Impacts of Elevated Dissolved CO_2 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_2 geological sequestration imposes on the environment is the impact of potential CO_2/brine leakage on shallow groundwater. The reliability of reactive transport models predicting the response of groundwater to CO_2 leakage depends on a thorough understanding of the relevant chemical processes and key parameters affecting dissolved CO_2 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_2-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_2 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_2 was injected. In

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

1. Introduction

Ever since the concept of CO_2 geologic storage was proposed about two decades ago, many studies have been undertaken to assess hydrological, geochemical and mechanical processes affecting deep injection and containment of CO_2 in storage reservoirs. Meanwhile, as part of environmental risk assessments for CO_2 storage sites, studies have also been undertaken to assess the impacts of potential CO_2 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_2
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_2 leakage. Most recently, reactive transport models have been used to
62 predict potential long-term change in aquifer in response to CO_2/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_2 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_2
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_2 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_2. Several field tests
88 have been conducted to further enhance our understanding of potential impacts of CO_2
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_2 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_2 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

100 days. As reported in Peter et al. (2012), CO_2 was injected through 3 wells for a period of 10 days into an aquifer at 18 m depth in Northeast Germany. All these tests involved an injection of CO_2 or CO_2-bearing water into the aquifer, and the monitoring of changes in water composition via monitoring wells downstream of the injection point. In general, observations made in field tests are largely consistent with those from laboratory tests in terms of concentration increases for major and trace elements, but there are two noticeable differences: first, the level of concentration changes observed in the field is typically much lower than in the laboratory. For example, an increase in major and trace element concentrations of 1 to 3 orders of magnitude has been observed in the laboratory compared to field tests, which never show an increase greater than one order of magnitude (i.e., 20% to 700%). Secondly, concentration increases in trace elements, especially for elements of environmental concern such as As, Pb, Ba, Cd, are more frequently observed in laboratory than in field tests.

A thorough understanding of key physical and chemical processes and related parameters is critical for building a reliable model to predict long term changes in aquifer response to CO_2/brine leakage. Researchers have postulated based on laboratory-scale experimental results (e.g. Lu et al., 2010), the simulation of laboratory-scale data (e.g. Humez et al., 2011; Viswanathan et al., 2012; Zheng et al., 2015b) or field tests (e.g. Zheng et al., 2012; Trautz et al., 2013) that a number of chemical processes are potentially responsible for the mobilization of trace elements. These include the dissolution of carbonates (e.g., Kharakha et al., 2006; McGrath et al., 2007; Lu et al., 2010), sulfides (e.g., Wang and Jaffe, 2004; Zheng et al., 2009; Apps et al., 2010) and iron oxyhydroxide minerals (e.g., Kharaka et al., 2006, 2009), as well as surface reactions such as adsorption/desorption

(Viswanathan et al., 2012) and ion exchange (Kharaka et al., 2006, 2009; Zheng et al., 2009; Apps et al., 2010; Zheng et al., 2012; Cahill et al., 2014). The degree to which these reactions contribute to water quality impacts depends on the specific aqueous chemistry and aquifer mineralogy for a given system. Field testing integrated with reactive transport modeling provides an effective and reliable way to identify reactions and parameters that are needed to build reliable simulation tools for risk assessments of CO_2 sequestration.

A comprehensive longer-term field study involving the controlled release of groundwater containing dissolved CO_2 was initiated in 2011 to investigate potential groundwater impacts in Mississippi, USA (Trautz et al., 2013). Injection of dissolved CO_2 lasted approximately 5 months followed by an extended phase of post-injection groundwater monitoring. The experiment involved extensive laboratory and field characterization of groundwater and sediments, an innovative fluid-delivery system, hydrologic monitoring, and geophysical monitoring for remote detection of dissolved CO_2. Trautz et al. (2013) presented the data from this test at one of the monitoring wells, including preliminary results of reactive transport simulations, and Varadharajan et al. (2013) reported laboratory test results for aquifer sediments collected while drilling wells for this test. In this paper, we present reactive transport simulations conducted to interpret groundwater monitoring data at the site over a significantly longer time frame than initially reported by Trauntz et al. (2013), with the goal to elucidate key chemical processes and parameters that could affect observed changes in long-term dissolved metal concentrations in groundwater at this test site.

