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REVIEW PAPER

# Potential $CO_2$ intrusion in near-surface environments: a review of current research approaches to geochemical processes

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**Abstract** Carbon dioxide ($CO_2$) capture and storage (CCS) plays a crucial role in reducing carbon emissions to the atmosphere. However, gas leakage from deep storage reservoirs, which may flow back into near-surface and eventually to the atmosphere, is a major concern associated with this technology. Despite an increase in research focusing on potential $CO_2$ leakage into deep surface features and aquifers, a significant knowledge gap remains in the geochemical changes associated with near-surface. This study reviews the geochemical processes related to the intrusion of $CO_2$ into near-surface environments with an emphasis on metal mobilization and discusses about the geochemical research approaches, recent findings, and current knowledge gaps. It is found that the intrusion of $CO_2(g)$ into near-surface likely induces changes in pH, dissolution of minerals, and potential degradation of surrounding environments. The development of adequate geochemical research approaches for assessing $CO_2$ leakage in near-surface environments, using field studies, laboratory experiments, and/or geochemical modeling combined with isotopic tracers, has promoted extensive surveys of $CO_2$-induced reactions. However, addressing knowledge gaps in geochemical changes in near-surface environments is fundamental to advance current knowledge on how $CO_2$ leaks from storage sites and the consequences of this process on soil and water chemistry. For reliable detection and risk management of the potential impact of $CO_2$ leakage from storage sites on the environmental chemistry, currently available geochemical research approaches should be either combined or used independently (albeit in a manner complementarily to one another), and the results should be jointly interpreted.

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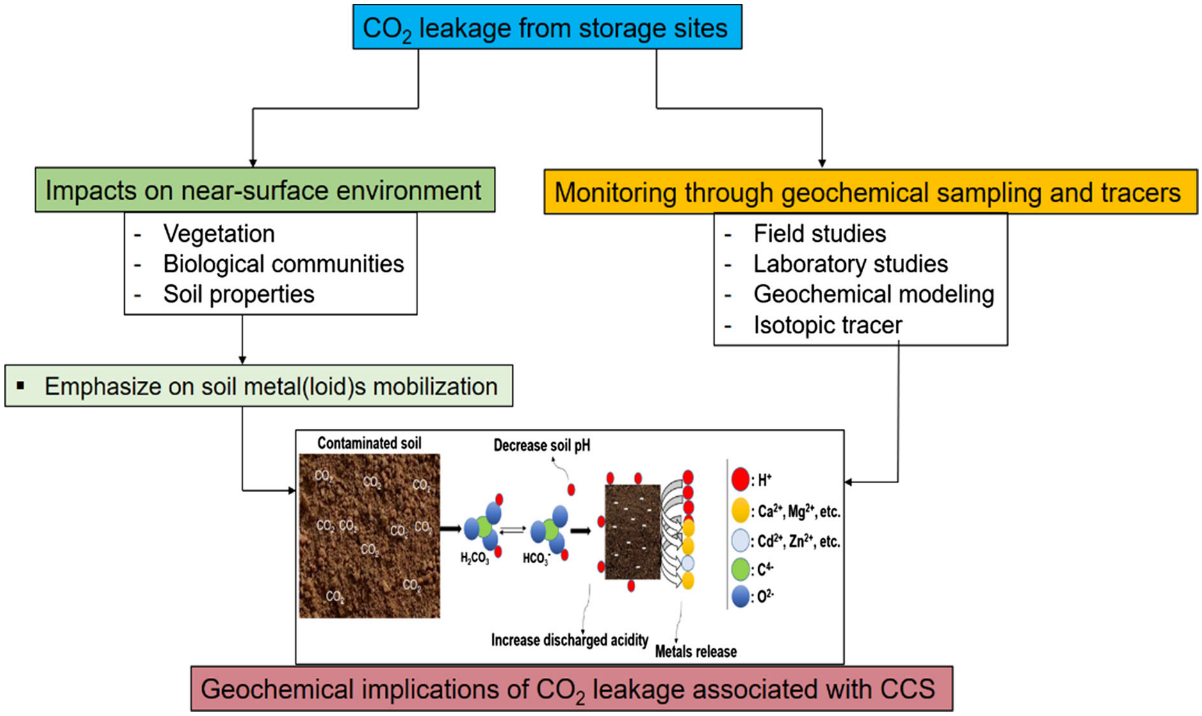
## Graphical abstract



**Keywords** $CO_2$ sequestration · $CO_2$ leakage · $CO_2$ capture and storage (CCS) · Near-surface environment · $CO_2$-induced geochemical processes

## Introduction

During the past century, the level of atmospheric $CO_2$ has risen by more than 39%, triggering the average global temperature increase of about 0.8 °C (Azdarpour et al. 2015). It is estimated that global greenhouse gas (GHG) emissions in 2030 would increase by 25–90% over the level of 2000, with the equivalent $CO_2$ concentration in the atmosphere growing to 600–1550 ppm (IPCC 2000; Leung et al. 2014). Apart from its significance as a GHG, $CO_2$ is also considered to aggravate the toxicity of CO when both are present in the same gas (Pauluhn 2016; Fabianska et al. 2018). Therefore, global concerns about GHG emissions have stimulated considerable research interest in $CO_2$ capture and storage (CCS) in deep geologic reservoirs.

As a climate change mitigation option, CCS technology reduces the industrial loadings of $CO_2$ as a GHG to the atmosphere (e.g., IEA 2004; IPCC 2005; Benson and Cole 2008; Gibbins and Chalmers 2008; Oelkers and Cole 2008; Harvey et al. 2012). In fact, CCS involves three distinct processes: (1) capturing $CO_2$ from the gas stream emitted during industrial activities; (2) transporting the captured $CO_2$ by pipelines, trains, trucks, or ships; and (3) storing $CO_2$ underground in deep saline aquifers. By ensuring a wide deployment of CCS, global $CO_2$ emissions can be reduced by approximately 70% by 2050 compared with the current emission levels (Stangeland 2007).

A major concern in the widespread deployment of $CO_2$ sequestration is whether $CO_2$ would leak from subsurface storage sites into the near-surface and subsequently back into the atmosphere to harm local populations and the environment (IEA 2008; Harvey et al. 2012; Wilkin and DiGiulio 2010; Boyd et al. 2013; Lions et al. 2014a; L'orange Seigo et al. 2014). It is known that natural disasters (e.g., earthquakes) or anthropogenic activities, which may happen during and/or afterward the operational (injection) procedure, may cause $CO_2$ leakage from geological storage sites (Bachu 2008; Zhou et al. 2016). There are three main potential pathways for escaping $CO_2$ and entry into the near-surface potable aquifers and soils (Bachu and Celia 2009; Liu et al. 2012): (1) leakage through the cap rock of the host reservoir; (2) migration along fracture networks and faults; and (3) migration via wells or abandoned wells (Fig. 1). Among the potential migration pathways to aquifers, leakage through fracture networks and faults is considered to be a rapid pathway (Oldenburg and Lewicki 2006). However, a leakage of $CO_2$ through wells is generally the primary risk of geological $CO_2$ storage installations (Oldenburg and Lewicki 2006), which can adversely influence the quality of the environment (Little and Jackson 2010; Wilkin and DiGiulio 2010).

$CO_2$ leakage from reservoirs may induce geochemical reactions and lead to degradation of water quality, which is likely the greatest concern associated with $CO_2$ migration from deep storage sites to near-surface environments. It is widely accepted that $CO_2$ intrusion induces acidification of groundwater and subsequently enhances the dissolution of contaminant-bearing soil and rock minerals (Wei et al. 2011; Saalfield and Bostick 2010; Harvey et al. 2012). In addition, the physicochemical properties of soils can change over the course of months or years in response to the rate of $CO_2$ leakage and the distance from a leakage point and subsequently impacts on terrestrial ecosystems. These properties include organic matter (OM), soil structure, mobilization/immobilization of the contaminants, infiltration rate, bulk density, and water- and nutrient-holding capacity (Mehlhorn et al. 2014, 2016; Ma et al. 2017; Moonis et al. 2017; Zhao et al. 2017).

