# Trace Metal Source Terms in Carbon Sequestration Environments

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ABSTRACT

Carbon dioxide sequestration in deep saline and depleted oil geologic formations is feasible and promising, however, possible $CO_2$ or $CO_2$-saturated brine leakage to overlying aquifers may pose environmental and health impacts. The purpose of this study was to experimentally define trace metal source terms from the reaction of supercritical $CO_2$, storage reservoir brines, reservoir and cap rocks. Storage reservoir source terms for trace metals are needed to evaluate the impact of brines leaking into overlying drinking water aquifers. The trace metal release was measured from sandstones, shales, carbonates, evaporites, basalts and cements from the Frio, In Salah, Illinois Basin – Decatur, Lower Tuscaloosa, Weyburn-Midale, Bass Islands and Grand Ronde carbon sequestration geologic formations. Trace metal dissolution is tracked by measuring solution concentrations over time under conditions (e.g. pressures, temperatures, and initial brine compositions) specific to the sequestration projects. Existing metrics for Maximum Contaminant Levels (MCLs) for drinking water as defined by the U.S. Environmental Protection Agency (U.S. EPA) were used to categorize the relative significance of metal concentration changes in storage environments due to the presence of $CO_2$. Results indicate that Cr and Pb released from sandstone reservoir and shale cap rock exceed the MCLs by an order of magnitude while Cd and

Cu were at or below drinking water thresholds. In carbonate reservoirs As exceeds the MCLs by an order of magnitude, while Cd, Cu, and Pb were at or below drinking water standards. Results from this study can be used as a reasonable estimate of the reservoir and caprock source term to further evaluate the impact of leakage on groundwater quality.

## 1. INTRODUCTION

Carbon capture and sequestration (CCS) technology is one prominent and feasible approach to help mitigate impacts from increasing rates of $CO_2$ release from emission point sources. The technology, in its most simplistic description, involves the capture of $CO_2$ from an industrial source such as a coal-fired power plant, compression and transport of $CO_2$ to an injection site and finally its sequestration to a deep underground geologic formation for long-term storage.

Many types of geologic formations have been proposed as the final receptors of $CO_2$ based on a suite of criteria, including their location, geomorphology, potential storage capacity, hydrocarbon potential, and structural characteristics for storage permanence. Among these, deep saline formations and depleted oil and gas fields are the most promising. The former is being considered based on for its large storage capacity with estimates ranging between 2,000 and 22,000 Gt for USA and Canada,[1] while the latter promises the additional potential for $CO_2$-enhanced oil and natural gas recovery[2] and long-term storage based on its inherent characteristic of maintaining oil and gas securely confined for thousands of years.

The sequestration of $CO_2$ in both saline geologic formations and depleted oil and gas fields involves upward brine displacement,[3] compression of both injected and resident fluids and

expansion of pore space.[4] Although, in the long geologic time scale the sequestered bulk $CO_2$ is unlikely to escape due to various trapping mechanisms, such as solution,[5,6] physical,[7] and mineral trapping,[8] slow leakage of buoyant $CO_2$ or $CO_2$ saturated brine even under favorable storage conditions may occur. Analog studies of geologic environments containing large, concentrated amounts of $CO_2$ have shown that leakage processes are inherent in CCS.[9] Carbon sequestration is viable only if those leakages account for less than 1% of stored $CO_2$ over 100 years.[10] Likely conduits for $CO_2$ migration to overlying aquifers are faults or fracture networks within caprock and wellbores.[11] The primary concern for such a leak is that dissolution of $CO_2$ within the storage reservoir and a drinking water aquifer will depress the pH and consequently dissolve trace metals from minerals, such as carbonate- or sulfide-bearing minerals, clays, and iron oxyhydroxides,[12-16] liberating naturally-occurring hazardous elements to the water table.[17,18] The resulting increase in concentration of hazardous trace elements can contaminate drinking water resources and detrimentally affect groundwater quality.[19] Lewicki et al.[20] have summarized $CO_2$ leakage incidents from natural and industrial analogues revealing that in more than 20 occasions worldwide, $CO_2$ escaped mainly through faults, fractures and wells causing adverse health, safety and environmental effects. In most of these occasions, $CO_2$ was naturally accumulated in highly fractured and/or porous rocks, such as sandstones and limestones, under low-permeability cap rocks or produced by thermal decomposition of carbonate-rich sedimentary rocks and degassing of magma.

