


Potential impacts of CO₂ leakage on groundwater quality of overlying aquifer at geological carbon sequestration sites: A review and a proposed assessment procedure

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Abstract: One of the risks of geologic carbon sequestration (GCS) is the leakage of injected CO₂ into overlying groundwater resources, resulting in potential deterioration of the quality of the groundwater due to the increase in acidity, the release of trace metals and organic compounds, and potential changes in microbial activities. A large number of studies have been conducted to evaluate various aspects of the impact of CO₂ leakage on overlying aquifers using natural analog, laboratory experiments, field tests, and numerical models. In this paper, we conducted an exhaustive review of the published work, focusing on the statistical assessment of the risk posed by the trace elements including Pb, As, Cd, Ba, and U and identifying the knowledge gaps. Key observations from the review include the following: (1) Pb, As, and U are metals of primary concern because multiple cases showed their concentration higher than maximum contaminant level (MCL) or other regulatory standards, (2) carbonate aquifers seemed more vulnerable to Pb and As contamination but not to U, (3) Cd and Ba are less a concern, only one case showed Cd/Ba concentration higher than MCL, (4) none of the field studies showed the concentrations of Pb and As higher than MCL, although one push–pull field test showed the concentration of U higher than MCL, (5) the order of aggressiveness in terms of releasing trace metals was determined to be as follows: batch experiment > column experiment > field test, and (6) there is no clear correlation between metal release and type of sediments, type of aquifer, the content of carbonate and clay. Evaluation likely has to be done on a case-by-case basis. For further operations of CO₂ storage overview and screening of potential sites, we suggest the use of an eight-step environmental risk assessment procedure comprising laboratory experiment, screening modeling work, and field testing for assessing the vulnerability of the overlying aquifers to degradation from CO₂ leakage from the GCS site. © 2021 Society of Chemical Industry and John Wiley & Sons, Ltd.

Keywords: CO₂ leakage; groundwater; risk assessment; review; procedure

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Introduction

Carbon capture and storage (CCS) is a promising technology to reduce net carbon dioxide (CO₂) emissions whereby CO₂ is captured from large point sources, such as power plants, and injected into deep geological formations. Geological carbon sequestration (GCS) is intended to persist for geological timescales¹; however, unintended leakage of injected CO₂ into overlying groundwater resources could occur due to either short-term, sudden releases of CO₂, such as in the case of a subsurface blowout or well failure, or due to slow, gradual leaks from undetected fractures or faults.² When CO₂ dissolves into groundwater, pH decreases, altering hydrogeochemical processes and leading to a subsequent mobilization of various ions,^{2–6} impacting water quality. The potential impacts of underground CO₂ storage on groundwater quality in the overlying aquifer due to leakage is an obstacle to widespread implementation.^{2,3,7,8} Therefore, a thorough understanding of the potential impacts of underground CO₂ storage on hydrogeochemical processes in overlying groundwater is crucial.

A combination of lab-scale tests, field-based tests, modeling, and analysis of natural analog sites provides the most thorough understanding of the potential impacts of CO₂ leakage on the groundwater quality of the overlying aquifer. Lab-scale batch experiments usually involve adding CO₂ to a preequilibrated sediment + water system with a high water-to-rock ratio and maximize the mobilization of ions from sediment allowing for slow geochemical processes to take place,⁹ which provide useful screening of the potential risk posed by the trace elements. Field-based studies provide water-to-rock ratios closer to natural systems and hydrological and geochemical conditions are expected to be more similar to actual GCS leakage scenarios.⁹ Models based on lab and field studies can be used to predict changes in groundwater quality based on site-specific parameters including aquifer mineral composition, flow rates, and CO₂ leakage rates. Natural CO₂ storage analog sites provide examples of both the long-term feasibility of GCS as well as potential long-term environmental impacts should leakage occur.¹⁰

In this study, we systematically reviewed current knowledge regarding the potential impacts of CO₂ leakage on groundwater quality of overlying aquifer that can be a resource for drinking water or other use.

From our synthesis of 350 published studies on groundwater quality impacts, we developed a workflow applicable to risk assessment of GCS in terms of the potential impact of leaking CO₂ on the overlying aquifer. This paper starts with a summary of the literature collected throughout this study, and then synthesizes the previously published results of impacts to groundwater from CO₂ leakage and identifies the data gaps and research needs. Finally, we describe a recommended workflow assessing the risk to shallow groundwater of CO₂ leakage.

Summary of literature

In this report, we collected a total of 139 papers/reports which encompass 350 cases. Note that one paper sometimes contains multiple cases and not all papers/reports are cited here. The break-down of these cases are as follows:

- 190 natural analog
- 16 review papers
- 19 modeling studies
- 81 laboratory batch and/or column tests
- 42 Field tests
- Eight studies motioned microbial activities:
 - Two studies involve field test
 - Two studies are related to deep storage formation
 - Four are natural analog
- Five studies mentioned organics:
 - Two modeling studies
 - Two studies from the deep storage formation
 - One batch experiment

Summary of literature: –*In situ* studies

Field injection and push–pull studies to determine the effects of CO₂ leakage from storage formation on overlying aquifer have been conducted around the world. A summary of field studies is provided in Table A1 in Appendix. Aquifer lithology at study sites includes chalk, granite, sandstone, gravel, and coarse and fine sand of varying composition. The carbonate composition of these aquifers ranges from undetectable to over 95%. Carbonates are expected to play a major role in ion mobilization during CO₂ leakage events, as their dissolution buffers pH and can be a source of released trace metals.¹¹

Overall, field studies found that simulated CO₂ leakage universally decreases pH and generally increases concentrations of water quality parameters

such as electrical conductivity (EC), alkalinity, major ions, and trace ions. In some studies, trace metals were addressed and noted to increase in concentration, but no numerical values were included.^{8,12–16} When values were provided, increases were typically minimal, or concentrations were close to detection limits. Increases in trace metal concentrations are likely due to pH-induced desorption or ion exchange with Ca, and Mg^{17,18} and dissolution of Fe and Mn oxides, as heavy metals tend to adsorb to oxide surfaces.¹⁹ Decreases in Mn and Fe are theorized to be the result of coprecipitations as impurities in gibbsite (Al(OH)₃) in Vrøgum studies²⁰; however, Mn and Fe show slight increases at the Brandenburg site, while ZERT site studies show fluctuations due to oxygenated water and ion exchange processes.²⁰

One exception was Mo, which was observed to decrease in concentration in the majority of studies where it was measured. No clear trends regarding the behavior of anions such as NO₃⁻ and SO₄²⁻ were obvious, as concentrations increase, decrease, or remain constant, depending on the study. K is relatively unaffected by exposure to a CO₂ plume in studies done at the ZERT site, Vrøgum, and the Paris Basin,^{17,20} and shows increases in other studies, but is unmeasured in most studies.

In carbonate-poor glacial and aeolian sands, dissolved ions such as Ca, Mg, Na, Si, Ba, and Sr and other water quality parameters such as EC and total dissolved solids (TDS) typically follow a pulse-like evolution trend, where concentrations rapidly increase following exposure to a CO₂ plume and gradually return to postexposure (or slightly elevated) levels after the CO₂ plume has passed.^{16,21,22} A separate study by Yang *et al.*¹¹ found that carbonate dissolution can play a significant part in ion mobilization in aquifers that are as little as 1% carbonates.

Studies in Svelvik, Norway demonstrated that isotope analysis can be used to isolate changes in ion concentrations due to water-rock interactions brought on by CO₂ injections from the effects of saline and freshwater mixing.^{23–25}

Although *in situ* field injection studies provide valuable data for the impacts of CO₂ leakage on groundwater quality, challenges exist when interpreting the data. Injection studies vary regarding the time period over which CO₂ is injected and the mineralogy of the target aquifers. Studies where CO₂ injection occurs for only a few days may result in observed changes to dissolved ion concentrations that appear as

a pulse, but are actually due to the short duration of the CO₂ injection, dilution, or flushing with fresh water.²¹ Push-pull studies, though simpler than studies that involve injection and monitoring, have limited time for reactions between CO₂ saturated water and aquifer minerals.²⁶ These differences in injection periods and timeframes complicate comparisons between studies done in aquifers of similar composition. It is clear that site-specific factors such as aquifer mineralogy, geology, groundwater chemistry, and flow and leakage rates result in varying responses to CO₂ leakage.^{8,17,24,27–31}

In summary, field tests have the following features in terms of aquifer response to CO₂ leakage:

- Increases in alkaline earth metals and alkali metals were observed in most studies.
- Increases in trace metal (As, Pb, Cd, Ba, and U) had been observed, but concentration remained below MCL.
- Change in concentrations of Fe and Mn depended on the condition of the test site and both increase and decrease had been observed.
- Site-specific conditions dominated the response of the aquifer to CO₂ leakage, conclusions from one site do not apply to other sites.

Summary of literature: Lab studies

A summary of lab scale batch and column experiments is provided in Table A2. Lab batch experiments used a variety of aquifer samples from around the world including sandstone, limestone, sand, basalt, and modified or synthetic minerals. Lab batch experiments typically utilized high water to rock ratio and allowed time for samples to equilibrate under an N₂ or Ar atmosphere, before pumping in CO₂.

Across nearly all lab studies, a decrease in pH and increase in alkalinity, TDS or EC, Na, Ca, Mg, Sr, Fe, and Ba is observed and can be attributed to the dissolution of carbonates such as calcite (CaCO₃) and dolomite (CaMg(CO₃)₂), Fe, and Mn-oxides, ion exchange, and desorption.^{2,9,19,32–34} Laboratory batch tests by Little and Jackson³⁵ is one of the representatives of lab studies and they found that concentrations of Co, U, and Ba continued to increase beyond the 300-day CO₂ exposure window and that Ca, Sr, Mn, and Ba fluctuated significantly over the same period, indicating that long term lab experiments and field monitoring are vital to accurately determine the effects of CO₂ exposure on groundwater quality. Laboratory batch tests by Little and Jackson³⁵ also

found that concentrations of Al, Cr, Co, Ni, Zn, As, and Se were highest in aquifer samples with limited carbonate minerals and, as a result, the lowest pH. U was shown to be released under oxidizing conditions. Variations in concentrations of released ions between samples from the same aquifer can be indicative of aquifer mineralogical heterogeneity.³⁵

Despite studies showing a general increase in trace element concentrations, only five studies we reviewed exceed World Health Organization (WHO), European Union (EU), or the United States Environmental Protection Agency (US EPA) drinking water standards for trace elements on the list of EPA primary drinking water regulations. Elevated trace metal concentrations during CO₂ leakage studies exceeded drinking water standards for Pb in one study,³⁶ As in three studies,^{34,36,37} Cd in one study,³² U in one study,³⁸ and Ba in one study.³² One of the most significant increase had been observed by Galeczka *et al.*³² investigating the effects of injecting CO₂ into a basalt aquifer saw a decrease in pH from 9–10 to 4.5 and an over 100 times increase in mobility in Sr, Fe, Al, Ca, Ba, Mn, and Mg. Dissolved Al, Fe, Mn, and Cr concentrations exceeded EU drinking water limits, with the majority of Al and Cr being in the Al⁺³ and Cr⁺³ forms, respectively. Carbonates such as calcite, siderite (FeCO₃), and ankerite (Ca(Fe,Mg,Mn)(CO₃)₂) were found to be supersaturated.

Although the increase in the concentration of major ions and trace elements had been observed in most cases, decreases in concentrations had also been observed. For example, a study by Montes-Hernandez *et al.*,³⁹ found that goethite (α -FeO(OH)) and calcite could, under the right conditions, adsorb Cu(II), Cd(II), Se(IV), and As(V) and prevent remobilization during CO₂ exposure. Similarly, Shao *et al.*⁴⁰ observed decreased concentrations in spiked Cd and As with unconsolidated sand and gravel samples that contained 0–4% carbonates by weight after CO₂ exposure.