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_2 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_2 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_2 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_2 injection (pumping continues)	18-Oct-2011	23-Mar-2012	5	MW, BG wells
Post-CO_2 injection	23-Mar-2012	15-Jan-2013	10	MW, BG wells

A decrease in groundwater pH by 1.5–3 units was observed at nearby monitoring wells as the dissolved CO_2 plume migrated through the sandy aquifer. In general, four groups of metals exhibiting different trends in metal/solute concentration changes (with limited exceptions) were observed during the test: (1) solutes below detection/background concentration levels (Type I: Al, Sb, As, Be, Cd, Cu, Pb, Hg, Ag, Tl, Zn, P, Se, Br^-, Cl^-, NO_2^-, NO3-, SO_4^{2-}, HS^-), (2) metals potentially leaching out of geophysical probes employed in the field experiment (Type II: Cr, Co Ni), (3) metals displaying an apparent concentration increase upon injection of CO_2 (Type III: Ba, Ca, Fe, Li, Mg, Mn, K, Si, Na, and Sr) and (4) those showing a concentration decrease (Type IV: Mo and F) after exposure to dissolved CO_2. It should be noted that none of the metal concentrations measured during the controlled release experiment exceeded primary drinking water standards (i.e., maximum contaminant levels) established by the U.S. Environmental Protection Agency under the Clean Water Act.

2.2. Trend analyses of observed metal concentrations

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

Here, we further evaluate the groundwater quality response to carbonation using the *full* set of analytical data collected *before* (13 months), *during* (5 months), and *after* the release of CO_2 (10 months after turning off the injection pump). Accordingly, the monitoring data were classified into three groups: *pre*-, *during*, and *post*-injection, with the '*pre*-injection' data defined as analyses before the arrival of the carbonated plume at specific wells, measured as the start of the pH decrease at these wells. Thus, these data may include samples that were technically sampled during the injection period but prior 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_2 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_2
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^{+2} 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_2 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_2
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

3. Groundwater Flow and Geochemical Model Development

The reactive transport models in this paper focus on the Type (III) metals/metalloids discussed earlier, because the increasing dissolved concentration of these metals upon exposure to CO_2-saturated water is obviously of more potential concern than the decreasing or un-detectable concentrations of the other metals. The simulations were conducted with TOUGHREACT V2 (Xu et al., 2011), a numerical model that was developed by introducing reactive chemistry into the existing framework of a non-isothermal multi-phase multi-component fluid and heat flow simulator, TOUGH (Pruess et al., 1999).

3.1. Model domain and discretization

Because the aquifer was found to be fairly homogeneous in the vertical direction, a 2-D planar (X-Y) model was employed. The spatial domain of the groundwater flow covers an area of about 500 m × 500 m. An area of 40 m × 100 m was finely discretized with a 1-m grid size. Areas of 20 m× 40 m surrounding the injection well and monitoring wells have even finer gridding with a 0.5-m grid size (Figure 5). A honeycomb mesh 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 1.45×10^{-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 1.65×10^{-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 1.55×10^{-11} m^2. The storativity used in the model was
296 taken as 0.00023, which was converted to a pore compressibility of 3.8×10^{-9} Pa^{-1}
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 ϕ	0.3