Geochemical modeling and reactive transport simulations have been conducted to systematically evaluate the potential for water quality changes due to $CO_2$ intrusion into shallow aquifers, but their results are difficult to extrapolate or generalize because these modeling runs are site specific

78 and the variation between sites is high.[21] Many of these investigations use the Maximum
79 Contaminant Levels (MCLs), as defined by the U.S. EPA, as a metric by which to gauge the
80 effects of geochemical reactions on water quality. According to the National Drinking Water
81 Regulations,[22] MCLs are divided into two categories: primary and secondary. Primary drinking
82 water standards, which are for trace metals such as As, Cd, Cr, Pb, and Cu, among others, are
83 legally enforced for the protection of public health by limiting the levels of contaminants in
84 drinking water. Secondary drinking water standards, which include standards for Fe, Mn, and Zn,
85 are non-enforceable guidelines regulating contaminants that may cause cosmetic or aesthetic
86 effects in drinking water. One of the modeling studies probed the potential for trace metal
87 mobilization due to $CO_2$ intrusion into United States drinking water aquifers, which resulted in
88 predictions that only As, Pb and Zn should exceed their MCLs.[23,24] Trace metal releases have
89 also been predicted due to acidification of shallow aquifers with low buffering capacity, and in
90 some of these cases trace metal concentrations were estimated to exceed their MCLs
91 (e.g.[19,24,25]).
92
93 Limited experimental data exist to date to assess the probability and the environmental impacts
94 of $CO_2$ leakage on groundwater quality. For field studies reported in shallow environments, a
95 few examples demonstrate the complexity of the reactions involved. In the U.S. Tri-state mining
96 district (Kansas-Missouri-Oklahoma) high concentrations of zinc, lead and cadmium in the $CO_2$-
97 rich water decreased as the $CO_2$ degassed and pH increased. In this system trace metal solubility
98 was governed by the dissolution of iron oxyhydroxide and carbonate minerals.[26] Investigations
99 suggest that trace metals dissolved from reaction of $CO_2$-rich brines with basalt at Mt. Hekla,
100 Iceland are reincorporated into solid phases as the groundwaters are neutralized by continued

basalt dissolution.[27] At Zero Emission Research and Technology Center (ZERT) in Bozeman MT, a field experiment showed that by injecting $CO_2$ in a shallow aquifer, Pb and As were readily mobilized and their respective concentrations in the water were increased, but not to a level that exceeded their respective MCLs at the end of the field experiment.[28,29] In the Frio formation in Texas, a demonstrative $CO_2$ injection was conducted into a sandstone section of the formation to investigate the potential for geologic storage in a saline sedimentary aquifer.[12] Fluid samples were collected before and after the $CO_2$ injection. Chemical and modeling results exhibited rapid mineral dissolution especially for calcite and iron oxyhydroxide which significantly increased Fe and Mn concentrations in the saline waters and were associated with early $CO_2$ breakthrough. Samples collected 15 months after injection showed much lower metal concentrations and higher pH, indicating that the reservoir had buffered any environmental impacts from this short test.[13] Investigations in Chimayo New Mexico, revealed upwelling trace metals via two pathways that have $CO_2$-rich or $CO_2$-poor brines. The former provided a source of As, Pb and U which significantly increased their concentration in the overlying aquifer, exceeding the MCLs in few cases; however, the increase was not attributed to in situ trace element mobilization caused by the presence of $CO_2$.[17]

The objective of this experimental study is to provide a range of concentrations that can be used as the trace element source term for reservoirs and leakage pathways in risk simulations (i.e.[30,31]). We report averaged trace metal concentrations after 20 days of reaction of $CO_2$-rich brines with cap and reservoir rock from different carbon sequestration demonstration projects and wellbore cements. The results rank rock systems and trace elements that require more systematic studies to establish the geochemical reactions that control solution concentrations.

Defining the magnitude of this source term is important for both understanding the role of $CO_2$ in liberating trace metals via dissolution of their parent minerals, and predicting the potential risks to shallow groundwaters if reacted brines leak from storage formations.