The role organics (including pristine organic acids such as humic acid in an aquifer and organic compounds from storage formation) play in releasing metals when sediments were exposed to CO₂ was not widely studied. A study by Lawter *et al.*⁴¹ for sediments collected from the formation in between storage formation and shallow aquifer examined the effects of organic matter on the release of major and minor ions during a lab column test and found that the presence of organic matter slowed the release of S, Sr, Ba, K, Si, and Ca and increased the rate of removal of As and Cd.

Although laboratory studies provide valuable insight into geochemical interactions within aquifers as a result of CO₂ leakage, they are limited in their ability to accurately replicate conditions within the aquifer of study. Lab studies are often done using relatively small samples of aquifer material that have been ground, dried, and are constantly stirred with large water-to-rock ratios. These conditions facilitate water–rock interactions due to greater surface area to volume ratios and results may not fully represent the complex heterogeneous aquifer system and associated reaction rates, microbial communities, and flow and transport behaviors.^{8,9,42} Batch experiments, in particular, fail to account for reactive transport and changes in hydrogeochemical conditions downstream which could result in reprecipitation or scavenging of trace elements.⁵ Additionally, CO₂ exposure and postmonitoring in batch experiments typically occur over the course of weeks, rather than months or years. Furthermore, changes to redox conditions could potentially occur during the collection of aquifer field samples, affecting hydrogeochemical reactions and associated lab results.⁸ Thus, *in situ* field experiments are necessary to confirm if laboratory studies reflect aquifer conditions and thoroughly understand the potential impacts of CO₂ leakage on groundwater quality.

In summary, lab tests have the following features in terms of aquifer response to CO₂ leakage:

- An increase in alkaline earth metals and alkali metals was observed in most studies.
- An increase in trace metals (As, Pb, Cd, Ba, and U) had been observed, some cases showed concentration higher MCL or other regulatory standards.
- Sediment–CO₂ reaction had been maximized during most studies and therefore metals are typically more aggressively released in comparison to field tests.
- The role of organics in releasing metals when sediments were exposed to CO₂ was not widely studied, but a few studies showed by organics could suppress the release of metals.
- Artifacts in the experiment such as exposure to O₂ lead to changes in the concentration of metals unrelated to CO₂ exposure.

Summary of literature–analog sites

Natural CO₂ reservoirs exist worldwide and can be classified into sites that show no evidence of leakage

and sites that show leakage over time.¹⁰ These GCS analog sites can provide useful information for demonstrating the long-term feasibility of GCS as well as the potential environmental impacts if leakage should occur.

A summary of studies examining groundwater at GCS analog sites is provided in Table A3. Large variations are seen among the suite of water quality parameters and ions measured among studies. However, practically all studies report pH, temperature, EC, or TDS, Na, Ca, Cl, Mg, Fe, and some form of carbon. Nearly all natural analog sites exhibit pH levels below 7.

In a study by Afsin *et al.*⁴³ of thermal mineral waters in Turkey, samples with pH below 7 had elevated EC, CO₂, Ca, Mg, Na, Cl, SO₄²⁻, NO₃⁻, and to a lesser degree Cd and K, compared to other mineral waters from the same region. Similarly, in a study by Cruz *et al.*⁴⁴ of waters from the Furnas volcano, samples with pH below 7 had elevated alkalinity, EC, dissolved inorganic carbon (DIC), total inorganic carbon (TIC), Al, Fe, K, Mn, Na, SO₄²⁻, SiO₂, and NH₄⁺ compared to other mineral waters from the same region. Studies of the Vesuvius volcanic complex found that CO₂-rich groundwater has increased concentrations of trace elements (As, Se, Mo, V, Li), and decreased levels of Al, Pb, Co, and Mn compared to unleached host rocks.⁴⁵ At Mt. Etna, Al, Th, Fe, and other poorly mobile elements tended to be retained in the host rock, while As, Se, Sb, and Mo are more readily released.⁴⁶ Other metals such as Mn, Cr, V, Zn, and Cu are more dependent on redox conditions and surface-related processes.⁴⁶

Studies by Arnórsson *et al.*⁴⁷ in Iceland found that CO₂-rich water (>200 ppm dissolved TIC) from basalt aquifers are higher in Ca, Mg, Fe, As, Ba, Mn, Co, Ni, and Sr, and are close to saturation with calcite and amorphous silica compared to similar nonCO₂-rich waters. The authors suggest that the dissolution of plagioclase is initially responsible for increased concentrations of Ba and Sr, but that concentrations decrease as they precipitate out as secondary minerals.⁴⁷ Keating *et al.*⁴⁸ reported contrasting results for a natural analog in New Mexico, USA, where the pH depression and consequent trace element mobility were relatively minimal due to the buffering capacity of the aquifer, despite relatively high levels of dissolved CO₂.

Studies by Pauwels *et al.*⁴⁹ and Lions *et al.*⁵⁰ thoroughly analyzed groundwater overlaying a natural

CO₂ reservoir in Montmiral, France. Despite measuring high CO₂ fluxes, the isotopic analysis found no evidence that CO₂ was leaking from the reservoir. They suggested that high CO₂ fluxes could be explained by carbonate dissolution and that changes in Ca, Mg, K, and SO₄²⁻ could be due to Mg-calcite or dolomite dissolution, and K-feldspar (KAlSi₃O₈) dissolution with subsequent kaolinite (Al₂Si₂O₅(OH)₄) precipitation.^{49,50} These results highlight the importance of isotopic analysis alongside major ion monitoring to ensure that CO₂ fluxes and associated groundwater quality changes are due to CO₂ reservoir leakage, instead of carbonate dissolution.

A study by Heath *et al.*⁵¹ of multiple CO₂-rich springs and a geyser in the Paradox Basin of the Colorado Plateau found the waters were slightly acidic (pH < 6.5), very saline (TDS > 13850 mg L⁻¹), and had elevated levels of HCO₃⁻ (> 3500 mg L⁻¹). All analyzed waters fell into the sodium-chloride chemical facies and are supersaturated with calcite, aragonite (CaCO₃), dolomite, and hematite (Fe₂O₃). Despite the presence of surface travertine deposits, the system has remained active for over 100 000 years, suggesting that leaky reservoirs may continue to leak even when mineralization is observed.

In addition to natural analog sites, multiple studies have analyzed major and trace ions in bottled sparkling waters and bottled mineral waters. A study by Fiket *et al.*⁵² analyzed ions and trace elements in 10 different brands of bottled sparkling spring and mineral waters from Croatia; however, the study did not indicate if sparkling waters were naturally or artificially carbonated. A study by Allen *et al.*⁵³ measured over 20 trace elements and ions in 16 different brands of naturally sparkling bottled water from various regions around Europe. Sparkling natural mineral waters had pH values ranging from 5.8 to 7.8, with most falling below 7. Alkalinity ranged from 60–3429 mg L⁻¹ as CaCO₃.

While analyzing analog sites for potential impacts of subsurface CO₂ storage and leakage on overlaying groundwater resources is valuable, it is not without issues. The effects of natural CO₂ seepage on groundwater resources at analog sites are difficult to elucidate because studies do not always measure or report groundwater quality parameters from similar or nearby groundwater that is not impacted by CO₂ seepage. Geological data regarding the composition and relative abundance of minerals such as quartz (SiO₂), feldspars, and clays of aquifers or locations

where water samples are collected is also limited. The geological descriptions provided are not always sufficient and limit the ability to draw direct comparisons between analog sites and potential CO₂ storage sites. Furthermore, studies often sampled CO₂-rich water from springs or geysers, where rapid degassing of CO₂ can occur. Accurate measurements of groundwater CO₂ concentrations and pH are vital for determining mineral-water interactions.⁵⁴

In summary, observations from analog sites have the following features:

- Lower pH and elevated EC and major ions have been observed in comparison to a typical groundwater composition.
- While analog sites provided useful information regarding the long-term impact of GCS, their implication to GCS has to be taken with caution because (1) the pristine condition before the exposure of CO₂ is missing (2) data from nearby site without CO₂ seepage which can serve as a reference point for analog sites were usually missing, (3) the time scale is too long for GCS operation.

Potential groundwater quality impacts

One of the primary risks of CO₂ leakage on groundwater quality is the release of trace elements and contaminants naturally found within aquifer rocks.⁵ These trace elements and contaminants are both adsorbed to mineral surface sites and contained within the minerals themselves.⁵ Changes in hydrogeochemical conditions (such as pH, redox potential, water composition, and CO₂ partial pressure) that promote the dissolution of aquifer minerals or remobilization of adsorbed contaminants are of high concern.

General water quality parameters

As groundwater is exposed to CO₂, whether through underground injection, leakage of CO₂-rich brines, or during lab-scale experiments, dissolved CO₂ increases, and the formation of carbonic acid results in a decrease in pH. A decrease in pH is observed in every CO₂ lab and field experiment and is further supported by modeling studies. This drop of pH is one of the major driving factors in subsequent hydrogeochemical reactions that affect groundwater quality after CO₂ exposure.

The degree of decrease in pH is dependent on the CO₂ partial pressure and the presence of carbonate minerals such as calcite or dolomite, for which dissolution is thermodynamically favorable under acidic conditions, increasing alkalinity and buffering capacity of the water.^{5,6,17,34} Indeed, multiple studies show a significant increase in alkalinity after CO₂ exposure,^{8,12,13,55} even in aquifer samples that are less than 4% carbonates.^{24,38} Similarly, TDS and EC also show similar increases after CO₂ exposure.

When reported, oxidation reduction potential (ORP) also typically shows a slight decrease after CO₂ injection. One likely explanation is that dissolved CO₂ displaces O₂, reducing ORP.³ This effect may have been lessened by the fact that many of the studies that reported ORP took place in shallow, unconfined aquifers. ORP plays an important role in determining the speciation and subsequent mobility of some trace elements of concern, such as As.^{3,5,25}

General trends regarding polyatomic anions such as SO₄²⁻ and NO₃⁻ are unclear, as they are observed to both increase and decrease in various studies. Although they are not directly affected by carbonates equilibrium, they could be impacted by CO₂ indirectly through mechanisms such as microbial activity.

General trends in major and trace elements

Overall, concentrations of most major and trace elements increase during CO₂ exposure studies. Increases in trace elements brought on by a decrease in pH due to dissolved CO₂ are thought to be caused by desorption, and ion exchange reactions along with the dissolution of carbonates, iron oxides, and oxyhydroxides, and sulfides.^{2,12,13,56} Iron oxides and hydroxides and clay minerals, when present, are often the primary minerals responsible for desorption/adsorption.² The effects of CO₂ on elemental release generally decrease with CO₂ pressure, an important factor to consider is that CO₂ pressure decreases as a plume migrates upward.^{41,57}

Increases in Na, Ca, Mg, Sr, and Ba are commonly observed in studies and are thought to be due to carbonate dissolution and Ca-driven cation exchange reactions.^{2,18} Concentrations of Ca, Mg, Fe, and Mn greatly increase in the majority of studies. This is explained by the dissolution of various carbonate species, such as calcite, siderite, magnesite (MgCO₃), and dolomite, as well as iron sulfides.^{5,6,8,17,27} Other

elements such as Ba and Sr saw only slightly elevated concentrations in comparison.⁴¹ This behavior is likely because Ba and Sr are often present on the exchangeable sites and as impurities in carbonate minerals.^{5,34} The dissolution of plagioclase may also be responsible for slow increases in Ca, Sr, and Ba due to the Ca-driven cation exchange.^{8,18,55,58} Trace elements such as Cd, Co, Cr, and Ni often show rapid increases in concentration following CO₂ exposure. Their rapid mobilization can be explained by desorption from Fe and Mn oxyhydroxides and clay minerals,^{5,18} while sustained steady increases in concentration are attributed to the dissolution of containing minerals due to a decrease in pH.³³ Increases in Si, Al, K, and to a lesser extent Na, can be partially attributed to silicate and clay dissolution.^{3,9,30}

Elements of concern, such as As and Pb saw increases in some studies and decreases in others. One study has shown that As and Pb desorb from illite and smectite when pH decreases, which increases aqueous concentrations of As and Pb.⁵⁹ Furthermore, increased concentrations of HCO₃⁻ have been shown to facilitate the desorption of arsenic and uranium from the surfaces of metal oxides and other aquifer minerals and clays.³ Other studies have found that As(V) and other metals such as Cu(II), Cd(II), and Se(IV), can be immobilized by the presence of carbonates after exposure to CO₂.^{39,40} Al and oxyanion-forming trace elements including As, Se, Sb, Mo, V, and Cr can be immobilized in oxidizing, moderately acidic aqueous systems but can see increased mobilization under highly acidic conditions.^{35,59} Other hazardous elements, such as U, were shown to be mobilized under oxidizing conditions.³⁵ Concentrations of Mo decrease in some CO₂ exposure studies,^{8,9,17,27,38,60} and increase in others.^{34,35,57} It is hypothesized that Mo adsorbs to sulfides and iron oxides at low pH.⁴¹

Although increases are observed in many major and trace elements, it is important to note that reactive transport mechanisms, including water–rock interactions downstream of the CO₂ leakage or injection site, can buffer pH and result in contaminant removal through scavenging or the precipitation of secondary minerals,⁵ release or scavenging is the result of a delicate dynamic balance of reactions such as precipitation/dissolution, adsorption/desorption,⁵⁹ natural attenuation can apparently alleviate the release of trace metals.

