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Geochemical Implications of CO₂ Leakage Associated with Geologic Storage: A Review

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July 2012



Pacific Northwest
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Pacific Northwest National Laboratory
Richland, Washington 99352

Abstract

Leakage from deep storage reservoirs is a major risk factor associated with geologic sequestration of carbon dioxide (CO₂). Different scientific theories exist concerning the potential implications of such leakage for near-surface environments. The authors of this report reviewed the current literature on how CO₂ leakage (from storage reservoirs) would likely impact the geochemistry of near surface environments such as potable water aquifers and the vadose zone.

Experimental and modeling studies highlighted the potential for both beneficial (e.g., CO₂ re-sequestration or contaminant immobilization) and deleterious (e.g., contaminant mobilization) consequences of CO₂ intrusion in these systems. Current knowledge gaps, including the role of CO₂-induced changes in redox conditions, the influence of CO₂ influx rate, gas composition, organic matter content and microorganisms are discussed in terms of their potential influence on pertinent geochemical processes and the potential for beneficial or deleterious outcomes.

Geochemical modeling was used to systematically highlight why closing these knowledge gaps are pivotal. A framework for studying and assessing consequences associated with each factor is also presented in Section 5.6.

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1.0 Introduction

The capture and storage of CO₂ in deep geologic formations (or geologic CO₂ sequestration) is widely considered a feasible option for reducing anthropogenic loadings of greenhouse gases to the atmosphere (Bergman and Winter 1995; Bachu 2000; Herzog 2001; Bachu and Adams 2003; Metz et al. 2005; Michael et al. 2010; Goodman et al. 2011; Benson and Cole 2008). Although oil and gas reservoirs (Kovscek 2002; Bachu and Shaw 2003; Hovorka et al. 2009; Esposito et al. 2010; Zhang et al. 2011) and unmineable coal seams (White et al. 2005; Faiz et al. 2007a; Kronimus et al. 2008a) formations have been identified as potential geologic repositories for CO₂, deep (often saline) nonpotable aquifers are preferred and are the most widely studied. Reasons include ubiquity, availability of mature technology, high storage capacities, and the potential for CO₂ conversion to carbonate minerals (Bachu and Adams 2003; Goldberg et al. 2008, 2010; McGrail et al. 2006). Estimates for CO₂ storage capacity in single, deep nonpotable aquifers range from 10⁻² to 10⁴ Gt (Herzog 2001; McGrail et al. 2006; Goldberg et al. 2008; Gislason et al. 2010; Donda et al. 2011; Medina et al. 2011) and would be sufficient for storing decades to centuries of future CO₂ emissions. For example, the estimated CO₂ storage capacity of deep basaltic aquifers on the Juan de Fuca ridge off Vancouver Island (part of British Columbia and northwestern Washington State), is believed to be equivalent to about 122–147 years of U.S. future CO₂ emissions (Goldberg et al. 2008).

Despite apparent promise, a major risk factor and potential barrier to widespread deployment of geologic CO₂ sequestration is leakage of CO₂ from the storage aquifer (Metz et al. 2005; Celia and Nordbotten 2009; Holloway et al. 2007; Shaffer 2010; Bachu 2008; Wilson et al. 2007; Celia and Bachu 2003). Shaffer (2010) suggested that leakage of 1% or less per thousand years from a storage reservoir, or continuous re-sequestration, would be required to maintain atmospheric CO₂ concentrations close to those projected for alternative approaches (e.g., lowering emissions). Concerns with CO₂ leakage may be considered globally or locally (Metz et al. 2005; Bachu 2008). On a global scale, increased atmospheric CO₂ concentration due to leakage of previously sequestered CO₂ is of greatest concern to the scientific community. Some global assessments indicate that even with leakage up to 2%, geologic sequestration would still be viable (van der Zwaan 2009; Hepple and Benson 2005; Pacala 2003). Hence, with 1000-year storage capabilities now approaching 99%, concerns about geological sequestration on a global scale will likely be a nonissue in the near future (Metz et al. 2005).

Locally, two CO₂ leakage scenarios are of concern (Metz et al. 2005; Bachu 2008). The first is where there is a sudden, fast and short-lived release of CO₂ as would occur in the case of well failure during injection or spontaneous blowouts (Holloway et al. 2007; Jordan and Benson 2009; Damen et al. 2005; Skinner et al. 2003). In general, this leakage scenario is anticipated to be rare (on the order of 1 every 10⁵ wells year⁻¹) with environmental damage confined to the vicinity of the accident (Holloway et al. 2007; Jordan and Benson 2009). However, in cases where CO₂ concentrations are high enough, there is the potential for loss of human and animal life (Bachu 2008; Hepple 2005). The second local leakage scenario is where the leak is more gradual, occurring along undetected faults, fractures or well linings (Celia and Nordbotten 2009; Bachu 2008; Damen et al. 2005; Nordbotten et al. 2005; Scherer et al. 2011; Lewicki et al. 2007; Annunziatellis et al. 2008). Without rigorous monitoring, such diffusive leakage may go undetected for prolonged periods of time, and has the greatest potential to cause broad-scale environmental impacts (Metz et al. 2005; Bachu 2008; Damen et al. 2005).

Knowledge on specific environmental consequences associated with leakage from geologic sequestration of CO₂ is continually evolving. Gaus et al. (2010) recently reviewed the literature pertinent to the effect of CO₂-rock interactions on rock porosity and permeability in deep formations suitable for CO₂ sequestration. Lemieux (2011) also reviewed the literature on what he termed “near-field” and “far-field” impacts of geological CO₂ sequestration on shallow groundwater. In this report, the current literature on the geochemical implications associated with CO₂ leakage from deep storage formations to near-surface environments is reviewed and synthesized. Specific attention is paid to CO₂-induced effects on pertinent geochemical processes (e.g., dissolution/precipitation and adsorption/desorption) and potential beneficial or deleterious consequences. Gaps in current knowledge and areas of future research are identified and discussed in the context of these processes. When possible, geochemical modeling was used to illustrate why closing current knowledge gaps is pivotal.

2.0 Carbon Dioxide in Subsurface Environments

In deep geologic formations suitable for CO₂ sequestration, the temperature and pressure conditions typically exceed those of the critical point of CO₂ (31.1°C/7.38 megapascals [MPa]). The CO₂ in storage aquifers will therefore exist primarily as a supercritical fluid (Celia and Nordbotten 2009; Bachu 2008; Bachu 2003). Several mechanisms for the sequestration of this supercritical CO₂ (scCO₂) in deep aquifers have been identified:

1. Geologic trapping through physical containment by geologic features
2. Solubility trapping through dissolution in the formation water or residual oil
3. Mineral trapping through the formation of carbonate minerals
4. Hydrodynamic trapping due to difference in viscosity between the CO₂ plume and formation water
5. Capillary trapping where CO₂ is held in formation due to capillary forces (Bachu and Adams 2003b; Han et al. 2010a; Carneiro 2009; Saadatpoor and Sepehrnoori 2010).

In uneconomical coal-bed formations, sorption of CO₂ to the coal surface is the primary sequestration mechanism identified (White et al. 2005; Bachu 2007; Ross et al. 2009; Kronimus et al. 2008b; Faiz et al. 2007b).

It is difficult to ascertain how much CO₂ is sequestered by a specific mechanism; however, estimates on coal-bed storage capacity indicate accessibility to sorption sites of less than 60% for CO₂ sequestration (Bachu 2007; Kronimus et al. 2008b; Faiz et al. 2007b). In the early years of sequestration in deep aquifers and reservoirs, geologic trapping of CO₂ is expected to be dominant with solubility, hydrodynamic and mineral trapping becoming increasingly significant with time (Metz et al. 2005; Bachu 2008; Han et al. 2010a). Several studies (Han et al. 2010b; Gunter et al. 1997; Wilkinson et al. 2009; Moore et al. 2005) suggest that even after centuries of operation, CO₂ sequestration via mineral trapping might be extremely small (less than 0.5%) in sedimentary formations.

Except at depths exceeding around 2000 m, scCO₂ will be less dense than the formation water (Bachu 2003). Any CO₂ not sequestered via solubility or mineral trapping would therefore be expected to form a buoyant scCO₂ plume within the storage aquifer. The distribution of CO₂ between the supercritical plume and aqueous phase (CO₂ sequestered via solubility trapping) will depend on aquifer temperature and

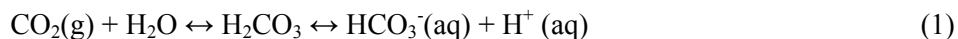
pressure, as well as formation water composition (Celia and Nordbotten 2009; Bachu 2003; Duan and Sun 2003; Kharaka et al. 2006). The reactivity of both phases towards geologic and manmade materials (e.g., cement and steel used in well construction) has been extensively studied under conditions consistent with deep storage formations (Loring et al. 2011; McGrail et al. 2009; Bearat et al. 2006; Shao et al. 2010a, 2010b, 2011; Hu et al. 2011; Jacquemet et al. 2008; Kutchko et al. 2007, 2008, 2009; Lu et al. 2011; Regnault et al. 2005; Palandri et al. 2005; Soong et al. 2004; Kaszuba et al. 2003; Sorai et al. 2003). Although results from some of these studies are discussed in this report, reactions in deep storage aquifers are not the primary focus of this review.