Investigation of the impact of $CO_2$ leakage on the subsurface and especially the near-surface systems (e.g., soils and aquifers) is one of the most crucial topics (e.g., Schloemer et al. 2013; Mayer et al. 2015). The tools required for such analysis must be able to detect a forerunner or an early-warning signal of leakage associated with geochemical modifications that are related to small amounts of $CO_2$ (Humez et al. 2014a). Recently, researches have started to discuss about the potential geochemical impacts of $CO_2$ migration into a vadose zone or potable aquifers (e.g., Altevogt and Jaffe 2005; Carroll et al. 2009; Zheng et al. 2009a, b; Humez et al. 2014a, b). These include some specific topics such as continuous soil gas monitoring related to CCS (Schloemer et al. 2013); various tools and isotopic compositions for tracing and monitoring $CO_2$ intrusions into storage sites (Humez et al. 2014a; Mayer et al. 2015); risk assessment associated with the impacts of $CO_2$ leakage on human health (Atchley et al. 2013; Hillebrand et al. 2016); geochemical processes controlling groundwater quality (Lemieux 2011; Lions et al. 2014a); and the integrity of existing wells (Zhang and Bachu 2011; Choi et al. 2013). A broad review of these recent investigations, however, indicated very

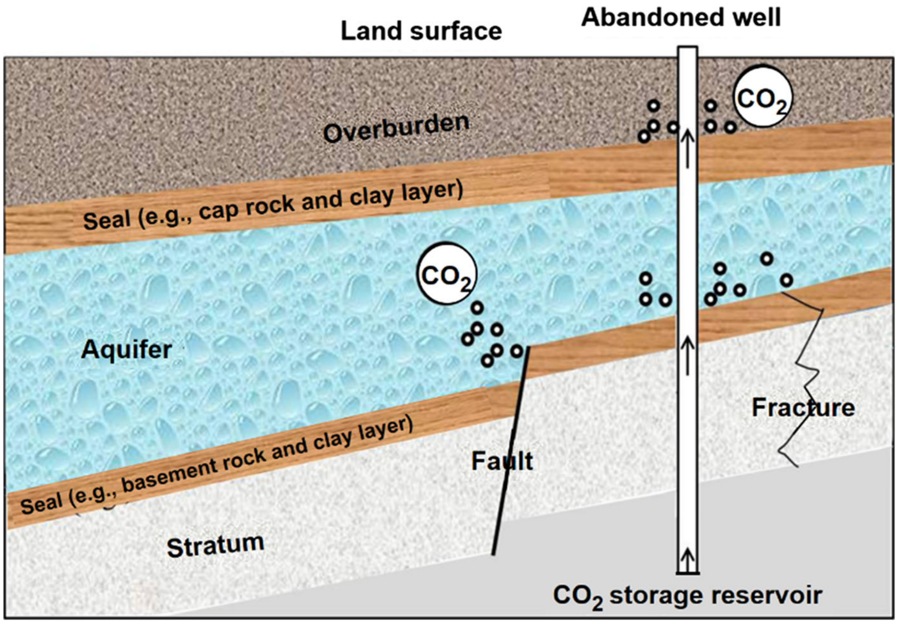


**Fig. 1** Schematic diagram of upward migration of $CO_2$ along faults, fracture, and abandoned wells. (Modified after Wilkin and DiGiulio 2010; Zhang and Song 2014)

limited studies and significant knowledge gaps on $CO_2$-induced changes in the geochemistry of near-surface soil and groundwater (Harvey et al. 2012). The primary concern about a $CO_2$ leakage is whether it would cause any harmful effect on the terrestrial ecosystem and finally on human beings. Because of this reason, previous studies in this subject, especially for near-surface soil, have examined many different aspects including the effects on plants and microbes but not limited to geochemical processes. Consequently, a comprehensive study is required to consider the interrelated aspects of diverse research subjects together linked to near-surface environments (including soil, water, plants, and microorganisms), which has been rare in the literature.

Hence, this review summarizes the geochemical processes and environmental consequences associated with potential $CO_2$ leakage into near-surface environments. Specifically, emphasis is placed on the metal(loid)s mobilization and subsequent physicochemical changes in shallow soil environment. And discussed are the geochemical research approaches using isotopic tracers, field studies, laboratory experiments, and geochemical modeling to assess such leakage to the near-surface. In addition, the knowledge gaps in the current studies on geochemical interactions in near-surface environments are examined and future research studies that should be followed are addressed.

## Environmental consequences of $CO_2$ leakage

Researchers have identified numerous detrimental effects that could occur following a $CO_2$ leakage from a storage reservoir on not only the soil and water quality but also the vegetation and biological communities (IEA 2007; Wei et al. 2011; Yang et al. 2017). Therefore, understanding the effects of possible leakage is essential for conducting risk analysis of CCS technology. Table 1 summarizes the experimental studies relevant for assessing the potential changes in physicochemical properties of the near-surface environment in response to a $CO_2$ leakage. Such leakage may pose deleterious effects to both humans and animals. The impacts of $CO_2$ leakage on the surrounding environment are divided into four main groups.

### Vegetation

The impacts of $CO_2$ emission on the vegetation are divided into two aspects: (1) impacts of the elevated atmospheric $CO_2$-induced plant growth on the geochemical reactions and (2) impacts of $CO_2$-induced geochemical reactions on the vegetation. It is reported that an elevated $CO_2$ concentration may enhance photosynthetic rates in plants (Tian et al. 2013; Sakurai et al. 2014). Thus, an elevated $CO_2$ is likely to stimulate the growth of many plant species (Sakurai et al. 2014). However, an increase in the growth of plants will need an increased supply of essential plant nutrients (e.g., N, P), which are taken up from the available nutrition pool in soil (Edwards et al. 2005; Gentile et al. 2012; Jin et al. 2012, 2013). Therefore, elevated $CO_2$-induced plant growth may influence the nutrients cycle, soil mineral composition, and the leachability of elements in ecosystems (Hungate et al. 2003; Luo et al. 2004; Schneider et al. 2004; Wang et al. 2013; Xu et al. 2013). For instance, Jin et al. (2015) reviewed the impacts of elevated $CO_2$ on the demand and utilization of P in plants and P acquisition from soil. They demonstrated a significant increase in P demand by plants under an elevated $CO_2$ ($>$ 16 mg/kg) due to the stimulation of photosynthesis. Elevated $CO_2$ altered P acquisition through changes in root morphology and caused an increase in rooting depth. Additionally, the quantity and composition of root exudates changed due to the changes in carbon fluxes along the glycolytic pathway and the tricarboxylic acid cycle. As a consequence, these root exudates led to P mobilization in the soil by forming soluble P complexes, by the alteration of the biochemical environment, and/or by changing microbial activity in the rhizosphere.

On the other hand, soil acidification due to $CO_2$ dissolution affects the quality and maturity of soil for vegetation. Generally, pH lower than 4 or higher than 9 will prevent or destroy the metabolism of plants (Zhao et al. 2017). Moreover, pH can affect the adsorption of nutrients such as Ca, Mg, N, P, and K by plants and impact plant growth (Zhao et al. 2017). Ekene et al. (2016) examined the effects of elevated soil $CO_2$ concentrations on spring wheat depending on the soil chemical properties in the Sutton Bonington Campus of the University of Nottingham, the UK, using Artificial Soil Gassing and Response Detection (ASGARD) facility, which artificially controlled $CO_2$

**Table 1** Potential changes in terrestrial ecosystem and groundwater chemistry in response to $CO_2$ leakage

| Soil parameters | Type of experiment | Observations | References |
|---|---|---|---|
| Vegetation | Natural analog | Moderate $CO_2$: improved plant growth. Intensive $CO_2$: reduced plant growth | Zhao et al. (2017) |
| | Field study | The clover biomass decreased by 79%, the grass biomass decreased by 42% | Smith et al. (2013) |
| | Greenhouse study | Root growth, leaf water, and nitrogen contents were considerably decreased | Kim et al. (2017a, b) |
| | A review | Significant increases in P demand, increased rooting depth, alteration of P acquisition, and P mobilization under elevated $CO_2$ | Jin et al. (2015) |
| | Field study | The wheat plant showed visible symptoms of wilting, chlorosis, and poor development | Ekene et al. (2016) |
| Biological communities | Laboratory study | Community of *Proteobacteria* increased to 67.93%, while *Acidobacteria* decreased to 9.29% | Ma et al. (2017) |
| | Field study | Bacterial numbers declined to $2 \times 10^4$ bacteria $g^{-1}$ during the 3 months of experiment | Smith et al. (2013) |
| | Field study | An increase in the relative abundance of *Bacteroidetes* and *Firmicutes* phyla, with a decrease in *Acidobacteria* and *Chloroflexi* phyla | Chen et al. (2016) |
| | Field study | Faunal biomass and trophic diversity were substantially lower compared to those at the reference site. Bacterial communities were also structurally affected | Molari et al. (2018) |
| Physicochemical properties of soil | Laboratory study | Soil acidification with an increase in metals (Al, Fe, Mn, K, and Pb) mobilization | Wei (2013) |
| | Laboratory study | Soil acidification with an increase in exchangeable fraction of Ni, Zn, and Pb | Wei et al. (2015) |
| | Laboratory study | A drop in pH with an increase in DOC content in organic soil and an increase in exchangeable fraction of $Al^{3+}$ in mineral soil | Moonis et al. (2017) |
| | Natural analog | A decrease in $Ca^{2+}$, $Cl^-$, TP, TN, and $SO_4{}^{2-}$ concentration with an increase in calcite content | Zhao et al. (2017) |
| | Field study | High concentration of $CO_2$ in soil enhanced the dependence of soil EC on soil moisture | Zhou et al. (2012) |
| | Laboratory study | An increase in N and P concentration, with a decrease in $SO_4{}^{2-}$, $Ca^{2+}$, $Na^+$, $K^+$, and $Cl^-$ concentration | Ma et al. (2014) |
| | Natural analog | A decrease in soil pH and Eh with an increase in OC contents | Mehlhorn et al. (2014) |
| | Laboratory study | A decrease in soil pH with an increase in Mn and Fe mobilization | Melhorn et al. (2016) |
| Groundwater chemistry | Geochemical modeling | Decreases in pH caused desorption of metals bound at the mineral–water interface or the dissolution of oxide and hydroxide minerals | Wilkin and DiGiulio (2010) |
| | Field study | Total IC concentration increased, and pH decreased | Peter et al. (2012) |
| | Laboratory and field studies | Changing pH conditions initially mobilize Ca, Mo, V, Zn, Se, and Cd | Mickler et al. (2013) |
| | Laboratory and modeling studies | A decrease in aquifer pH with desorption/resorption of As on clay-/Fe-rich minerals | Xiao et al. (2017a, b) |
| | Geochemical modeling | The induced low pH caused dissolution of aquifer minerals and As mobilization | Kim et al. (2018) |