## 2. EXPERIMENTAL SECTION

### 2.1. Rock – Brine – $CO_2$ Experiments

Rock and cement samples used in the experiments from different depths and geologic formations in the United States, Canada and Algeria (Table 1). In all experiments, rock fragments were reacted with synthetic or natural brine and supercritical $CO_2$ at the temperature and pressure conditions of their respective site. The $pCO_2$ for a given set of experiments depends on pressure, temperature, and salinity and can be calculated from various equations of state found in the literature.[32-35] Most of the brine compositions used in this study were synthesized to simulate the actual brine composition of the site, because collecting adequate mass to conduct experiments and preserving natural brine samples from each site is rarely possible. Only the brines used in experiments studying the Lower Tuscaloosa rocks were collected from the actual site. The rest of the brine compositions, except for one (i.e. Bass Island) were representative of the sites trying to mimic the actual composition of the natural brines. Details about the depth, brine type, mass of solids and brine, temperature, pressure and reaction times for individual experiment are reported in Table 1.

Static Dickson-type Au reactors housed in water-filled pressure vessels were used to react rock or cement samples with the brine and supercritical $CO_2$ for most of the experiments. Here we provided a brief description of the experimental setup, details are available in the literature.[13,36]

149 The reaction kinetics and the approach to equilibrium were monitored by sampling the solution
150 as a function of time. The impact of $CO_2$ on dissolved trace metal solubility was made from the
151 comparison of the solution composition before and after injection of supercritical $CO_2$. After one
152 month of reaction to achieve constant concentrations in absence of $CO_2$, supercritical $CO_2$ was
153 injected into the reactor-cell (gold bag) and reacted for an additional month. Supercritical $CO_2$
154 was added in excess to the reaction vessel to ensure that both dissolved and supercritical $CO_2$
155 were present for the duration of the experiment. Brine samples were taken and analyzed for
156 solution chemistry over the duration of the experiment. Samples for dissolved trace metal
157 analysis were filtered, acidified with high purity nitric acid, and diluted with distilled and
158 deionized water. $CO_2$ concentrations were measured continuously throughout the experiment.
159 Measuring the $CO_2$ saturation was essential to the experiment, not only because we wanted to
160 mimic the reservoir conditions, but also as an indicator of possible leaks of the reactor-cell (gold
161 bag) during the experiment. $CO_2$ values are reported in accompanied studies (Table 1). Control
162 experiments using the same protocol but without any rock sample show that some trace metals
163 are leached from the passivated titanium parts when exposed to supercritical $CO_2$ and high brine
164 concentrations, but these values are 10 to 1000 times lower than the concentrations from rock-
165 water interactions. Results for all control experiments are reported in Table 2 for direct
166 comparison with the rock-water-$CO_2$ experiments. Initial trace metal concentrations were 1 to
167 1000 times greater in the solids compared to the solution composition.
168
169 Experiments for Grand Ronde basalt and Bass Islands dolomite rock samples were conducted in
170 300-mL Parr® pressure vessels (Parr Instrument Company, Moline, Illinois) with a Teflon liner.
171 Parallel experiments were conducted with $CO_2$ and $N_2$, respectively, for each rock sample under

the same conditions (pressure, temperature, brine concentration, solid to solution ratio) to compare the effect of $CO_2$ on rock dissolution. Synthetic brine and rock samples were equilibrated with $CO_2$ or $N_2$ gas under a designated pressure and temperature. Rock samples were not equilibrated with saline solution before $CO_2$ or $N_2$ injection as previously described for other rocks. All wetted parts of the pressure vessel were made of either teflon, titanium or zirconium. No Ti or Zr was detected above its quantification limit (20 and 30 ppb, respectively) in aqueous samples throughout the experiment. Aqueous samples were collected at selected time intervals, and during sampling, the vessels were pressurized with a syringe pump to maintain constant pressure throughout the experiment.

**2.2. Sample Analysis**

Major and trace metals in the aqueous samples and the stock solution were analyzed using ICP-MS or ICP-OES. Samples were prepared volumetrically with a 20:1 dilution using an internal standard solution in 2% nitric acid. A fully quantitative analysis using a linear calibration curve based on known standards was performed. The internal standard was corrected for instrument drift and suppression from the sodium chloride matrix. Detection levels were established from duplicate blanks and serial dilution preparations. Matrix spike samples were analyzed for quality control.