It is the CO₂ that would migrate upward (in the case of a leak) from the storage aquifer, through various leakage paths and into near surface environments (e.g., potable aquifers or vadose zone) that is of primary concern in this review. Celia and Nordbotten (2009) provide a good overview of leakage pathways and their significance. In contrast to deep storage aquifers, temperature and pressure conditions in near surface environments, where most potable water aquifers can be found, are below the critical point of CO₂. Under these subcritical conditions, CO₂ exists predominantly in the gaseous phase. If CO₂ leaks from the storage aquifer, it is the lower pressure and temperature conditions (associated with near surface environments) that drive the transition of CO₂ from its supercritical-fluid to subcritical-gas phase.

What happens to the leaked CO₂ gas after migrating from the deep storage aquifer and reservoir depends largely on the physical and chemical characteristics of the receiving subsurface environment. For instance, although the potential for re-sequestration in the vadose zone does exist, in the absence of a confining zone (e.g., a confined aquifer), some of the leaked CO₂ will eventually diffuse into the atmosphere (Oldenburg and Unger 2003; Klusman 2003). Klusman (2003) estimated that about 170 tons of CO₂ is lost annually through leakage from deep storage to the atmosphere, at the Rangely CO₂-Enhanced Oil Recovery (EOR) site in Colorado. If a confining zone was present above the injection zone at Rangely, losses of CO₂ to the atmosphere would be significantly less due to physical containment of the gas, as well as continued dissolution of CO₂ into the groundwater. It is the chemical reactivity of this dissolved CO₂ phase in solution, especially its effect on aqueous phase pH, that drives the current thoughts on the potential impact of CO₂ leakage (from deep storage reservoirs) on the geochemistry of near surface environments.

2.1 CO₂-Induced Changes in Aqueous Phase pH

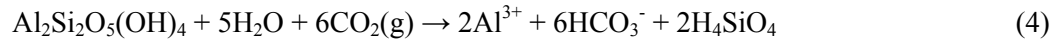
The dissolution of CO₂ in water to form carbonic acid and its subsequent dissociation is known to cause a decrease in pH as a result of aqueous phase proton enrichment:



Changes in pH and the production of HCO₃⁻ will influence or control the dissolution of minerals and the subsequent release of chemical elements and contaminants into the aqueous phase, as well as precipitation reactions and formation of neophases. In addition, these changes may significantly affect the extent and rate of chemical, biological, and hydrological processes and reactions, which may control contaminant mobility in the subsurface.

Experimental and modeling studies indicate that CO₂ intrusion into the vadose zone or potable aquifers could induce a decrease in aqueous pH of 1 to 3 units (Altevogt and Jaffe 2005; Little and Jackson 2010; Lu et al. 2010; Vong et al. 2011; Wang and Jaffe 2004; Wei et al. 2011; Wilkin and

DiGiulio 2010; Zheng et al. 2009; Kharaka et al. 2010). Decreases in pH on the lower end is typical of well-buffered systems where CO₂-induced dissolution of reactive carbonates (Equation 2), feldspars (Equation 3), and/or the dissolution/precipitation of clays (Equation 3 and 4) provide enough buffering capacity (via HCO₃⁻ alkalinity) to resist drastic changes in pH.



Poorly buffered systems (e.g., sandy soils in aquifers) are devoid of sufficient quantities of alkalinity-producing minerals and therefore lack the ability to resist changes in pH. In such systems, the decrease in pH due to the dissolution of CO₂ into solution is generally more apparent and the risk for pH-induced perturbation to environmental quality is more significant and prolonged compared to well-buffered systems (McGrail et al. 2006; Wang and Jaffe 2004; Wilkin and DiGiulio 2010).

The synthesis of the current literature suggest the potential for both beneficial and deleterious effects resulting from the subsurface sediments exposure to the CO₂ gas leaking from the deep reservoirs. These effects are detailed in the following two sections.

3.0 Beneficial CO₂-Induced Interactions in the Near Surface Environments

The migration of CO₂ from deep geologic storage into near surface environments could be considered beneficial if it resulted in enhanced carbon sequestration (or re-sequestration) and/or reduced mobility and bioavailability of contaminants.

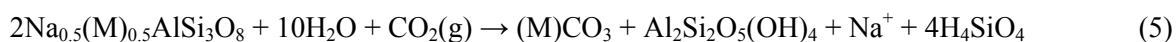
3.1 CO₂ Re-Sequestration

Estimates of up to 96% attenuation of leaked CO₂ over a 1000-year period have been reported in the vadose zone (Oldenburg and Unger 2003). Processes identified for such enhanced CO₂ retention/re-sequestration in the subsurface include the accumulation of the CO₂ gas at the water table (due to CO₂ being denser than soil air), permeability trapping (due to anisotropy favoring the horizontal flow of CO₂) and solubility trapping (due to dissolution of CO₂ into infiltrating or residual soil water).

The mineralogical trapping of CO₂ in carbonate minerals provides another potential mechanism for CO₂ re-sequestration in near surface environments. From an environmental and sequestration perspective, this is the most desirable outcome for CO₂ intrusion into near surface environments because of the immobility of carbonate minerals compared to other CO₂ trapping mechanisms. Several studies have demonstrated mineralogical trapping of CO₂ under conditions associated with deep geologic CO₂ storage, but such assessments have not been considered in near surface environments due to thermodynamic and kinetic limitations (Loring et al. 2011; McGrail et al. 2009; Bearat et al. 2006; Oldenburg and Unger 2003).

Thermodynamic limitations to carbonate precipitation are because many soil solutions and potable groundwater are undersaturated (saturation index, $SI < 0$) with respect to carbonates, while kinetic limitations are due to the slow nucleation rates of carbonates. However, given the potential for 1) CO_2 to increase the thermodynamic favorability of carbonate precipitation via enhanced CO_2 -induced weathering of soil and aquifer minerals; and 2) the current literature on microbially mediated nucleation of carbonates, the authors of this report believe the consideration of mineral trapping of CO_2 in near surface environments (as a consequence of a CO_2 leak) is warranted (Kenward et al. 2009; De Choudens-Sánchez and González 2009; Dean et al. 2007; Power et al. 2011; Vasconcelos and McKenzie 1997; Roberts et al. 2004; Douglas and Beveridge 1998; Dong 2010; Ferris et al. 2004; Tobler et al. 2011; Mitchell and Ferris 2005).

A generalized reaction for the CO_2 -induced weathering of a plagioclase mineral to carbonate is shown in Equation (5) (simplified from McGrail et al. 2006).



where M could be Ca^{2+} , Mg^{2+} , Fe^{2+} or a combination of these metals. In this reaction, the dissolution of CO_2 in water would cause a decrease in solution pH, leading to enhanced dissolution of the plagioclase, and increase chemical activity of Ca, Mg, or Fe and HCO_3^- . The increasing activity of Ca, Mg or Fe and HCO_3^- could lead to super-saturation ($SI \gg 0$) and precipitation of carbonate minerals (e.g. calcite [$CaCO_3$], magnesite [$MgCO_3$], siderite [$FeCO_3$] or their metastable intermediates).

3.2 Contaminant Immobilization

Some modeling and direct experimental evidence indicates the introduction of CO_2 into the near-surface environment may reduce the mobility of some contaminants (Altevogt and Jaffe 2005; Lu et al. 2010; Smyth et al. 2009). In simulating the effect of intruding CO_2 on soil biogeochemistry, Altevogt and Jaffe (2005) concluded the displacement of O_2 by CO_2 in soil gas and the decrease in soil solution pH (due to CO_2 dissolution) would favor the reduction of soil NO_3^- to NH_4^+ . Because of the greater tendency for NH_4^+ (compared to NO_3^-) to be adsorbed to negatively charged soil minerals and organic matter, such CO_2 -induced changes in nitrogen speciation would be useful in reducing nitrate contamination of groundwater in agricultural areas.

Based on laboratory experiments, Lu et al. (2010) and Smyth et al. (2009) concluded that introduction of CO_2 into a fresh water aquifer could reduce the aqueous concentration of some contaminants (including As, Cr, U and V). The behavior of these contaminants was attributed to CO_2 -induced changes in dissolution and adsorption characteristics of organic matter, clays, and other aquifer minerals.