injection into the soil of the test site. They demonstrated a significant increase in the leachability of essential plant nutrients (e.g., N, P, and K), which caused a decrease in plant growth under elevated $CO_2$ conditions. Therefore, $CO_2$ leakage upward to the surface may result in vegetation die-off due to an increase in soil $P_{CO_2}$, which leads to root asphyxiation and plant death (IEA 2007; Pierce and Sjogersten 2009). It has been reported in previous studies that when $CO_2$ gas concentration was higher than 5 vol% in soil, it was dangerous for plants and that it may be fatal for vegetation at 20 vol% and above (IEA 2007; Muradov 2014; Witkowski et al. 2015). For example, Zhao et al. (2017) utilized a naturally occurring $CO_2$-leaking site in the Qinghai–Tibet Plateau with the aim of systematically investigating the response mechanisms of plants to the influence of long-term (> 10 years) $CO_2$ leakage on the shallow ecological environment. In case of a large $CO_2$ concentration (> 112,000 ppm) in the soil gas system, they demonstrated adverse effects on the plant community distribution and growth, the physiological and biochemical systems of plants, and the quality of plants. The possible reasons for such effects include pH change, lack of nutrients such as available N or P, inhibition of soil respiration induced by replacement of $O_2$ with excess $CO_2$, and depression of photosynthesis in plant leaves. However, moderate $CO_2$ concentration (< 110,000 ppm) in soil gas could improve the plant growth and enhance the fat and starch contents in rapeseeds and potatoes, respectively. Smith et al. (2013) conducted a study to define the sensitivity of the plant variety to high concentrations of $CO_2$ in ASGARD facility with a gas leakage for 16 months. They demonstrated a significant change in biomass of all plant varieties but to different extents. The total biomass collected during the experiment showed that at a high concentration of $CO_2$ the biomass of both grass and clover decreased 42% and 79%, respectively. In addition, Kim et al. (2017a, b) investigated the growth of plants under a short-term $CO_2$ exposure (11 days) in a pilot-scale greenhouse setup. Their results showed a reduction of 47% in the root length of cabbages exposed to 99.99 vol% $CO_2$, whereas no change in a leaf biomass was shown. Indeed, the above-ground biomass was not influenced by $CO_2$ exposure, which indicates that the effects of soil $CO_2$ injection were more evident in the roots than in the shoots. Madhu and Hatfield (2013) also found a higher correlation of $CO_2$ concentration with root length than with shoot height. Overall, species of dicots showed more sensitivity than monocots in most studies to the elevated $CO_2$ concentration (Ko et al. 2016). Although species-specific response of plants to different soil $CO_2$ concentrations is a useful approach in investigating $CO_2$ leakage at the vegetated areas of $CO_2$ storage sites, the plant response to elevated levels of soil $CO_2$ has not been well understood yet as those of atmospheric $CO_2$. Hereupon, further investigations are required to clarify plant species' stress responses to an elevated soil $CO_2$ condition and compare seasonal variations in plant physiological parameters, as a tool for a long-term monitoring of $CO_2$ leakage in near-surface environments.

### Biological communities

$CO_2$ leakage in near-surface alters biological diversity throughout the ecosystem and changes the compositions and the numbers of species in the local environment (IEA 2007; Patil 2012). Moreover, $CO_2$ leakage may change the biogeochemical processes occurring in soil, which can lead to changes in the soil chemistry such as soil pH (IEA 2007). This can be associated with the negative effects on some microbial populations within the soil, which can lead to changes in the indigenous nutrients that would disturb the food chain, finally affecting the entire ecosystem (IEA 2007). In this regard, Ma et al. (2017) conducted a pot experiment with various $CO_2$ gas fluxes of 400, 1000, and 1500 $g/m^2$/day to investigate short-term (4 months) effects of $CO_2$ leakage on the bacterial community. Their results showed that an increase in $CO_2$ concentration led to an increase in the abundant proportion of *Proteobacteria* with a decrease in the abundance of *Acidobacteria*. Moreover, the abundances of other phyla such as *Verrucomicrobia*, *Actinobacteria*, *Gemmatimonadetes*, *Firmicutes*, *Planctomycetes*, *Cyanobacteria*, *Chloroflexi*, and *Nitrospirae* decreased with an increase in $CO_2$ flux. In a field-scale study conducted by Smith et al. (2013), the numbers of bacteria in the $CO_2$-exposed plots decreased by one order of magnitude during the gassing period, which suggests that $CO_2$ exposure to the soil affects microbial populations. In addition, Chen et al. (2016) conducted a study in an open field with a $CO_2$ injection to examine the threshold $CO_2$ concentration affecting the composition and structure of soil bacterial communities. Their results showed an increase in the relative abundances of *Bacteroidales*, *Firmicutes*, and *Lactobacillus* with respect to the $CO_2$ flux. In contrast, the relative abundances of *Acidobacteria* and *Chloroflexi* phyla decreased along with the $CO_2$ flux. Although $CO_2$ leakage obviously affects soil microbial communities, its impacts on biological processes have been poorly understood yet. For this, Molari et al. (2018) compared the ecological functions of naturally $CO_2$-vented seafloor of the Mediterranean island Panarea (Tyrrhenian Sea, Italy) to those of non-vented sands, with a focus on biogeochemical processes and microbial and faunal community composition. Their results showed a local shift in bacterial communities and enhanced microphytobenthos growth, but also decreased benthic meiofauna and macrofauna density and composition. Furthermore, $CO_2$ leakage altered the ecosystem functions in terms of remineralization and carbon transfer along the food web. Hence, there is a substantial risk that $CO_2$ leakage from CCS sites may locally lead to negative impacts on the ecosystem and the function of the seafloor as carbon sink. A review of the recent findings on impacts of $CO_2$ leakage triggering microorganism's activities and communities showed that the concentration of $CO_2$ and duration of exposure to $CO_2$ gas did not necessarily explained the differences in microbial responses at different experimental studies (Ko et al. 2016). This suggests that the other environmental factors may influence soil microbial communities and activities more than soil $CO_2$ concentration. Microbial responses to the elevated $CO_2$ concentration can also be covered up by natural responses to ambient environmental changes. Thus, a large number of short-term temporal and seasonal samplings along with long-term investigation on soil biological communities and activities are required to understand their response to $CO_2$ leakage.