Permeability [m^2]	1.55×10-11
Hydraulic conductivity (m/day)	13.4
Pore compressibility (Pa^{-1})	3.8×10-9
Average molecular diffusion coefficient (m^2/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_2 pressure (P_{CO2}) of 3.8 bar,
313 corresponding to full saturation of the water with CO_2 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	7.10×10^{-5}	Zn	2.14×10^{-7}
Al	4.45×10^{-6}	Li	6.97×10^{-6}	S(-2)	3.70×10^{-5}
Ba	4.07×10^{-7}	Mg	5.35×10^{-5}	Cr	4.81×10^{-8}
Br	8.27×10^{-7}	Mn	1.16×10^{-6}	Se	7.00×10^{-9}
Ca	7.34×10^{-5}	Mo	4.41×10^{-8}	As	9.22×10^{-9}
Cd	8.45×10^{-10}	Na	6.70×10^{-3}	N(+5)	1.67×10^{-4}
Cl	7.31×10^{-4}	Ni	3.41×10^{-8}	Acetic acid (aq)	5.31×10^{-5}
Co	9.67×10^{-9}	Pb	9.65×10^{-10}	Methane(aq)	9.87×10^{-6}
Cu	1.73×10^{-8}	S(+6)	1.02×10^{-5}	Ethane(aq)	2.51×10^{-5}
F	2.40×10^{-5}	Sb	1.33×10^{-8}	Hg	3.49×10^{-10}
Fe(II)	4.00×10^{-6}	Si	1.75×10^{-4}	Fe(III)	3.46×10^{-6}
C(+4)	6.22×10^{-3}	Sr	1.13×10^{-6}	O_2(aq) #	1.08×10^{-74}
P	3.18×10^{-6}	Na	6.70×10^{-3}		

324 # Computed from redox couple HS^-/SO_4^{-2}

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 $Fe(OH)_3(s)$) is the adsorbent. The reaction
332 constants for surface complexation of H+ 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, $Fe(OH)_3(s)$ and amorphous iron sulfide (mackinawite, FeS_m),
337 in addition to major aquifer minerals such as quartz, K-feldspar and plagioclase (Table 4).
338 The amount of iron sulfide (FeS_m) was estimated from selective extractions (~0.02
339 vol%), and the amount of $Fe(OH)_3(s)$ 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 ^{o}C)	Potential Secondary Minerals allowed to form	logK(25^{o}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
$Fe(OH)_3(s)$	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^+ 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^+ adsorption occurs dominantly
369 onto ferric iron (oxy)hydroxides (here modeled as ferrihydrite in the form of $Fe(OH)_3(s)$).
370 Using these data, the volume fraction of $Fe(OH)_3(s)$ 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_2 at the surface and then
389 injected through IW-1. The dissolved CO_2 dissociates into bicarbonate and protons (CO_2
390 + $H_2O \rightleftharpoons HCO_3^- + H^+$), 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 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 (HCO_3^-) is the dominant component of total alkalinity, with much
414 lower concentrations of carbonate (CO_3^{-2}). Hence, the simulated alkalinity values are
415 taken as the sum of the predicted concentrations of HCO_3^- and 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 ($H_2CO_3^0$) 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 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_2 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 $Fe(OH)_3(s)$, 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_2 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 $Fe(OH)_3(s)$ surfaces, and the slow-reacting (unlimited) pool
499 is represented by the dissolution of plagioclase (Ab80An20). 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_2-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):

531 $HFO\_wOH_2^+ = HFO\_wOH + H^+$ (1)

532 $HFO\_wCO_2H + H_2O \rightleftharpoons HFO\_wOH + HCO_3^- + H^+$ (2)

533

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

4.2.2. Sensitivity to calcite volume fraction and dissolution rate

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

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

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

4.2.3. Sensitivity to cation exchange capacity (CEC)

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

4.2.4. The Effect of Cation Exchange on Iron Concentrations

In the base case, the desorption of Fe from $Fe(OH)_3(s)$ surfaces is used to interpret the initial pulse shown in the breakthrough curve of Fe. One question, however, is whether Fe could be rather present in exchangeable surface sites, thus whether cation exchange is rather the process that leads to the increase in Fe concentrations. In order to test this hypothesis, we conducted a simulation (Model C in Figure 13a) in which Fe(II) was included as an exchangeable cation and excluded from sorption sites. With this conceptual model, the release of Fe via cation exchange with Ca is responsible for the initial pulse of Fe. Figure 13a shows the model results of this simulation, using exchange 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 3.5×10^{-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_2 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_2 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 ($Fe(OH)_3(s)$) 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 ofcarbonated 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_2 injection and post-injection time-
688 periods at CO_2 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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877 **Appendix A**