A statistical assessment of the risk associated with trace elements

Based on the data collected in the current work, we conducted a statistical assessment of the risk associated with trace elements, that is, among all the studies, how many of them showed the risk of trace elements. The risk was grouped in the following three categories based on the EPA regulated MCLs:

- Green flag: There is no change of concentration of trace metals when CO₂ was added to the system, or trace metals were not detected either in the background or after CO₂ was added.
- Yellow flag: Changes in the concentration of trace metals were detected, but the level of change was lower than MCL.
- Red flag: Concentrations increase to a level higher than MCL.

The studies selected for such statistical assessments are laboratory experiments and field tests. However, modeling studies, natural analog studies, and lab studies on pure minerals to study release processes (e.g., Montes-Hernandez *et al.*³⁹) are not included.

Pb was the focal point for risk assessment of GCS sites in terms of impact on shallow groundwater since the issue of GCS impact on shallow groundwater was brought up in some early studies (e.g., Zheng *et al.*⁵⁹). Among all the 21 eligible cases, four of them show a red flag for Pb (Table 1) and all of them are from column tests of samples from Edward aquifer, an unconfined carbonate aquifer.³⁶

Many studies measure As and 11 out of 60 studies show a red flag for As (Table 2), which were reported in Lu *et al.*,³⁴ Wunsch *et al.*,^{37,57} and Wang *et al.*³⁶ The red flag cases are not clearly related to any type of features of the aquifer, except that all these studies are batch experiments.

Cd seems not to pose a great risk to the aquifer—only one out of 44 cases shows a red flag for Cd (Table 3) and it is a quite unusual type of aquifer: basalt.³²

Ba is quite ubiquitously observed in studies—40 out of 43 studies show the yellow flag for Ba (Table 4), Increase in concentrations of Ba had been observed but was not above MCL. The only red flag for Ba was observed in a lab test with basalt.³²

Seven out of 46 studies show a red flag for U (Table 5). It is noteworthy that two of these red-flag cases are field push–pull tests³⁸ for sediments about 240–300 m deep.

Table 1. Summary of risk of contamination in terms of Pb and some relevant aquifer characteristics.

Total eligible studies (21)	Green	Yellow	Red
Case/sample	9	8	4
Type of sediments	Two limestone, 7 sandstone	7 sandy sediment or Sandstone and 1 Limestone	4 Edward aquifer, carbonate aquifer
Carbonate rich (>5%)	6	1	
Carbonate poor (<5%)	3	7	
Lab or field	5 field, 4 lab	5 Lab and 3 Field	4 Column tests
Confined/unconfined	4 confined, 3 unconfined	2 confined, 5 unconfined	4 unconfined
Clay%	3 studies <1%; 6 studies >1%;	1 study <1%; 3 studies >1%; 4 not reported (NR)	0 studies <1%; 2 studies >1%; 2 NR*

Table 2. Summary of risk of contamination in terms of As and some relevant aquifer characteristics.

Total eligible studies (60)	Green	Yellow	Red
Case/sample	24	25	11
Type of sediments	1 limestone, 23 sandstone	21 sandy sediment or Sandstone and 4 Limestone	9 limestone, 2 sandstone
Carbonate rich (>5%)	4	4	9
Carbonate poor (<5%)	17	10	2
Lab or field	4 field, 20 lab	22 Lab and 3 Field	Batch experiments
Confined/unconfined	14 confined, 2 unconfined, 8 not reported (NR)	7 confined, 7 unconfined, 11 NR	0 confined, 4 unconfined, 4 NR
Clay%	2 studies <1%; 3 studies >1%; 19 NR	1 studies <1%; 6 studies >1%; 18 NR	2 studies <1%; 5 studies >1%; 4 NR

Table 3. Summary of risk of contamination in terms of Cd and some relevant aquifer characteristics.

Total eligible studies (44)	Green	Yellow	Red
Case/sample	18	25	1
Type of sediments	5 limestone, 13 sandstone	24 sandy sediment or Sandstone and 1 Limestone	Basalt
Carbonate rich (>5%)	10	2	
Carbonate poor (<5%)	6	16	
Lab or field	4 field, 20 lab	21 Lab and 4 Field	Column experiments
Confined/unconfined	9 confined, 7 unconfined, 2 not reported (NR)	11 confined, 6 unconfined, 8 NR	1 NR
Clay%	2 studies <1%; 5 studies >1%; 11 NR	1 studies <1%; 6 studies >1%; 18 NR	1 NR

In summary, the following observation can be drawn from the statistical analyses:

- Pb, As and U are metals of primary concern: four of 21 cases showing Pb concentration above MCL, 11 of 60 cases for As, and seven of 46 cases for U show red flags.
- Carbonate aquifers seemed more vulnerable to Pb and As contamination, but not to U.
- Cd and Ba are less a concern: only one out of 44 cases for Cd and one of 43 cases for Ba showing the red flag and both for one study on basalt.
- None of the field studies show the red flag of Pb and As, one push-pull field test showed a red flag for U.

Table 4. Summary of risk of contamination in terms of Ba and some relevant aquifer characteristics.

Total eligible studies (43)	Green	Yellow	Red
Case/sample	2	40	1
Type of sediments	2 limestone,	33 sandy sediment or Sandstone and 7 Limestone	Basalt
Carbonate rich (>5%)	2	12	
Carbonate poor (<5%)	2	20	
Lab or field	2 lab	21 Lab and 4 Field	Column experiments
Confined/unconfined	0 confined, 2 unconfined	17 confined, 11 unconfined, 12 not reported (NR)	1 NR
Clay%	1 studies <1%; 1 studies >1%;	1 studies <1%; 11 studies >1%; 28 NR	1 NR

Table 5. Summary of risk of contamination in terms of U and some relevant aquifer characteristics.

Total eligible studies (46)	Green	Yellow	Red
Case/sample	14	25	7
Type of sediments	3 limestone, 11 sandy sediments	23 sandy sediment with clay and 2 Limestone	Sedimentary formation mixed with sand and clay (2); Sand from the shallow formation (5)
Carbonate rich (>5%)	3	5	1
Carbonate poor (<5%)	11	20	6
Lab or field	1 field, 3 column and 10 batch	24 batch and 1 Field	1 field and 6 batch experiments
Confined/unconfined	5 confined, 4 unconfined, 5 not reported (NR)	12 confined, 5 unconfined, 8 NR	5 confined, 0 unconfined, 2 NR
Clay%	0 studies <1%; 2 studies >1%; 12 NR	1 studies <1%; 6 studies >1%; 18 NR	2 studies <1%; 1 studies >1%; 4 NR

- Order of aggressiveness in terms of releasing trace metals: Batch > column > field.
- Releasing of organics were not reported for shallow aquifer (there was one study for Frio formation at 1500 m showing increasing organics).
- There is no clear correlation between metal release and type of sediments, type of aquifer, the content of carbonate and clay. Evaluation likely has to be done case by case.

Microbial impacts on water quality

Data regarding the effects of microbial communities on changes to groundwater quality due to CO₂ leakage is limited, partially because lab-scale studies purposefully limit microbial activity by drying samples and sediments before CO₂ experimentation.⁴² Although there are relatively few studies investigating the effects of CO₂ leakage on microbial communities in aquifers with respect to water quality, it is clear that changes in micro-

bial communities brought on by the leakage of CO₂ into overlying groundwater have the potential to negatively impact water quality and must be further studied.

Leakage of CO₂ into groundwater is expected to impact microbial activity by altering environmental conditions or penetrating cells and interfering with metabolic functions.⁵ Increases in CO₂ concentration are generally expected to negatively impact microbial activity.⁵ Indeed, a field injection of CO₂ in Escatawpa, Mississippi analyzed by Gulliver *et al.*⁶¹ found an overall decrease in microbial diversity with increased CO₂ concentrations, but also found increasing evidence of CO₂ fixation, methanogenesis, and the oxidation of reduced organics including nitrogen, hydrogen, sulfur, and iron species, impacting water quality.

Studies by Kirk *et al.*^{62,63} of the Frio Formation and the ZERT site found that in lab batch experiments with lower partial pressures of CO₂, SO₄²⁻ reducing bacteria were dominant, while Fe(III) reducers were

dominant in high partial pressure CO₂ experiments. Injection of CO₂ and subsequent drop in pH increases the energy available for microbial Fe(III) reduction and has been shown to increase CO₂ trapping^{62,63} through the biomineralization of siderite and calcite.⁶⁴

However, these same conditions also led to the increase in Fe(II) and dissolution of goethite and sulfide minerals such as pyrite (FeS₂), minerals that play an important role in adsorbing trace elements such as As.^{62,63,65} In aquifers where iron oxides and oxyhydroxides are present and natural Fe(III) reduction is normally limited, the introduction of subsurface CO₂ can increase microbial activity and lead to negative impacts on groundwater quality.^{62,63,65}

In a push–pull study in the Newark Basin by O'Mullan *et al.*⁴² increases in the concentration of U by up to 100-fold were likely caused by enhanced desorption due to uranyl carbonate complex formation, however, increases in bacterial communities associated with anaerobic oxidation of U were also observed during the early and mid-phases of injection and may have also contributed to the increase in U. No significant changes were observed in levels of As, but bacterial communities shown to mobilize arsenic under sulfide oxidizing conditions. Under the right conditions, these bacterial communities could play a significant role in trace metals geochemistry during CO₂ leakage.

Subsurface microbial activity is generally slow and changes in groundwater quality due to CO₂-induced microbial activity may be minimal during short-term lab and field injection experiments.^{64,66}

Organic matter

There are two types of organic matters that could affect the response of groundwater quality to CO₂ leakage: one is the pristine soil organic matters such as humic and fulvic acid in the aquifer, which could affect the release of trace metals because of their association with metals in groundwater, the other is organic compounds that usually exist in the deep formation such as BTEX. The current review did not find studies regarding soil organics, but there are a few studies that examined the effects of organic compounds of deep sources on the impacts of CO₂ leakage on groundwater quality. It is generally agreed that mobilization of BTEX and other non- to moderately polar organic compounds from reservoir rock due to supercritical CO₂ injection is a possibility.^{5,13,67–70} This is of particular concern for CO₂ injection for EOR, but also has implications for injection of CO₂ into nonoil-bearing saline aquifers.⁷⁰

Migration of CO₂-rich brine high in toxic organic compounds such as BTEX can negatively impact overlying groundwater quality.^{5,13,67–71} In these cases, understanding the redox conditions of the aquifer is important for determining the biodegradation potential and persistence of organic contaminants.²

Few studies detected elevated concentrations of organic compounds during CO₂ injection. One notable field study that detected elevated BTEX levels after CO₂ injection determined that the source was contaminated CO₂, rather than mobilization from reservoir rock.^{17,67} Fewer studies have investigated the effects of organic matter on the release of major and trace elements during CO₂ exposure. One key lab study by Lawter *et al.*⁴¹ found that concentrations of Ca, Mo, Ba, Si, K, Sr, and S were lower and removal rates of As and Cd were slightly increased in CO₂ exposure tests with increased levels of organic matter (toluene spike). Decreases in trace elements due to organic matter are typically attributed to surface adsorption.⁵ Note that Lawter *et al.*,⁴¹ tested sediments collected from the formation in between storage formation and the shallow aquifer that is a groundwater resource.