## Physicochemical properties of soil

$CO_2$ leakage may change the quality of near-surface soil, particularly pH and heavy metal contents (Harvey et al. 2012). Studying the effects of $CO_2$ leakage is useful for identifying sensitive parameters if a leakage does happen. In this perspective, Wei (2013) investigated the impacts of $CO_2$ leakage on the properties of various soil types using a closed reactor experiment and a flow-through column system. Soil mineralogy did not significantly change, while soil acidification due to $CO_2$ dissolution caused an increase in mobilization of Al, Fe, Mn (highest mobilization), K, and Pb after the 3-day reaction at $P_{CO_2} = 25$ bar. Wei et al. (2015) also investigated the impacts of soil moisture content for the effect of $CO_2$ on the mobility and speciation of the exchangeable fraction of metals in soil samples collected from an artificial soil gassing site. Their results showed an increase in soil pH but not a decrease, which they speculatively ascribed to the escape of $CO_2$ during the sample collection or to the soil mineral dissolution induced by $CO_2$ exposure. Moreover, no changes were observed in the soil OC, inorganic carbon (IC) contents, or mineralogy following the $CO_2$ exposure with an increase in the exchangeable concentrations of Ni, Zn, and Pb in the soils. In another study, Moonis et al. (2017) compared the effect of a high $CO_2$ concentration on the physicochemical properties of a soil with a high concentration of OM (organic soil) with that of very low OM contents (mineral soil) by exposing samples to $CO_2$ gas in a greenhouse chamber for 32 days. Their results showed a significant decrease in soil pH in the $CO_2$-treated samples. They attributed a greater pH decrease for the mineral soil than for the organic soil to the higher buffering capacity of the organic soil. No change in the cation exchange capacity (CEC) of either soil was observed after the $CO_2$ exposure. However, a significant increase (28%) in the dissolved organic C (DOC) of organic soil was observed, whereas a significant reduction in DOC was observed in the $CO_2$-exposed mineral soil. The increase in DOC in the $CO_2$-treated organic soil could be attributed to its increased mobilization through a depletion of polyvalent cation bridges with OM due to proton exchange processes. However, a decrease in DOC in the mineral soil under $CO_2$ treatment was attributed to its adsorption on the mineral surfaces (Zech et al. 1994; Kalbitz et al. 2000). Besides the laboratory studies, soil properties were monitored in a natural $CO_2$ leakage site in the Qinghai–Tibet Plateau (Zhao et al. 2017). $CO_2$ intrusion resulted in the changes in soil properties, such as soil pH, a reduction in nutrients such as N and P, and some changes in soluble ions. The transformation of soil minerals was confirmed by X-ray diffraction (XRD), which demonstrated that $CO_2$ intrusion could change the soil mineralogy, in which $CaCO_3$ formation was pronounced mainly due to the long-term $CO_2$ exposure (> 10 years) in the naturally occurring site. Zhou et al. (2012) investigated the changes in bulk soil electrical conductivity (EC) during $CO_2$ leakage by conducting in situ continuous monitoring of soil EC, soil moisture, soil temperature, rainfall, and soil $CO_2$ concentration. Their observation showed that a high soil $CO_2$ concentration (20 vol%) enhanced the dependence of soil EC on soil moisture. In addition, Ma et al. (2014) conducted a pot experiment for 30 days by varying $CO_2$ concentrations (10,000–80,000 ppm) to monitor the physicochemical properties of a soil exposed to $CO_2$ gas. They showed that changes in $CO_2$ concentration had no significant impact on the soil particle size distribution. Their results showed that the concentrations of N and P in soil slightly increased with an increase in $CO_2$ concentration in the pots in 30 days after planting. The concentration of $K^+$ in soil changed significantly with an elevation of $CO_2$ concentration. The concentrations of ${SO_4}^{2-}$, $Ca^{2+}$, $Na^+$, $K^+$, and $Cl^-$ reached minimum values at 10,000 ppm $CO_2$ concentration in the soil, and that of $Mg^{2+}$ reached a minimum value at 20,000 ppm. It is noteworthy that metals were affected by $CO_2$ in different ways. Compared with the control conditions, the concentrations of total Zn and As (Cr and Ni) increased (decreased) slightly with an elevated $CO_2$ concentration (e.g., Zn from 49 to 53 mg/kg and As from 63 to 69 mg/kg). However, total concentrations of Cu, Pb, Cd, and Hg did not change at different $CO_2$ concentrations. Mehlhorn et al. (2014) investigated natural $CO_2$ exhalation through mofettes in a wetland area in the Czech Republic to document the soil properties. Compared with the control site, mofette soils showed a lower pH ($3.8 \pm 0.2$ vs. $4.1 \pm 0.2$) and a redox potential (Eh $270 \pm 50$ vs. $360 \pm 40$ mV) but a higher OC content (41 vs. 21%). Furthermore, they recognized lower contents of poorly crystalline or crystalline Fe (hydr)oxides, which are the most important sorbents of metal(loid)s in soil, due to a long-term $CO_2$ exposure (> 20 years) in the mofette. In turn, this increased the mobility of As in that the As concentration was 2.5 times higher than that of the control site. Likewise, Melhorn et al. (2016) studied the influence of $CO_2$ exposure on the metal mobilization processes for 6 weeks at 3 different temperatures (16, 22, and 35 °C) in a Fe (oxyhydr)oxide-rich soil. After 1 d of $CO_2$ exposure, weakly adsorbed metal cations were mobilized (especially Mn at 16 °C) due to surface protonation. After 3 days, Fe was significantly mobilized mainly due to microbially triggered reductive dissolution of Fe (oxyhydr)oxide. Noteworthily, a higher temperature (35 °C) and OM content (45 mg/g) accelerated microbially triggered Fe (oxyhydr)oxide dissolution. This study increased our understanding regarding the kinetics and temperature dependency of soil properties following $CO_2$ emission.

The main impact of $CO_2$ emission on soil properties was found to be a drop in soil pH, which triggered the mobilization of metal(loid)s from soils depending on soil types, soil moisture content, OM contents, and the period of $CO_2$ exposure. Hence, an abrupt change in pH would be a primary parameter to indicate the $CO_2$ intrusion into soil once a background has been set. Among soil metals, Fe and Mn showed a higher sensitivity to soil acidification to be mobilized by $CO_2$ dissolution. The response of Ca to $CO_2$ intrusion highlights that carbonate minerals are sensitive to an elevated $CO_2$ concentration and could possibly be used as an indicator of $CO_2$ leakage once the baseline for the pre-injection concentration has been established. However, studies on the dissolution of OC induced by $CO_2$ leakage have produced contradictory results. For instance, Titeux and Delvaux (2010), Moonis et al. (2017), and Derakhshan-Nejad et al. (2018) reported an increase in DOC under elevated $CO_2$ conditions, while You et al. (1999) found a decrease in DOC. Indeed, the molecular composition of OC in soil and soil water has a wide range and varies substantially as a function of pH (Roth et al. 2015). Therefore, a change in pH may influence the degradation of OM/OC contents and thereby the types and the distribution of soil organic molecules (You et al. 1999; Titeux and Delvaux 2010). In addition, the sorption/desorption of $H^+$ ions by OM is dependent on the dissociation constants of the weak organic acids, which differs by OM types (Spadotto and Hornsby 2003). Hence, the effect of $CO_2$ leakage on soil pH and its subsequent effects on a type-specific OM decomposition ratio in near-surface environments need to be well studied. In contrast to laboratory experiments (e.g., Wei 2013), a change in the mineralogy of the soil was found in a natural $CO_2$ leakage site. Indeed, since elevated soil $CO_2$ concentrations can enhance the weathering of minerals, it may be possible to assess the impact of $CO_2$ leakage on the soil mineralogy if the experiments are carried out for a substantially long period of time.

### Groundwater chemistry

Upward migration and dissolution of $CO_2$ in potable groundwater may adversely affect groundwater chemistry by increasing mineral dissolution as a result of a decrease in pH. Desorption and ion exchange reactions may increase water salinity and mobilize hazardous elements (Zheng et al. 2009a; Apps et al. 2010). Wilkin and Digiulio (2010) used analogous reaction paths and kinetic models to explore possible geochemical impacts to underground sources of drinking water. Reaction paths and kinetic models indicated that geochemical shifts caused by $CO_2$ leakage were closely linked to mineralogical properties of the receiving aquifer. The distribution and abundance of carbonates, silicates, and phyllosilicates were identified as key variables in controlling changes in groundwater geochemistry. Peter et al. (2012) conducted a controlled $CO_2$ injection test in a shallow aquifer to investigate the geochemical impact of $CO_2$ on the aquifer and to apply and verify different monitoring methods (i.e., isotope analysis, geoelectrical borehole monitoring, and multi-parameter probes). Due to $CO_2$ injection, total IC concentrations increased, but pH decreased. Associated reactions resulted in the release of major cations and trace elements. Geoelectrical monitoring as well as isotope analyses and multi-parameter probes were proved to be suitable methods for monitoring injected $CO_2$ and/or the alteration of groundwater. In addition, Mickler et al. (2013) examined the effects of an increase in $P_{CO_2}$ on groundwater chemistry in a siliciclastic-dominated aquifer by comparing the results from a laboratory batch experiment with those from a field single-well push–pull test on the same aquifer sediment and groundwater. Although the aquifer was mainly comprised of siliciclastic sediments, carbonate dissolution was the primary geochemical reaction. In the batch experiment, Ca concentration increased until the solution was saturated with respect to calcite at ~ 500 h. The concentrations of the elements such as Ca, Mg, Sr, Ba, Mn, and U were controlled by carbonate dissolution. In contrast, silicate dissolution controlled Si and K concentrations and was ~ 2 orders of magnitude slower than carbonate dissolution. Changing pH conditions through the experiment initially mobilized Mo, V, Zn, Se, and Cd. In that study, there was a considerable variation in the mobilization of the elements between the batch and push–pull experiments. So it was concluded that a combination of these two methods would be more precise to predict metals mobilization than using a single method. In another study, Xiao et al. (2017b) developed an integrated framework of a batch experiment and a reactive transport modeling to investigate water–rock–$CO_2$ interactions and As mobilization. In the beginning of $CO_2$ intrusion, pH decreased and As released from clay-/Fe-rich minerals (especially kaolinite). However, the buffering capacity of the water–rock system induced As re-adsorption onto clay-/Fe-rich minerals. Kim et al. (2018) also modeled the potential impacts of $CO_2$ leakage on As contamination in a simulated shallow groundwater aquifer with As-bearing minerals as a variable using simple 2D multi-species reactive transport models. The induced low-pH plume appeared to cause dissolution of aquifer minerals and subsequently increase the calculated permeability of the aquifer; in particular, the most drastic increase in permeability appeared at the rear margin of the $CO_2$ plume where two different types of groundwater mixed in their models. They argued based on their modeling results that water–rock interactions induced by $CO_2$ dissolution mobilized As species to the shallow potable aquifer and suggested that the aquifer should be well characterized and the amount of leached $CO_2$ and its plume size should be well evaluated to develop a proper remediation protocol.