Recent studies show that, in addition to carbonates, the enhanced weathering effect of CO_2 on primary soil and aquifer minerals could also yield secondary clay minerals or metal (hydr)oxides (Hu et al. 2011; Shao et al. 2010b, 2011; Lu et al. 2010). The formation of these new mineral phases could serve to reduce the mobility of contaminants in near-surface environments via incorporation into the mineral structure and/or sorption to the mineral surface. For example, the ability of secondary minerals (e.g., allophane (Lu et al. 2011), goethite (Hu et al. 2011), and highly weathered soils with pH-dependent, positively charged reactive surface groups to adsorb oxyanion contaminants (e.g., nitrate, arsenate, arsenite, chromate, selenate) under acidic conditions is well known (Opiso et al. 2009; Arai et al. 2005;

Giménez et al. 2007; Rovira et al. 2008). In addition, clays (e.g., illite and smectites [Lu et al. 2011] with permanent negatively charged surfaces are also known to adsorb cationic contaminants (Bradbury and Baeyens 1999; Poinssot et al. 1999). In basaltic systems, the weathering effect of the intruding CO₂ on basalts to form the ferrogenous smectite-like minerals, such as nontronite, could also serve to enhance the immobilization of redox-sensitive contaminants (Vingiani et al. 2004; Mason et al. 1997; Benson and Teague 1982; Jaisi et al. 2009).

4.0 Deleterious CO₂ Interactions in Near Surface Environments

CO₂-induced reactions leading to the degradation of water quality is probably the greatest concern associated with migration of CO₂ from deep geologic storage to near surface environments. Such degradation may involve the increase mobilization of contaminants or changes in other water quality parameters such as alkalinity, salinity or total dissolved solids (TDS). Research in this area is relatively new and at the time of this review, applicable work included several modeling studies (Vong et al. 2011; Wang and Jaffe 2004; Zheng et al. 2009; Apps et al. 2011; Apps et al. 2010; Jacquemet et al. 2011; Zheng et al. In Press), batch experiments (Little and Jackson 2010; Lu et al. 2010; Wei et al. 2011; Smyth et al. 2009) and short-term field studies (Kharaka et al. 2006, 2010; Assayag et al. 2009; Mito et al. 2008).

4.1 Mobilization of Contaminants

The potential for CO₂-induced mobilization of contaminants have been reported in experimental and modeling studies, and have been attributed largely to the activity of H⁺ and HCO₃⁻.

Wang and Jaffe (2004) modeled potential changes in aqueous Pb concentration as a result of intrusion of CO₂ into hypothetical aquifers comprising of PbS/CaCO₃ or PbS/quartz. For an 8-year simulation, Wang and Jaffe (2004) predicted that CO₂-induced decrease in pH would result in increased dissolution of the PbS and subsequent increases of aqueous concentrations of Pb. Vong et al. (2011) modeled the potential for the intrusion of CO₂ into a glauconitic-sandstone aquifer system to induce excessive release of heavy metals into solution. Vong et al. (2011) also predicted that a decrease in aqueous pH associated CO₂ intrusion into the aquifer would adversely affect potable groundwater quality due to CO₂-enhanced dissolution of galena and other trace-metal bearing minerals resulting in increased aqueous concentrations of Pb, Cd, Cu, Fe, Mn and Zn. Similar predictions were made by Zheng et al. (2009) who also considered the significance of sorption on the mobility of Pb and As in a typical eastern U.S. coastal plain aquifer impacted by the intrusion of CO₂ gas.

Laboratory and field studies have also highlighted the potential for CO₂-induced changes in near-surface environments to negatively affect water quality. Wei et al. (2011) found that, although still tolerable by plants, exchangeable concentrations of a wide range of metals (including Cu, Pb, Cr, V and U) in an agricultural soil increased by up to 500% during a 3-day incubation period with CO₂ (25°C and 25 bars). Little and Jackson (2010) tracked metal releases from various aquifer sediments (exposed to CO₂) and reported that CO₂ intrusions resulted in increased aqueous concentrations of several metals (e.g., Al, V, Cr, Mn, Zn and Co) by up to 3 orders of magnitude. Kharaka et al. (2010) during a 30-day field study, found the injection of CO₂ into a shallow freshwater aquifer (2 to 2.3 m) resulted in increased

aqueous concentrations of Fe, Mn, As, Cu, Zn, Cd, Pb, Al, and Se. In all cases, the increase in aqueous concentration of the contaminants was attributed to enhanced dissolution and/or desorption from the surfaces of soil and aquifer minerals.

Wilkin and Digiulio (2010) cautioned that although increased HCO_3^- concentrations—associated with enhanced weathering effects of dissolved CO_2 on soil and aquifer minerals—may be favorable for carbonate precipitation, such concentrations may also enhance the desorption of some contaminants from the surfaces of minerals. The ability of HCO_3^- to desorb negatively charged species of arsenic and naturally occurring uranium from metal oxides, soils, and aquifer sediments is well recognized (Mason et al. 1997; Anawar et al. 2003; Saalfield et al. 2010). Mason et al. (1997) found that in the presence of HCO_3^- , 75–90% uranium could be desorbed from contaminated soils. Anawar et al. (2003) found that arsenic desorption from Bangladeshi aquifer sediments was enhanced in the presence of HCO_3^- . Saalfield and Bostick (2010) found that desorption of As from ferrihydrite increased by 1–3 orders of magnitude with increasing HCO_3^- concentrations.

4.2 Other Water Quality Parameters

In addition to decreases in pH and enhanced mobilization of contaminants, the intrusion of CO_2 into near-surface environments can also induce changes in other pertinent water quality parameters such as alkalinity, salinity/TDS and total metal concentrations. Kharaka et al. (2010) found that in addition to a change in pH (from 7.0 to 5.6), the introduction of CO_2 into a shallow groundwater aquifer over a 2-week period caused HCO_3^- alkalinity to increase from 400 to 1300 mg/L, salinity (measured as electrical conductivity) to increase from 600–1800 $\mu\text{S cm}^{-1}$, and TDS from 600 to 1500 mg/L. Kharaka et al. (2010) and other studies (Little and Jackson 2010; Lu et al. 2010; Smyth et al. 2009) have also shown the potential for the aqueous concentrations of nontoxic metals such as Ca, Mg, K, Ba and Na to increase significantly in response to CO_2 introduction. Excessive amounts of these metals, although not a serious environmental risk, could cause a compromise in potable water quality due to their contributions to TDS.

5.0 Knowledge Gaps and Research Needs

A notable absence from current literature concerning the impacts of CO_2 intrusion on the biogeochemistry of near-surface environments is a substantive discussion on the potential role of CO_2 -induced shifts in redox condition. Carroll et al. (2009), in recognizing the potential significance of redox conditions, noted that robust predictions of the geochemical impact of a CO_2 leak will require the coupling of CO_2 plume modeling with laboratory experiments under a range of redox conditions. However, in contrast to pH, Eh is far less prevalent as a quantitative variable in studies concerning the geochemical effects of CO_2 intrusion into the vadose zone or potable aquifers. Instead, most studies (e.g., Zheng et al. (2009) and Vong et al. (2011) attribute CO_2 -induced geochemical chemical changes in the subsurface solely to changes in solution pH- even in the presence of redox-sensitive minerals/elements.

As a result of CO_2 intrusion, the redox condition of the subsurface will change due to CO_2 -induced reactions and/or O_2 depletion/replacement with the CO_2 gas (Altevogt and Jaffe 2005; Ardelan and Steinnes 2010; Huesemann et al. 2002) or changes in biological activity (Kirk 2011). As with pH, changes in redox condition (measured as redox potential, Eh) will influence or control the extent and rate

of chemical, biological, and hydrological processes/reactions (because of its influence on the speciation of redox-sensitive elements and the dissolution/precipitation characteristics of redox-sensitive minerals). Therefore, detailed assessments of how CO₂ influences redox conditions is also crucial to determining biogeochemical impacts of CO₂ migration from deep storage into potable aquifers and the vadose zone.

In reality, pH and Eh in the subsurface will be interrelated. This interrelation is reflected in the fact that most redox reactions involve protons (oxidation releases H⁺ and reduction consumes H⁺) and will simultaneously influence solution pH. A change in pH will also impact Eh due to pH effects on dissolution, and subsequently the distribution of reduced versus oxidized species in solution. The impact of CO₂ on speciation of elements and the dissolution and precipitation characteristics of minerals in the subsurface will therefore be a combined effect of Eh and pH. The relationship between Eh and pH and their combined influence on system geochemistry is commonly represented on pH-Eh stability diagrams based on the Nernst Equation:

$$Eh = E^0 - \frac{0.059}{n} \log \frac{a_{red}}{a_{oxid} a_{H^+}^m} \quad (6)$$

where

- Eh = Redox potential of the reaction
- E^0 = Standard state redox potential
- n = Number of electrons involved in the reaction
- m = Number of proton involved in the reaction
- a_{red} , a_{oxid} and a_{H^+} = Chemical activity of the reduced species, oxidized species and protons, respectively (McBride 1994).