Data gaps and further research

Inconsistencies between studies, such as variations in CO₂ injection and post monitoring time frames for both field and lab studies, variations in the major and minor ions measured or reported, and the lack of data reporting consistency (e.g., ion concentration data presented in chart form only), hinder the ability to compare study results. The limited time frames of post-CO₂ exposure monitoring, in particular, limits data regarding the post CO₂ exposure behavior of mobilized trace metals and time frames required to return to background levels after pH and dissolved CO₂ concentrations also return to background levels.² Furthermore, studies sometimes omit a detailed breakdown of aquifer mineralogy according to carbonate, quartz, clay, k-feldspars, plagioclase, and other relevant minerals, as well as elemental composition. As discussed previously, aquifer mineralogy plays an important role in contaminant mobilization, and information regarding mineral composition would facilitate analyzing and comparing the effects of various aquifer mineralogies on contaminant mobilization from CO₂ exposure.^{5,94}

A thorough review of available studies regarding impacts on groundwater quality from CO₂ injection

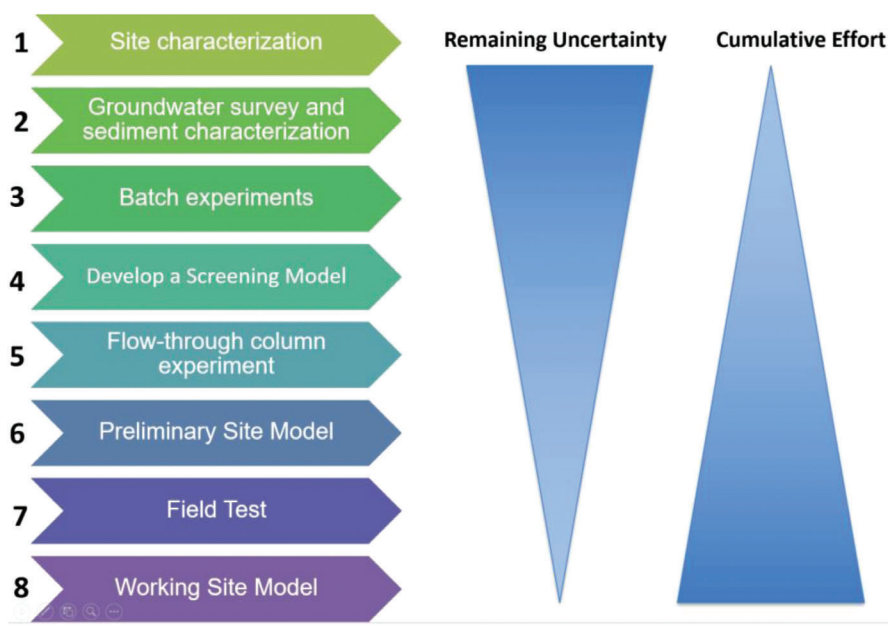


Figure 1. Summary of eight-step procedure for assessing the vulnerability of the shallow aquifer overlying the GCS site.

reveals that significant data gaps still exist. While the release of trace metals has been studied extensively, the response of microbial communities to CO₂ intrusion into aquifer and their role in the mobilization of trace metals requires further study. Organic matter, either as contaminants or an agent that enhance the mobilization of trace metals warrant further studies. Even for trace metals, a major hurdle is that aquifer responses to CO₂ injection or leakage are site-specific.^{2,5,25,68}

The knowledge gap regarding organics has two folds:

1. Impact of organic matter preexisting in the impacted aquifer in the response to CO₂ intrusion.
 - Impact on buffering capacity
 - Impact on CEC
 - Impact on supporting microbial activity
2. Impact of organics that carried by leaking CO₂ onto the aquifer.
 - CO₂ leaching of cap rock materials
 - Transportability of leached species
 - Decomposition pathways of released organics
 - Sorption/desorption behavior of released organics

The knowledge gap regarding microbial activities is about assessing the effects of CO₂-induced changes in the microbial community and Fe cycling in GCS-relevant aquifer sediments.

Proposed site assessment procedure

Based on the risk that CO₂ leakage could pose on shallow aquifers and the various studies in this regard that have been conducted, we propose the following eight-step procedure for assessing the vulnerability of the shallow aquifer overlying the GCS site. The procedure uses activities with different levels of effort, for example, from batch experiments and simple models to field tests and complex site models to screen the potential risk by gradually reducing the uncertainties with increasing effort (Fig. 1).

Step 1: Site survey

The purpose of Step 1 is to gather information from a literature survey in preparation for sample collection and testing/modeling in the next steps. Specifically, Step 1 is composed of the following tasks:

- Gather as much existing information on the site as possible, primarily through a literature survey, including hydrological and geochemical conditions.
- Based on current knowledge, perhaps supplemented by a geophysical survey, a statistically valid sampling procedure to obtain aquifer materials will be determined.
- Use statistical decisions and collected sediment samples from the aquifer to plan the next steps in the procedure.

Note that in Step 1, the work can be conducted for multiple sites simultaneously.

Step 2: Groundwater survey and sediment characterization

Unless thorough information can be collected in Step 1, it is likely that a groundwater survey and sediment characterization has to be conducted, which is the purpose of Step 2:

- If the concentration of a contaminant in the groundwater is below the detection limit in groundwater, the chance that this contaminant will rise above MCL upon the leakage of CO₂ is very low, but an increase in concentration is still possible (e.g., Varadharajan *et al.*⁷² and Zheng *et al.*⁵⁵).
- Knowledge of the mineralogical composition of the sediment can be a useful indicator of potential contamination:
 - The existence of clay minerals indicate potential cation exchange and desorption, leading to the release of Ba, Cd, Pb, and As.
 - The existence of sulfide minerals is an indicator of a potential release of As and Pb (also Cu and Zn).
 - The amount of carbonate minerals is related to the aquifer pH buffering capacity and the degree of metal release is related to the magnitude of pH drop driven by CO₂ dissolution.
- Sediment titration to assess buffering capacity is a key test to evaluate the aquifer response.
- Selective extraction is recommended because it reveals the metal-mineral associations which are good indicators of potential contamination.

Step 3: Batch experiments

The batch experiments in which sediments are mixed with field or synthetic groundwater and reacted with CO₂ are recommended in Step 3:

- If contaminants are released in the batch experiment, further studies are warranted.
- If contaminants are NOT released in the batch experiments, further studies are NOT warranted.

Step 4: Screening model

The purpose of Step 4 is to screen the potential risk before investing in expensive experimental work. It has the following two substeps:

- Prepare the screening model

The geochemical model will be built based on all the information collected in Steps 1–3, that is, the groundwater survey, sediment characterization, metal-mineral association revealed by sequential leaching.

- Establish contaminant release mechanisms/reaction network
- Calibrate key parameters such as pH buffering capacity, parameters related to adsorption/desorption, and kinetic reaction rates
- Screening model
 - 1D, horizontal homogenous
 - Pore velocity from ambient flow gradient and estimated hydraulic conductivity and specific charge
 - Typical average aquifer mineralogy/ geochemical properties
 - Test many combinations of key input parameters

Step 5: Flow-through column experiment

The purpose of Step 5 is to assess the risk of contamination at the solid-to-liquid ratio close to the aquifer.

- Design column tests to validate and explore the results of the screening model
- Because of the large liquid to solid ratio, batch experiments are very aggressive in releasing contaminants, column experiments provide conditions more similar to field conditions in terms of liquid to solid ratio
 - Pay special attention to the contaminants released in batch experiments or screening model runs
 - If contaminants are released in the batch experiment with less than a moderate increase in concentration and are not released in column experiments, further studies are NOT warranted.
 - If contaminants are released in column experiments, further studies are warranted.

Step 6: Preliminary site model

The purpose of Step 6 is to further evaluate the risk without resorting to expensive field tests. The model has the following features:

- 2D horizontally homogenous
- Vertically heterogenous
- Permeability and flow rate yield ambient typical pore velocity range

- Distinct zones of average aquifer mineralogy and geochemical properties
- Evaluate different leakage scenarios
- Understand the long-term behavior.

Step 7: Field test

The ultimate measure of risk assessment is to conduct a field test at the GCS site.

- Field tests are warranted if column tests and reactive transport modeling show release of contaminants, especially to a level higher than MCL.
- Use the preliminary site model to design a field test.
- A closed-loop experiment like the Mississippi field test (Trautz *et al.*⁸; Zheng *et al.*⁵⁵) is recommended to constrain the CO₂ plume, but the induced groundwater flow rate should not be much higher than ambient conditions (ideally about the same).
- Groundwater monitoring for an extended period before the test is necessary to provide good baseline data.

Step 8: Working site model

The working site model can be used to interpret the data from the field test and eventually developed into the model of the GCS site. It has the following features:

- Full 3-D heterogenous model
- Calibrated and refined from the field test
- Used for monitoring and risk assessment
- Complexity limits the number of uncertainty analyses.

Conclusion

In this paper, we collected data for 350 cases that were documented in 139 papers/reports, with 81 cases of laboratory batch and/or column tests and 42 cases of field tests. In general, we observed that:

- Increases in alkaline earth metals and alkali metals were observed in most studies.
- Solid phase aquifer chemistry and mineral phases are dominant factors in the release of major and trace elements.

In light of the release of trace metal from sediment upon the intrusion of CO₂ into the shallow aquifer, there are the following general observations:

- An increase in trace metals (As, Pb, Cd, Ba, and U) had been observed, some cases showed

concentration higher MCL or other regulatory standards.

- Pb, As and U are metals of primary concern: four cases have Pb concentration higher than MCL, and 11 for As; seven for U.
- Carbonate aquifers seemed more vulnerable to Pb and As contamination, but not to U.
- Cd and Ba are less a concern, only one of 44 case show Cd concentration higher than MCL, and one of 43 cases has Ba concentration higher than MCL.
- None of the field studies show the concentration of Pb and As higher than MCL; one push-pull field test showed the concentration of U higher than MCL.
- Order of aggressiveness in terms of releasing trace metals: Batch experiment > column experiment > field test.
- There is no clear correlation between metal release and type of sediments, type of aquifer, the content of carbonate and clay. Evaluation likely has to be done on a case-by-case basis.

Despite a large number of studies being conducted, there are still knowledge gaps: one is about organics, in light of the impact of organic matter preexisting in the aquifer in the response to CO₂ intrusion and the impact of organics that carried by leaking CO₂ on the shallow aquifer. Another knowledge gap regards microbial activities; further studies are needed to assess the effects of CO₂-induced changes in the microbial community and Fe cycling in GCS-relevant aquifer sediments.

Based on the literature review, using MCL as a simple risk assessment threshold, an 8-step risk assessment procedure was proposed to assess the risk of GCS site on overlying groundwater aquifers:

- Step 1: Site survey
- Step 2: Groundwater survey and sediment characterization
- Step 3: Batch experiments
- Step 4: Screening model
- Step 5: Flow-through column experiment
- Step 6: Preliminary site model
- Step 7: Field test
- Step 8: Working site model

Acknowledgment

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Appendix

Table A1. Summary of field injection and push-pull studies.