Table 1. Summary of general experimental parameters.

| Lithology | Location | Depth (m) | Solid (g) | Brine (g) | Brine Type[a] | Temperature (°C) | Pressure (MPa) | Reaction Time before $CO_2$ injection (days) | Reaction Time after $CO_2$ injection (days) |
|---|---|---|---|---|---|---|---|---|---|
| **Sandstone Reservoirs** | | | | | | | | | |
| **Mt Simon**[36] | Illinois, USA | 1954 | 12.4 | 245.9 | A | 51 | 19.5 | 40 | 31 |
| **Mt Simon**[36] | Illinois, USA | 2062 | 12.0 | 320.7 | A | 51 | 19.5 | 35 | 43 |
| **Frio**[13] | Texas, USA | 1547 | 10.6 | 210.0 | B | 60 | 10.0 | 4 | 21 |
| **Lower Carboniferous**[15] | In Salah, Algeria | 2062 | 5.6 | 301.2 | C | 95 | 10.0 | 33 | 28 |
| **Lower Tuscaloosa**[37] | Mississippi, USA | 3190 | 10.0 | 193.2 | D | 120 | 34.4 | 43 | 46 |
| **Lower Tuscaloosa** | Mississippi, USA | 3193 | 8.55 | 170.8 | D | 120 | 34.4 | 53 | 50 |
| **Bunter**[38] | UK | 2000 | NA | NA | E | 60 | 30 | 5 | 57 |
| **Navajo Sandstone**[39] | Arizona, USA | NA | 4.0 | 40 | F | 200 | 30 | 0 | 1-58 |
| **Shale Caprocks** | | | | | | | | | |
| **Eau Claire**[36] | Illinois, USA | 1675 | 15.3 | 262.6 | A | 51 | 19.5 | 41 | 31 |
| **Eau Claire**[36] | Illinois, USA | 1675 | 10.0 | 364.3 | A | 95 | 19.5 | 29 | 64 |
| **Lower Carboniferous**[15] | In Salah, Algeria | 2087 | 6.4 | 301.2 | C | 95 | 10 | 31 | 31 |
| **Carbonate Reservoirs** | | | | | | | | | |
| **Vuggy**[40] | Weyburn, Canada | 1463 | 11.6 | 253.7 | G | 60 | 12.4 | 35 | 31 |
| **Vuggy**[40] | Weyburn, Canada | 1448 | 11.3 | 340.5 | G | 60 | 12.4 | 28 | 32 |
| **Marly**[40] | Weyburn, Canada | 1447 | 10.4 | 265.4 | G | 60 | 12.4 | 35 | 31 |
| **Bass Islands**[41] | Michigan, USA | 1367 | 4.0 | 180 | H | 75 | 10.0 | 35 | 35 |
| **Evaporite Caprocks** | | | | | | | | | |
| **Three Fingers**[40] | Weyburn, Canada | 1389 | 12.1 | 285.5 | G | 60 | 12.4 | 29 | 64 |
| **Basalt** | | | | | | | | | |
| **Grand Ronde**[42] | Washington, USA | 1074 | 4.0 | 180 | H | 75 | 10.0 | 35 | 35 |
| **Wellbore Cement** | | | | | | | | | |
| **Class G** | NA | NA | 4.0 | 280.5 | C | 95 | 10 | 11 | 30 |
| **Class G** | NA | NA | 20.0 | 204.5 | C | 95 | 10 | 21 | 22 |
| **Class G + Lower Carboniferous**[15] | In Salah, Algeria | 2087 | 4.8 | 252.5 | C | 95 | 10 | 26 | 44 |
| **Class G + Lower Carboniferous**[15] | In Salah, Algeria | 2062 | 8.6 | 246.5 | C | 95 | 10 | 40 | 35 |

[a]Brine Type: A) 2.1 m NaCl, 0.2 m KCl, 0.55 m $CaCl_2$, and 0.1 m $MgCl_2$; B) 1.5 m NaCl; C) 1.8 m NaCl, 0.55 m $CaCl_2$ and 0.1 m $MgCl_2$; D) Natural brine from Cranfield MI (salinity of 15%wt); E) 1 m NaCl; F) 0.2 m KCl; G) 1.1 m NaCl equilibrated with calcite and anhydrite prior to injection of $CO_2$; H) 0.1 m NaCl.

## 3. RESULTS AND DISCUSSION

Our collective experimental dataset shows that reaction of $CO_2$-rich brines with reservoir rocks (sandstone, carbonate, and basalt), caprocks (shale and evaporite), and wellbore cement enhance trace metals in solutions. The trace metals generally achieve constant concentrations within about 20 days after $CO_2$ injection, but not in all cases. Relative standard deviation for the trace metal concentrations was generally less than 2% for As, Cr, Cu, Fe; less than 6% for Pb; less than 10% for Cd and Mn; and often as high as 100% for Zn. For some experiments where the trace metal concentrations were low, the relative standard deviation was between 15 and 35%. An example of the change in trace metal concentrations with time is shown in Figure 1 for carbonate rocks from the Weyburn storage project. The results of these specific carbonate experiments suggest that storage of supercritical $CO_2$ will result in As, Cr, Fe, and Mn concentrations that are at or above EPA drinking water standards. We observed a wide variation in the absolute trace metal concentrations from the other experiments (see Supplementary Information Figures S2 to S13).