878 Table A1. List of aqueous complexes used in the model and log(*K*)'s for reactions that

879 are written with the primary species listed the first column

880

Primary species	Aqueous complex	logK(25 °C)	Aqueous complex	logK(25 °C).	Aqueous complex	logK(25 °C).	Aqueous complex	logK(25 °C).
H^+	ClO_2^-	23.107	$CaCO_3$(aq)	7.009	$FeOH^{+2}$	2.205	$Mg_4(OH)_4^{+4}$	39.758
H_2O	HSO_5^-	17.29	$CaCl^+$	0.297	$FeSO_4$(aq)	-2.2	$MgOH^+$	11.681
AlO_2^-	$S_2O_3^{-2}$	133.549	$CaCl_2$(aq)	0.654	$FeSO_4^+$	-1.917	$MgSO_4$(aq)	-2.22
Ba^{+2}	SO_3^{-2}	46.625	$CaHCO_3^+$	-1.043	H_2O_2(aq)	16.626	$Mn_2(OH)^{3+}$	23.9
Ca^{+2}	$Al(SO_4)_2^-$	-27.104	$CaOH^+$	12.834	H_2SO_4(aq)	1.021	$MnCl^+$	0.143
Cl^-	$Al_{13}O_4(OH)_{24}$	-189.919	$CaSO_4$(aq)	-2.1	H_2Se(aq)	-3.807	$MnCl_3^-$	0.772
Fe^{+2}	$Fe_{13}O_4(OH)_{24}$	58.85	$Fe(CO_3)_2^{-2}$	13.498	$HAlO_2$(aq)	-6.596	$MnHCO_3^+$	-0.442
HCO_3^-	$Al_2(OH)_2^{+4}$	-36.717	$Fe(OH)_3^-$	31	$HFeO_2$(aq)	12.021	MnO(aq)	22.203
K^+	$Al_3(OH)_4^{+5}$	-52.731	$Fe(OH)_4^{-2}$	46	$HFeO_2^-$	29.202	MnO_2^{-2}	48.28
Li^+	$Al_2(OH)_2CO_3^+$	-38.721	$Fe(SO_4)^{2-}$	-3.214	$HMnO_2^-$	34.796	MnO_4^-	20.219
Mg^{+2}	$Al_3(OH)_4HCO_3$	-58.025	$Fe_2(OH)_2^{+4}$	2.95	$HS_2O_3^-$	131.867	$MnOH^+$	10.62
Mn^{+2}	$Fe_2(OH)_2CO^{3+}$	0.627	$Fe_3(OH)_4^{+5}$	6.3	HSO_4^-	-1.975	$MnSO_4$(aq)	-1.903
Na^+	$Fe_3(OH)_4HCO_3$	0.986	$FeCO_3$(aq)	4.879	KCl(aq)	2.541	$NaCO_3^-$	9.814
SO_4^{-2}	AlO^+	-11.857	$FeCl^+$	0.165	$KHSO_4$(aq)	1.502	NaCl(aq)	0.782
SiO_2(aq)	Al^{+3}	-22.199	$FeCl^{+2}$	-1.475	KOH(aq)	14.44	$NaHCO_3$(aq)	-0.149
Sr^{+2}	$AlOH^{+2}$	-17.2	$AlCl^{+2}$	-21.685	KSO_4^-	-0.875	NaOH(aq)	14.206
Zn^{+2}	$AlSO_4^+$	-25.214	$FeCl_2$(aq)	8.181	LiCl(aq)	1.517	$NaSO_4^-$	-0.696
HS^-	$BaCO_3$(aq)	7.691	$FeHCO_3^+$	-1.47	LiOH(aq)	13.65	OH^-	13.991
Fe^{+3}	$BaCl^+$	0.503	FeO(aq)	20.412	$LiSO_4^-$	-0.77	$SrCO_3$(aq)	7.47
O_2(aq)	$BaHCO_3^+$	-1.012	MgO(aq)	24.491	$MgCO_3$(aq)	7.356	$SrCl^+$	0.253
	$BaOH^+$	13.502	CaO(aq)	24.851	$MgCl^+$	0.139	$SrHCO_3^+$	-1.226
	CO_2(aq)	-6.341	FeO^+	5.652	$MgHCO_3^+$	-1.033	$SrOH^+$	13.303
	CO_3^{-2}	10.325	FeO_2^-	21.618	$FeOH^+$	9.315	$SrSO_4$(aq)	-2.3