In addition to consideration of redox conditions, the authors of this report believe that development of consistent experimental and assessment protocols, as well as the identification and systematic evaluation of the influence of all pertinent system properties, are crucial to advancing current knowledge on how the migration of CO₂ gas from deep storage would impact the biogeochemistry of near-surface environments. The identification and systematic evaluation of pertinent system properties is critical in ensuring that all major reaction drivers are accounted for, and appropriately weighted in both our experimental and modeling assessments. A consistent set of experimental and assessment protocols is therefore needed to address current discrepancies, allow effective interstudy comparison, provide context for experimental results, and facilitate sound science-based decisions and policy making.

The following sections discuss four factors that require immediate attention from the scientific community. These are as follows:

1. The influence of the gas intrusion rate
2. Composition of the intruding gas stream
3. Organic matter (type and amount) and microbial activity
4. Sediment mineralogy.

The first two factors pertain to the nature of the migrating gas stream while the latter two pertain to impacted systems (e.g., shallow groundwater aquifer, capillary fringe, or the vadose zone). A possible framework within which the geochemical consequences of CO₂ could be effectively assessed and experimental protocols developed is also proposed.

Throughout the discussions, results from some of the authors' geochemical modeling efforts are used to highlight why closing current knowledge gaps is pivotal. Details on the model setup (including input parameters and data used) are presented in Appendix A. Note that geochemical modeling results are largely based on hypothetical scenarios and therefore are intended to be illustrative. Laboratory and field scale experimental work will be needed to confirm the results derived from modeling.

5.1 Importance of CO₂ Intrusion Rates

One criticism of current experimental studies is that the rate of CO₂ intrusion used is disproportionately high, is unlikely to occur at geologic sequestration sites, and would overwhelm any chemical buffering provided by minerals, resulting in unrealistic mineral dissolution and release of undesirable trace metals and elements (Gilfillan and Haszeldine 2011). Although such a criticism is refutable on the basis the solubility of CO₂ in water is limited and excess CO₂ in experiments would have been vented (Little and Jackson 2010), the reality is that no experimental data currently exists on how the rate of CO₂ intrusion would likely influence geochemical changes in a potable aquifer. In the authors' search of the literature, only the modeling studies by Zheng et al. (2009) and Vong et al. (2011) considered the likely impact of intrusion rate on aquifer geochemistry. In both studies, increasing CO₂ intrusion rates led to lower pH that in turn led to enhanced dissolution of sulfide minerals—such as galena (PbS), sphalerite (ZnS), and arsenopyrite (FeAsS)—and subsequently compromised groundwater quality due to increased aqueous concentrations of trace metals (e.g., Pb, Zn and As).

While the concept that lowering pH could enhance the dissolution of aquifer minerals and increase aqueous concentrations of contaminants in groundwater is reasonable, in the case of sulfides or other redox-sensitive minerals, redox conditions would be expected to have the greatest effect on their precipitation and dissolution behavior (Abdelouas et al. 1999; Lee and Hering 2005; Rashid et al. 2002; Sasaki et al. 2010; Nickson et al. 2000; Noubactep et al. 2008; Smedley and Kinniburgh 2002; Edwards et al. 2000). Thus, considering the influence of CO₂ intrusion rate on both pH and Eh and their coupled effects on the beneficial and deleterious reactions in the subsurface would provide a more complete scenario of what to expect within a particular environment.

To account for the wide array of possible environments, these studies could be conducted under different conditions including open versus closed systems, oxic versus suboxic/anoxic systems and saturated versus unsaturated conditions. The authors conducted 100-year simulation runs using hypothetical CO₂ intrusion rates of 0.01, 0.1, 1, and 10 g day⁻¹ into a model system with the fugacity of oxygen fixed at initial system conditions (closed system), or allowed to vary (open system with respect to oxygen). Predicted changes in pH and Eh (superimposed onto pH-Eh diagrams for CO₂/HCO₃⁻, Fe, As, and Pb) are presented in Figure 5.1.

For CO₂ re-sequestration, modeling results indicate mineral trapping is likely to become less favorable as CO₂ intrusion rate increase due to lower equilibrium pH (associated with higher CO₂ rates) favoring dissolution, rather than precipitation of carbonates (Figure 5.1a). Figures 5.1b-d indicate that although CO₂ rates may have no apparent effects on Fe, Pb, and As speciation in closed anaerobic systems, in an open (with respect to oxygen) system increasing CO₂ rates could favor either mineral dissolution, or formation of new mineral phases (in the case of Fe)-, depending on the accompanying shift in system redox condition.

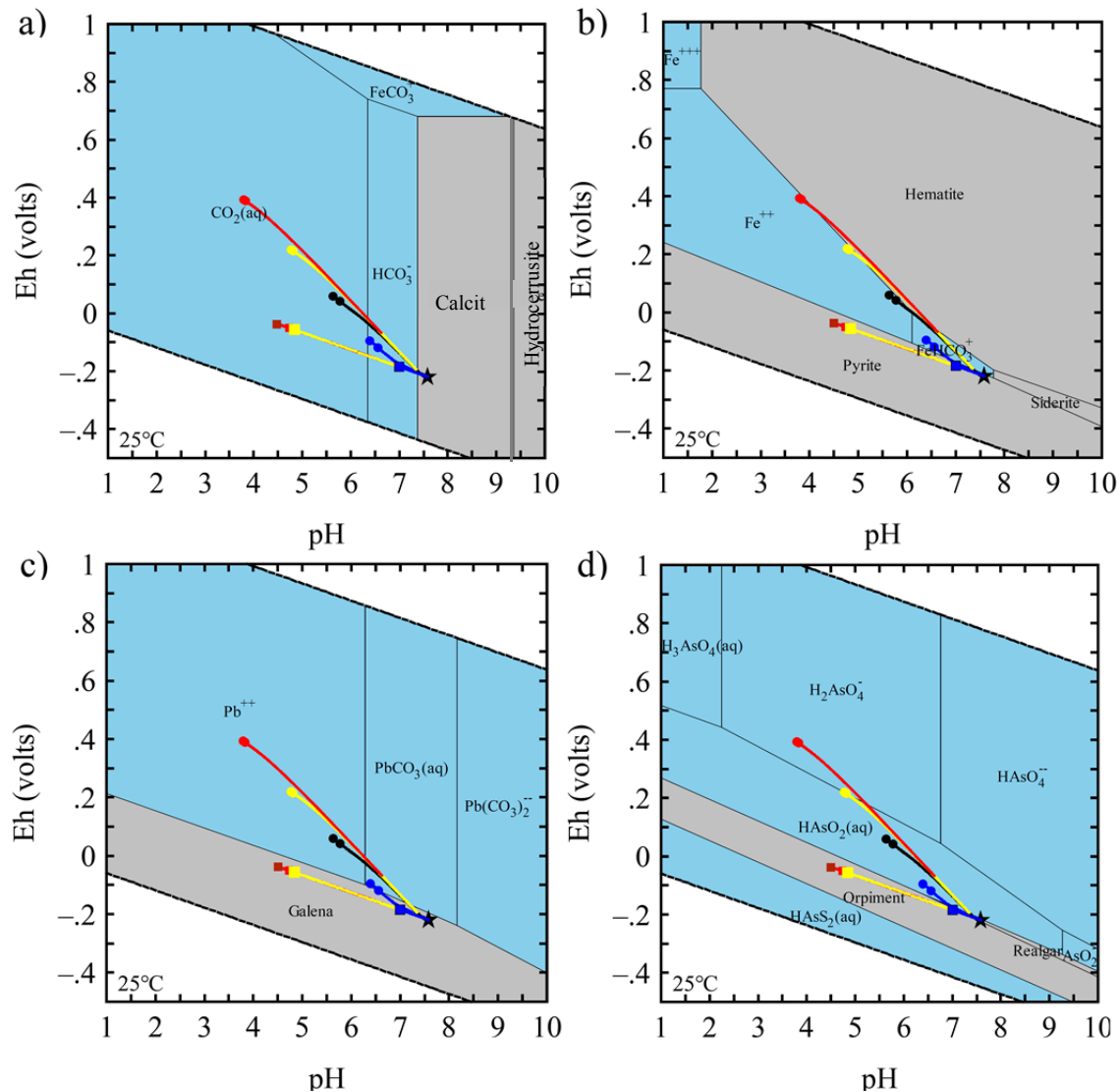


Figure 5.1. Predicted changes in pH and Eh at different CO₂ intrusion rates, and implications for aqueous speciation of (a) CO₂, (b) Fe, (c) Pb, and (d) As. Simulation was for 100 years at CO₂ intrusion rates of 0.01 (blue), 0.1 (black), 1 (yellow) and 10 (red) g d⁻¹ into a model aquifer assuming a closed (squares) or open (circles) system with respect to oxygen. The star is indicative of the starting point. Points on the lines represent status after 1 year and 100 years. In cases where points are undifferentiable, the 1-year results coincide with that for 100 years. Details on the model aquifer system are provided in Appendix A.

