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Modeling the potential impacts of CO₂ sequestration on shallow groundwater: The fate of trace metals and organic compounds before and after leakage stops

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Abstract: Large-scale deployment of CO₂ geological sequestration requires understanding and assessing the risks of such an operation. One of these risks is the potential contamination of groundwater by CO₂/brine leakage into shallow aquifers. Although our understanding of this issue has improved significantly over the last decade, several questions still need to be better addressed, including the fate of organic constituents, the dominant source of trace metals (are they mainly coming from aquifer sediments, or leaking brine), and whether the trace metals released during the leakage phase recover to background levels if the leakage were to be detected and stopped. In this paper, reactive transport simulations that model the behavior of trace metals and organic compounds in response to the leakage of CO₂ and brine into a shallow aquifer are presented to address these questions. Model results show that the metals and organic compounds brought by the leaking brine form a plume at the bottom of the aquifer because the density of the brine is higher than that of groundwater. In contrast, metals are mobilized by CO₂ over a larger vertical extent because of the spreading of gaseous CO₂ by buoyancy. The concentration of organic contaminants is strongly attenuated by adsorption and degradation, with degradation playing the major role in the modeled scenarios. Although the leaking brine is assumed to contain elevated concentrations of As, Pb, Cd, and Ba, it does not contribute significantly to the contamination of the modeled shallow aquifer by these elements. Once the leakage stops, mobilized organic compounds that undergo degradation vanish, while less degradable compounds linger for a longer time; the dissolved concentrations of trace metals decrease significantly, as a result of re-sorption and reversal of processes leading to Ca-driven cation exchange. Published 2017. **This article is a U.S. Government work and is in the public domain in the USA.**

Keywords: risk assessment; groundwater; CO₂ leakage; reactive transport model; brine

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Introduction

CO₂ capture and deep geologic storage is being considered as a potential mitigation measure against rising anthropogenic emissions of greenhouse gases (GHGs). One potential risk from CO₂ geologic storage is that CO₂ and deep brines could leak from a deep storage formation into overlying shallow, potable groundwater aquifers. Investigators considering the feasibility of geologic storage must therefore consider the impact of potential CO₂ and brine leakage from deep subsurface reservoirs on overlying groundwater aquifers, to ensure the safety of drinking-water resources at these locations.

The primary concern regarding potential leakage into shallow aquifers is the mobilization of trace metals – which has been the focus of many studies, as reviewed by Lemieux¹ and Harvey *et al.*,² and references therein. The dissolution of CO₂ into an aquifer would increase the concentration of dissolved carbonic acid in groundwater and thus increase its acidity, which could mobilize trace elements through mineral dissolution, desorption reactions, and/or exchange reactions involving H⁺ and other mobilized constituents.^{3–13} The transport of deep metal-bearing brines along leakage pathways, with or without CO₂, in response to an increased formation pressure from injection operations could also directly mobilize salts and metals to shallow aquifers. In addition, because supercritical CO₂ is an excellent solvent for organic compounds,^{14,15} concerns have been raised about the potential mobilization of organic constituents from depth and subsequent transport to shallow drinking water bodies via leakage pathways.^{7,16}

The potential mobilization of trace elements in response to CO₂ intrusion into potable groundwater has been investigated by laboratory experiments,^{10,11,17–23} natural analogues,^{24–26} and field experiments.^{13,27–30} Numerical models have also been used to perform generic evaluations of the potential impact of CO₂ leakage on the water quality of shallow aquifers,^{3–5,9} identify potential issues such as the leaching out of organic compounds at depth by supercritical CO₂ and their release in shallow aquifers,⁷ and interpret laboratory experiments^{10,11,31} as well as field tests.^{13,32,33} These interpretations enable understanding of the underlying transport and chemical processes that control the mobilization of major and trace elements upon CO₂ dissolution in groundwater.

It has been shown in laboratory experiments^{10,11,17–22} – which typically involved the release of CO₂ into a pre-equilibrated water-rock environment, followed by monitoring of the geochemical changes in the aqueous phase – that the concentrations of many dissolved major and trace elements increase noticeably upon reaction of the water with CO₂. Because the range of experimental conditions and sediment types covered by these experiments is wide, results vary significantly between different experiments in terms of the types of elements being released and their dissolved concentrations. However, one commonality among these experiments is the rapid increase of alkali and alkaline earth metals in solution. Trace metals of environmental concern that have been found to be released include As, Pb, Ba, and Cd. Observations from field tests^{13,27–30} are largely consistent with observations from laboratory experiments, in that both field and laboratory experiments show a general increase in the dissolved concentrations of major and trace elements upon CO₂ release. However, there are two noticeable differences between results of field and laboratory tests. First, the rise in concentration observed during field tests is typically much less pronounced than in laboratory experiments – field tests show increases of less than about one order of magnitude (20% to 700% in the studies cited), in comparison with orders-of-magnitude increases observed in laboratory tests. Second, increases in trace elements, especially those of environmental concern such as As, Pb, Ba and Cd, are more frequently observed in laboratory tests than in field tests. As pointed out by Apps *et al.*,⁸ eventually how an aquifer responds to the leakage of CO₂ and/or brine depends on the site-specific conditions, including metal-sediment associations and brine characteristics.

Laboratory experiments, field test and modeling studies over a decade have greatly improved our understanding of which, and to what extent, trace elements could be mobilized in shallow aquifer upon the intrusion of CO₂/brine. These investigations have also provided a better understanding of the chemical processes that control the mobilization of major and trace elements upon CO₂ dissolution in groundwater. Nevertheless, several questions still need further answers. One question is related to the potential impact on groundwater from organic constituents. Although the presence and possible extraction of organic compounds by supercritical CO₂ inside deep reservoirs has been documented,^{7,34} the potential for

groundwater contamination from mobilized organic constituents transported to shallow aquifers has been much less studied. Kharaka *et al.*¹⁵ advocated further investigation of this issue when elevated DOC concentrations were observed in the injection formation at the Frio test site in Texas. Zheng *et al.*⁷ and Zhong *et al.*¹⁶ investigated the transport of organic compounds along with leaking CO₂ via leakage pathways, but not the fate of organics in shallow aquifers. Another question remains about the dominant source of potential trace metal contamination; would metals originate mainly by mobilization from aquifer sediments, triggered by the increase in acidity from dissolved CO₂, or would they be mainly brought up by leaking brine? Also, if the leakage were to be detected and stopped, would the trace metals released during the leakage phase recover to their background level if pH recovered?

As revealed by model interpretation of laboratory^{22,35} and field test,^{32,33} the reactions that control the release trace metals are mostly pH-mediated. Once the leakage stops, pH within the impacted zone is expected to slowly increase and recover to its background value upon mixing with upstream fresh groundwater and neutralization reactions with minerals. In this case a remaining question is whether trace metal concentrations would recover to their background values or not. If this was the case, as suggested by Zheng *et al.*,³³ would such recovery occur within the same period as the pH recovery?