881

882 Table A2. Cation exchange reactions and selectivity coefficients, using the Gaines-
883 Thomas convention (Appelo and Postma, 1994)

Cation exchange reaction	$K_{Na/M}$
$Na^+ + X\text{-}H = X\text{-}Na + H^+$	1
$Na^+ + X\text{-}K = X\text{-}Na + K^+$	0.2
$Na^+ + 0.5X\text{-}Ca = X\text{-}Na + 0.5Ca^{+2}$	0.4
$Na^+ + 0.5X\text{-}Mg = X\text{-}Na + 0.5Mg^{+2}$	0.45
$Na^+ + 0.5X\text{-}Ba = X\text{-}Na + 0.5Ba^{+2}$	0.35
$Na^+ + 0.5X\text{-}Mn = X\text{-}Na + 0.5Mn^{+2}$	0.55
$Na^+ + 0.5X\text{-}Sr = X\text{-}Na + 0.5Sr^{+2}$	0.35
$Na^+ + X\text{-}Li = X\text{-}Li + Li^+$	1.1

884

885 Table A3. Surface complexation reactions and surface complexation constants (logK) on
886 ferrihydrite (double diffuse layer model) (Dzomback and Morel, 1990; Appelo et al.,
887 2002; Jordan et al., 2007)

Surface complexation	logK
$HFO\_sOH_2^+ = HFO\_sOH + H^+$	-7.29
$HFO\_wOH_2^+ = HFO\_wOH + H^+$	-7.29
$HFO\_sO^- + H^+ = HFO\_sOH$	8.93
$HFO\_wO^- + H^+ = HFO\_wOH$	8.93
$HFO\_sOFe^+ + H_+ = HFO\_sOH + Fe^{+2}$	0.95
$HFO\_wOFe^+ + H^+ = HFO\_wOH + Fe^{+2}$	2.98
$HFO\_wOFeOH + 2H^+ = HFO\_wOH + Fe^{+2} + H_2O$	11.55
$HFO\_wCO_2^- + H_2O = HFO\_sOH + HCO_3^-$	-2.45
$HFO\_wCO_2H + H_2O = HFO\_sOH + HCO_3^- + H^+$	-10.4
$HFO\_sH_3SiO_4 + 3H_2O = HFO\_sOH + SiO2(aq)$	-2.75
$HFO\_sH_2SiO_4^- + 3H_2O + H^+ = HFO\_sOH + SiO2(aq)$	1.4

$HFO\_sOCrOH^{+} + 2H^{+} = HFO\_sOH + Cr^{+3} + H_2O$ 2.98

888

889

890 A general form of rate law is implemented for the dissolution and precipitation of solid

891 phases (Lasaga et al., 1994):

892

$$r = kA\left|1 - (\frac{\mathrm{K}}{\mathrm{Q}})^{\theta}\right|^{\eta} \quad \text{(A1)}$$

893

894 where *r* is the kinetic rate, *k* is the rate constant (mol/m^2/s) which is temperature

895 dependent, *A* is the reactive surface area per kg water, *K* is the equilibrium constant for

896 the mineral–water reaction written for the dissolution of one mole of mineral, and *Q* is

897 the ion activity product of the dissolution reaction. Here, for simplicity, the exponents θ

898 and η are assumed to be equal to 1. *A* is a function of the mineral specific surface area

899 (e.g., cm^2/g mineral), the volume fraction and density of each mineral in the sediment,

900 and porosity.