Project site	Experiment type	Aquifer type	Experimental setup	Constituent release trends	Major details	Source
Vrørum, Western Denmark	<i>In situ</i> field injection	Aeolian sand and glacial sand. Carbonate poor (<1%), with 5% clays, 1–15% plagioclase, and 1–5% K-feldspars	Pilot study: Injected food grade CO ₂ (12 L min ⁻¹) for 14 days after which injection rate reduced to 6 L min ⁻¹ for 58 days. Injection depth of 5–10 m Main release study: 1600 kg of gas phase CO ₂ was injected through four inclined injection wells at 5 and 10 m depth, over 72 days.	Decrease: pH, Mn, Fe, and EC DO pH dependent: Al and Zn Pulse increase: EC, Ca, Mg, Na, Si, Ba, and Sr Unaffected: K	EC was the most stable indicator of migrating CO ₂ . Ba, Ca, Mg, Na, Si, and Sr mirror EC, suggesting a common mobilization mechanism, possibly primarily ion exchange and proton induced desorption from Fe/Al and Mn-oxi-hydroxides. Al and Zn are pH dependent and are initially mobilized and continue to increase in concentration as pH decreases throughout injection. Only Al exceeded WHO guidelines.	Cahill and Jakobsen ⁷³ ; Cahill <i>et al.</i> ²⁰ ; Cahill and Jakobsen ²¹ ; Auken <i>et al.</i> ⁷⁴
Brandenburg, Germany	<i>In situ</i> field injection	Carbonate-free, relatively homogeneous medium-to-coarse sand formation	397,938 L (1 bar, 0°C) CO ₂ injected over 10 days through three injection wells at a depth of 18 m.	Decrease: pH Pulse decrease: NO ₃ , SO ₄ , Na Pulse increase: EC, TIC, Ca, Mg, K, Al, Si, Cu, Ni, Zn, Ba, Cd, and Pb (to a lesser degree Mn and Fe)	Continuous pH decrease after injection stopped. Na decreased, indicating fixing due to cation exchange or due to interference from a previous salt tracer test. All trace metals, major cations, and anions return to background levels after plume passed.	Schulz <i>et al.</i> ¹² ; Peter <i>et al.</i> ¹⁶
Lodève, Southern France	<i>In situ</i> – Push-pull	Fractured sandstone with iron hydroxide, siderite, and trace pyrite. 25% carbonates, 15% quartz, 30% k-feldspars, 20% plagioclase, and 10% clays	3 m ³ pumped out and bubbled with CO ₂ for 12 hr. Reinjecting over 6 hr at 0.5 m ³ hr ⁻¹ at 56 m depth. 80 hr incubation period before 72 hr pull phase.	Decrease: pH and Mo Increase: alkalinity, As, Ca, Fe, Mg, Mn, and Zn, redox potential Undetected: Cd, Co, Cr, Cu, and Pb.	Increase in alkalinity, Ca, and Mg were due to dolomite dissolution; Fe increases due to ferrhydrite and siderite dissolution. Pb, Cu, and Ba are present in reservoir rock, but not influenced by CO ₂ . Remobilization of bivalent metal cations (Fe, Mn, and Zn) is relatively high compared to other elements like As, Ca, or Mg.	Rillard <i>et al.</i> ²⁷

(Continued)

Table A1. (Continued).

Project site	Experiment type	Aquifer type	Experimental setup	Constituent release trends	Major details	Source
Paris Basin, Catenoy, Oise, France	<i>In situ</i> - field injection	Shallow, chalky aquifer. Senonian chalk covered by a few meters of thanetian sands and colluvium. >95% carbonates	10 m ³ water pulled from aquifer, saturated with 20 kg CO ₂ at atmospheric pressure. Injected 12–25 m over 40 hr.	Decrease: pH, B, and Zn, Increase: EC, alkalinity, DO, HCO ₃ , Ca, Sr, and redox potential	Aquifer is primarily calcite and only Ca and Sr saw appreciable increases in concentrations.	Frédérick et al. ^{7,5}
	<i>In situ</i> - Push-pull		3 m ³ water pulled from aquifer, saturated with CO ₂ at atmospheric pressure. Injected 16–17 m deep and left for 1 weekend, before 328 m ³ water being pumped out.	Minimal or no change: Cl, K, Mg, Na, SO ₄ , NO ₃ , and SiO ₂ . Not detected: Mn		
Svelvik, Norway	<i>In situ</i> - field injection	Sandy phreatic aquifer consisting of well sorted coarse-grained sand with gravel lenses. Transition from fresh to salt water below 12 m. Quartz (35–50%), plagioclase feldspar (albite 23–33%), K-feldspar (ortho) 8–12%, and calcite (2–4%).	1.67 t CO ₂ injected over 6 days at 20 m	Decrease: pH, Cl, Na, Mg, and SO ₄ Increase: EC, alkalinity, As, Ca, Co, Al, Si, Sr, Fe, Ba, Li, Mn, Ni, and Zn. Erratic or minor changes: B	Isotope analysis reveals Cl, Na, Mg, and SO ₄ changes were primarily due to seawater mixing, while other ions were due to water-rock interactions.	Humez et al. ²⁴
Florianopolis, Brazil	<i>In situ</i> - field injection	Argillite, siltite, and sandstone with pebbles, organic matter, and iron oxides. Particle size classified as fine to medium sand.	Injection rate of 90 g day ⁻¹ for 12 day (32 kg CO ₂ in total) at 3 m	Decrease: pH and redox potential Increase: Ca, Mg, Na, P, Ag, Al, As, B, Ba, Cd, Pb, Cu, Cr, Ni, Mn, S, V, and Zn. No change: EC, alkalinity	Slight decreases in ORP were observed ranging from 308 to 229 mV. Ppb level increases detected for the major cations (Ca, Mg, Na, and P) and trace elements (Ag, Al, As, B, Ba, Cd, Pb, Cu, Cr, Ni, Mn, S, V, and Zn). Electrical conductivity and alkalinity remained constant throughout.	Oliva et al. ¹⁵

(Continued)

Table A1. (Continued).

Project site	Experiment type	Aquifer type	Experimental setup	Constituent release trends	Major details	Source
Yaojia Formation, Inner Mongolia, China	<i>In situ</i> - field injection	Grayish or hoary fine sand; mainly quartz, feldspars, clay minerals, and a small amount of ankerite, calcite, and other trace minerals. 56.2–79.5% quartz, 6.8–11.9% K-feldspar, 7.2–19.3% anorthose, 3.6–13.0% clay mineral, 1.3%–10.1% ankerite/dolomite, and 0.7%–5.4% calcite.	27 tonnes of gaseous CO ₂ injected at constant rate over 19.5 days at depth 242 m. Samples were taken at monitoring well (20 m offset) at 4 hr intervals at 183 m.	Decrease: pH Increase: TDS, HCO ₃ , Ca, Cl, F, and Mg Not detected: Pb, Fe No change: SO ₄ , Na, and redox potential	Ca and Mg increase due to calcite and dolomite dissolution, with calcite being dominant. Cause for Cl increase is unclear. Linear correlations between F:HCO ₃ and F:Ca, but no proposed explanation.	Zhu <i>et al.</i> ³¹
Eumseong, Chungcheongbuk-do, South Korea	<i>In situ</i> - field injection	Biotite granite of the Jurassic age.	390 kg of CO ₂ released at 12 L min ⁻¹ at 2.5 m depth across three zones in unsaturated zone for 96 hr. 23 days of monitoring soil water in unsaturated zone.	Decrease: pH, Ba, Increase: EC, Al, As, Cu, Fe, Mn, and U	Preliminary study that presents results for CO ₂ release in unsaturated zone on water quality of soil water in unsaturated zone.	Jun <i>et al.</i> ²⁶
Escatawpa, Mississippi	<i>In situ</i> - field injection	Fine silty sand with minor clay interbedding at depths between 46.9 and 54.6 m. The borings penetrated 30.5 m of sand and gravel of the Citronelle Formation, underlain by low-permeability clay from 30.5 to 46.9 m.	Groundwater pumped out, infused with CO ₂ , and reinjected in a closed loop system, for 5 months at depth 50 m. 10 months post injection monitoring	Decrease: pH, Mo, and F Increase: EC, alkalinity, Ca, Ba, Mg, Mn, K, Li, Na, Sr, Si, and Fe Not detected/Background concentrations: Al, Sb, As, Be, Cd, Cu, Pb, Hg, Ag, Ti, Zn, P, Se, Br-, NO ₂ , NO ₃ , SO ₄ , and HSN Unaffected: Cl	pH and total dissolved carbon are promising indicators of CO ₂ leakage. Pulse release Ca, Ba, Mg, Mn, K, Li, Na, and Sr suggest a fast release pH dependent mechanism with an overlapping slow release from mineral dissolution. No MCLs were exceeded.	Trautz <i>et al.</i> , ⁸ Zheng <i>et al.</i> ⁵⁵

(Continued)

Table A1. (Continued).

Project site	Experiment type	Aquifer type	Experimental setup	Constituent release trends	Major details	Source
Catahoula Aquifer, Mississippi	<i>In situ</i> – Push–pull	Catahoula aquifer. Primarily fluvial to marginal deltaic. Three subaquifers: the upper unconfined-confined subaquifer and the middle and lower confined subaquifers. 53% quartz, 17% k-feldspars, 2% plagioclase, and 29% clays	3825 L groundwater was bubbled with CO ₂ at 10 ⁵ Pa in headspace and injected over 10 hr at 73 m. Incubation period of 55 hr. 15 000 L groundwater pulled over 11 hr.	Decrease: pH Increase: DIC, Ca, Na, K, Mg, Si, Na, Sr, Mo, Mn, Co, Ba, B, As, Pb, and Ni No change: Cl, SO ₄ , NO ₃	Increases in Si, Na, and K due to dissolution of silicates. Increases in Ca and Mg may have been caused by trace calcite dissolution. Sr, Mo, Mn, Co, Ba, and B were correlated to Ca, indicating carbonate dissolution. No MCLs were exceeded.	Yang et al. ³⁰
Blackenridge, Texas	<i>In situ</i> - Field injection	Silticlastic-dominated alluvial aquifer. 18% carbonates, 50% quartz, 13% k-feldspars, 14% plagioclase, and 5% clays. Sediments vary in grain size from clay-rich layers, ~0.2 m thick, to coarse sands and gravel, with most of the sediment in the medium- to coarse-grained sand range.	Two pulse-like releases of CO ₂ using a peristaltic pump for 2–3 hr at 6 m, 10 days apart	Decrease: pH, Na, Increase: DIC, alkalinity, and dissolved CO ₂ , Ca, Br, and Mg	Monitoring of dissolved CO ₂ is promising for detecting leakage. Analysis confirms decreases in pH, and increases in DIC and dissolved CO ₂ were from dissolution of CO ₂ , while alkalinity was from carbonate dissolution.	Yang et al. ¹¹
	<i>In situ</i> – Push–pull		Single well push pull. 950 L pumped out to equilibrate with CO ₂ . Maintains slightly above atmospheric pressure with 100% CO ₂ in head space. Injected over 1 hr at 6 m. Sampled after 23–80 hr	Decrease: pH, Mo, and Al, Increase: DIC, alkalinity, dissolved CO ₂ , Ca, Mg, Sr, Ba, Mn, U, Si, K, As, Zn, V, P, Ni, Na, Mg, Fe, Co, B, U, Ti, and Sr Not detected or too dilute: Zr, Se, Cd, Cs, Sb, and Pb	Ca, Mg, Sr, Ba, Mn, and U are controlled by carbonate dissolution, while Si and K are controlled by silicate dissolution that is two orders of magnitude slower. Most ions returned to near baseline levels. MCLs were not exceeded for any ions except Mn.	Mickler et al. ⁹

(Continued)

Table A1. (Continued).