In this paper, to tackle some the aforementioned questions, we design a large-scale reactive transport model based on the High Plains Aquifer to simulate the hypothetical leakage of CO₂ and of brine bearing metals and organic compounds. These simulations consider both a leakage and post-leakage period. The High Plains Aquifer is used as a basis for this effort because it is one of the largest aquifer in the USA, and has been used as a typical confined aquifer to develop a risk assessment tool for the US Department of Energy GCS National Risk Assessment Partnership (NRAP; Keating *et al.*³⁶).

Model development

Simulator

The multiphase flow and reactive transport modeling is performed with TOUGHREACT V2,³⁷ using the flow module ECO2N.³⁸ This simulator was developed by introducing reactive chemistry into the existing

framework of a non-isothermal, multiphase, multicomponent fluid and heat flow code, TOUGH.³⁹ The ECO2N fluid property module⁴⁰ includes a comprehensive description of the thermodynamics and thermophysical properties of an H₂O–NaCl–CO₂ system.³⁸ Flow processes can be modeled isothermally (as done in this study) or non-isothermally, and phase conditions may include a single (aqueous or CO₂-rich) phase, as well as two-phase mixtures. Depending on the temperature and pressure conditions, CO₂ may be in a supercritical or gaseous form. Aqueous chemical complexation and gas (CO₂) dissolution/exsolution are assumed to be at local equilibrium. For the conditions assumed in this study, the intrusion of gaseous CO₂ into a freshwater aquifer is modeled as a two-phase flow system, with dissolution of CO₂ into water occurring instantaneously using a local equilibrium assumption, while gaseous CO₂ migrates within the aquifer, driven mainly by buoyancy.

Model set-up

Because effects of potential CO₂ leakage on groundwater quality in ongoing GCS operations have not been reported, we rely on a generic model based on the High Plains Aquifer used in NRAP.³⁶ The simulation domain is 10 000 m long, 5000 m wide and 250 m deep. A nested mesh is used, with refined space discretization in the area where CO₂ and brine leakage occurs and a coarser mesh for the area where the CO₂ and brine plumes are less likely to migrate (Fig. 1). A regional hydraulic gradient of 0.005 (from left to right) is applied by fixing the pressure at gridblocks on the left and right model boundaries. The modeled domain is assumed isothermal with a temperature of 17°C, and under pressure values ranging from about 27–29 bar at the bottom model boundary to 7–9 bar at the top.

A single leaking point is assigned at location $x = 2000$ m, $y = 2500$ m, and $z = 250$ m, with CO₂ and brine leakage rates shown in Fig. 2. These rates represent a hypothetical leakage pathway related to a deep, leaky well connecting a deep geologic reservoir for CO₂ storage with a shallow groundwater resource.⁴¹ The temporal evolution and magnitude of leakage is based on the generalized leakage scenario of Carroll *et al.*⁴¹

The aquifer is assumed to be confined, with a uniform thickness of 240 m, which corresponds to the average thickness of the High Plains Aquifer. The following two lithologic facies are considered within

Figure 1. Numerical mesh used in the model and the lithologic facies in the aquifer; gray represents sand facies and black represents clay facies. Note that the Z axis is exaggerated by ~20 times.

Table 1. Mass fraction (%) of primary minerals in the two modeled lithofacies: sand and clay.

Primary Mineral	Sand facies	Clay facies
Quartz	73.82	34
Albite	2	3
K-feldspar	4.18	3
Kaolinite	2.5	10.5
Smectite-Na	1.5	15
Illite	1.5	20
Goethite	10	10
Calcite	4.5	4.5

the aquifer: a 'sand lithofacies,' mainly composed of medium and coarse sand, and a 'clay lithofacies,' mainly composed of very fine sand and silty clay. The sand lithofacies has a porosity of 0.25 and a permeability of $2 \times 10^{-12} \text{ m}^2$, whereas the clay lithofacies has a porosity of 0.35 and a permeability of 10^{-18} m^2 . The mineralogical compositions of these two facies are listed in Table 1, and fall largely into the range reported by McMahon *et al.*⁴⁸ and Lawter *et al.*²³

Figure 2. The leakage rate of CO₂ and brine as a function of time. The leakage rate of CO₂ and brine as a function of time is taken from Carroll *et al.*⁴¹.

The initial water chemistry used in the model, listed in Table 2, represents the arithmetic average of major and trace inorganic element data collected in two surveys in 1999 and 2010, as part of the High Plains Regional Ground-Water Study conducted by the US Geological Survey' (USGS's) National Water-Quality Assessment Program.⁴³ The surveys carried out

Table 2. Chemical composition of groundwater in the aquifer and leaking brine. Concentrations of trace metals in the brine are based on experiments⁵⁵ and organic concentrations in brine are from Zheng *et al.*⁵.

Primary species	Concentration in the groundwater (M)	Concentration in the leaking brine (M)	Primary species	Concentration in the groundwater (M)	Concentration in the leaking brine (M)
Ca ⁺²	1.37E-03	1.37E-03	Sb(OH) ₃ (aq)	5.59E-10	5.59E-10
Mg ⁺²	8.74E-04	8.74E-04	H ₃ AsO ₃ (aq)	2.33E-08	2.33E-08
Na ⁺	1.60E-03	4.30E-02	Ba ⁺²	8.10E-07	1.99E-04
K ⁺	1.13E-04	1.13E-04	Cd ⁺²	6.91E-10	3.17E-08
Cl ⁻	1.85E-03	4.30E-02	Pb ⁺²	1.57E-09	1.78E-07
HS ⁻	6.48E-04	6.48E-04	Benzene	1E-15	2.51E-07
SO ₄ ⁻²	5.77E-05	5.77E-05	Phenol	1E-15	1.41E-07
HCO ₃ ⁻	3.95E-03	9.8E-02*	Naphthalene	1E-15	8.91E-08
H ₄ SiO ₄ (aq)	5.33E-04	5.33E-04	HSe ⁻	5.34E-08	5.34E-08
Fe ⁺²	1.01E-06	1.01E-06	Eh	-0.26 volts	-0.26 volts
Fe ⁺³	8.97E-16	8.97E-16	pH	7.4	5.2*
AlO ₂ ⁻	1.57E-07	1.57E-07			

* The pH and the total dissolved carbonate concentration (as HCO₃⁻) were calculated assuming equilibrium of the solution with CO₂ at the leaking point.

analyses of 30 to 74 randomly selected wells. Very small values (10⁻¹⁵ M) were assigned to the initial concentration of benzene, phenol, and naphthalene, because their concentrations were all below the detection limits in the 2010 survey.

The composition of brines that could migrate from a storage reservoir varies a great deal from site to site. In this model, to simplify the simulation and more clearly evaluate the impact of brine leakage on groundwater (in terms of potential concentration change of trace metals and organic compounds), the brine is assumed to have the same composition as groundwater except for higher concentrations of Na, Cl, Pb, Cd, As, benzene, phenol, and naphthalene, as listed in Table 2.

The CO₂ and brine leakage rate are based on the assumption that CO₂ and brine could be transported from a pressurized reservoir, through a borehole, and into groundwater.⁷ Conceptually, CO₂ leakage flux increases to a plateau during the onset of CO₂ injection into the storage reservoir, maintains a constant value during injection, and then decrease over time to some minimal level. The brine-leakage profile is assumed different from that of CO₂: it is characterized by a maximum and constant flux during injection, then falling to a final value after injection stops. The CO₂ and brine leakage rates are shown in Fig. 2. The simulations assume that leakage occurs continuously

for a period of 100 years. In addition, we simulate a 100-year post-leakage period, during which the leakage is assumed to have been detected and stopped.