CO₂-induced changes in system pH and Eh favoring the formation of Fe-oxides such as hematite could be beneficial in two ways: 1) sorption of contaminants onto their surfaces (Giménez et al. 2007; Goldberg and Johnston 2001; Bowell 1994), or 2) incorporation of contaminants into their structure (Kaur et al. 2009; Davranche and Bollinger 2000; Paige et al. 1997). However, CO₂-induced changes in system pH and Eh favoring the dissolution of contaminant-containing minerals could be deleterious especially in the absence of a suitable sorbent. Based on Figure 5.1c, the release of Pb²⁺ from galena would be most favored in an open system and increasing higher CO₂ intrusion rates. An open system and higher CO₂ rates would also favor the release of As(V) and As(III) from As-bearing minerals but these

conditions also favor the precipitation of Fe-oxides, which are excellent sorbents for As(V) and less so for As(III) under acidic conditions. Understanding the potentially delicate balance between the CO₂ intrusion rate, system properties, pH, Eh, precipitation and dissolution, and adsorption and desorption is therefore vital to assessing the geochemical impact of CO₂ on the environment.

5.2 Importance of Co-Injected/Co-Transported Gas

All geologic sequestration programs will need to be permitted and therefore composition of the injected CO₂ stream will depend on responsible regulatory agencies. The composition of injection streams into deep storage aquifers will likely vary from site to site and is likely to be more reflective of flue gas (that has been denitrogenated and deoxygenated to improve compressibility), rather than the food-grade CO₂ usually used in current studies.

Results from the authors' geochemical modeling efforts that compared a mixed gas (99.4% CO₂, 0.1% CO, 0.1% NO_x, 0.3% SO_x and 0.1% CH₄) to a CO₂-only stream indicate that co-injected or co-transported gases could potentially influence aqueous speciation of redox-sensitive elements such as Fe and As (Figure 5.2). Such effects further indicate that gas composition could have significant implications for the mobility of As and other redox-sensitive contaminants (e.g., V, U, Se and Cr) in the subsurface, since their mobility is strongly influenced by speciation (Abdelouas et al. 1999; Lee and Hering 2005; Rashid et al. 2002; Sasaki et al. 2010; Nickson et al. 2000; Noubactep et al. 2008; Smedley and Kinniburgh 2002). In cases where gas composition favors a shift from more to less mobile species (e.g., As(III) or Cr(VI) to As(V) and Cr(III), respectively), CO₂ intrusion could be considered beneficial, while in cases where the alternative shift is favored, then CO₂ intrusion would be deleterious.

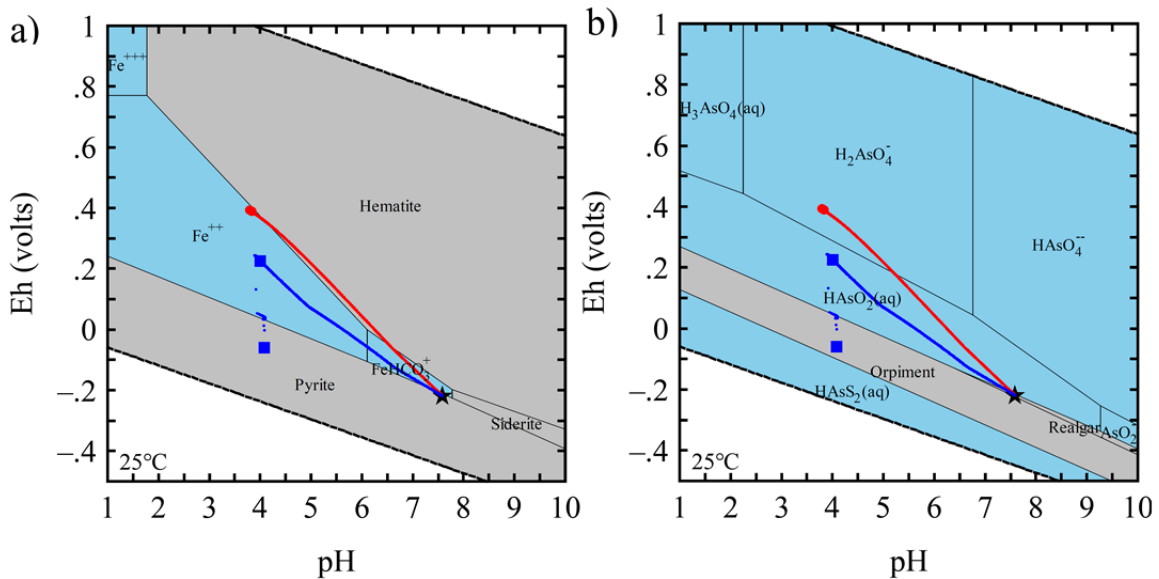


Figure 5.2. Predicted changes in pH and Eh with composition of intruding gas, and implications for aqueous speciation of (a) Fe and (b) As. Simulation was for 100 years at gas intrusion 10 g d⁻¹ using pure CO₂ (red) and a mixed gas stream (blue; 99.4% CO₂, 0.1% CO, 0.1% NO_x, 0.3% SO_x and 0.1% CH₄) into a model aquifer assuming an open system with respect to oxygen. The star is indicative of the starting point. Points on the lines represent status after 1 and 100 years. In cases where points are undifferentiable, the 1-year results coincide with that for 100 years. Details on the model aquifer system are provided in Appendix A.

The dissolution of co-transported NO_x or SO_x into potable groundwater or soil pore water could also be considered deleterious given the health effects associated with nitrites and nitrates (Manassaram et al. 2006; Raczuk 2010; Sandor et al. 2001; Fowler et al. 2005) or negative implications associated with the acidifying effects of NO_x and SO_x on rainwater (Fowler et al. 2005; Goyer et al. 1985; Matson et al. 1999). Similar acidifying effects of NO_x and SO_x gases are expected if these gases leak into potable aquifers or the vadose zone. A recent study by Jacquemet et al. (2011) indicates that even at low concentrations, SO₂ and NO may lower pH by an additional 1 unit compared to CO₂ alone. Jacquemet et al. (2011) predicted an increased release of metals as a consequence of the additional decline in pH. However, such pH declines may also enhance other undesirable reactions. For example, the formation of carcinogenic *nitroso* compounds from NO₂ and organic matter is known to be enhanced under acidic conditions (Mitch et al. 2003).

From a beneficial perspective, dissolved SO_x and NO_x could also potentially serve as an important source of oxidant in microbially mediated mineralization (of CO₂ to carbonate minerals) coupled to sulfate or nitrite/nitrate reduction (Aloisi et al. 2002; Blair and Aller 1995; Chen et al. 2007; Michaelis et al. 2002; Peckmann et al. 2001). Understanding the coupled geochemical influence of contaminant gases found in flue gas (e.g., H₂S, NO_x, and SO_x) and CO₂ is therefore pivotal to assessing the potential geochemical impact of CO₂ leakage on potable aquifers and the vadose zone at sequestration sites. Research focused on understanding the beneficial and deleterious outcomes of contaminant gases in the CO₂ injection stream needs to be established.

5.3 Importance of Native Aquifer Gases

In addition to having formation waters in equilibrium with CH₄, deep aquifer formations suitable for CO₂ storage are likely to have gaseous environments dominated by gases other than CO₂. Kharaka et al. (2006) found that gas samples collected from a deep abandoned oil well in the Frio formation, Texas, contained 95 ± 3% CH₄ (compared to 0.3% CO₂), with the bulk of the remaining gas comprised of N₂, C-2, and higher hydrocarbon gases. High concentrations of CH₄ and H₂ have also been observed in deep basaltic aquifers (Stevens and McKinley 1995). Any leakage of injected gas from the storage aquifer will likely occur in conjunction with native aquifer gases.

The authors simulated the potential influence of CH₄ as a co-intruding aquifer gas by increasing its concentration, in the mixed gas stream described above, from 0.1 to 1% at the expense of CO₂. Increasing the CH₄ in the gas stream was predicted to have the greatest effect on the redox condition of the system by favoring more reduced species as CH₄ content in the intruding gas stream increases (Figure 5.3). As noted prior, with respect to co-injected gases, such changes in redox condition could be considered beneficial or deleterious depending on the redox-sensitive species present in the system.

The transformation of native aquifer gases in the subsurface could also be crucial to assessing their overall influence on the environment. Klusman (2003, 2006) found that most of the CO₂ in oxic soils above exploited oil fields was attributable to the methanotrophic oxidation of methane and other hydrocarbons that migrated upwards from the reservoir. The formation of CH₄ from H₂ and CO₂ via methanogenesis under anaerobic conditions and in the presence of methanogens is also possible (Stevens and McKinley 1995). Methanotrophic oxidation of native hydrocarbons would further increase CO₂ concentrations in the aquifer and likely enhance its impact on geochemical processes. However, methanogenesis could potentially reduce the direct effects of CO₂ by converting injected CO₂ to CH₄.