Overall, spatial variability in the flux rate of $CO_2$ in the aquifer, heterogeneity within the aquifer, and/or spatially variable $CO_2$-consuming reactions (e.g., calcite or plagioclase dissolution) may change the levels of the dissolved $CO_2$ in the aquifer and the subsequent chemical reactions (Keating et al. 2010). For a risk assessment, it is important to fully understand the effects of mineral dissolution/precipitation within the aquifer because these reactions may induce/reduce a risk to human health since the mobility of the metal(loid)s, caused by pH reduction, may be improved/prevented. However, it is hard to detect the $CO_2$ leakage through a simple measurement of groundwater pH or mineral dissolution/precipitation. Accordingly, combining geochemical models and geochemical sampling together is suggested to examine the behavior of hazardous elements in an aquifer over a range of pH, IC concentrations, and redox and mineralogical conditions.

## Geochemical processes associated with $CO_2$ leakage in near-surface environments

$CO_2$ leakage can significantly alter the geochemical processes occurring in subsurface and near-surface environments. The fate of leaked $CO_2$ gas and the subsequent induced reactions depend mostly on the physicochemical characteristics of the shallow soil containing the leakage. The highly complicated deleterious effects of $CO_2$ intrusion on the near-surface environments are summarized in this section.

### Mineral interactions and geochemical changes associated with $CO_2$ leakage

Injection of supercritical $CO_2$ into a reservoir (e.g., deep brine formations) alters the physicochemical reaction balance between fluid and rocks in the system (Kaszuba and Janecky 2013). Complex fluid–rock interactions are expected to occur during the injection of $CO_2$, which may affect $CO_2$ injectivity, storage capacity, geochemical reactions, and safety to successfully storing $CO_2$ (Nghiem et al. 2004; Andre et al. 2007; Fritz et al. 2010; Andre et al. 2014; Shao et al. 2015; Jin et al. 2016; Miri and Hellevang 2016; Cui et al. 2017). Generally, $CO_2$ injection breaks the original chemical equilibrium between the rock and water, resulting in the dissolution of some minerals (e.g., mainly primary minerals) and the precipitation of others (e.g., clays and oxides) (Cui et al. 2018).

The effects of $CO_2$ leakage from storage reservoirs and of the subsequent $CO_2$–soil mineral interactions give an outlook on how the leakage would impact the geochemistry of near-surface environment. $CO_2$ leakage imposes a decrease in pH (Little and Jackson 2010; Vong et al. 2011; de Orte et al. 2014; Moonis et al. 2017) and/or a change in Eh (Mehlhorn et al. 2014) and thereby influences the dissolution of minerals (Jaffe and Wang 2003; O'Malley 2010; Peter et al. 2011; Harvey et al. 2012; Al-Khoury and Bundschuh 2014; Mehlhorn et al. 2014; Zheng et al. 2015; Melhorn et al. 2016; Xiao et al. 2017a), resulting in the release of chemical elements into solution. In fact, pH is strongly linked to the concentration of dissolved $CO_2$ in the soil/water. The dissolution of $CO_2$ in water (e.g., soil water, pore water, and potable water) forms carbonic acid ($H_2CO_3$). Subsequently, the changes in pH influence the dissolution of soil minerals (e.g., calcite, dolomite, K-feldspar, and plagioclase) (Eqs. 1–5).

$$CO_{2(g)} + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-} \tag{1}$$

$$CaCO_3(\text{calcite}) + H_2O + CO_2 \Leftrightarrow Ca^{2+} + 2HCO_3^- \tag{2}$$

$$CaMg(CO_3)_2(\text{dolomite}) + 2H_2O + 2CO_2 \Leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \tag{3}$$

$$KAlSi_3O_8(\text{K - feldspar}) + Na^+ + H_2CO_3 \Leftrightarrow NaAlCO_3(OH)_2(\text{dawsonite}) + 3SiO_2 + K^+ \tag{4}$$

$$CaAl_2Si_2O_8(\text{Ca - plagioclase}) + 2H^+ + H_2O \Leftrightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4 \tag{5}$$

The extent and direction of pH and Eh changes control the rate and extent of mineral dissolution/precipitation as well as the sorption/desorption of contaminants from related sorbents such as clays, OM, and metal (hydr)oxides. Indeed, carbonate minerals, clay minerals, and feldspars tend to buffer the pH (Eqs. 2–5) (Vernet 1993). Gaus (2010) suggested that carbonate minerals rapidly buffer the pH and cause the brine to be less acidic (Eqs. 2, 3). The reactions in Eq. 2 can rapidly reach equilibrium under suitable conditions (Gaus 2010). However, dissolution of clays and feldspars is characterized by slow reaction kinetics (Eqs. 4–5) and would require thousands of years (Gaus 2010). Poorly buffered systems with primary minerals such as feldspar have a low resistance to changes in pH. Previous research indicated that sandy soils with a lower buffering capacity are likely to be more sensitive to an increase in $CO_2$ concentration to change their pH compared to clay-rich soils, with a higher buffering capacity (Harvey et al. 2012). However, in well-buffered systems $CO_2$-induced dissolution of carbonates or the dissolution/precipitation of clays would provide a sufficient buffering capacity (Harvey et al. 2012). Therefore, such systems are expected to provide a required buffering capacity (via $HCO_3^-$ alkalinity) to resist dramatic changes in pH with secondary mineral precipitates (Gunter et al. 1997). However, this pH buffering process through mineral dissolution at a high

$CO_2$ concentration may increase the mobilization of metals (Cui et al. 2018).

It is worthy to note that feldspars are one of the most prevalent groups of potentially reactive minerals in reservoirs. Feldspar dissolution causes precipitation of secondary minerals such as phyllosilicates. For this, Fu et al. (2009) conducted a batch experiment to investigate dissolution of perthitic K-feldspar at a high temperature (200 °C) and pressure (300 bar) for CCS at an initial pH of 3.1. They reported coexistence of K-feldspar with kaolinite and/or sometimes illite in sandstone and suggested that K-feldspar dissolution was coupled by the growth of the secondary phases. Indeed, secondary clay minerals are very important for reducing sandstone permeability. Previous studies showed that $CO_2$–$H_2O$ interactions result in acid-dominated reactions and alteration of K-feldspar to clay (Kaszuba and Janecky 2013). On the contrary with feldspars, not much attention has been paid to the solubility of quartz in the context of CCS because quartz solubility is not sensitive to pH at $< 9$ (Knauss and Wolery 1986). For this, Carroll et al. (2013) investigated reactivity of reservoir and cap rocks to $CO_2$ exposure and demonstrated an amorphous silica precipitation from dissolved silica released during clay transformations. As to carbonates, it is well known that many carbonates react more quickly than silicates with acidified fluids under elevated $CO_2$ conditions. Carbonates control the pH and the chemical composition of the fluid in a rapidly moving fluid packet ahead of a $CO_2$ plume. The dissolution rates of calcite and dolomite have been assessed in a number of the studies, whereas there has been a lack of studies on those of magnesite, siderite, and other carbonates (e.g., Morse and Arvidson 2002; Golubev et al. 2009; Pokrovsky et al. 2009a, b; Schott et al. 2009). For instance, Cui et al. (2017) conducted laboratory experiments on $CO_2$–water–rock interactions to investigate the geochemical reactions from both sandstone and carbonate reservoirs. The experimental results of the sandstone reservoir showed an increase in the dissolution rate of ankerite and clay minerals and precipitation of plagioclase, which caused an increase in the concentrations of $Ca^{2+}$, $Mg^{2+}$, and $Fe^{2+}$. For a carbonate reservoir, $CO_2$ exposure induced the dissolution of dolomite and precipitation of ankerite and calcite, which resulted in an increase in the concentrations of $Ca^{2+}$ and $Mg^{2+}$.