Geochemical system

The geochemical system is extensive and includes over 70 aqueous species, dissolution, and precipitation kinetics for 14 minerals, 5 cation exchange reactions, 36 sorption reactions, and oxidation kinetics for 3 organic species. Kinetic constants, minerals, cation exchange, and sorption reactions stoichiometries and constants are summarized in Tables A1–A3 in Appendix 1. Equilibrium constants for aqueous complexes and minerals are taken primarily from the THERMODDEM database version 1.0.0.8.⁴⁴ For those reactions that are not listed in THERMODDEM, thermodynamic data are taken from database data0.ymp.r5 in the EQ3/6 V8.1 geochemical modeling package⁴⁵ and Birkholzer *et al.*⁴⁶ Cation exchange reactions are included for Na, K, Ca, Mg, and Ba, as are surface complexation reactions for As, Cd, and Pb on goethite, illite, kaolinite, and montmorillonite. Surface complexation reactions on calcite are not considered in the model, because calcite is a much weaker adsorbent in comparison with goethite, illite, kaolinite, and montmorillonite, and is

Table 3. Kinetic properties of minerals considered in the model (see text for data sources): ‘Primary’ minerals are initially present in the aquifer; ‘Secondary’ minerals are those that are allowed to form by precipitation.

		Parameters for Kinetic Rate Law							
		Neutral Mechanism		Acid Mechanism			Base Mechanism		
Mineral	A (cm ² /g)	k ₂₅ mol/m ² /s	E _a kJ/mol	k ₂₅	E _a kJ/mol	n(H ⁺)	k ₂₅	E _a kJ/mol	n(OH ⁻)
Primary:									
Calcite	221	2.2 × 10 ⁻⁸	23.5	6.9 × 10 ⁻⁴	14.4	1.0			
Illite	2124	1.66 × 10 ⁻¹³	35.00	1.05 × 10 ⁻¹¹	23.60	0.34	3.02 × 10 ⁻¹⁷	58.9	-0.40
Kaolinite	2309	6.91 × 10 ⁻¹⁴	22.20	4.89 × 10 ⁻¹²	65.90	0.78	8.91 × 10 ⁻¹⁸	17.9	-0.47
Smectite	2149	1.66 × 10 ⁻¹³	35.00	1.05 × 10 ⁻¹¹	23.60	0.34	3.02 × 10 ⁻¹⁷	58.9	-0.4
Goethite	141	2.51 × 10 ⁻¹⁵	66.20	4.07 × 10 ⁻¹⁰	66.20	1.00			
Albite	229	3.89 × 10 ⁻¹³	38.00	8.71 × 10 ⁻¹¹	51.70	0.50	6.31 × 10 ⁻¹²	94.1	-0.82
Quartz	227	3.98 × 10 ⁻¹⁴	87.7						
K-feldspar	234	3.89 × 10 ⁻¹³	38.00	8.71 × 10 ⁻¹¹	51.70	0.50	6.31 × 10 ⁻¹²	94.1	-0.82
Secondary:									
Dolomite	209	2.95 × 10 ⁻⁸	62.76	2.34 × 10 ⁻⁷	43.54	1.00			
Magnesite	199	4.57 × 10 ⁻¹⁰	23.50	4.17 × 10 ⁻⁷	14.40	1.00			
Dawsonite	247	3.89 × 10 ⁻¹³	38.00	8.71 × 10 ⁻¹¹	51.70	0.50	6.31 × 10 ⁻¹²	94.1	-0.82
Muscovite	212	3.89 × 10 ⁻¹³	38.00	8.71 × 10 ⁻¹¹	51.70	0.50	6.31 × 10 ⁻¹²	94.1	-0.82
Gibbsite	246	3.89 × 10 ⁻¹³	38.00	8.71 × 10 ⁻¹¹	51.70	0.50	6.31 × 10 ⁻¹²	94.1	-0.82
Pyrite	120	2.52 × 10 ⁻¹²	62.76						
A: specific surface area									
k ₂₅ : rate constant at 25°C									
E _a : activation energy									
n(H ⁺): exponent on H ⁺ activity term									
n(OH ⁻): exponent on OH ⁻ activity term									

thus unlikely to make a significant impact on the adsorption of metals. Kinetic-rate parameters for most rock-forming minerals are taken from Palandri and Kharaka;⁴⁷ these are based mainly on experimental studies conducted under far-from-equilibrium conditions. The overall rate equation is tied to mineral equilibria through the saturation ratio (Q/K) with a pH-dependent rate consisting of acid, neutral, and base mechanisms of the following form:

$$r = \pm k A a_i^n \left[1 - \left(\frac{Q}{K} \right)^\theta \right]^m \quad (1)$$

where r is the kinetic rate for a given mechanism, k is the rate constant computed at different temperatures

from a value at 25°C and activation energy, A is the specific reactive surface area, a_i is the activity of either H^+ or OH^- at some exponent n , K is the equilibrium constant for the mineral–water reaction, and Q is the activity product of that reaction (refer to Palandri and Kharaka,⁴⁷ for the full rate equation). θ is the inverse of the Temkin coefficient (the stoichiometric number of the activated complex involved in the rate-limiting step) and m is an empirical constant. In this study, the parameters θ and m are assumed equal to unity. The mineral specific surface areas are calculated assuming a grain diameter of 0.1 mm for non-clay minerals and 0.01 mm for clay minerals (Table 3).

Organic compounds are modeled to undergo adsorption and degradation, with the distribution coefficient, K_d , and the degradation coefficient control

Table 4. Compilation of published K_d values for benzene partitioning between soil and water.

Reference	K_d (mL/g)	f_{oc}	Comments
Larsen <i>et al.</i> ⁵⁶	0.05–0.65	0.00063–0.0082	Measured for a range of different aquifer samples at various locations in Denmark
Donahue <i>et al.</i> ⁵⁷	0.1–1.0	0.0013–0.013	Measured for Regina clay in Canada
Jean <i>et al.</i> ⁵⁸	0.16–0.5	0.0021–0.0063	Measured in a laboratory experiment for artificial medium-sized sand
Hawthorne and Miller ⁵⁹	28–59	0.35–0.75	Measured for manufactured gas plant soils (contaminated by organic compounds)

the concentration of benzene, phenols, and naphthalene. K_d value were derived from the partitioning of a specific compound between water and organic carbon and the amount of organic carbon in sediments, by the equation:

$$K_d = f_{oc} \times K_{oc} \quad (2)$$

where $f_{oc} = m_{oc}^s / m^s$ is the mass fraction of organic carbon in sediments, defined as the mass of organic carbon in sediments m_{oc}^s divided by the mass of sediments m^s . K_{oc} may be thought of as the ratio of the amount of chemical adsorbed per unit weight of organic carbon in the soil, to the concentration of the chemical in solution at equilibrium.