Averaged concentrations measured throughout the duration of the experiment capture the likely range of As, Cd, Cr, Cu and Pb (primary elements of concern) and Fe, Mn, and Zn ( secondary elements of concern) that could leak from geologic sequestration environments to overlying aquifers. Table 2 reports averaged concentrations normalized to the appropriate MCL for each element and experiment, as well as results reported by Wigand et al.[38] and Lu et al..[39] Figure 2 is a cumulative distribution profile of the normalized concentrations plotted against the percentage of the experiments with trace metals at or below a given concentration. Normalized concentrations from all experiments generally span 2 to 3 orders of magnitude where values may

be either above or below the standard threshold (MCL). Concentration thresholds of primary MCLs are As = 10 ppb, Cd = 5 ppm, Cr = 100 ppb, Cu = 1300 ppb, and Pb = 15 ppb, and of secondary MCLs are Fe = 300 ppb, Mn = 50 ppb, and Zn = 5000 ppb. Figure 2 suggests that leakage of brines containing Fe and Mn could impact groundwater quality because normalized concentrations for these elements were consistently higher than the secondary MCLs. Leakage of brines containing Pb, Cr, Cd, and As also need to be considered for integrated risk assessment modeling, as between 50% to 75% of the experiments reported here yielded concentrations for these elements that were above the groundwater thresholds. Of the elements studied, only Cu and Zn are unlikely to affect groundwater quality during mixing of reacted brine, because the concentrations measured from 80% to 90% of the experiments were generally below the thresholds.