Geochemical reactions in $CO_2$–water–rock systems induce changes in the reservoir porosity, permeability, pH, mineral dissolution, etc. In the event of a $CO_2$ gas stream intruding into a potable aquifer or the vadose zone, it is the mineralogy of the system that will dictate how the system is buffered, the type and amount of contaminants likely to be mobilized, and what sorbents are likely to precipitate. All the mineralogical reactions induced by the dissolution of $CO_2$ in soil/rock–water systems are highly complex. Mineralogical reactions may occur in the bulk of the reservoir rock/cap rock and/or in the fractures (Czernichowski-Lauriol et al. 2006). Dissolution of minerals in cap rocks might result in the formation of flow pathways that might boost $CO_2$ migration. The geochemical consequences of the $CO_2$-induced changes in fractures and bulk rock physical properties need to be assessed as they have an impact on the long-term storage stability and security. In addition, these geochemical reactions are highly site specific, depending on the fluid chemistry, mineralogy, time dependence (due to the wide range of reaction kinetics), pressure and temperature of the host formation. Therefore, when a geologic reservoir for $CO_2$ storage is selected, all the reservoir conditions, site-to-site basis, should be thoroughly analyzed and all the possible leakage pathways as well as subsurface properties (especially pertinent minerals) should be well characterized to be able to assess the impact of $CO_2$ on subsurface and near-surface environments.

## Impacts of $CO_2$ leakage on the mobilization of metal(loid)s

Basic information regarding the capacity of soils to retain or release metal(loid)s is essential for predicting the environmental impact of $CO_2$ leakage on the shallow surface. Sorption/desorption reactions are expected to play a crucial role (Zheng et al. 2009a) not only in metal mobilization, but also in buffering pH in the absence of significant amounts of fast-reacting minerals such as carbonates (e.g., calcite and its polymorphs). Sorption competition with bicarbonate/carbonate ions could also release oxyanions (e.g., As, Se). In addition, released metal(loid)s may trigger subsequent ion exchange reactions to cause further release of other metal(loid)s into solution. Generally, pH can be considered as an indicator of the $CO_2$ intrusion rate and subsequently the fate and transport of constituents of concern in $CO_2$-impacted sites (Harvey et al. 2012). Eh also controls many geochemical processes occurring in subsurface systems. The intrusion of $CO_2$ gas into soil, aquifers, or vadose zones may induce changes in Eh due to $CO_2$-induced reactions resulting in the redistribution of oxidized and reduced aqueous species or $O_2$ depletion/displacement with $CO_2$ gas (Huesemann et al. 2002; Altevogt and Jaffe 2005; Ardelan and Steinnes 2010; Kirk 2011). Table 2 summarizes the results of previous studies examining the impacts of $CO_2$ intrusion on metal(loid)s mobilization in near-surface environments.

Wang and Jaffe (2004) demonstrated that a decrease in aqueous pH associated with $CO_2$ intrusion increased the aqueous concentrations of Cd, Cu, Pb, Zn, Mn, and Fe mainly due to the dissolution of these metal-bearing minerals. In addition, Wei et al. (2011) reported an increase by more than 5 times in the exchangeable fractions of heavy metals (e.g., Cu, Cr, Pb, V, and U) in a $CO_2$-exposed agricultural soil. Wilkin and DiGiulio (2010) also reported desorption of some contaminants from mineral surfaces associated with $CO_2$ dissolution in an aquifer. Mehlhorn et al. (2014) reported that the dissolution of Fe (oxyhydr)oxides affected by $CO_2$ intrusion under acidic or reducing conditions significantly increased metal(loid)s mobilization. However, despite the fact that many studies have been conducted on metal(loid)s mobilization in aquifers and saturated soils, less attention has been paid to the influence of $CO_2$ leakage on partially wet soils or near-surface environments. In this regard, only Wei et al. (2015) investigated the effects of soil moisture content on metal mobilization in soils exposed to $CO_2$. They recognized that soil exposure to $CO_2$ significantly ($p < 0.05$) increased the exchangeable concentrations of Ni, Zn, and Pb. In addition, As, Ar, Cr, Cu, and Fe showed different mobilization patterns depending on the soil moisture content. This study demonstrated that moisture content played an essential role in the uptake of $CO_2$ by pore water and caused the soil to mobilize heavy metal(loid)s, but no information was provided on the distribution and origin of the minerals responsible for the observed changes. This increase in the release of soil metals likely corresponded to the dissolution of the soil and aquifer minerals and/or the

**Table 2** Impacts of $CO_2$ intrusion on the mobilization of metal(loid)s near-surface environment

| Elements | Investigation area | Experimental setup | Observations | References |
|---|---|---|---|---|
| Cu, Cr, Pb, V, and U | Agricultural soil | 3 days of exposure | 500% increase in exchangeable fraction of metals | Wei et al. (2011) |
| Al, Co, Cr, Mn, Zn, and V | Aquifer sediments | > 300 days of exposure | A significant increase in metals leaching | Little and Jackson (2010) |
| Pb | Into hypothetical shallow aquifers | 8 years of simulation (modeling) | An increase in dissolution of PbS and subsequent increases in Pb leachability | Wang and Jaffe (2004) |
| Al, As, Cd, Cu, Fe, Mn, Pb, Se, and Zn | Shallow freshwater aquifer | 3 days of field study | An increase in metals leaching | Kharaka et al. (2009) |
| Cd, Cu, Fe, Mn, Pb, and Zn | Glauconitic-sandstone aquifer | > 10 years of simulation | A significant increase in metals leaching | Vong et al. (2011) |
| As, Cu, Fe, Mn, and Ni | Agricultural soil near to mofette site | 30 days of field test | An increase in metals leaching | Mehlhorn et al. (2014) |
| Al, B, Co, K, Li, Mg, Mn, Na, Ni, Pb, Sr, and Zn | Albian aquifer | 30 days of batch experiment | An increase in metals leaching | Humez et al. (2013) |
| As, Ba, Ca, Co, Mg, Ni, Sr, Tl, and U | Limestone aquifers | 40 days of rock–$CO_2$ reaction | An increase in dissolution of calcite and pyrite and stimulation of metals leaching | Wunsch et al. (2014) |
| As, Ba, Ca, Cd, Fe, Mn, Mg, Pb, Sr, and U | Sandstone aquifers | 27 days of rock–$CO_2$ reaction | An increase in dissolution of calcite and stimulation of metals leaching | Kirsch et al. (2014) |

desorption of easily leachable fractions of metals in response to $CO_2$ intrusion, which caused an alteration of groundwater and soil quality. Therefore, a systematic understanding of the factors influencing the dissolution of metal-bearing minerals and fractionation of metal(loid)s in a $CO_2$–soil–water system is an essential prerequisite of any attempt to predict metal(loid)s mobilization under an elevated $CO_2$ condition.

## Geochemical research approaches for assessing $CO_2$ leakage

Owing to the important consequences of $CO_2$ leakage on the environment, adequate investigation of $CO_2$-induced reactions is necessary. Investigating $CO_2$-induced geochemical reactions provides a basis of risk assessment and management to ensure that $CO_2$ injected into a storage site remains constant within the pre-defined geological structures and does not leak into subsurface zones or to the near-surface environments.

It is noted that $CO_2$ can leak out over lateral distances of several tens of kilometers from the storage sites depending on the properties of the multi-phase flow and the heterogeneous structures of the cap rocks (Dethlefsen et al. 2013). In CCS studies, it is common to combine some of the present tools and options to increase the understanding of the $CO_2$-induced geochemical reactions. In general, isotopic tracers and geochemical sampling are considered as appropriate tools for investigating $CO_2$ leakage and the following reactions in the near-surface environment over a wide range of $CO_2$ fluxes and its influences on the soil and water chemistry (Carroll et al. 2009; Olive et al. 2014). Co-injection of specific compounds together (as tracers) with $CO_2$ can generate a specific "fingerprint" of $CO_2$ leakage. These tracers have been reported to detect any seepage from a reservoir even in a very small amount in parts per million (Jenkins et al. 2012). In geochemical sampling, soil or water samples are collected from storage sites or adjacent sites that might be potentially affected, to observe the physicochemical variation induced by $CO_2$ leakage. These research approaches are used in field and laboratory scales and can be combined with geochemical modeling for prediction of $CO_2$-induced reactions or with tracers as a leakage monitoring method.

### Isotopic tracer

Tracer approaches are essential tools to identify the distribution of a $CO_2$ plume in the target hydrogeologic formations and to enable a tracking of potential leakage of $CO_2$ outside the storage reservoir (Mayer et al. 2015). Thus, it is indispensable to develop effective geochemical tracer tools or markers of these interactions, particularly an isotopic tracer.