Project site	Experiment type	Aquifer type	Experimental setup	Constituent release trends	Major details	Source
Frio Formation, Dayton, Texas	<i>In situ</i> - Field injection	Poorly cemented subarkosic sandstone comprised dominantly of fine grained, moderately sorted quartz with minor amounts of illite/smectite, feldspar and calcite. Na-Ca-Cl brine type.	1600 tons of CO ₂ injected over 10 days at depth of 1540 m. 60 samples were taken before, during, and after injection	Decrease: pH Increase: alkalinity, EC, DOC, Ca, Fe, Mn, Mo, Pb, and Zn	Sharp increase in Fe and alkalinity Modeling indicates that buffering by dissolution of calcite and Fe oxyhydroxides prevented further pH reduction. This could also lead to trace metal mobilization	Kharaka <i>et al.</i> ¹²⁻¹⁴
Newark Basin, Palisades, New York.	<i>In situ</i> - Push pull	Palisades dolerite sill is 230 m thick from the surface and underlain by metamorphosed sedimentary rocks of the Passaic Formation. 1% carbonates, 78% quartz, 18.7% k-feldspars, 1.7% plagioclase, and 0.5% clays	3100 L aquifer water enhanced with 1 atmosphere pressure CO ₂ gas for 16 hr. 3060 L injected back over 11.1 hr at 364 m depth. 20 days incubation; 33 days pull phase.	Decrease: pH, SO ₄ , Mo, and As Increase: alkalinity, Ca, Mg, Si, Fe, Mn, Cr, Co, Ni, Cu, Zn, Rb, Sr, Ba, U, Be, Zr, and Sb	Release rates for Ca, Mg, and Si are comparable to batch experiments, dependent on pH and pCO ₂ . Carbonate dissolution contributed significant changes to ion concentrations despite low aquifer abundance. Simultaneous changes in pH, EC, and associated ions could be used as indicator for CO ₂ leakage. MCLs were exceeded for pH, Fe, Mn, and Zn under CO ₂ leakage conditions.	Yang <i>et al.</i> ³⁸

(Continued)

Table A1. (Continued).

Project site	Experiment type	Aquifer type	Experimental setup	Constituent release trends	Major details	Source
ZERT Site, Bozeman, Montana	<i>In situ</i> - Field injection	Topsoil of organic-rich silt and clay with some sand ranges in thickness from 0.2 to 1.2 m, and a caliche layer, high in calcite (~15%), is observed at depths of ~50–80 cm. Beneath the topsoil layer is a cohesionless deposit of coarse sandy gravel extending to 5 m, the maximum depth investigated. Gravels comprise ~70% of rock volume, and andesite is the chief rock fragment among the gravels and coarse sands, but minor amounts of detrital limestone and dolostone are also observed. The sand and silt sized fraction of this sediment consists of approximately 40% quartz, 40% magnetite and magnetic rock fragments, and 20% grains of amphibole, biotite/chlorite, and feldspar.	300 kg days ⁻¹ CO ₂ injected underground from July 9–August 7 2008 at 2–2.3 m. Samples were collected from July 7–August 14, 2008.	Decrease: pH, As, Cu, and Mo, alkalinity could provide early detection for CO ₂ leakage. BTEX increase: alkalinity, EC, TDS, Ca, Mg, Fe, Mn, Sr, Ba, Al, B, Ba, Br, Cd, Cl, Co, Cr, Li, Mg, Sr, Zn, NO ₃ , SiO ₂ , and SO ₄ . No change: Na, K	Changes in Ca, Mg, Mn, Fe, EC, and alkalinity could provide early detection for CO ₂ leakage. BTEX detection caused by CO ₂ contamination. Trace metals and BTEX are below MCLs. DOC saw slight variation not related to CO ₂ injection.	Kharaka et al. ¹⁷ ; Apps et al. ^{7,6}

Table A2. Summary of laboratory studies.

Sample site	Experiment type	Sample description	Experimental setup	Constituent release trends	Major details	Source
Cranfield formation; Mississippi; Dockum, Trinity, Ogallala, Carrizo-Wilcox, and Hickory Formations, Texas	Lab batch	Various types of fine and coarse sandstone. Quartz, dolomite, illite/smectite, albite, microcline, and chlorite	95 g disaggregated rock sample with 500 mL DI water. 2 weeks of Ar gas, followed by 2 weeks of CO ₂	Increased then decreased below starting levels: Fe, Al, Mo, U, V, As, Cr, Cs, Rb, Ni, and Cu Increasing: Ca, Mg, Si, K, Sr, Mn, Ba, Co, B, and Zn Decrease: pH	Dissolution of dolomite and calcite caused the largest increase in concentrations for Ca, Mg, Mn, Ba, and Sr. Cation release rates decreased linearly as pH increased during mineral buffering. Experiment results suggest that carbonate minerals are the dominant contributor of changes in groundwater quality	Lu <i>et al.</i> ³⁴ ; Yang <i>et al.</i> ²⁹
Ogallala, Texas; Mahomet, Illinois; Aquia & Virginia Beach, Virginia/Maryland	Lab batch	Various types of fine sand, medium and coarse quartz sands, and sands containing N/Na/Ca feldspars, dolomite, and Fe oxides, and calcite	400 g of dry disaggregated aquifer sediment from 17 locations were incubated with CO ₂ pumped in at 0.2 L min ⁻¹ for 300 days	Increase: B, Ca, Mn, Co, Ni, Fe, U, Ba, Cu, Li, Mg, Sr, U, Rb, Al, Zn, Cd, Se, and Ti Decrease: As and Mo No clear trend: Cr	Mn, Fe, Ca, and pH could be used as geochemical markers of a CO ₂ leak, as their concentrations increase within 2 weeks of exposure to CO ₂ . Carbonate poor aquifers had lower concentrations of Ca, and lowest pH. Al, Mn, Fe, Zn, Cd, Se, Ba, Ti, and U approached or exceeded MCLs.	Little and Jackson ³⁵
Medina, Bexar, and Atascosa, Texas	Lab batch	Core plugs came from the San Antonio region in Texas; Medina, Bexar, and Atascosa counties. Relatively high organic matter and carbonates ranging from 23–100%, quartz 0–51%, K-feldspar 0–15%; and clays 0–13%.	0.3 cm thick slices of core plugs were quartered (about 0.8–0.9 g) and exposed to CO ₂ and N ₂ (control) in 25 mL Parr vessels and 15 mL 0.01 M NaCl solution for 7 days. As/Cd were spiked for some experiments, and pressure was changed for others.	Decrease: pH, Zn, As, and Cd Increase: Ba, Ca, K, and Mg No clear trend: Mo and Na	Tests containing organics showed slower release of S, Sr, Ba, K, Si, and Ca and faster removal of As and Cd. Decreases in Zn likely due to initial Zn contamination from pressure vessel. Highest pCO ₂ results in increase calcite dissolution rates.	Lawter <i>et al.</i> ⁴¹
N/A	Lab column	Modified sand with precipitated metal oxides of Cr, Co, Ni, Zn, Cd, Cu, Mn, and Fe.	0.0028 m ³ of modified sand. Distilled water flow at 0.3 mL min ⁻¹ and CO ₂ flow at 2 mL min ⁻¹ . Two month long experiment.	Increase: Cd, Cu, Mn, Ni, and Zn	CO ₂ dissolution and drop in water pH significantly mobilizes Mn, Ni, Cu, Zn, and Co, with moderate mobilization in Cr, and acceleration in Cd dissolution. Fe remained bound to sand as goethite.	Terzi <i>et al.</i> ⁷⁷

(Continued)

Table A2. (Continued).

Sample site	Experiment type	Sample description	Experimental setup	Constituent release trends	Major details	Source
Blackenridge, Texas	Lab batch	Siliclastic-dominated alluvial aquifer. 18% carbonates, 50% quartz, 13% k-feldspars, 14% plagioclase, and 5% clays.	100 g disaggregated ground aquifer sample with 400 mL aquifer groundwater (4:1 water to rock ratio). 1 week argon gas, followed by CO ₂ injection 1 min/20 min at 5 PSI above atmospheric pressure. Run time 27 days	Decrease: pH, As, Mo, V, Zn, Se, and Cd Increase: B, Ba, Ca, Mg, Sr, Mn, U, Si, K, Co, and Ni Not detected: Cs, Fe, Pb, and Ti	As, Mo, V, Zn, Se, and Cd were highest after argon flush and decreased when CO ₂ was introduced. No trace metals exceed MCLs.	Mickler et al. ⁹
N/A	Lab batch	Synthesized pure calcite	3 g of sample (calcite, goethite, or goethite-calcite composite) with 1 L of metalloid ion solution with 400 rpm agitation. 24 hr of Ar gas at 10 bar allowed for solution equilibrium. CO ₂ injected at 8 bar over 2 days.	Remobilization: As(III) and Se(VI) Resorption: Se(IV), No effect: Cd(II) and Cu(II)	Results indicate calcite and goethite may prevent mobilization of Cu(II), Cd(II), and Se(IV), and As(V) during CO ₂ intrusion and reactivate adsorption of Se(IV) and As(V) if present in sufficient amounts. Results suggest Ca and Cu adsorption increases with calcite dissolution.	Montes-Hernandez et al. ³⁹
		Synthesized goethite		Remobilization: As(III), Cd(II), and Cu(II) Re-sorption: Se(IV) and Se(VI),		
		Synthesized goethite-calcite composite		Remobilization: As(III), Re-sorption: Se(IV) No effect: Se(VI), Cu(II), and Cd(II)		

(Continued)

Table A2. (Continued).

Sample site	Experiment type	Sample description	Experimental setup	Constituent release trends	Major details	Source
ZERT Site Wells, Bozeman, Montana	Lab batch	Topsoil of organic-rich silt and clay with some sand ranges in thickness from 0.2 to 1.2 m, and a caliche layer, high in calcite (~15%), is observed at depths of ~50–80 cm. Beneath the topsoil layer is a cohesionless deposit of coarse sandy gravel extending to 5 m, the maximum depth investigated. Gravels comprise ~70% of rock volume, and andesite is the chief rock fragment among the gravels and coarse sands, but minor amounts of detrital limestone and dolostone are also observed. The sand and silt sized fraction of this sediment consists of approximately 40% quartz, 40% magnetite and magnetic rock fragments, and 20% grains of amphibole, biotite/chlorite, and feldspar	15 g of sediments from wells 6 and 7 at ZERT site and 150 mL synthetic ZERT groundwater was synthesized. Samples were allowed time to equilibrate before exposure to 1 atm of food grade CO ₂ for 15 days.	Decrease: pH and Pb Increase: EC, TDS, HCO ₃ , Ca, Mg, Fe, Mn, Co, U, Ba, SiO ₂ , SO ₄ , Zn, Sr, Na, Li, K, and As Minimal or No effect: PO ₄ , and Fe,	Increase in alkalinity, EC, Mg, Ca, Fe, and Mn linked to dissolution of calcite, dolomite, minor Mn-oxides, and ion exchange and desorption. Heavy metal mobilization linked to these processes.	Kharaka <i>et al.</i> ^{4,19}
High Plains Aquifer, Kansas	Lab batch	The High Plains aquifer is a heterogeneous, unconsolidated aquifer consisting of clay, silt, sand, and gravels. Samples have carbonate percentage ranging from 0–3.8%	Batch experiments using 5 g soil, 15 mL synthetic groundwater spiked with As and Cd and equilibrated for 15 hr before CO ₂ introduction. CO ₂ was continuously flowed at 70 mL min ⁻¹ at 1 atm for 14 days.	Decrease: As Pulse increase: Cd Increase: Ba, Ca, K, Mg, Mn, Si, Sr, and Na (minor increase)	Results suggests that aquifers containing 0–4% carbonates can adsorb As and Cd. Cd will initially remobilize with introduction of CO ₂ , but will readsorb with time.	Shao <i>et al.</i> ⁴⁰

(Continued)

Table A2. (Continued).