Based on published K_{oc} values and a typical range of f_{oc} values for the High Plains Aquifer, Carroll *et al.*⁴¹ obtained plausible K_d ranges for benzene, phenol, and naphthalene. Here, we take the median values of these data, which are 0.012 L/kg, 0.0012 L/kg and 0.28 L/kg, respectively. For comparison, Table 4 lists some published K_d values for benzene, which show a large variation. Also shown in Table 4 is the weight fraction of organic carbon in sediments, f_{oc} , calculated based on a K_{oc} of 79 ($\log K_{oc} = 1.9$) for benzene. The large range of measured K_d values primarily results from the dependence of K_d on the organic matter content of soils, which is quite variable. In other words, K_d is soil specific, and the same K_d value is not necessarily applicable to a range of different soil types.

The degradation of the organic compounds is calculated with a first-order degradation kinetic rate:

$$\frac{dC}{dt} = -kC \quad (3)$$

where C is the concentration of the organic compound and k is the first-order rate constant. Organic compounds are much more degradable under aerobic conditions than anaerobic conditions. Because the aquifer is under reducing conditions in the current

model, anaerobic degradation constants should be used. Values of such constants for anaerobic systems have been sparsely reported. Here, we select these constants based on work reported by the US Environmental Protection Agency,⁴⁷ adopting values of 3.7×10^{-7} 1/s for phenol and an assumption of 0 (no degradation) for benzene and naphthalene.

Model results

Release of metals

The intrusion of CO₂ into the aquifer forms a separate gaseous phase, which is carried horizontally down the regional hydraulic gradient by groundwater flow and at the same time driven upward by buoyancy (Fig. 3), following the zones of higher permeability (sand facies). After the CO₂ leakage stops at 100 years, the free CO₂ phase gradually fades, as shown by the simulated CO₂ concentration map at 110 years, and completely vanishes after about 120 years (by dissolution) (Fig. 3). It should be noted that at higher groundwater flow rates (simulated by increasing permeability) the disappearance of the CO₂ gas phase occurs sooner due to increased mixing with upgradient CO₂-free water.

The dissolution of CO₂ in water produces carbonic acid, which decreases pH and increases the dissolved carbonate content in impacted groundwater:

The simulated concentration map of dissolved CO₂ (expressed as total inorganic carbon, TIC, Fig. 4) occupies a much larger area than the free CO₂ phase, because of diffusion and dispersion in groundwater. The highest concentration of TIC (slightly higher than 0.9 M) appears in the vicinity of the leakage point. After the CO₂ leakage stops at 100 years, the TIC

Figure 3. Simulated spatial distribution of the free CO₂ gas phase (physical) saturation along a cross section at Y = 2500 m at 10 (a), 100 (b), 110 (c), and 130 (d) years.

plume is carried downgradient and the TIC concentrations gradually decrease, from 0.8 M at 110 years to 0.3 M at 200 years (Fig. 4).

The evolution of pH closely follows the evolution of TIC (Fig. 5), with pH decreasing as the concentration of TIC rises. In pure water, the dissolution of CO₂ at pressure > 5 bars yields a pH near 3.5; however, in natural systems, the pH drop is not as pronounced (values typically near or above 5) because of buffering by various reactions. For example, at the Frio deep CO₂ injection test site,¹⁵ injection of supercritical CO₂ at pressures ~150 bar into a deep sandstone aquifer resulted in pH dropping from about 6.5 to 5.7. Under totally different conditions in shallow sandy gravels, a few meters below the ground surface at the Montana State University-Zero Emissions Research and Technology (MSU-ZERT) field test in Montana,²⁷ the pH decreased from around 7 to 6 after injection of gaseous CO₂. A more significant pH decrease, from about 8 to 5.1, was observed in a field test in Mississippi¹³ upon injection of groundwater carbonated at a pressure near 4 bars into confined, poorly consolidated sandy and carbonate-depleted sediments. By comparison, in the present model, the lowest pH is predicted to be around 5.2 within the

two-phase zone (Fig. 5). The pH is buffered primarily by the dissolution of calcite, with also a slight contribution from protonation/deprotonation reactions on clay minerals and goethite surfaces. Once the CO₂ leakage stops, the pH is predicted to recover slowly from a minimum values of 5.2 at 100 years to near 5.9 at 200 years at the center of the plume, which is primarily a result of mixing with groundwater from upstream, and secondarily a result of the continuous dissolution of calcite (albeit at a lower rate as the pH increases) and dissolution of siderite formed during the CO₂ leakage phase.

The decrease in groundwater pH upon carbonation can lead to the release of metals (M) by the dissolution of minerals, especially carbonates and sulfides:

Adsorption-desorption reactions are also expected to play an important role in metal mobilization, and also in buffering pH in the absence of significant amounts of fast-reacting carbonate minerals:

Figure 4. Simulated spatial distribution of Total Inorganic Carbon (TIC, M) along a cross section at $Y = 2500$ m at 10 (a), 100 (b), 110 (c), and 200 (d) years.

Competitive sorption with bicarbonate ions (e.g. As, Se) can also mobilize metal oxyanions:

In addition, metals released by the above reactions (e.g. Ca) may trigger exchange reactions that then further mobilize other metals into solution:

All these reactions are plausible in controlling the release of trace metals from sediments upon exposure to carbonated groundwater. The dissolution of sulfide minerals was originally proposed (from modeling studies) as reactions controlling the release of trace metals in groundwater after a CO₂ leak. For example, Wan and Jaffe³ simulated the release of Pb as a result of the dissolution of galena, and Zheng *et al.*⁵ and Apps *et al.*⁸ considered the control of galena on Pb, and arsenian pyrite on As. However, Zheng *et al.*⁵ suggested that adsorption/desorption reactions should more typically dominate the release of trace metals from sediments, because these reactions are typically much faster than mineral dissolution and precipitation, and sulfide minerals are not ubiquitous in aquifers. Moreover, the increases in concentrations of trace

metals reported in laboratory experiments exposing sediments to CO₂^{22,23} are not elevated enough, and do not follow the trends required to suggest that the dissolution of sulfide minerals controls the concentrations of metals such as Pb and As in groundwater. For this reason, in the present model, the dissolution of sulfide minerals is not considered.

The dissolution of calcite with impurities of Sr and Ba has been proposed by Lu *et al.*¹⁸ and tested by Zheng *et al.*³⁵ to explain increased concentrations of these metals in laboratory experiments. An alternative mechanism proposed by Zheng *et al.*³⁵ involves calcite dissolution accompanied by Ca-driven cation exchange reactions. Simulations of these coupled processes give satisfactory results when compared to field measurements at two CO₂-release test sites.³⁵ For this reason, in the present model, we consider the dissolution of pure calcite and a series cation exchange and desorption reactions (Tables A2 and A3), rather than the dissolution of impure calcite, as the reactions that control the release of metals.