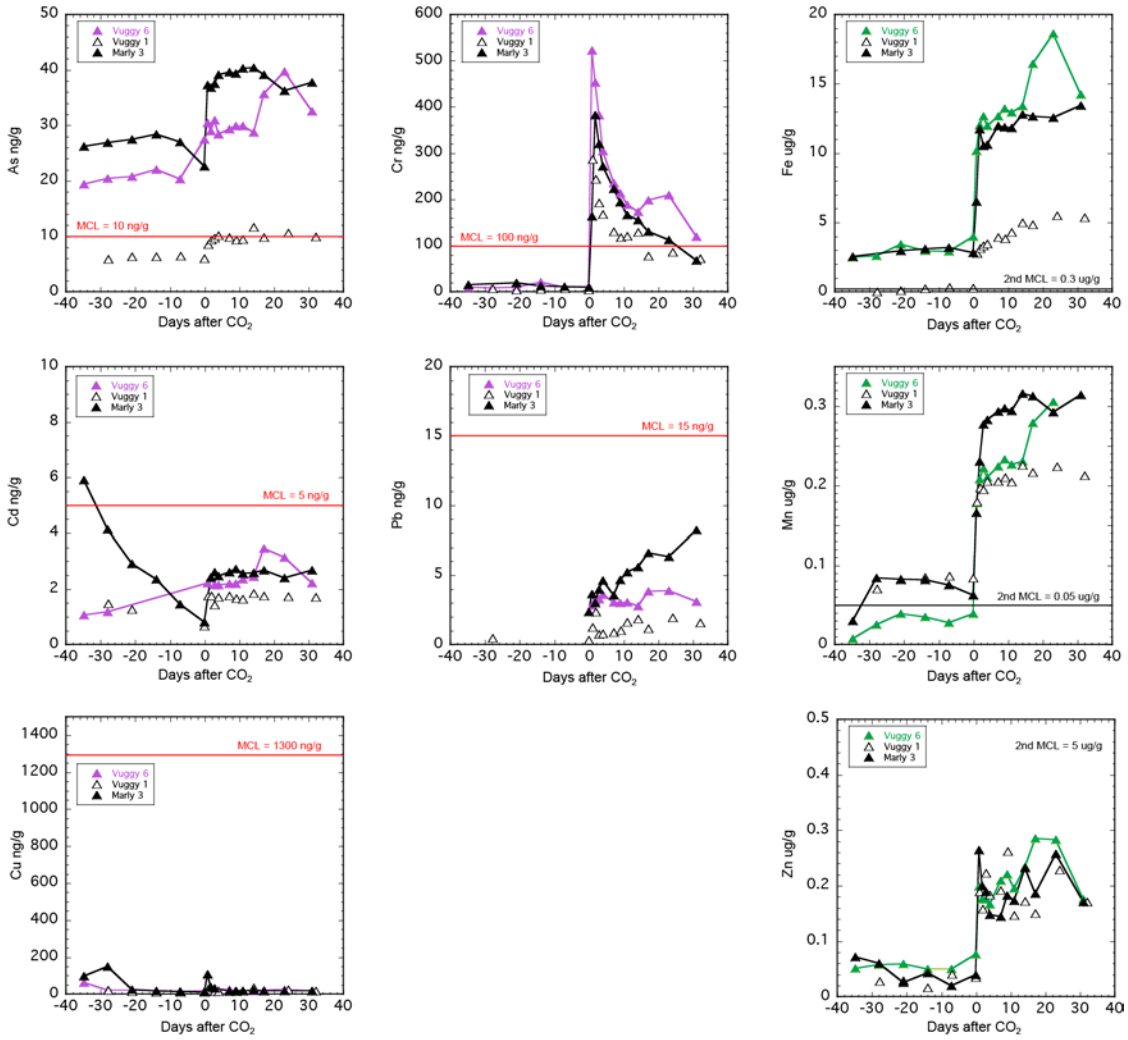


Figure 1. Total concentrations (ng/g or µg/g solution) of dissolved trace metals released from three carbonate samples originated in Weyburn, Canada (Vuggy and Marly) when they reacted with synthetic brine with or without $CO_2$ as a function of reaction time (days). Time 0 hours denotes the beginning of $CO_2$ injection in the system.

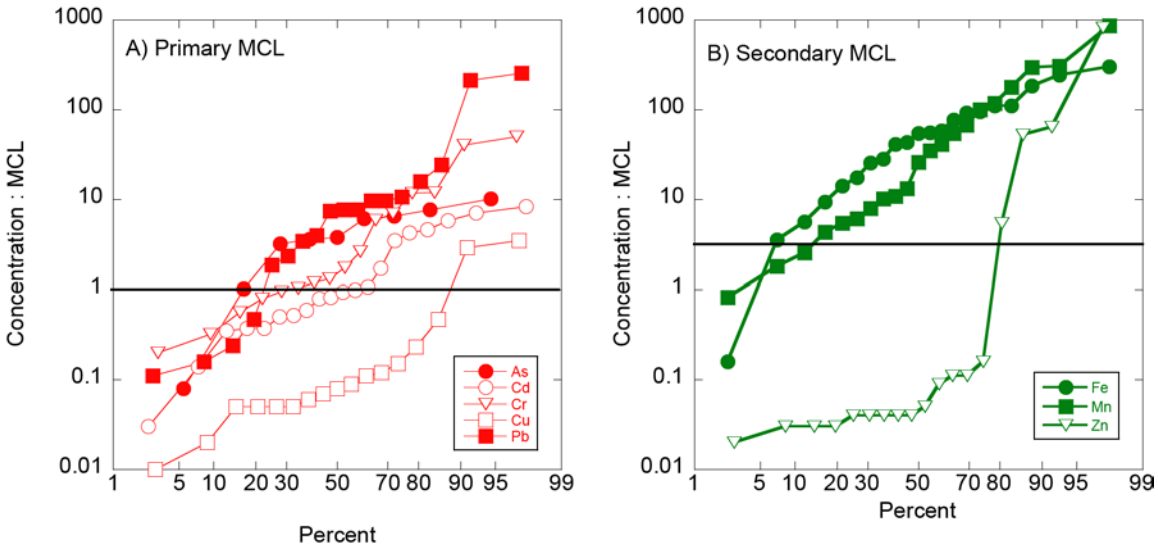


Figure 2. Cumulative distribution profiles of averaged concentrations normalized to MCL plotted against the percentage of the experiments with trace metals at or below a given concentration.