Sample site	Experiment type	Sample description	Experimental setup	Constituent release trends	Major details	Source
High Plains Aquifer, Kansas	Lab batch	Sand/sandstone aquifer. Quartz was the major component and varying amount of feldspar, mica, kaolinite, and carbonate minerals (calcite and dolomite) were also present. Calcite ranged from 0–4.7%	Batch experiments at room temp and atmospheric pressure with 15 mL synthetic groundwater and 5 g sand/sandstone sample, and 72 L min ⁻¹ CO ₂ flow. Synthetic groundwater was made using CaCO ₃ , MgCO ₃ , Na ₂ SO ₄ , NaCl, HNO ₃ , and KOH for final pH of 7.59. Experiment run for 14 days	Decrease: pH, Mo, and Cu (1 of 4 samples), Increase: Ba, Ca, Mg, Mn, Si, Sr, and As (1 of 4 samples)	Significant increase of Ca, Ba, Sr, Mg, and Si observed. Mobilization of trace metals occurred in low concentrations. Occurrences of mobilization was more frequent in calcite free sediments. Mo concentration consistently lower in CO ₂ exposed samples, and steadily increased in controls.	Qafoku et al. ⁶⁰
Stapafell Mountain, Iceland	Lab column	Basaltic glass used in this study was collected from the Stapafell Mountain located in SW Iceland. The composition of the material is similar to that of mid-ocean ridge basalt (MORB).	8.3 kg of basaltic glass particle size 45–100 µm was placed in titanium reactor. Liquid CO ₂ and degassed DI water pumped through at 8 Mpa at 0.22 mL min ⁻¹ and 3.5 mL min ⁻¹ , respectively, for 100 hr.	Decrease: pH and V Increase: Ba, Mn, Mg, Sr, Fe, Al, Ca, Cr, As, Ti, Si, Pb, Na, Mg, Li, K, and Cd	All measured ions saw increase in mobility. Mn, Al, Fe, and Cr exceeded EU limits for drinking water.	Galezka et al. ³²
Dongying Depression, China	Lab batch	Sandstone from the Shahejie formation in Dongying Depression. 29% carbonates, 35% quartz, 7% plagioclase, 19% clays, and 7% k-feldspars	1.8 g of sandstone with 25 mL of NaCl solution (0.02, 0.1, and 0.5 mol L ⁻¹) at 50 °C and CO ₂ at 2.5, 8, and 10 Mpa for 12–144 hr	Decrease: Increase: HCO ₃ , Ca, Mg, and Na. No change: K	HCO ₃ increased due to carbonic acid decomposition, dissolution of calcite. Ca increase caused by calcite dissolution. Precipitation of dawsonite led to large decrease in Na after experiment was over.	Liu et al., ⁷⁸
Paris Basin, France	Lab batch	Sandy multilayered aquifer, consisting of quartz rich sand, with the presence of illite/smectite, microcline, apatite, and glauconite. Albian sands from outcrops and borehole cuttings were used.	Water samples were collected at 600 m depth. 40 g sand with 400 mL formation water were equilibrated with N ₂ . CO ₂ injected until 2.0 bar at 20°C was reached. Monitored over 1 month period	Increase: DIC, alkalinity, Al, As, B, Ca, Co, F, Li, Ni, Si, Na, K, Mg, Mn, Pb, and Zn Decrease: pH, Ba, Be, Fe, SiO ₂ , and PO ₄ Minor change/not detected: Cl, F, U, and SO ₄ ,	Ca, SiO ₂ , HCO ₃ , F, PO ₄ , Na, Al, B, Co, K, Li, Mg, Mn, Ni, Pb, Sr, and Zn increased after initial CO ₂ influx. Be and Fe declined at the start of CO ₂ injection. No variation seen in Cl and SO ₄ . No ions exceeded EPA or WHO guidelines.	Humez et al. ³³

(Continued)

Table A2. (Continued).

Sample site	Experiment type	Sample description	Experimental setup	Constituent release trends	Major details	Source
N/A	Lab batch	Idealized limestone (1:1 calcite and dolomite with 1% pyrite).	Simulated limestone and limestone shale mixtures were reacted with synthesized brine for 28 days for equilibrium before CO ₂ was injected for 48 days.	Increase: SO ₄ , SiO ₂ , V, Ti, Pb, Ni, Mn, Fe, F, Co, Cl, Cu, Ba, and Cd Decrease: pH, K, Sr, Cr, Ca, and Zn Minor change/not detected: Al, Na, and Mg	Mineral dissolution increased Ba, Co, Cu, Pb, and V for both experiments; Fe, Ni, and Zn for mixed shale experiment, and Ba and Cd in carbonate experiment. Shale caprock plays active role in trace metal mobilization as well as immobilization due to presence of clays, smectites and other silicates. Fe, Pb, and Cr exceeded EPA MCLs for both experiments. Zn exceeded limits in shale carbonate experiment, while Ba, Cu, and Cd exceeded limits in carbonate experiment.	Marcon <i>et al.</i> ⁷⁹
N/A	Lab batch	50% idealized limestone and 50% gothic shale (sapropelic (organic rich) dolomite and dolomitic shale to silty carbonate mudstone)	150 g of each crushed rock with 750 mL water in N ₂ atmosphere for 18 days to equilibrate. CO ₂ partial pressure increased from 0.01 bar to 1 bar in 15 d stages for 75 days total	Increase: SO ₄ , SiO ₂ , V, Ti, Pb, Ni, Mn, Fe, F, Co, Cl, Cu, and Zn Decrease: pH, K, Cr, and Ba Minor change/not detected: Al, Na, Mg, Ca, and Sr Erratic: Cd	Dissolution of carbonates due to pH drop will buffer pH changes, but also release impurities. Carbonates the dominant source of Sr, Co, Mn, Ni, Ti, Zn, and other associated metals.	Wunsch <i>et al.</i> ⁵⁷
N/A	Lab batch	Kindblade Dolomite (Colorado): 89% carbonates, 2% quartz, and 9% clays Sevy Dolomite (Colorado): 37% carbonates, 57% quartz, and 6% clays Cotter Dolomite (Missouri): 80% carbonates, and 19% quartz				

(Continued)

Table A2. (Continued).

Sample site	Experiment type	Sample description	Experimental setup	Constituent release trends	Major details	Source
Bryan and Carter Counties, Oklahoma	Lab batch	Joins Limestone: 83% carbonates, 7% quartz, 7% clays, 2% and K-feldspars Kindblade Limestone: 96% carbonates, 3.6% quartz, 0.4% and clays	150 g of disaggregated rock. 5:1 water to rock ratio. CO ₂ headspace pressures varied from 0.01 bar to 1 bar over 10 days	Increase: As, Ba, Ca, Co, Mg, Ni, Sr, U, SO ₄ , Pb (1 of 2 samples), and Ti (1 of 2 samples) Decrease: pH	As and Ni exceeded MCLs. Calcite dissolution was primary driver of metal release, over pyrite dissolution or metal desorption. Calcite dissolution is more important to metal release under oxic or sub-oxic conditions. Pyrite dissolution may play important role in long term dissolution.	Wunsch et al. ³⁷
Scurry Area Canyon Reef Operators Committee (SACROC) oilfield, Texas	Lab batch	Core samples from University of Texas at Austin used with the goal of representing various aquifers present in Texas and throughout the Gulf Coast region.	95 g disaggregated rock sample combined with 500 mL DI water with 40 ppm Cl as NaCl. Ar gas bubbled for 2 weeks, then CO ₂ bubbled for 2 weeks.	Increase: Al, As, B, Ba, Ca, Co, Cs, Cu, Fe, K, Mg, Mn, Mo, Ni, Rb, Sr, U, V, and Zn Decrease: pH	Identified cations that increased rapidly and then slowly increase or remained constant (B, Ba, Ca, Co, K, Mg, Mn, Sr, and Zn), and cations that increased rapidly and slowly decreased (Al, As, Cs, Cu, Fe, Mo, Ni, Rb, U, and V). Correlations between Ca and Mg suggest dolomite is their source mineral. K and Si may be release from K-feldspars.	Smyth et al. ⁸⁰
Edward aquifer, San Antonio, Texas	Lab batch	Soluble limestone formation, dominated by karst dissolution features and is representative of carbonate aquifers overlying potential CO ₂ sequestration repositories within the continental United States	5 g of <2 mm particle size samples were mixed with 15 mL synthetic groundwater. Pure CO ₂ injected continuously at 70 mL min ⁻¹ , with vessel open to atmosphere for venting for 15 days	Increase: Ca, Cu, Mn, Na, Si, and K Decrease: pH, Ba, Mg, Sn, and Sr Not detected: Fe and Pb	CO ₂ exposure caused decrease in pH by 2 units, and subsequent release of Ca, Mg, Ba, Sr, Si, Na, K, and the slow release of Mo, Cs, and Sn. Other element such as Al and Mn may have seen rapid mobilization followed by rapid immobilization. (Pulled from abstract, some element conc data only in supplemental material)	Wang et al. ³⁶
	Lab column		Columns packed with ground sediments and exposed to CO ₂ saturated synthetic ground water at a rate of 0.03 mL min ⁻¹ with two stop flow events of duration 143 hr and 69 hr at experimental times of 170 and 240 h, respectively.	Increase: As, Ba, Cr, Cu, Mn, Ni, Pb, Se, and Zn Decrease: pH and redox Not detected: Be, Cl, Fe, U, SO ₄ , and NO ₃ .		

Table A3. Summary of groundwater quality studies regarding CO₂ storage analog sites.

Analogue site	Water type	Geological description	Constituents measured	Source
Kayseri, Turkey	Thermal mineral springs (Na-Mg-Ca-Cl-HCO ₃ and other variations)	Central Anatolian crystalline complex. Metamorphic/crystalline rocks in the area occurring as the basement, sedimentary units of Upper Cretaceous-Quaternary age form the cover. Metacarbonates are of primary confined aquifers	pH, Temp, EC, DO, CO ₂ , HCO ₃ ⁻ , CO ₃ ²⁻ , B, Ca, Cd, Cl, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn, SO ₄ , NO ₃ , NH ₃ , PO ₄ , and isotope analysis	Afsin <i>et al.</i> ⁴³
Chungcheng; Chojeong; Bugang; Bangadari, South Korea	Carbonated and noncarbonated groundwater, surface water, and wells	Varies between granitic, gneissic, and Precambrian terrains. Granitic terrain consisting of Precambrian gneiss intruded by age-unknown gneiss, Jurassic sedimentary layer, and Mesozoic granite. Gneissic terrain consisting of consist of age-unknown arenaceous phyllite layer and metasedimentary rocks of the Okcheon metamorphic belt. Precambrian metamorphic rocks and Jurassic granites composed of biotite granite, two-mica granite, and porphyritic granite. The main constituent minerals of biotite granite are quartz, orthoclase, plagioclase and biotite, and minor minerals include muscovite and chlorite. The two-mica granite is relatively weathered, which mainly consists of quartz, feldspar, biotite, and muscovite. Porphyritic granite consists of quartz, orthoclase, plagioclase, and biotite.	pH, temp, EC, alkalinity, TDS, DO, CO ₂ , HCO ₃ ⁻ , TIC, Al, Ba, Be, Br, Ca, Cl, Cr, Cs, F, Fe, K, Li, Mg, Mn, Na, Ni, Rb, Sr, U, SO ₄ , SiO ₂ , NO ₃ , redox potential, and isotope analysis	Choi <i>et al.</i> ⁸¹
Chungcheong; Gangwon; Gyeongsang, South Korea	CO ₂ rich, acidic, and ordinary groundwater	Bedrock in Gangwon Province consists of various types of granite (Jurassic biotite granite, muscovite granite, and graphic granite) and banded gneiss. Gyeongsang Province consists mainly of sedimentary bedrock from the Gyeongsang Supergroup, which has a thickness of 8–10 km and includes conglomerate, sandstone, shale, mudstone, marl, and other lithologies, along with volcanic rocks and thin layers of limestone above and below the supergroup. In Gyeongsang Province, the CO ₂ -rich groundwater occurs in the sedimentary rocks of this supergroup. Chungcheong Province is composed largely of granite, but with a wide variety of additional rock compositions including sedimentary protoliths, Jurassic biotite granite, chalk, gneiss, mineralized acidic dikes containing sphalerite, scheelite, chalcocopyrite, and pyrrhotite, as well as quaternary rocks.	pH, temp, EC, alkalinity, TDS, DO, HCO ₃ ⁻ , Al, Ca, Cl, F, Fe, K, Li, Mg, Mn, Na, Sr, SO ₄ , SiO ₂ , NO ₃ , and redox potential	Kim <i>et al.</i> ⁸²
100 km Southeast of Seoul, South Korea	CO ₂ rich and CO ₂ poor groundwater	The geology of the study area mainly consists of Precambrian gneiss and Jurassic-biotite granite. The CO ₂ -rich waters are located at the geological boundary between Jurassic granites and their adjacent Precambrian gneisses. The granites are mainly composed of K-feldspar, quartz, plagioclase, and biotite. The origin of CO ₂ gas in this area was known as magmatic CO ₂ gases migrating along faults or fractures.	pH, temp, EC, alkalinity, TDS, DO, DOC, CO ₂ , Al, Ba, Be, Br, Ca, Cl, Cr, Cs, F, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Rb, Sr, Zn, SO ₄ , SiO ₂ , NO ₃ , and redox potential	Ham <i>et al.</i> ⁸³

(Continued)

Table A3. (Continued).