The pH drop induced by CO₂ dissolution (Reactions 4 and 5) triggers a series of desorption reactions (following Reaction 8) that lead to increases in Pb in

Figure 5. Simulated spatial distribution of pH along a cross section at $Y = 2500$ m at 10 (a), 100 (b), 110 (c), and 200 (d) years.

solution. As seen in Fig. 6, a plume with elevated Pb concentration develops and closely follows the plume with low pH surrounding the CO₂ intrusion. In our case, Pb⁺² is initially adsorbed onto goethite, illite, kaolinite, and montmorillonite. Montmorillonite and illite are the most important adsorbent of Pb, with (mon)₂Pb and (ill)₂Pb (Table A3) being the dominant surface complexes. The concentration of dissolved Pb peaks at about 4.2×10^{-8} M (~ 9 ppb) during the CO₂ leakage period. After CO₂ leakage stops at 100 years, the plume becomes diluted by upstream groundwater but the Pb concentration at the center of the plume decreases only slightly to about 4×10^{-9} M (~ 8 ppb) at 200 years because the pH at this location is still significantly lower than background values (Fig. 5).

The case of Cd is similar to that of Pb: an increase in dissolved concentration is predicted as the result of pH-driven desorption reactions, although the increase in concentration is less pronounced than with Pb. In this case, the dominant surface complexes are (mon)₂Cd and (ill)₂Cd (Table A3), and the maximum dissolved Cd concentration is $\sim 8 \times 10^{-9}$ M (~ 1 ppb) during the CO₂ leakage period, decreasing to

about 7×10^{-9} M (~ 0.7 ppb) at the center of the plume after 200 years (Fig. 7).

Arsenian pyrite was initially postulated by Zheng *et al.*⁵ and Apps *et al.*⁸ as the mineral that thermodynamically controls the concentration of As in groundwater, based on statistical analyses of groundwater samples in a range of aquifers within the USA.⁴⁶ However, laboratory and field tests since then do not seem to support this hypothesis. First, not all laboratory tests published to date show a release of As when sediments are exposed to CO₂. Even for those laboratory tests that did show a release of As,^{10,19,22} either the sediments were taken from aquifers known to have high background levels of As¹⁰ or the concentration of As observed in the laboratory was too low to be attributed to the dissolution of arsenian pyrite. Moreover, it is known that laboratory tests are more aggressive than field tests in leaching out trace metal with dissolved CO₂.^{30,35} Among field tests that have been reported in the literature so far,^{13,27–30} only Yang *et al.*³⁰ reported a release of As after the injection of CO₂. The measured As concentration by these authors ($\sim 3 \times 10^{-9}$ M As, or 0.2 ppb) is orders of magnitude lower than if As concentrations were

Figure 6. Simulated spatial distribution of dissolved Pb concentrations (M) along a cross section at $Y = 2500$ m at 10 (a), 100 (b), 110 (c), and 200 (d) years.

controlled by equilibrium with arsenian pyrite. For this reason, arsenian pyrite is not considered in the present model, and the geochemical behavior of As is simulated as being controlled solely by surface and aqueous complexes, with $\text{goe2_H}_2\text{AsO}_4^-$, goe2_HAsO_4^{2-} , and mon_HAsO_3^- (Table A3) dominating the surface complexation of As. Figure 8 shows the simulated As concentration map at four different times. The maximum dissolved As concentration appears at the leakage point, where it is up to 1.1×10^{-7} M (~ 8 ppb) during the leaking period. After the CO₂ leakage stops, the dissolved As concentration at the center of the plume decreases somewhat to about 8×10^{-8} M (~ 6 ppb).

Pb, Cd, and As were included in the model because they are typical elements of environmental concern and were observed in laboratory studies being leached out from sediments by carbonated water. However, as mentioned earlier, laboratory leaching experiments appear too aggressive compared to conditions expected for an actual CO₂ leak in the field. This seems supported by field experiments,^{13,28,29} which show no release of Pb, Cd, or As in groundwater. In contrast, the mobilization of Ba has been typically observed in both laboratory and field studies. Modeling interpretations

of CO₂ leakage, laboratory³⁵ and field experiments^{7,13} showed that Ca-driven cation exchange provides a robust explanation for the release of Ba in groundwater upon carbonation. The drop of pH leads to the dissolution of calcite, and then the increase in the concentration of Ca triggers a series of cation-exchange reactions that cause an increase in the concentrations of alkaline earth metals in groundwater. This explains the parallel temporal and spatial distribution of dissolved Ba (Fig. 9), Ca, and pH (Fig. 5), which is also observed in the field experiments mentioned above. In the present case, the model predicts a maximum Ba concentration of 7×10^{-4} M (~ 96 ppm) during the 100-year leakage phase, which then decreases to 6×10^{-5} M (~ 8 ppm) after 200 years. The similarity between the plumes of pH, TIC and trace metals suggests that the release of metals, as simulated in the present model (Figs. 5 through 9), is driven primarily by the CO₂ dissolution in the aquifer and not by brine leakage. This is confirmed by simulations of brine leakage without CO₂ presented later in this section.

Fate of organic compounds

In the case of CO₂ geological storage in deep saline aquifers, the type of organic contaminants that could

Figure 7. Simulated spatial distribution of dissolved Cd concentration (M) along a cross section at $Y = 2500$ m at 10 (a), 100 (b), 110 (c), and 200 (d) years.

be transported to shallow aquifers once leakage occurs depends on the type of organic compounds present in the brine. Organic compounds present in deep saline aquifers are seldom reported. However, their occurrence and concentrations in brines produced in the vicinity of gas and oil fields have been documented.^{48–51} From such studies, benzene, toluene, ethylbenzene, and xylenes (BTEX), as well as polycyclic aromatic hydrocarbons (PAHs) and phenols, were identified as potentially relevant candidates for our study. Obviously, many other organics could also warrant attention. Such compounds include carboxylic acids, which are commonly present at much higher concentrations (up to 5000 mg/L) in oil field brines,³⁴ and are also expected to be present in deep saline aquifers. Although these compounds are essentially nontoxic, they are good ligands for metal complexation, and their mobilization could exacerbate the release of trace metals upon CO₂ leakage into fresh water.

In the present model, we selected benzene as a representative for BTEX, phenol for phenols, and naphthalene for PAHs. Because the aquifer is assumed free of these organic contaminants, the contamination

of organic compounds comes exclusively from the leaking brine. Once reaching the aquifer, degradation and adsorption is predicted to essentially immobilize these organic compounds. Phenol, as shown in Fig. 10, undergoes both degradation and adsorption, and its plume is very small. After the brine leakage stops at 100 years, degradation quickly consumes the remaining phenol, and its plume vanishes. Although naphthalene undergoes stronger adsorption, its dissolved plume (Fig. 11) is much larger than that of phenol (Fig. 10) because it is assumed to suffer no degradation. After the brine leakage stops at 100 years, the concentration of naphthalene decreases owing to dilution, but the size of the plume increases slightly. Benzene (Fig. 12) forms the largest plume of the three organic compounds included in the model, because it undergoes less adsorption than naphthalene and is also assumed not to degrade. These modeling results show that organic compounds in the leaking brine spread out at the bottom of the aquifer, but can be quickly consumed by degradation. If no degradation takes place, they can linger within the aquifer for a long time, even after the leakage stops.

Figure 8. Simulated spatial distribution of As concentration (M) along a cross section at $Y = 2500$ m at 10 (a), 100 (b), 110 (c), and 200 (d) years.