There is also the risk of dealing with a new set of challenges associated with CH₄ (stronger reducing agent and lower solubility than CO₂). Accounting for the fate and transport of native aquifer gases (e.g., H₂, CH₄, and other volatile organic compounds) is therefore critical to assessing geochemical changes associated with leakage of CO₂ from deep storage aquifers.

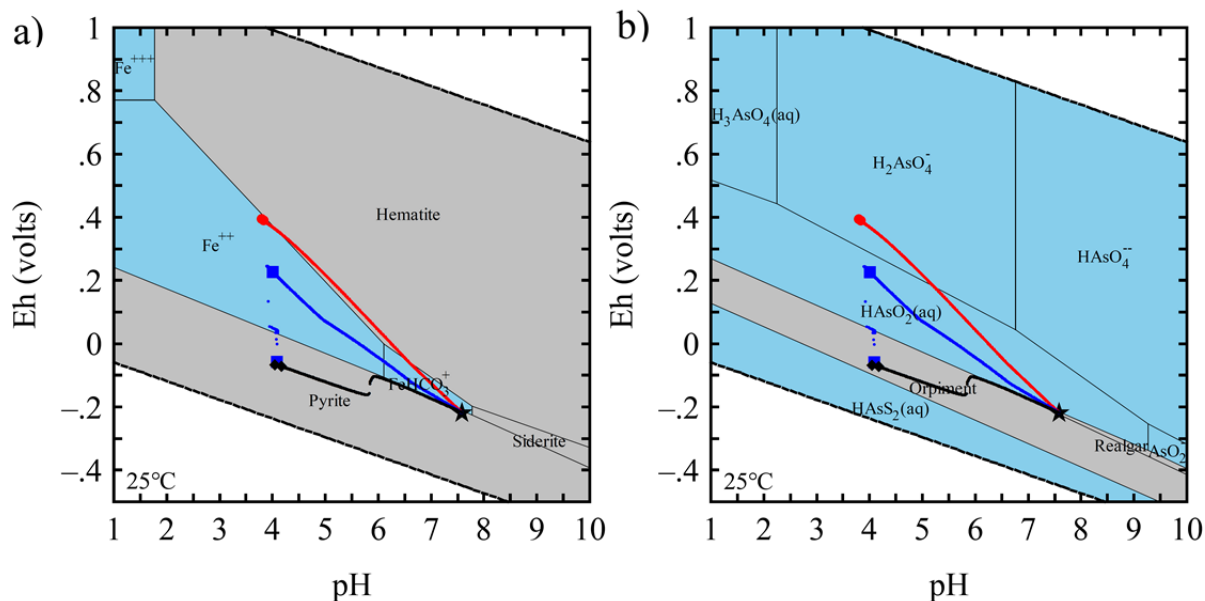


Figure 5.3. Predicted changes in pH and Eh with CH₄ content of intruding gas, and implications for aqueous speciation of (a) Fe and (b) As. Simulation was for 100 years at gas intrusion 10 g d⁻¹ using pure CO₂ (red) and one mixed gas stream with 0.1% CH₄ (blue; 99.4% CO₂, 0.1% CO, 0.1% NO_x, 0.3% SO_x and 0.1% CH₄) and one with 1% CH₄ (black; 98.5% CO₂, 0.1% CO, 0.1% NO_x, 0.3% SO_x and 1% CH₄) into a model aquifer assuming an open system with respect to oxygen. The star is indicative of the starting point. Points on the lines represent status after 1 year and 100 years. In cases where points are undifferentiable, the 1-year results coincide with that for 100 years. Details on the model aquifer system are provided in Appendix A.

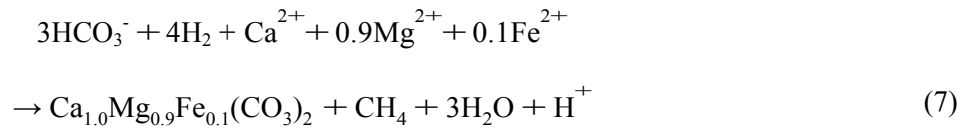
5.4 Importance of Organic Matter and Microorganisms

Studies of the behavior of scCO₂ in deep saline formations, unmineable coal seams, and depleted oil and gas reservoirs highlight the need for significant consideration to be given to the role of organic contaminants in the event of CO₂ leakage into a potable aquifer. For example, Kharaka et al. (2006) found that breakthrough of injected CO₂ in deep formations was accompanied by the release of a “slug” of organic matter, with dissolved organic carbon concentrations exceeding 100 times prebreakthrough levels. Analysis for a limited number of dissolved organic species revealed significant concentrations of C1-C5 organic anions, plus toluene concentrations in excess of the U.S. Environmental Protection Agency’s drinking water standard of 1 ppm. In another study, Zheng et al. (2012) used computer simulations to illustrate how benzene could be mobilized from a deep storage formation to an overlying aquifer, with benzene building up in the leading edge of a scCO₂ plume because of preferential partitioning in scCO₂ relative to water. Therefore, given the solvent properties of scCO₂, the influx of organic contaminants would be a plausible outcome of the intrusion of CO₂-rich water into a potable aquifer.

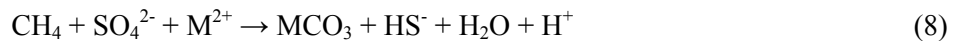
For water-soluble organic compounds, in addition to exceeding water standards for organic contaminants, the consequence of an influx of previously stored CO₂ into a potable aquifer may be two-fold. In the absence of suitable redox conditions or micro-organisms, the influx of organic contaminants could also serve to enhance metal mobility through the formation of soluble organo-metal complexes, enhanced dissolution reactions, and the inhibition of precipitation or adsorption reactions. However, under suitable redox conditions and in the presence of a suitable microbial community, the influx of organic contaminants may actually enhance the immobilization of some redox-sensitive contaminants and metalloids via assimilatory or dissimilatory microbial-mediated redox reactions (Lloyd 2003, Lovley 1993).

There is also some evidence to indicate that microorganisms could enhance CO₂ re-sequestration in near-surface environments via direct assimilation (Pedersen and Ekendahl 1992) or biogenic carbonate formation (Vasconcelos and McKenzie 1997; Roberts et al. 2004; Douglas and Beveridge 1998; Dong 2010). Many microorganisms likely to be encountered in near-surface environments above geologic sequestration sites (e.g., sulfate-reducers, nitrate-reducers, iron-reducers, urea-degraders, and methanogens) are capable of biogenic carbonate formation (Roberts et al. 2004; Douglas and Beveridge 1998; Dong 2010; Ferris et al. 2004; Tobler et al. 2011; Mitchell and Ferris 2005; Mitchell et al. 2010). The formation of carbonate minerals by urea-degraders has been extensively studied (Ferris et al. 2004; Tobler et al. 2011; Mitchell and Ferris 2005; Mitchell et al. 2010). A recent study (Mitchell et al. 2010) showed that under conditions consistent with CO₂ storage conditions, urea-degraders incorporated up to 37% of total carbon into carbonate minerals. Because the high pressure conditions of deep storage formations could significantly inhibit cellular activity, a higher incorporation of CO₂ into carbonates might be expected in near-surface environments (Wu et al. 2010).

Roberts et al. (2004) found that iron-bearing dolomite formed after 3 months of suspending sterile Columbia River basalt fragments into a fresh water aquifer (to a depth of 7 m) was associated with the colonization of the basalt by a consortium of methanogens and fermenters. Dolomite formation was indicated to occur via local microbially enhanced weathering of the basalt coupled with methanogenesis (with dissolved CO₂ as a source of carbon) and crystal nucleation on the cell walls of the microorganism as seen in Equation (7).



There is also ample evidence in the literature that indicates CH₄ produced in Equation (3) could be re-oxidized via anaerobic methane oxidation (AMO) by reducing bacteria (including iron-, nitrate- and sulfate reducers), resulting in further biogenic carbonate formation as seen in Equation (8) (Aloisi et al. 2002; Blair and Aller 1995; Chen et al. 2007; Michaelis et al. 2002; Peckmann et al. 2001):



where M²⁺ could be any carbonate forming divalent metal (e.g., Ca²⁺, Mg²⁺, or Fe²⁺). If M²⁺ was Cd²⁺ or Pb²⁺, biogenic carbonate formation could also potentially serve to enhance natural attenuation of toxic metals through the formation of CdCO₃ and PbCO₃.