901 The rate constant for calcite dissolution is given as a combination of neutral, acid and

902 carbonate mechanisms (Plummer and Parkhurst, 1979):

903

$$k_c = 1.5 \times 10^{-6} e^{-E_a^{nu}/RT} + 0.5 e^{-E_a^{H}/RT} a_H + 9.6 \times 10^{-5} e^{-E_a^{CO2}/RT} a_{CO2} \quad \text{(A2)}$$

904

905 where E_a^{nu}, E_a^H and E_a^{CO2} are activation energies with values of 23.5, 14.4 and 35.4
906 (kJ/mol), respectively. The rate constant for the neutral, acid and carbonate mechanisms,
907 are respectively 1.5×10^{-6}, 0.5 and 9.6×10^{-5}. a_H is the H^+ activity and a_{CO2} is the activity
908 of dissolved CO_2. In the model, the specific surface area of calcite (9.8 cm^2/g) was
909 calibrated, together with the initial calcite volume fraction, to match the breakthrough of
910 observed alkaline earth metals concentrations of Ca, Ba and Sr in MW-3. Assuming
911 spherical grains, the value of the calibrated surface area would correspond to the
912 geometric surface area of millimeter-sized grains. Because the product of the specific
913 surface area and volume fraction is of relevance to the reaction rate (not each value
914 individually), calibrated values of specific surface area or volume fraction should be
915 viewed as non-unique (co-linearly varying) values.

916 The specific surface areas and kinetic rates of minerals other than calcite are listed in
917 Table A4. Most rate constants were taken from Palandri and Kharaka (2004). The
918 dissolution rate constant of plagioclase (Ab80An20) was calibrated based on Ca
919 concentration changes observed at MW-3. The rate constant is higher than that of albite
920 but lower than that of anorthite (Palandri and Kharaka, 2004). The rate constant for
921 FeS_m was taken from Pankow and Morgan (1980). Specific surface areas for most
922 minerals were arbitrarily set to the same value as for calcite, except for FeS_m, for which
923 the surface area was increased (56 cm^2/g) to match Fe concentrations at MW-3.

924

925 Table A4. Kinetic properties for minerals considered in the model (see text for sources)

Mineral	A	Parameters for Kinetic Rate Law

	(cm^2/g)	Neutral Mechanism		Acid Mechanism			Base Mechanism		
		k_{25} (mol/m^2/s)	E_a (KJ /mol)	k_{25}	E_a	n(H^+)	k_{25}	E_a	n(H^+)
Primary:									
Quartz	9.8	1.023×10^{-14}	87.7						
K-feldspar	9.8	3.89×10^{-13}	38	8.71×10^{-11}	51.7	0.5	6.31×10^{-12}	94.1	-0.823
Ab80An20	9.8	1.95×10^{-12}	65	2.95×10^{-4}	69.8	0.457			
Kaolinite	9.8	6.91×10^{-14}	22.2	4.89×10^{-12}	65.9	0.777	8.91×10^{-18}	17.9	-0.472
Smectite-Ca	9.8	1.66×10^{-13}	35	1.05×10^{-11}	23.6	0.34	3.02×10^{-17}	58.9	-0.4
Illite	9.8	1.66×10^{-13}	35	1.05×10^{-11}	23.6	0.34	3.02×10^{-17}	58.9	-0.4
$Fe(OH)_3(s)$	9.8	2.51×10^{-15}	66.2	8.7×10^{-11}	66.2	1.0			
FeS_m	56.0	3.27×10^{-7}	0						
Secondary:									
Gypsum	9.8	1.62×10^{-3}	0						
Dolomite	9.8	2.51×10^{-9}	95.3	1.74×10^{-4}	56.7	0.5			
Siderite	9.8	2.51×10^{-9}	95.3	1.74×10^{-4}	56.7	0.5			
Witherite	9.8	2.51×10^{-9}	95.3	1.74×10^{-4}	56.7	0.5			
Rhodochrosite	9.8	2.51×10^{-9}	95.3	1.74×10^{-4}	56.7	0.5			
Strontianite	9.8	2.51×10^{-9}	95.3	1.74×10^{-4}	56.7	0.5			
Dawsonite	9.8	1×10^{-7}	62.8						

926

927