Table 2. Average trace metal concentrations normalized to primary or secondary MCL. Concentrations were averaged after about 20 days of reactions. Relative standard deviation for the trace metal concentrations was generally less than 2% for As, Cr, Cu, Fe; less than 6% for Pb; less than 10% for Cd and Mn; and often as high as 100% for Zn.

| Lythology | As | Cd | Cr | Cu | Fe | Mn | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| **Sandstone Reservoirs** | | | | | | | | |
| **Mt Simon**[36] | -[a] | 0.50 | 40.61 | 0.23 | 55.31 | 10.13 | 9.66 | 0.04 |
| **Mt Simon**[36] | - | 1.06 | 50.19 | 0.12 | 77.11 | 10.84 | 2.35 | - |
| **Frio**[13] | 0.08 | 0.82 | 1.21 | 0.08 | 14.13 | 8.00 | 7.67 | - |
| **Lower Carboniferous**[15] | - | 0.98 | 5.90 | 0.05 | 303.43 | 40.96 | 1.88 | 0.03 |
| **Lower Tuscaloosa**[37] | - | 7.06 | - | 2.90 | 111.33 | 308.00 | 212.67 | 53.18 |
| **Lower Tuscaloosa** | - | 3.48 | 1.33 | 3.52 | 25.70 | 296.00 | 254.00 | 5.48 |
| **Bunter**[38] | - | 0.79 | - | 0.47 | 94.99 | 865.00 | 7.67 | 820.52 |
| **Navajo Sandstone**[39] | - | - | - | 0.05 | 5.67 | 1.80 | - | 64.00 |
| **Shale Caprocks** | | | | | | | | |
| **Eau Claire**[36] | - | 1.73 | 7.03 | 0.05 | 241.95 | 67.61 | 7.48 | - |
| **Eau Claire**[36] | 6.10 | 0.37 | 11.90 | - | 110.00 | 34.80 | 4.00 | 0.03 |
| **Lower Carboniferous**[15] | - | 0.93 | 0.32 | 0.15 | 184.00 | 2.55 | 24.48 | 0.11 |
| **Carbonate Reservoirs** | | | | | | | | |
| **Vuggy**[40] | 3.77 | 0.52 | 1.04 | 0.01 | 43.00 | 6.14 | 0.47 | 0.04 |
| **Vuggy**[40] | 1.02 | 0.35 | 0.79 | - | 17.47 | 4.36 | 0.11 | 0.04 |
| **Marly**[40] | 3.60 | 0.59 | 1.76 | 0.02 | 54.77 | 5.48 | 0.24 | 0.05 |
| **Bass Islands**[41] | - | 0.03 | - | 0.09 | 0.16 | 0.82 | - | 0.02 |
| **Evaporite Caprocks** | | | | | | | | |
| **Three Fingers**[40] | - | 0.37 | 11.99 | 0.05 | 58.10 | 13.19 | 0.16 | 0.03 |
| **Basalt** | | | | | | | | |
| **Grand Ronde**[42] | - | 0.14 | - | 0.06 | 40.99 | 99.87 | - | 0.04 |
| **Wellbore Cement** | | | | | | | | |
| **Class G** | 10.12 | 8.41 | 2.65 | - | 3.55 | 54.15 | 9.71 | 0.16 |
| **Class G** | 3.20 | 4.24 | 0.56 | - | 9.45 | 26.08 | 3.43 | 0.04 |
| **Class G + Lower Carboniferous**[15] | 7.72 | 4.63 | 0.96 | 0.11 | 91.52 | 177.20 | 10.62 | 0.11 |
| **Class G + Lower Carboniferous**[15] | 6.51 | 5.83 | 0.20 | 0.07 | 28.18 | 118.64 | 15.97 | 0.09 |
| **Blanks** | | | | | | | | |
| **0.1 m NaCl** | - | - | 0.64 | 0.07 | 0.14 | - | 0.39 | - |
| **1 m NaCl + 0.8 m $NaHCO_3$** | 0.014 | 0.05 | 0.35 | 0.04 | 0.69 | 0.21 | 0.38 | 0.005 |
| **3.6 m NaCl + 0.015 m $NaHCO_3$** | 0.59 | 0.09 | 0.12 | 0.02 | - | 0.86 | 0.09 | 0.009 |
| **DI water** | - | - | - | - | - | - | - | - |

[a]The dashes in the table indicate insufficient data. Concentrations were below the limit of detection.