Theoretically, Equation (7) indicates mineral trapping alone could account for 66% of dissolved CO₂. In cases where Equation (8) is thermodynamically and kinetically favorable, and if the system is not limited by oxidants (e.g., SO₄²⁻, NO₃⁻, or Fe³⁺) or dissolved metal (e.g., Ca²⁺, Mg²⁺, or Fe²⁺) concentrations, the number would be closer to 100%. It is therefore plausible that at geologic sequestration sites where biogenic carbonate formation is favorable, mineral trappings could be very important in determining the fate of leaked CO₂ in near-surface environments. At potential geologic sequestration sites (e.g., CO₂-EOR operations, exploited oil reservoirs or basaltic formations) where anaerobic subsurface microbial ecosystems have been shown to be comprised of significant quantities of methanogens and reducing bacteria (Stevens and McKinley 1995; Lin et al. 2011; Chapelle et al. 2002), methanogenesis and AMO coupled to biogenic carbonate formation are processes that should be considered. Gypsum-rich formations or co-injected acid gases (e.g., SO_x or NO_x) could serve as a source of oxidant.

Acidity (due to CO₂ dissolution in water) may inhibit microbially mediated processes through heavy metal-induced toxicity or direct inhibition of microbial enzymatic activity (vanBeelen and FleurenKemila 1997; Wang et al. 2006). However, acidity may thermodynamically favor microbial reductive dissolution of Fe(III) hydroxides (Kirk 2011), which are ubiquitous in the subsurface and are good sorbents of trace metals. Therefore, whether CO₂-induced inhibition of microbial activity could be considered beneficial or deleterious will depend on the microbial process impacted. For example, CO₂-induced inhibition of microbially mediated conversion of NH₄⁺ to NO₃⁻ (nitrification) in the vadose zone could minimize the risk for nitrate contamination of groundwater (since unlike NO₃⁻, NH₄⁺ adsorbs to soil and aquifer minerals). Thus, CO₂ leakage from the storage aquifer could be considered beneficial due to contaminant immobilization.

From a contaminant mobilization perspective, CO₂-induced inhibition of methane-oxidation that results in the accumulation of CH₄ in the vadose zone or capillary fringe could create anoxic zones and favor reductive mobilization of some contaminants that could then leach into the groundwater. Considering such multi-fold effects should be a primary focus of studies examining CO₂-intrusion into potable aquifers and the vadose zone. Understanding and assessing the impact of co-released CO₂ and organic contaminants on subsurface microbial populations and microbial-mediated processes is also important.

5.5 Importance of Sediment Mineralogy

Geology and subsequently mineralogy at geologic sequestration sites will differ. While capturing the complete variability across sites will be impossible, some understanding of the minerals present and their chemical and physical behavior is crucial to assessing potential outcomes of CO₂ migration into potable aquifers or the vadose zone.

In many studies reviewed, the significance of mineralogy to outcomes of CO₂-intrusion is evident. In studies by Lu et al. (2010) and Smyth et al. (2009), the dissolution of carbonate minerals and adsorption and desorption to hydrous oxides, organic matter, and clay minerals were highlighted as controlling the total aqueous concentration of various metals. Kharaka et al. (2010) also attributed observed increases in aqueous metal concentrations at the ZERT field site in Bozeman, Montana, to CO₂-induced dissolution of carbonates, iron oxides and/or desorption-proton exchange reactions possibly from clay minerals. Zheng et al. (In Press) further showed that ion exchange reactions driven by Ca²⁺ release from calcite dissolution

could explain the observed increase of dissolved trace metal concentrations at this site. Little and Jackson (2010) found that CO₂ intrusion had no effect on aqueous Cd concentration in calcite-rich sediments but induced a 1000% increase in Cd for the calcite-deficient sediments. The aqueous concentrations of Al, V, and Cr were also found to increase in chalcopyrite-containing sediments but decreased in other sediments.

The lack of effect on Cd concentrations in the calcite-rich sediments of Little and Jackson (2010) is attributable to CO₂-induced dissolution of calcite that would serve to buffer the pH and thereby prevent dissolution of Cd-bearing minerals. However, oxidative dissolution of chalcopyrite would decrease solution pH-, resulting in acid-enhanced dissolution of Al, V, or Cr-bearing minerals and the increase in aqueous concentrations of Al, V, and Cr.

Mineralogy knowledge could also be crucial in designing and conducting laboratory experiments with material from field sites. For example, many groundwater contaminants are redox-sensitive, or contained in redox-sensitive minerals (Birkholzer et al. 2012; Edmunds et al. 1989). It is the dissolution and precipitation of these minerals that will drive the total aqueous concentrations of redox-sensitive contaminants (Abdelouas et al. 1999; Lee and Hering 2005; Rashid et al. 2002; Sasaki et al. 2010; Nickson et al. 2000; Noubactep et al. 2008; Smedley and Kinniburgh 2002). Therefore, laboratory studies involving aquifer sediments and seeking to assess how CO₂ intrusion would impact the geochemistry of the aquifer should be conducted under redox and solution conditions relevant to that system.

The lack of matching laboratory (i.e., solution and redox) conditions as closely as possible to those observed in the field is one area where current laboratory studies could be improved. For example, Little and Jackson (2010) noted all of their experiments were conducted in deionized water under oxidized conditions. However, the presence of sulfide minerals in some of their sediments was more representative of sediments originating from a reduced environment. Thus, despite Little and Jackson (2010) pointing to pH as the primary factor responsible for the discrepancies between their study and that of Lu et al. (2010), it is more plausible that a change in redox conditions was the factor controlling metal release (especially because pH values between the two systems were comparable). Rather than the oxic conditions of Little and Jackson (2010), conditions existing in Lu et al. (2010) experiments were likely anoxic (purged with argon prior to CO₂ introduction). This difference in redox could potentially explain why, in contrast to Little and Jackson (2010), Lu et al. (2010) observed no significant changes in the aqueous concentrations of redox-sensitive metals (e.g., Fe, Cu, and U) or metals (e.g., Ni) that were likely contained in redox-sensitive minerals.

5.6 Need for Experimental and Assessment Protocols

Alleviating discrepancies between studies and the closing of current knowledge gaps are pivotal to the effective prediction of how the migration of CO₂ from storage reservoirs would impact the biogeochemistry of near-surface environments. The likelihood of experimental discrepancies can be minimized if experiments are conducted under rigorous experimental and assessment protocols, developed from a comprehensive process-based understanding of geochemical reactions in CO₂-rich environments. Such protocols will also provide a framework within which to explain discrepancies, compare findings from different studies, and facilitate the systematic closing of current knowledge gaps.

There is also a wealth of information from analog or comparable systems that need to be reconciled to highlight their value as geochemical signatures of what can be expected if CO₂ should migrate from storage into near-surface environments. For example, studies at analog sites show no or only localized compromise in water quality caused by the natural intrusion of CO₂ (Aiuppa et al. 2005; Keating et al. 2010, 2011; Flaathen et al. 2009). It has also been emphasized that such natural CO₂ analogs highlight the low risk for CO₂-induced contamination associated with geological sequestration—especially considering that water from these systems are often potable and consumed with no adverse health effects (Gilfillan and Haszeldine 2011). However, before such conclusions can be made, it is important to consider pertinent factors, such as the duration of time that sediments have been exposed to CO₂ (Lu et al. 2010). In contrast to sediments in aquifers subject to recent influx of CO₂ (as in gas leakage from geological storage), sediments at natural analog sites would have a comparatively long time to equilibrate with CO₂-rich water. Therefore, both systems would be expected to exhibit very different solution and mineral chemistry.

However, expected differences in solution and mineral chemistry at geological sequestration versus natural analog sites does not negate the geochemical value of natural analogs in understanding the likely impact of CO₂ migration from geological storage. In fact, it can be incurred that the geochemistry of natural analogs is indicative of what long-term consequences can be expected from CO₂ leakage into a potable aquifer. Hence, in addition to providing valuable information on potential flow paths and estimating leakage size, analog studies could provide significant insights into reaction kinetics, equilibration time, and equilibrium mineral phases. Such information would also be important in terms of policy and strategic decisions on remediation approaches in the event of significant CO₂-induced compromise in potable water quality.

Similar reconciliation as described for natural analog studies is also needed to evaluate the geochemical value of other systems (e.g., landfills and acid-mine sites) that exhibit some characteristics (shifts in pH and Eh) that could be expected in near-surface environments impacted by CO₂ from geological sequestration. Although such reconciliation is beyond the scope of this review, the authors believe that, as with minimizing experimental discrepancies and the systematic closing of current knowledge gaps, a rigorous set of experimental and assessment protocols would be useful in assessing their value in understanding of the potential geochemical implication of CO₂ migration into near-surface environments.

A possible framework within which to assess the geochemical impact of CO₂ on near-surface environments and to develop experimental and assessment protocols is presented in Figure 5.4. In this framework, shifts in pertinent geochemical processes (such as adsorption and desorption or dissolution precipitation) are driven by changes in solution pH and Eh that are in turn controlled by the properties of impacted systems (e.g., mineralogy and organic matter content) and the characteristics of the intruding gas stream (e.g., composition of gas stream and duration of intrusion).