A comparison of the available $CO_2$ monitoring techniques and the geophysical methods such as seismic reflection, electrical, and electromagnetic methods (Arts et al. 2004; Eiken et al. 2011) revealed that isotopic tools could provide more valuable and reliable information for detection of $CO_2$ leakage even in small amounts (e.g., Assayag et al. 2009; Bakk et al. 2012; Caritat et al. 2013; Dillen et al. 2009; Humez et al. 2014b). To ascertain the chemical reactions in a specific carbonate system and to establish their mass balance, it is crucial to identify the dynamic characteristics of C, H, and O isotopes of $CO_2$, carbonates, silicates, and water molecules. An overview of the previous studies on the isotopic tracer methods associated with $CO_2$ intrusion in subsurface systems is shown in Table 3. $\delta^{13}C_{CO2}$, $\delta^{18}O_{H2O}$–$\delta^{2}H_{H2O}$, and $\delta^{18}O_{SO4}$–$\delta^{34}S_{SO4}$ displayed the source of salinity or recharge, mixing processes, mineral dissolution (e.g., sulfide), and the fractionation processes induced by the changes in the geochemical conditions due to $CO_2$ migration (Assayag et al. 2009; Johnson and Mayer 2011; Larson and Breecker 2014; Lions et al. 2014b; Humez et al. 2014a, b). Additionally, Ca, Sr, B, and Li isotopes are useful for understanding water–rock interactions, particularly ion exchange, dissolution, and precipitation processes (Dogramaci and Herczeg 2002; Millot and Negrel 2007). Additionally, to illustrate the sources of contaminants and the geochemical processes induced by $CO_2$ intrusion, multi-isotopic approaches have been developed such as the mixing of different salinities, the interaction of rocks with saline or fresh water, and the reaction of $CO_2$ with water, rocks, and soil. For example, Bachelor et al. (2008) obtained detailed information about the pathways involved in a $CO_2$ leakage by using $^{14}C$ as a radiological tracer. Choi et al. (2017) examined a baseline hydrochemistry of an aquifer for the potentiality of early $CO_2$ detection using oxygen, hydrogen, and carbon isotope components. Results showed that groundwater parameters such as pH, EC, bicarbonate

**Table 3** An overview of the isotopic tracer method to detect the impact of $CO_2$ intrusion on the geochemistry of subsurface systems

| General purposes | Methodology description | Observations | References |
|---|---|---|---|
| Reaction and migration of $CO_2$ | Using carbon isotope compositions for $CO_2$ eluted from one-dimensional flow-through column experiments. | The adsorption isotope effects may significantly change the δ13C value of $CO_2$ | Larson and Breecker (2014) |
| | Using δ13C of DIC, $^{87}Sr/^{86}Sr$, and stable isotopes of water to monitor geochemistry of the aquifers | A $^{13}C$-enriched subset of samples shows signs of dissolution of Mg–Sr–calcite or dolomite by $^{87}Sr/^{86}Sr$ ratios | Lions et al. (2014b) |
| Water–rock interactions | Combined use of $^{87}Sr/^{86}Sr$ and $\delta 13C$ to constrain the extent of carbonate–solution interactions | Results showed that incongruent dissolution predominantly took place in the $CO_2$-saturated zone | Dogramaci and Herczeg (2002) |
| | Evaluation of redox fronts using O-, H-, B-, and Li-isotope ratios of groundwater in the sand aquifer | $\delta^{18}O$ and $\delta^{2}H$ correlate with the present-day and old recharge. The large range of $\delta^{11}B$ reflects interactions | Négrel et al. (2012) |
| | Application of $\delta^{11}B$, $\delta^{7}Li$, $^{87}Sr/^{86}Sr$, $\delta^{18}O_{SO4}$, $\delta^{34}S_{SO4}$, $\delta^{18}O_{H2O}$, and $\delta^{2}H_{H2O}$ isotopes in the context of CCS | $CO_2$–water–rock interactions enhanced by dissolved $CO_2$ | Humez et al. (2014b) |

($HCO_3$), $\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C$ were relatively sensitive to the introduction of $CO_2(g)$ and thus suggested that they could potentially be monitoring parameters for early detection of $CO_2$ leakage. Schulz et al. (2012) measured an artificial $CO_2$ leakage into a shallow aquifer by using a stable C isotope ($^{13}C/^{12}C$) of both soil and groundwater at a field site to monitor the distribution of the injected $CO_2$. Their results demonstrated that this approach could be applied appropriately to identify the $CO_2$ sources and the potential migration of $CO_2$ from CCS sites into shallow aquifers or even into the upper surface. In addition, Humez et al. (2014b) measured the ratios of multi-isotopes ($\delta^{11}B$, $\delta^{7}Li$, $^{87}Sr/^{86}Sr$, $\delta^{18}O_{SO4}$, $\delta^{34}S_{SO4}$, $\delta^{18}O_{H2O}$, and $\delta^{2}H_{H2O}$) during $CO_2$ injection to test various geophysical and geochemical monitoring tools. Significant changes in the isotope signatures of water showed acidification by $CO_2$ dissolution, which enhanced the mineral dissolution. Overall, as a key advantage, the tracer methods can provide direct information about the reactive transport processes and reservoir parameters. Within the context of CCS projects, this method could improve the understanding of subsurface movement of a $CO_2$ plume (Freifeld et al. 2005; Boreham et al. 2011; Underschultz et al. 2011; Vandewijer et al. 2011), the characterization of geochemical processes (Matter et al. 2007; Assayag et al. 2009), the assessment of the residual trapping capacity (Myers et al. 2012; LaForce et al. 2014; Rasmusson et al. 2014), the determination of leakage rates for monitoring, and the verification of the programs (Strazisar et al. 2009), and facilitate acquiring information about individual trapping mechanisms. However, isotopic analyses have addressed two disadvantages: insufficient spatial resolution for realistic monitoring tools and a low degree of discrimination between biogenic and fossil-derived $CO_2$. In many cases, isotopic data from field campaigns have been limited due to either complex sample retrieval or the need for verifying the fractionation factors under controlled boundary conditions (Barth et al. 2014). Sufficiently large differences among isotopic ratios are desirable for the tracer studies.

## Geochemical sampling

### *Field studies*

Field study conducted in a natural setting is a pivotal approach to examine $CO_2$-induced interactions in the near-surface environment. Only field studies can truly reflect the impacts of $CO_2$ gas in situ on the subsurface environments to form a basis for examining the performance and effectiveness of geochemical modeling codes. However, it is difficult to select proper sites and parameters in the field because of complex geological settings, mineral phases, aquifer formations, heterogeneous components of subsurface soil, and temperature. Proper site selection and CCS management are important considerations for reducing the potential of $CO_2$ leakage (Lemieux 2011). Selected sites should be adequately characterized on the basis of (1) geological settings (e.g., preexisting or induced factures and faults); (2) mineral compositions (i.e., carbonates, aluminosilicates, and metal (oxyhydr)oxides); (3) aquifer features (e.g., types, depth, thickness, geologic material); (4) soil properties (e.g., microbial community, organic content, and moisture content); and (5) pressure/temperature and salinity related to $CO_2$ solubility at each selected site. Field studies are comprised of natural analog studies and/or leak simulations (e.g., $CO_2$ injection directly into the subsurface) (Keating et al. 2010). Natural analog studies can be used to further refine reaction pathways, identify the intermediate mineral phases, and provide evidence for $CO_2$ storage safety and feasibility based on both temporal and spatial scales. However, observations from natural sites that are exposed to an elevated $CO_2$ for a considerable period may not directly correspond to the effects of a $CO_2$ leakage from a storage facility. Therefore, characterization of soil, water, or plants in artificial $CO_2$ injected sites would be more feasible to assess the actual impacts of a controlled injection of $CO_2$. However, a knowledge gap exists in field data characterizing the nature of potential impacts (Keating et al. 2010). In general, a variety of factors should be considered in a field study for the impact of $CO_2$-induced interactions on near-surface environments, such as proper site selection, leakage pathways, and well location. The primary parameters considered in examining the effects of $CO_2$ intrusion include pH, temperature, pressure, Eh, anions (e.g., Br, Cl, F, and $SO_4$), exchangeable cations (e.g., K, Na, Ca, and Mg), heavy metal(loid)s (leachable/soluble), OC/IC contents, mineral composition, EC, alkalinity, and moisture content (Kirsch et al. 2014; Yang et al. 2014; Mehlhorn et al. 2014, 2016).

Recently, a number of field-scale $CO_2$ injection studies have been conducted to address many of the uncertainties in the characterization of near-surface environment induced by $CO_2$ leakage. The experimental setup differed in a number of ways, from the geological conditions, surface environments, injection rates, and monitoring strategies (Trautz et al. 2012; Mickler et al. 2013; Yang et al. 2013; Feitz et al. 2014; Gal et al. 2014; Rillard et al. 2015; Roberts and Stalker 2017). Field studies allow us to identify knowledge gaps that future experiments should seek to address.

