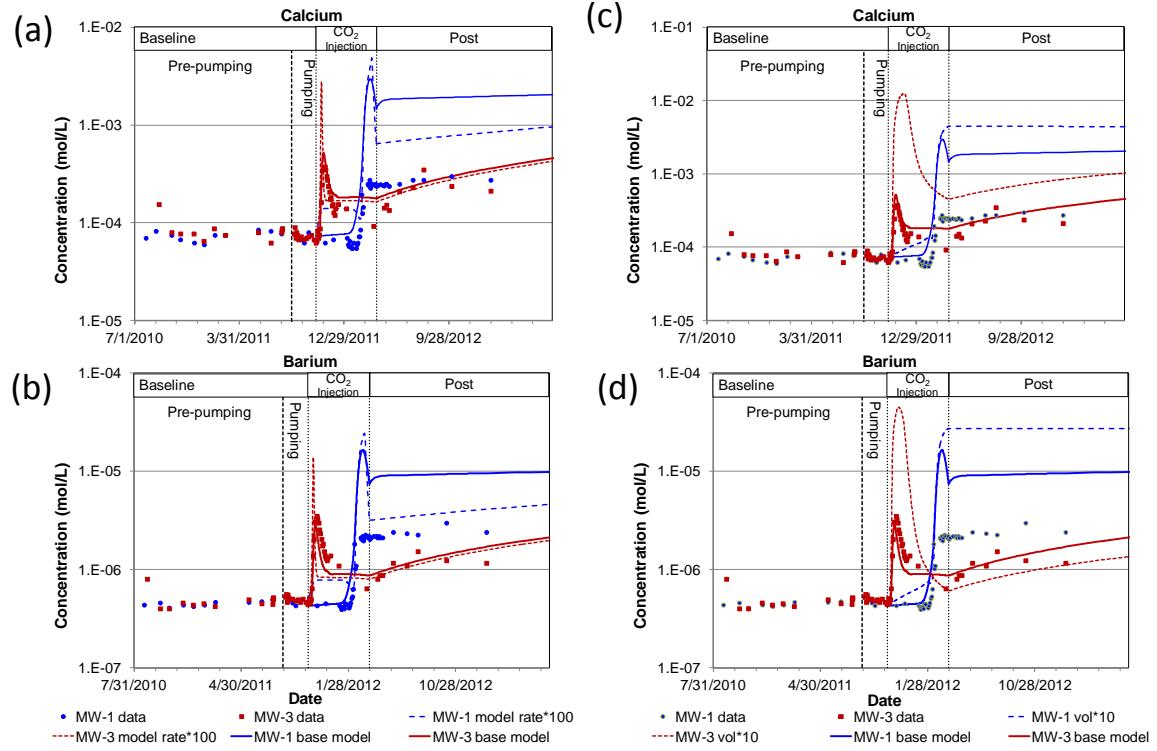


**Figure 9.** Simulated and observed breakthrough curves of total Ba (a), Fe (b), Si (c), and Cr (d)

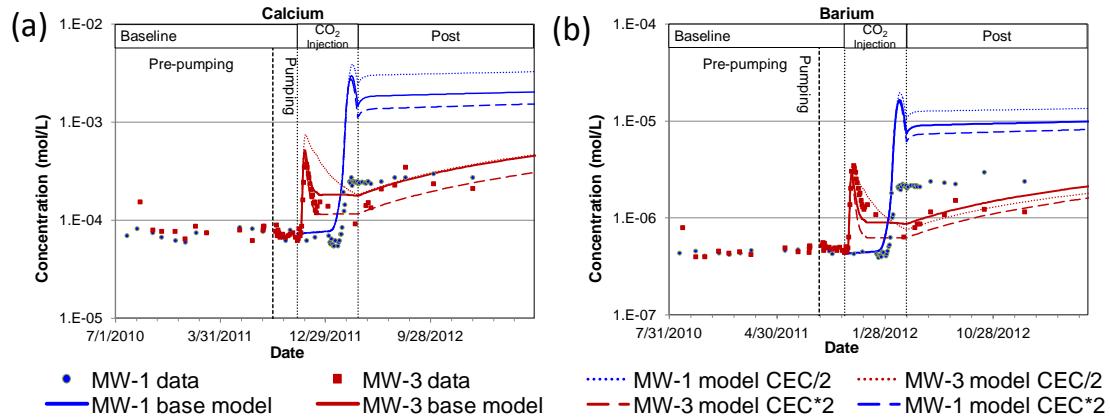
concentrations at monitoring wells MW-1, MW-2, MW-3, and MW-4.



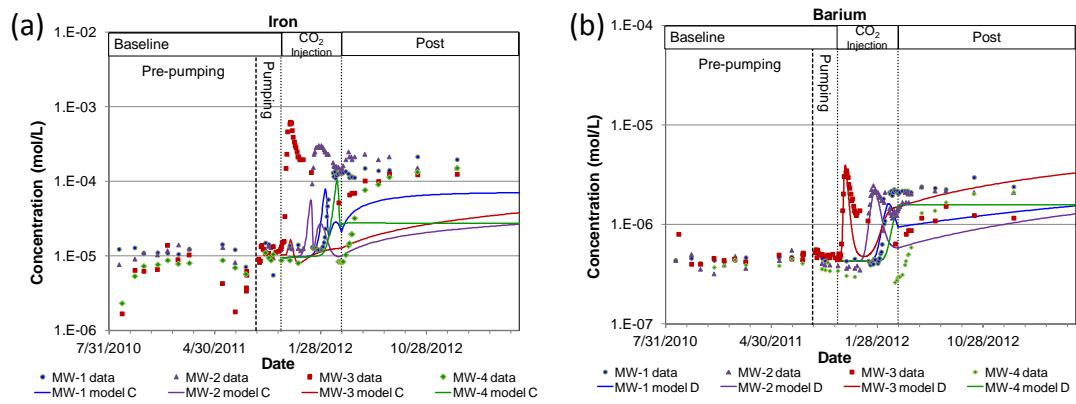
**Figure 10.** Simulated and observed breakthrough curves at MW-1, MW-2, MW-3 and MW-4, comparing the base-case model with Model A (no  $\text{HCO}_3^-$  surface complexation) for pH (a) and alkalinity (b), and with Model B (no  $\text{H}^+$  and no  $\text{HCO}_3^-$  surface complexation) for pH (c) and alkalinity (d).



**Figure 11.** Computed breakthrough curves at MW-1 and MW-3 for Ca (a) and Ba (b) after increasing the specific surface area of calcite (Equation A1) by two orders of magnitude, and for Ca (c) and Ba (d) after increasing the initial calcite volume fraction by a factor of ten relative to the base-case model.



**Figure 12.** Sensitivity of the breakthrough curves of Ca (a) and Ba (b) at MW-1 and MW-3 to CEC value, while testing CEC values that are either twice as large (“CEC\*2”) or half of the value (“CEC/2”) initially used in the base-case model.



**Figure 13.** Model sensitivity to different modeling concepts: (a) Fe at monitoring wells MW-1, MW-2, MW-3, and MW-4 for a simulation (Model C) in which Fe(II) is included as an exchangeable cation while excluding Fe desorption from  $\text{Fe(OH)}_3(s)$  surfaces (compare with Figure 9b); (b) Ba at monitoring wells MW-1, MW-2, MW-3, and MW-4 computed with a model (Model D) considering increased trace metal release in the vicinity of the injection well (MW-3) (compare with Figure 9a).