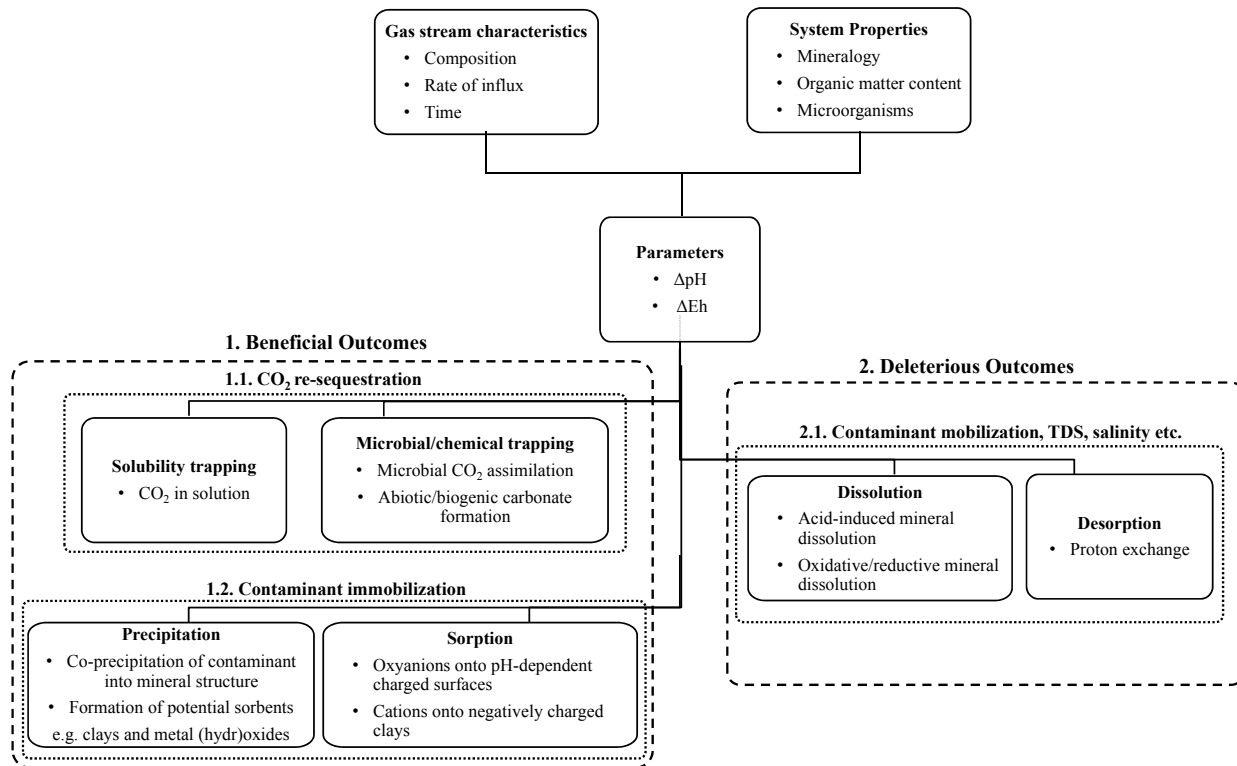


Figure 5.4. A conceptual framework for assessing geochemical impact of CO₂ on near surface environments

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Appendix A

Model Input Data, Modeling Approach and Construction of Pourbaix (pH-Eh) Diagrams

Appendix A

Model Input Data, Modeling Approach and Construction of Pourbaix (pH-Eh) Diagrams

Input data used for geochemical modeling was taken from Zheng et al. (2009) and Birkholzer et al. (2012); these data represent the mineralogy and groundwater composition of a reduced aquifer along the eastern coastal plain of the United States. Some substitutions were made for various minerals due to differences in the thermodynamic database used (Tables A.1 and A.2). Initial pH and Eh of the system was 7.6 and -0.23 V, respectively (Zheng et al. 2012). All simulations were done using the React module of Geochemist Workbench (release 6.0) with the Lawrence Livermore National Laboratory combined thermodynamic database (thermo.com.V8.R6+.dat). Simulations were set up as a one-dimensional flow experiment with kinetic reaction pathway. The rate equation used for kinetic reaction modeling was of the form:

$$r = A_s k_{25} (1 - Q/K)(a_{H^+})^n$$

where

- r = Reaction rate (mol s^{-1})
- A_s = Mineral surface area ($\text{cm}^2 \text{g}^{-1}$)
- k_{25} = Rate constant ($\text{mol cm}^{-2} \text{s}^{-1}$)
- Q and K = Activity product and equilibrium constant, respectively for the dissolution reaction
- a_{H^+} = Activity of H^+
- n = “Power” of H^+ in the rate law.

Values used for all kinetic parameters are provided in Table A.1. In cases where n is not specified, the rate equation used is reduced to the following:

$$r = A_s k_{25} (1 - Q/K)$$

where r , A_s , k_{25} , Q and K are as defined earlier.

Precipitation for minerals listed in Table A.1 are assumed to be governed by the same rate law as described for dissolution and occurs when r is negative. For minerals not listed in Table A.1, their precipitation or dissolution were assumed to occur when thermodynamically favorable. The precipitation of C, ice, and pyrophyllite were suppressed in all simulations.

The initial system at equilibrium contained a rock: solution ratio of 17:1 (100 kg: 6L) and a porosity of 0.145. Solution flow rate in and out of the system was set to achieve a mean residence time of 1 year.

When modeling an open versus closed system (with respect to oxygen), the fugacity of oxygen was fixed to the system initial value (closed system; $\log f_{O_2} = -65.9$) or allowed to vary as reactions progress (open system). When modeling the impact of mixed gas streams on aquifer geochemistry, the flow rates of component gases were set to reflect their proportions in the gas stream. For example, to achieve an

overall gas intrusion rate of 10 g d^{-1} for a mixed gas stream containing 99.4% CO_2 , 0.1% CO , 0.1% NO_x , 0.3% SO_x and 0.1% CH_4 , gas input rates were set to 9.94, 0.1, 0.1, 0.3 and 0.1 g d^{-1} for CO_2 , CO , NO_2 , SO_2 and CH_4 , respectively.

Pourbaix (pH-Eh) diagrams were constructed using the Act2 module of Geochemist Workbench (release 6.0) with the Lawrence Livermore National Laboratory combined thermodynamic database (thermo.com.V8.R6+.dat). Chemical activity and speciation of CO_2 , S, Fe, As, and Pb were based on groundwater composition data presented in Table A.2. Al species and organo-metal complexes were not considered in the diagrams.

Table A.1. Mineralogical composition of aquifer material and kinetic parameters used for geochemical modeling experiments. Data were obtained from Zheng et al. (2009) and Birkholzer et al. (2012).

Mineral	Volume fraction (%)	Surface area, A_s $\text{cm}^2 \text{g}^{-1}$	Kinetic Parameters	
			Rate constant, k_{25} $\text{mol m}^{-2} \text{s}^{-1}$	n
Quartz	68.9	9.8	1.023×10^{-14}	
K-feldspar	6.10	9.8	3.89×10^{-13}	0.5
Albite ^(a)	9.90	9.8	1.44×10^{-12}	0.457
Kaolinite	1.70	1.95×10^5	6.91×10^{-14}	0.777
Smectite-Ca	1.30	5.64×10^5	1.66×10^{-13}	0.34
Illite	2.80	6.68×10^5	1.66×10^{-13}	0.34
Nontronite-Mg ^(b)	1.00	9.8	3.02×10^{-13}	0.5
Calcite	1.50		Assumed at equilibrium	
Goethite	6.00	1.47×10^5	2.52×10^{-12}	
Arsenopyrite ^(c)	0.51	12.9	2.52×10^{-12}	
Galena	8.00×10^{-4}	12.9	2.34×10^{-7}	1.0

(a) Used in place of Oligoclase.

(b) Used in place of Chlorite.

(c) Used in place of Arsenian pyrite.

Table A.2. Groundwater composition used for geochemical modeling experiments. Data were obtained from Zheng et al. (2009) and Birkholzer et al. (2012). Concentrations are in $\mu\text{mol L}^{-1}$. Initial pH and Eh was 7.6 and -0.23 V, respectively.

Species	Concentration, $\mu\text{mol L}^{-1}$
Ca^{++}	9.0×10^2
Mg^{++}	2.2×10^1
Na^+	2.0×10^3
K^+	2.7×10^2
Fe^{++}	5.6×10^1
$\text{SiO}_2 \text{ (aq)}$	9.3×10^2
HCO_3^-	3.3×10^3
SO_4^{2-}	1.9×10^2
Al^{+++}	4.2×10^{-5}
Cl-	2.1×10^2
Pb^{++}	1.3×10^{-3}
H_2AsO_4^-	4.4×10^{-2}

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