Analog site	Water type	Geological description	Constituents measured	Source
Daylesford, Victoria, Australia	High CO ₂ mineral water from various springs, pipes, pumps, and trenches	The mineral water resides primarily in fractures and fissures in the Ordovician sediments that form the Ordovician Aquifer. The upper 50 m of the Ordovician sediments are highly weathered and contain kaolinite throughout the sediments and Fe oxyhydroxides along fracture zones. In this weathered zone, groundwater flow occurs both through fractures and the weathered bedrock. Where they are sufficiently thick, the basalt flows that cover parts of the weathered Ordovician sediments form the unconfined quaternary basalt aquifer	pH, temp, EC, CO ₂ , HCO ₃ ⁻ , B, Ba, Ca, Cl, Fe, K, Li, Mg, Mn, Na, Sr, Zn, SO ₄ , SiO ₂ , NO ₃ ⁻ , and redox potential	Weaver <i>et al.</i> ⁸⁴
Snaefellsnes; Grimsmes; Torfajökull, Iceland	CO ₂ -rich spring, surface water, and well samples	Basalt aquifers. CO ₂ -rich waters are found in two types of environments, as cold and hot springs on the periphery of volcanic geothermal systems that are located within the zones of active volcanism and rifting and in areas of present-day alkalic volcanism that occurs in the nonrifting volcanic zones.	pH, temp, CO ₃ ²⁻ , Al, As, B, Ba, Be, Br, Ca, Cl, Co, Cr, Cs, Cu, F, Fe, Ga, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sr, V, W, Zn, SO ₄ , SiO ₂ , and H ₂ S	Arnósson <i>et al.</i> ⁴⁷
Mt. Hekla, Iceland	Springs	Mt. Hekla volcano. Bulk of erupted material is andesitic basaltic volcanic glass. Rock forming phases of the basaltic andesitic tephra are glass (97.9%), plagioclase (1.6%), magnetite (0.2%), olivine (0.2%), and pyroxene (0.1%)	pH, CO ₂ , Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V, Zn, Mg, Ca, Cl, K, Na, Si, and Al	Flaathen <i>et al.</i> ⁸⁵
Southern Alps, Italy	CO ₂ -rich gas fed springs	Seven major geological structures: Fella-Sava line, Val Pesarina Line, But-Chiarso line, M.Dof-M.Auda lineament, Barcis-Staro Selo – joints, Sauris line, Monte Pala line. Geology varies from Upper Triassic dolomites, dolomitic and marly limestones, Mesozoic carbonate terranes, and carbonatic silico-clastic deposits.	pH, temp, EC, CO ₂ , HCO ₃ ⁻ , Al, As, B, Ba, Ca, Cl, Co, Cs, Fe, Ga, K, Li, Mg, Mn, Mo, Na, Ni, Rb, Si, Sr, U, Zn, SO ₄ , redox potential, and isotope analysis	Slejško <i>et al.</i> ⁸⁶ and Italiano <i>et al.</i> ⁸⁷
Apennine, Italy	CO ₂ -rich springs	The Apennine area is characterized by 12 well-defined regional aquifers hosted by Mesozoic permeable limestones.	pH, temp, alkalinity, DIC, Ca, Cl, K, Mg, Na, SO ₄ , and isotope analysis	Chiodini <i>et al.</i> ⁸⁸
Mt. Vesuvius, Italy	Volcanic groundwaters	Two major aquifers. The deep-carbonate aquifer, hosted in the Mesozoic series buried beneath the volcanoclastic and sedimentary deposits of the Campanian Plain and is recharged by carbonate massifs of the Apennine Chain. The shallower Vesuvian volcanic aquifer hosted by fractured lavas and coarse-grained pyroclastic deposits produced by eruptions of both nearby Phlegrean Fields and Somma–Vesuvius complex.	pH, temp, EC, alkalinity, Al, As, Ba, Ca, Cd, Cl, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sr, Th, U, V, Zn, SO ₄ , SiO ₂ , and redox potential	Aiuppa <i>et al.</i> ⁴⁵ and Federico <i>et al.</i> ⁸⁹

(Continued)

Table A3. (Continued).

Analog site	Water type	Geological description	Constituents measured	Source
Mt. Etna, Sicily	CO ₂ enriched groundwater from springs, wells, and drains	The Etnean aquifer is hosted by the permeable basaltic lavas that form the volcanic pile. All groundwaters are meteoric in origin. They seep rapidly into the fractured volcanic strata and flow at the contact with the underlying impermeable sedimentary basement	pH, temp, EC, alkalinity, Al, As, Ba, Ca, Cd, Cl, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sr, Th, U, V, Zn, SO ₄ , SiO ₂ , and redox potential	Aiuppa <i>et al.</i> ⁴⁶
Sainte-Marguerite, France	Mineral springs and geyser	Southern part of the Limagne d'Allier basin in the French Massif Central; mainly filled by limestones with frequent sandy-clay intercalations that are contemporary of the Oligocene to Miocene West European rifting. Alluvial and colluvial deposits from the Allier River partly overlie these tertiary strata and from place-to-place volcanic series crosscut the sedimentary formations. Mineral waters in the basin are strongly influenced by their deep circulation in the crystalline basement and the occurrence of deep CO ₂ sources	pH, temp, EC, HCO ₃ ⁻ , Br, Ca, Cl, F, Fe, K, Li, Mg, Mn, Na, Sr, SO ₄ , SiO ₂ , NO ₃ , PO ₄ , redox potential, and isotope analysis	Gal <i>et al.</i> ⁹⁰
Montmiral, France	CO ₂ -rich brine	Triassic sandstone consisting mainly of quartz and K-feldspar and some mica. Other minerals present are small amounts of ankerite and traces of sphalerite and rutile	pH, alkalinity, Al, B, Br, Ca, Cl, F, Fe, I, K, Li, Mg, Na, Rb, Sr, SO ₄ , SiO ₂ , NH ₄ , H ₂ S, redox potential, and isotope analysis	Pauwels <i>et al.</i> ⁴⁹ Lions <i>et al.</i> ⁵⁰
Furnas volcano, Azores, Portugal	Heated and cold CO ₂ -rich and poor springs	Furnas volcano. Pumice rings and associated trachyte domes. Several fumaroles and thermal springs across the caldera floor	pH, temp, EC, alkalinity, DIC, TIC, Al, As, B, Br, Ca, Cl, F, Fe, K, Li, Mg, Mn, Na, P, Sr, Zn, SO ₄ , SiO ₂ , NH ₄ , and H ₂ S,	Cruz <i>et al.</i> ⁴⁴
California coastal range, California	CO ₂ -rich travertine-depositing spring	Clear Lake Volcanics consists of quaternary volcanic rocks of varying lithologies which overlie meta-sedimentary and sedimentary rocks of marine origin. Region consisting primarily of meta-sedimentary rocks with occasional outcrops of ultrabasic igneous rock which, in places, have been metamorphosed to serpentinite.	C, Ca, Mg, Mn, Fe, and isotope analysis	Amundson <i>et al.</i> ⁹¹
Springerville-St. Johns CO ₂ field, Arizona & New Mexico	Springs and groundwater above CO ₂ field	Springerville-St. Johns CO ₂ field lies within a broad, northwest trending asymmetrical anticline at the northeastern border of the volcanic field, adjacent to the Little Colorado River. The aquifers immediately above the Springerville-St. Johns CO ₂ field are in the Glorietta Sandstone and San Andres Limestone.	pH, temp, TDS, HCO ₃ ⁻ , B, Ca, Cl, F, Fe, K, Mg, Na, Sr, SO ₄ , and SiO ₂	Moore <i>et al.</i> ⁹²

(Continued)

Table A3. (Continued).

Analog site	Water type	Geological description	Constituents measured	Source
Jackson dome, Mississippi; McElmo dome, Paradox Basin, Colorado	CO ₂ reservoir formation water	Jackson dome: Jurassic sandstone and dolomite reservoir rocks ~ 4660–4960 m Jurassic Formations Norphlet (~150–365 m thick), Smackover, and Buckner (10–30 m thick) McElmo dome: lower Carboniferous carbonate reservoir; dolomitic carbonate; main reservoir is Mississippian Leadville Limestone–sequence of carbonate rocks (interbedded limestone and dolomite)	Na, Ca, Mg, Fe, Cl, SO ₄ , HCO ₃ ⁻ , TDS, and pH	Stevens et al. ⁹³
Little Grand Wash & Salt Wash, Paradox basin, Colorado Plateau, Utah	CO ₂ rich seeps, springs, and geysers	Faults along the Cane Creek–Big Flat salt anticline cut sandstones, shales, and siltstones which typically are sealed by clay–shale smear and cataclasis. CO ₂ leaks to the surface through low-temperature springs, seeps, geysers, and abandoned oil wells located along the surface trace. The field area includes the Little Grand Wash and Salt Wash fault zones, which are located at the northern edge of the Paradox Basin of the Colorado Plateau near Green River	pH, temp, TDS, HCO ₃ ⁻ , B, Ca, Cl, Fe, K, Mg, Mn, Na, Si, and Sr	Heath et al. ⁵¹
Green river area, Utah	Wells and springs	Entrada Sandstone, Carmel Formation, and Navajo Sandstone. The Carmel Formation is underlain by the ~122 m thick Navajo Sandstone which regionally and locally is a homogenous unit comprising thick sets of high-angle cross-bedded, well-sorted, fine- to medium grained aeolian sandstone with internal stratification The Navajo Sandstone in the northern Paradox Basin is a quartz–arenite to subarkosic fine-to medium-grained sandstone, dominated by quartz (72–86 wt. %) and K-feldspar (6–11 wt. %) with minor amounts of plagioclase (1–3 wt. %) and trace heavy mineral fractions of tourmaline, apatite and rutile (b1 wt. %)	pH, temp, alkalinity, DIC, Al, B, Ba, Br, Ca, Cl, F, Fe, K, Li, Mg, Mn, Na, Rb, Sr, Zn, SO ₄ , SiO ₂ , and isotope analysis	Kampman et al. ⁵⁴
Chimayo, New Mexico	Wells and geysers	These sediments are quartz and feldspar rich; approximately 50–70% of the felspars are plagioclase	pH, DIC, TDS, alkalinity, Ag, Al, As, B, Ba, Ca, Cl, Cr, Cu, F, Fe, K, Li, Mg, Mn, Na, Ni, NO ₃ , Pb, Sr, U, V, Zn, SO ₄ , SiO ₂ , and isotope analysis	Keating et al. ⁴⁸

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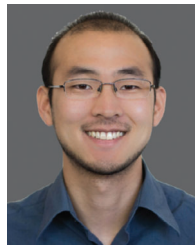
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