Source of metals release: leaking brine or aquifer sediments?

In the present model, trace metals released into the aquifer come from two sources: (i) the leaking brine and (ii) the aquifer sediments resulting from the pH-driven (though CO₂) desorption and dissolution reactions. Figures 5 to 9 show that the spatial distribution of the contaminant plume is largely dictated by the transport of CO₂, as manifested by the parallel behavior of pH, TIC, and trace metals. To clearly distinguish the effect of the leaking brine from CO₂-related metal mobilization, we conducted a simulation of brine leakage without CO₂. The simulated concentration map of trace metals obtained in this manner at 100 years is shown in Fig. 13. Because the brine is denser than the groundwater, the dissolved metals associated with brine leakage always stay near the bottom of the aquifer and only partially overlap with the TIC plume (compare Fig. 13 with Fig. 4); the concentrations of trace metals mobilized in this way are quite low, in the present case several folds larger than background concentrations, because of the dilution by clean groundwater and adsorption to mineral surfaces. For this reason, the plume of trace

metals caused by brine leakage is overshadowed by the effect of CO₂ leakage. This finding suggests that if leakage of both CO₂ and brine occurred, at the anticipated relative rates assumed for this study,⁴¹ the CO₂ leakage would most likely dictate the spatial distribution of trace-metal contamination. However, when the leakage rate of CO₂ is small enough such that no buoyant gaseous phase CO₂ forms and migrates upwards, the mobilization of metals by CO₂ is expected to be more limited in vertical extent; under these conditions, a high brine leakage rate relative to CO₂ might become the dominant factor leading to groundwater contamination.

The issue of reversibility

During the post-injection phase, if the leakage were to be detected by the monitoring system and measures were to be taken to stop the leakage, it is expected that the plume of elevated CO₂ concentration and low pH would become diluted by mixing with groundwater. Neutralization reactions with carbonates as well as mineral surfaces would also continue to take place. As a result, pH would be expected to eventually rebound to original near-neutral values, but it is less clear if

Figure 9. Simulated spatial distribution of dissolved Ba concentrations (M) along a cross section at $Y = 2500$ m at 10 (a), 100 (b), 110 (c), and 200 (d) years.

metal concentrations would drop concurrently with the pH rebound. Previous modeling, laboratory, and field investigations^{22,32,33,35} suggest that reversibility is expected to a large degree but on time scales that may exceed the time required for pH to fully rebound. Here we examine the predicted temporal change of trace metal concentration at several locations in our model to shed further light on this question.

Figure 14 shows the temporal evolution of pH and several trace metals at the leak point. After the leakage stops at 100 years, as expected, pH starts recovering immediately, from 5.3 at 100 years to 6.7 at 200 years, partially because the migration of the CO₂ plume downstream and partially because the mixing with pristine groundwater coming upstream and further neutralization reactions with minerals and their surfaces. As soon as pH recovers, the concentrations of As and Ba drop continuously, but the concentrations of Cd and Pb continue to increase for another 10 years (concurrent with a pH increase from 5.2 to 6.0) and only then start to decrease for the remainder of the simulation. This appears to result from the competition between aqueous complexation and adsorption, with the formation of Pb and Cd bisulfide aqueous complexes causing some desorption of these metals when the pH increases from 5.2 to 6.

Figure 15 shows the temporal evolution of pH and trace metals at a point 200 m downstream of the leak point. At this location the pH recovers at a slower pace than closer to the leaking point because this area is further downstream of the low-pH plume trailing edge. As a result the pH only rises to about 6.4 after 200 years. As predicted at the leak point, the decrease in As concentrations follows closely the increase in pH while the concentrations of Cd and Pb continue to increase during the period when pH increases from 5.2 to about 6, and then decrease until the end of simulation. Ba at this downstream point behaves differently: its concentration decreases slightly for about 40 years and drops at a faster pace than predicted at the leak point. Because this point is located downstream, the migration of low-pH and high-Ba groundwater maintains a low pH and high Ba concentration at this location for a while until the arrival of fresh groundwater.

Sensitivity analyses to permeability and leakage rate

The spatial and temporal evolution of groundwater impacted by the leakage of CO₂ and brine depends on many model input parameters, with the respective rates

Figure 10. Simulated spatial distribution of phenol concentration (M) along a cross section at $Y = 2500$ m at 10 (a), 100 (b), and 110 (c) years.

of CO₂ and brine leakage as well as groundwater flow being the most important ones (as revealed by uncertainty quantification studies reported in Carroll *et al.*,⁵¹ Dai *et al.*,⁵² and Bacon *et al.*⁵³ In this study, additional simulations with different leakage rates and groundwater flow rates were conducted to assess the effect of these parameters on model results.

Given that the initially modeled CO₂ and brine leakage rates are relatively high (Fig. 2; compare for example with Xiao *et al.*⁵⁴), additional simulations were performed with CO₂/brine leakage rates two orders (run1) and four orders (run2) of magnitude lower than initial values, respectively. In the run2 case, the leakage rate was found to be too small to cause a significant pH change, and for this reason the run2 model results are not shown here.

We previously predicted two trends of trace metal concentrations with time during the simulated post-leakage period: a continuous decrease of As and Ba concentrations accompanying the rising pH, and in contrast a short-term increase in the concentrations of Pb and Cd before their decrease. Figure 16 shows that these trends do not differ significantly with lower leakage rates. However, during leakage, the pH does not decrease as much as that in the initial base-case run

(minimum values ~ 5.8 versus ~ 5.2) and the concentrations of As do not rise as much as predicted in the base case. In contrast, the lower leakage rate yields higher Pb concentrations during the leakage phase compared to the base-case run, because the higher pH values favor the formation of Pb bisulfide aqueous complexes. Similar differences between the base and run1 cases are predicted at a point 200 m downstream (Fig. 17).

The interaction between leakage rate and flow rate largely dictates the spatial distribution of impacted groundwater. A decrease in groundwater flow rate was implemented by changing the permeability for the sand facies to half its original value (run3 case) while keeping the hydraulic gradient at its original value. When doing so, at the leak location, during the leakage period, the pH and concentrations of As and Pb in the run3 case are very similar to that in the base-case run (Fig. 18). However, once the CO₂ and brine stop leaking, the recovery of pH and As and Pb concentrations is slower than predicted in the base-case, because of slower dilution by clean upstream groundwater. At a point 200 m downstream (Fig. 19), concentration trends with time modeled with the base and run3 simulations are similar but shifted in time as

Figure 11. Simulated spatial distribution of naphthalene concentration (M) along a cross section at $Y = 2500$ m at 10 (a), 100 (b), 110 (c), and 200 (d) years.

would be expected from the lower groundwater flow rate in the run3 case compared to the base case. Consequently, during leakage the drop of pH and increase in concentrations of As and Pb is delayed, and the post-leakage recovery of these concentrations is slower.