The rock type (or cement) has significant control on the release of trace metals both in terms of mineral dissolution and carbonate content that can buffer solution pH. Table 3 recasts the information in Table 2 for a given rock type to highlight which types of rock yield trace metal concentrations that exceed EPA primary or secondary MCLs during reaction with $CO_2$. Values highlighted with red shading indicate that the respective trace metal concentration exceeds the MCL, whereas those values below or equal to MCL are shaded in green, indicating that they are of less concern when developing models to predict the effects of leaked brine on shallow groundwaters. The amount of trace metals that can be leached from rock types are generally greater for sandstone and shale, followed by cement, and then carbonate, evaporite, and basalt. Dissolved Fe and Mn routinely exceeded the secondary standards for nearly all rock types and their impact to groundwater quality should be evaluated closely. Any impacts to groundwater quality from Fe and Mn would contribute to an economic risk by altering groundwater aesthetics. Dissolved Pb concentrations were highest for sandstones, shales, and cements, but were released in limited amounts for carbonates, evaporites and basalt. Higher releases of Pb generally correspond to those experiments at higher temperatures, with the highest concentrations in the 120 °C sandstone experiments. Elevated Cr release occurred in all rock types (sandstones, shales, carbonates, evaporites or cements) except basalt. The As source term from sandstones and shales were inconclusive because the As concentration of the synthetic brines was generally higher than concentrations measured after the reaction with $CO_2$-rich brines. Slight As release was observed for carbonates, cements and evaporites.

Table 3. Median trace metal concentrations normalized to primary or secondary MCL for all the experiment. Shading below indicates those rock types that yielded trace metal concentrations that were at, below or above the MCL.

| Metal | Median | Basalt | Sandstone | Shale | Carbonates | Evaporite | Cement |
|---|---|---|---|---|---|---|---|
| | | | | **Primary** | | | |
| Cu | 0.08 | <MCL | <MCL[a] | <MCL | <MCL | <MCL | <MCL |
| As | 3.8 | <MCL[b] | | | > MCL | <MCL | >MCL |
| Cd | 0.93 | <MCL | <MCL[a] | ~MCL | ~MCL | <MCL | >MCL |
| Cr | 1.27 | <MCL | >MCL | >MCL | >MCL | >MCL | ~MCL |
| Pb | 4.0 | <MCL | >MCL | >MCL | <MCL | <MCL | >MCL |
| | | | | **Secondary** | | | |
| Zn | 0.04 | <MCL | <MCL[a] | <MCL | <MCL | <MCL | <MCL |
| Mn | 26.08 | >MCL | >MCL | >MCL | >MCL | >MCL | >MCL |
| Fe | 54.7 | >MCL | >MCL | >MCL | >MCL | >MCL | >MCL |

[a]Two points from the experiment were above the MCL; [b]Samples were below the limit of detection. MCLs in drinking water (µg/L or ppb): Cu,1300; As, 10; Cd, 5; Cr (total), 100; Pb, 15; Zn, 5000; Mn, 50; Fe, 300.

## Implications of brine leakage on groundwater quality

The increased acidity associated with brines in equilibrium with supercritical $CO_2$ will increase trace metal concentrations in the storage reservoir and along cap rock and wellbore leakage pathways. Although these carbon sequestration experiments show that some trace metals exceeded their respective MCLs, their impact on groundwater quality will be dependent on many processes along the leakage pathway and within the shallow aquifer. This will involve degassing of $CO_2$, an increase in pH, and precipitation of carbonate and iron hydroxide minerals as temperature and pressure decrease.[13,27-29] All of these processes are likely to lower the trace metal concentration. Leakage into many groundwaters will also be accompanied by a change from reducing to oxidizing conditions that should result in much lower Fe and Mn concentrations

from hydroxide precipitation.[26] Even for elements such as Pb with fairly high concentrations, it is likely that degassing of the brines could lower the concentrations along the leakage pathway through precipitation or adsorption. Lower Pb concentrations in experiments with cement suggest that Pb released from the caprock would be removed from solution possibly by amorphous silica and carbonate minerals (the primary cement alteration products). Natural dispersion and sorption reactions also have the potential to lower Pb concentrations within a dilute aquifer. The range of trace metal concentrations from these 21 experiments can be used as source terms to overlying aquifers to assess risk during the site selection and permitting process. Once site-specific core is available additional experiments may be performed to narrow the uncertainty of risk assessment calculations.

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## ASSOCIATED CONTENT

**Supporting Information**

Details of the individual dissolved trace metals release from different types of rocks and locations, when reacted with or without $CO_2$ saturated synthetic or natural brine as a function of time and their comparison with regulatory maximum contaminant levels. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
The authors declare no competing financial interest.

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**TABLE OF CONTENTS ARTWORK**

Range of trace metal concentrations normalized to maximum contaminant levels that could leak from geologic carbon storage reservoirs by on experiments