Summary and conclusion

Large-scale deployment of CO₂ geological storage operations requires the assessment of the risks associated with each storage site. One of these risks is that CO₂ and/or brine from the storage reservoir could leak into overlying shallow, potable groundwater aquifers. Within the last decade, laboratory experiments, field tests, and numerical models have been used to study and understand which, and to what extent trace elements could be mobilized in shallow aquifer upon such leakage. Although these studies provided much insight into chemical processes that control the release of major and trace elements following the dissolution of CO₂ in groundwater, several questions have not yet been fully answered. To what extent could potentially mobilized organic

constituents impact groundwater quality? Are trace metals more likely to be released from sediments by the increased groundwater acidity from CO₂ dissolution, or are they more likely to be advected with leaking brine. If the leakage were to be detected and stopped, would the trace metals released during the leakage phase recover to background levels? The reactive transport simulations presented in this paper were developed to help answer these questions. These simulations consider a leak of CO₂, a brine containing metals and organic contaminants into an aquifer modeled after the High Plains Aquifer in Kansas, using a model setup and properties previously developed for the US Department of Energy GCS National Risk Assessment Partnership (NRAP).

Model results show that the organic compounds brought up by leaking brine form a plume at the bottom of the aquifer that is carried downgradient. The concentration of these organic contaminants is strongly attenuated by adsorption and degradation, with degradation playing the major role in the modeled scenarios. Once the leakage stops, as would be expected, mobilized organic compounds that undergo degradation vanish, while less degradable compounds

Figure 12. Simulated spatial distribution of benzene concentration (M) along a cross section at $Y = 2500$ m at 10 (a), 100 (b), 110 (c), and 200 (d) years.

linger for a longer time. Model results also suggest that brine leakage (at rates anticipated for typical leakage scenarios) may not impact groundwater quality as much as the acidity from CO₂ dissolution, because (i) the dense leaking brine tends to remain at the bottom of the aquifer, in contrast to buoyant CO₂ migrating over a much larger vertical extent, and (ii) trace-metal concentrations in typical brines, may not be high enough to yield levels in groundwater, upon leakage, as high as those resulting from the carbonic acid-driven mobilization of adsorbed and exchangeable metals in aquifer sediments.

A comparison of the predicted metal concentrations during the period of CO₂ leakage and after leakage is stopped provides insight on whether trace metals released during the leakage phase recover to background levels when pH recovers. During the leakage period, As, Pb, Cd, and Ba are predicted to be released as a result of the pH decrease. Once the leakage is stopped and pH recovers, two trends are predicted: the concentration of As and Ba decrease immediately as the pH rises, whereas the concentrations of Pb and Cd continue to increase for some time before decreasing. This is attributed to the formation of

aqueous bisulfide complexes that predominate at pH around 6 and compete with adsorption in this pH range. Similar trends are predicted for cases with different leakage rates and groundwater flow rates.

Obviously, the use of models alone to investigate an aquifer's response to intrusion of CO₂ and brine is seriously limited, because such a response depends on site-specific conditions – such as metal-sediment associations, groundwater composition and redox conditions, leakage rate versus regional groundwater flow rates, and many other hydrologic and geochemical parameters. The leakage impact on groundwater is expected to be quite sensitive to the complex (and coupled) interaction between hydrological and chemical processes, as well as to the degree of mixing between the leaking fluid and groundwater. Although reactive transport models to investigate these complex coupled processes yield useful insights, the results of such modeling are qualitative or semi-quantitative at best, because simulations require many input parameters, most of which are site-specific and often unknown or poorly constrained. The models presented in this paper were used to illustrate the types of

Figure 13. Simulated spatial distribution of As (a), Ba (b), Cd (c) and Pb (d) concentrations (M) along a cross section at $Y = 2500$ m at 100 years, without CO₂ leakage.

Figure 14. Temporal evolution of pH and trace metals at the leak location.

Figure 15. Temporal evolution of pH and trace metals at a point 200 m downstream of the leak location.

reaction mechanisms that could be expected in typical leakage scenarios. When conducting a risk assessment of specific CO₂ geological storage sites, it is recommended that extensive site characterization be

conducted first, including the determination of hydrogeological and geochemical conditions in the storage reservoir, sediment-metal associations in overlying aquifers, and types of potential leakage

Figure 16. Temporal evolution of pH, As and Pb at the leak location for the initial base-case simulation (base) and a sensitivity case (run1) in which the leakage rate of CO₂ and brine are two orders of magnitude smaller than that in the base-case run.

Figure 18. Temporal evolution of pH, As and Pb at the leak location for the initial base-case simulation (base) and a sensitivity case (run3) in which the permeability for the sandy facies is half of that in the base-case run.

Figure 17. Temporal evolution of pH, As and Pb at a point 200 m downstream of the leak location for the initial base-case simulation (base) and a sensitivity case (run1) in which the leakage rate of CO₂ and brine are two orders of magnitude smaller than that in the base-case run.

Figure 19. Temporal evolution of pH, As and Pb at a point 200 m downstream of the leak location for the initial base-case simulation (base) and a sensitivity case (run3) in which the permeability for the “sand layer” is half of that in the base-case run.

pathways (e.g. wellbore, faults). Geochemical modeling integrated with laboratory experiments should also be carried out, to establish a robust conceptual model of contaminant mobilization. Only then can reactive transport modeling be applied with some confidence to

predict the long-term impact on specific aquifers. These investigations should include uncertainty quantification to assess the effect of parameter and concept uncertainties on the model results, such as in the approach developed by the CO₂ geologic storage National Risk Assessment Partnership.^{50,51}

Appendix A

Table A1. Equilibrium constants of minerals considered in the simulations.

Minerals	logK (25°C)
Calcite + H ⁺ = Ca ⁺² + HCO ₃ ⁻	1.853
Illite + 6.3 H ₂ O = H ⁺ + 0.25Mg ⁺² + 0.85K ⁺ + 3.4 H ₄ SiO ₄ (aq) + 2.35AlO ₂ ⁻	-43.490
Kaolinite + 3H ₂ O = 2H ⁺ + 2H ₄ SiO ₄ (aq) + 2AlO ₂ ⁻	-39.262
Smectite + 7.32 H ₂ O = 0.68H ⁺ + 0.17Ca ⁺² + 0.335Mg ⁺² + 3.99 H ₄ SiO ₄ (aq) + 1.68AlO ₂ ⁻	-32.834
goethite + 3H ⁺ = 2H ₂ O + Fe ⁺³	0.363
Albite + 6H ₂ O = Na ⁺ + 3H ₄ SiO ₄ (aq) + AlO ₂ ⁻	-20.126
Quartz + 2H ₂ O = H ₄ SiO ₄ (aq)	-3.740
K-Feldspar + 6H ₂ O = K ⁺ + 3H ₄ SiO ₄ (aq) + AlO ₂ ⁻	-22.394
Dolomite + 2H ⁺ = Ca ⁺² + Mg ⁺² + HCO ₃ ⁻	3.545
Magnesite + H ⁺ = Mg ⁺² + HCO ₃ ⁻	1.420
Dawsonite = H ⁺ + Na ⁺ + HCO ₃ ⁻ + 2.35AlO ₂ ⁻	-18.535
Muscovite + 6H ₂ O = 2H ⁺ + K ⁺ + 3H ₄ SiO ₄ (aq) + 3AlO ₂ ⁻	-57.264
Ferrihydrite + 3H ⁺ = 3H ₂ O + Fe ⁺³	3.404
Gibbsite = H ₂ O + H ⁺ + AlO ₂ ⁻	-15.129

Table A2. Cation exchange reactions and selectivity coefficients, using the Gaines-Thomas convention⁶⁰.

Cation exchange reaction	K _{Na/M}
Na ⁺ + X-H = X-Na + H ⁺	1
Na ⁺ + X-K = X-Na + K ⁺	0.2
Na ⁺ + 0.5X-Ca = X-Na + 0.5Ca ⁺²	0.4
Na ⁺ + 0.5X-Mg = X-Na + 0.5Mg ⁺²	0.6
Na ⁺ + 0.5X-Ba = X-Na + 0.5Ba ⁺²	0.2

Table A3. Surface sorption reactions for As, Cd, and Pb on goethite, illite, kaolinite, and montmorillonite (DLM = double layer model, CCM = constant capacitance model).

Reactions	Log k _{int}	Site density mol/m ²	Surface area m ² /g	Type of SCM model (and capacitance as needed)	Reference
Goethite					
goe ¹ _OH ₂ ⁺ = goe ¹ _OH + H ⁺	-7.38	3.9-e8	80	DLM	61
goe ¹ _O ⁻ + H ⁺ = goe ¹ _OH	10.74	3.9-e8	80	DLM	
goe ² _OH ₂ ⁺ = goe ² _OH + H ⁺	-7.38	3.8e-6	80	DLM	61
goe ² _O ⁻ + H ⁺ = goe ² _OH	10.74	3.8e-6	80	DLM	
goe ¹ _OCd ⁺ + H ⁺ = goe ¹ _OH + Cd ⁺²	-1.29	3.9-8	80	DLM	61
goe ² _OCd ⁺ + H ⁺ = goe ² _OH + Cd ⁺²	1.83	3.8e-6	80	DLM	

(Continued)

Table A3. Continued

Reactions	Log k_{int}	Site density mol/m ²	Surface area m ² /g	Type of SCM model (and capacitance as needed)	Reference
$goe^1_{OPb^+} + H^+ = goe^1_{OH} + Pb^{+2}$	-4.78	3.9-e8	80	DLM	61
$goe^2_{OPb^+} + H^+ = goe^2_{OH} + Pb^{+2}$	-1.52	3.8e-6	80	DLM	
$goe^2_{OH_2AsO_3} + H_2O = goe^2_{OH} + H_3AsO_3(aq)$	-5.19	3.32e-6	80	DLM	62
$goe^2_{OHAsO_3^-} + H_2O + H^+ = goe^2_{OH} + H_3AsO_3(aq)$	2.34	3.32e-6	80	DLM	
Illite					
$ill_{OH_2^+} = ill_{OH} + H^+$	-8.02	2.27e-6	66.8	CCM, = 2.0 F/m ²	63
$ill_{O^-} + H^+ = ill_{OH}$	8.93	2.27e-6	66.8	CCM, = 2.0 F/m ²	
$ill_{OCd^+} + H^+ = ill_{OH} + Cd^{+2}$	3.62	2.27e-6	66.8	CCM, = 2.0 F/m ²	63
$(ill)_2Cd + 2H^+ = 2ill_H + Cd^{+2}$	-0.63	1.3e-6	66.8	CCM, = 2.0 F/m ²	
$ill_{CdOH} + 2H^+ = ill_H + Cd^{+2} + H_2O$	6.49	1.3e-6	66.8	CCM, = 2.0 F/m ²	
$ill_{OPb^+} + H^+ = ill_{OH} + Pb^{+2}$	0.70	2.27e-6	66.8	CCM, = 2.0 F/m ²	63
$(ill)_2Pb + 2H^+ = 2ill_H + Pb^{+2}$	-1.37	1.3e-6	66.8	CCM, = 2.0 F/m ²	
$ill_{PbOH} + 2H^+ = ill_H + Pb^{+2} + H_2O$	3.65	1.3e-6	66.8	CCM, = 2.0 F/m ²	
$ill_{H_2AsO_3} + H_2O = ill_{OH} + H_3AsO_3$	-2.12	3.83e-6	66.8	CCM, = 1.06 F/m ²	64
$ill_{HAsO_3^-} + H_2O + H^+ = ill_{OH} + H_3AsO_3$	5.66	3.83e-6	66.8	CCM, = 1.06 F/m ²	
Kaolinite					
$kao_{OH_2^+} = kao_{OH} + H^+$	-4.63	2.24e-6	22.42	CCM, = 1.2 F/m ²	65
$kao_{O^-} + H^+ = kao_{OH}$	7.54	2.24e-6	22.42	CCM, = 1.2 F/m ²	
$Kao_{OCd^+} + H^+ = Kao_{OH} + Cd^{+2}$	3.23	2.24e-6	22.42	CCM, = 1.2 F/m ²	65
$(Kao)_2Cd + 2H^+ = 2Kao_H + Cd^{+2}$	-1.22	3.57e-7	22.42	CCM, = 1.2 F/m ²	
$Kao_{OPb^+} + H^+ = Kao_{OH} + Pb^{+2}$	0.64	2.24e-6	22.42	CCM, = 1.2 F/m ²	65
$(Kao)_2Pb + 2H^+ = 2Kao_H + Pb^{+2}$	-2.36	3.57e-7	22.42	CCM, = 1.2 F/m ²	
$kao_{HAsO_3^-} + H_2O + H^+ = kao_{OH} + H_3AsO_3$	5.43	3.83e-6	22.42	CCM, = 1.06 F/m ²	64
$kao_{AsO_4^{-2}} + H_2O + 2H^+ = kao_{OH} + H_3AsO_4$	4.69	3.83e-6	22.42	CCM, = 1.06 F/m ²	64
Montmorillonite					
$mon_{OH_2^+} = mon_{OH} + H^+$	-6.04	4.41e-6	46	CCM, = 3.2 F/m ²	66
$mon_{O^-} + H^+ = mon_{OH}$	6.63	4.41e-6	46	CCM, = 3.2 F/m ²	
$mon_{Na^+} + H^+ = mon_H + Na^+$	-0.18	1.53e-5	46	CCM, = 3.2 F/m ²	
$mon_{OCd^+} + H^+ = mon_{OH} + Cd^{+2}$	2.93	4.41e-6	46	CCM, = 3.2 F/m ²	66
$(mon)_2Cd + 2H^+ = 2mon_H + Cd^{+2}$	-2.37	1.53e-5	46	CCM, = 3.2 F/m ²	
$mon_{OPb^+} + H^+ = mon_{OH} + Pb^{+2}$	-0.49	4.41e-6	46	CCM, = 3.2 F/m ²	66
$(mon)_2Pb + 2H^+ = 2mon_H + Pb^{+2}$	-2.56	1.53e-5	46	CCM, = 3.2 F/m ²	
$mon_{H_2AsO_3} + H_2O = mon_{OH} + H_3AsO_3$	-1.19	3.83e-6	46	CCM, = 1.06 F/m ²	64
$mon_{HAsO_3^-} + H_2O + H^+ = mon_{OH} + H_3AsO_3$	3.92	3.83e-6	46	CCM, = 1.06 F/m ²	64

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