### *Laboratory studies*

Owing to their low cost and the relative ease of operation, batch and column studies conducted at a laboratory scale have attracted significant attention in an effort to understand the mobilization of trace elements in response to $CO_2$ intrusion into shallow soil and groundwater. Due to the known corrosive properties of $CO_2$, the assessment of $CO_2$–rock interactions has been an important topic of many laboratory studies since CCS has emerged (e.g., Gunter et al. 1997; Kharaka et al. 2006; Gaus 2010; Wilkin and DiGiulio 2010; Pham et al. 2011; Hellevang et al. 2013). Initially, researchers focused on the short-term impacts on host rocks through simple batch experiments combined with a long-term geochemical modeling (Gaus 2010). These experiments focused on the determination of dissolution rates, dissolution/precipitation mechanisms of specific minerals, or thermodynamic properties of minerals that would potentially participate in $CO_2$–rock interactions. To discuss these fundamental reaction mechanisms, laboratory experiments should be conducted in a well-controlled system. The various conditions of laboratory experiments for $CO_2$–sediment interaction examined in previous studies are summarized in Table 4.

The parameters sensitive to $CO_2$ leakage identified from laboratory experiments can be applied for cost- and time-effective experimental setup in the field. Laboratory experiments can provide basic clues to geochemical processes associated with $CO_2$ intrusion into subsurface soil. For a direct comparison of field with laboratory conditions, natural materials can be collected from a field (e.g., aquifer sediment), or artificial materials can be used depending on the various perspectives and objectives of the study. However, one or two orders of magnitude higher mineral dissolution rates are generally observed in laboratory experiments than those assessed in the field (Lu et al. 2010). Although laboratory experiments can facilitate the understanding of the potential impact of $CO_2$ on the subsurface environment, they may not accurately represent in situ conditions due to the inherent complexity of nature. As a consequence, field studies give data on $CO_2$ storage safety, leakage, and

**Table 4** Batch experiments of $CO_2$ intrusion interactions conducted at different conditions

| Materials | Weight (g) | Elapsed time (day) | Incubation condition | pH | Pressure (MPa) | Temperature (°C) | Gas velocity or ratio (L/min) | Material ratio | References |
|---|---|---|---|---|---|---|---|---|---|
| Field sediment | 100 | 30 | Exposed to $CO_2$ | 5.63–8.63 | 0.13 | – | – | 4/1 (water/sediment, ml/g) | Mickler et al. (2013) |
| | 95 | 30 | Ar (the first 14 days); $CO_2$ (the following 14 days) | 3.1–8.7 | 0.1 | Room temperature | – | 5/1 (water/rock) | Yang et al. (2014) |
| | – | 26 | Exposed to $CO_2$ | 6.5–7 | 1.5 | 6.5 ± 0.3 | 2.7 | Sediment + brine | Ardelan and Steinnes (2010) |
| | 5 | 26 | Exposed to $CO_2$ | 5.1–7.6 | 0.1 | 21 | 0.07 | 5 g + 15 ml (synthetic groundwater) | Shao et al. (2015) |
| Aquifer sediment | 2–400 | 320–340 | Exposed to $CO_2$ | 3.1–5.9 | 0.1 | 20 | 0.2 | 3/1 (v/v, water to sample) | Little and Jackson (2010) |
| Aquifer rock | – | 28 | Ar (the first 14 days); $CO_2$ (the following 14 days) | 3.8–4.6 | 0.1 | Room temperature | – | 5.3/1 (mass ratio, water/rock) | Lu et al. (2010) |
| Core sample | 95 | 30 | Ar (the first 14 days); $CO_2$ (the following 14 days) | 2–9.5 | 0.1 | – | – | 95/500 (g/ml, core sample/deionized water) | Smyth et al. (2009) |
| Minerals | 40 | 30 | Exposed to $CO_2$ | 5–5.3 | 0.1-0.2 | 20 | – | 10/1 (v/v, liquid/solid) | Humez et al. (2013) |
| Gleyic Fluvisol | 50 | 42 | Exposed to $CO_2$ | 4.5–4.8 | 0.1 | 16, 22, and 35 | 0.03 | 50 g + 250 ml (river water) | Melhorn et al. (2016) |

geochemical interactions, while laboratory studies give those of basic, repeatable, and being applied across a variety of disciplines.

### *Geochemical modeling*

Modeling and computer simulation is also an efficient approach for quantitative evaluation or prediction of some critical geochemical processes in subsurface or near-surface environments especially for long-term behaviors. In fact, modeling studies can provide valuable information for risk assessment associated with the effects of $CO_2$ introduced into subsurface environments. A variety of modeling parameters such as water–rock interaction, $CO_2$ solubility, reactive transport, reaction paths, and kinetics have been primarily used to examine the effects of $CO_2$ in subsurface systems. Several different codes (e.g., PHREEQC, TOUGHREACT, Geochemist's Workbench, and MINTEQ) have been used in the modeling studies (e.g., Altevogt and Jaffe 2005; Smyth et al. 2009; Song and Zhang 2012; Cahill and Jakobsen 2013). In addition, National Risk Assessment Partnership (NRAP) funded by US Department of Energy (US DOE) developed tools and approaches to quantitatively assess and predict the long-term behavior of CCS sites. This approach uses an integrated assessment model (IAM) that couples models for various CCS components in a stochastic modeling framework. Indeed, the NRAP-IAM was developed to simulate $CO_2$ injection, migration, and associated impacts at a geologic carbon storage site and to quantify leakage risk of $CO_2$ to the atmosphere and groundwater (Pawer et al. 2016). Table 5 summarizes the key results of some of the previous modeling studies that evaluated the impacts of $CO_2$ intrusion on the geochemistry of subsurface systems. For example, Humez et al. (2011) used a numerical code of TOUGHREACT to investigate the impacts of $CO_2$ leakage on water quality in terms of the chemical composition during $CO_2$ geological storage. $CO_2$ dissolution into the aquifer induced a pH drop, but the decrease in pH was limited due to buffering by calcite dissolution. Dissolution of glauconite in this aquifer resulted in a substantial increase in dissolved Si concentration from 0.21 to 11.2 mmol/kg near the intrusion point. Darcis et al. (2009) coupled light non-aqueous phase liquid (LNAPL) and isothermal three-phase (3p) models to

**Table 5** An overview of the geochemical modeling to monitor the impact of $CO_2$ intrusion on the geochemistry of subsurface systems

| General purposes | Modeling description | Observation | References |
|---|---|---|---|
| Mineral surface area and mobilization of trace metals | Inverse multi-component geochemical model | Mobilization of trace metals was due to mineral dissolution and surface complexation on clay mineral surface | Yang et al. (2014) |
| Impact of $CO_2$ on aquifer mineralogy and water chemistry | PATH.ubc and GeoCalc | Dissolution of calcite and adsorption of dissolved calcium on clays | Gunter et al. (1993) |
| Water–rock reactions in aquifers to sequester injected $CO_2$ waste | PATHARC model | Substantial trapping of $CO_2$ by formation of siderite, calcite, and aqueous bicarbonate ions | Gunter et al. (1997) |
| Problems in a $CO_2$ storage in geologic formations | GEO-SEQ Code | The problems deal with leakage through a leaky well, methane recovery, and a reservoir-scale injection scenario | Class et al. (2009) |
| Impact of $CO_2$ leakage on water chemistry | Reactive transport simulation model | Finding pH and carbonate chemistry as a good indicator for $CO_2$ leakage | Carroll et al. (2009) |
| Simplifying an approach for modeling post-combustion $CO_2$ capture with solvents | gPROMS®, an equation-oriented process modeling | The model significantly reduced CPU time (up to 60%) with reasonable model accuracy | Oko et al. (2015) |
| Impacts of leaking $CO_2$ on the water quality | TOUGHREACT model | A drop in aquifer pH and an increase in glauconite dissolution | Humez et al. (2011) |

reduce the model complexity for simulating $CO_2$ storage in saline aquifers and to increase the model efficiency. Elaine et al. (2009) estimated the physical and chemical changes induced by $CO_2$ injection in saturated near-surface zones under varying geological conditions by using numerical simulations employing a TOUGHREACT code. Their results demonstrated that the site-specific characterizations of soil, rock, and groundwater compositions were critical for quantifying water–rock interactions. Kim et al. (2017a, b) simulated geochemical evolution pathways of various $CO_2$-rich spring water (CSW) and carbonate water via equilibrium phase modeling (EPM) incorporated into PHREEQC code to interpret the carbonate–water–rock interactions in subsurface environments and connect them to the occurrence of surface CSW. For this, varieties of modeling conditions such as mixing ratios of the carbonate to shallow groundwater, temperature, and rock-forming minerals were considered. The simulation results demonstrated that a Na–$HCO_3$-type CSW was interpreted to be formed at a higher temperature range than a Ca–$HCO_3$-type CSW, indicating that a Na–$HCO_3$-type CSW was formed at a deeper depth. Therefore, modeling approaches could be applied to predict the behavior of $CO_2$ after its geological storage and to estimate the stability and security of geologically stored $CO_2$.

On the other hand, however, a major limitation of applying these modeling codes is that the technique requires reasonably complete and accurate chemical analyses, which are not always available (Bethke 1996). To increase the accuracy of geochemical modeling, it is crucial to obtain constraints on the boundary and the initial conditions that are as close as possible to the natural conditions. The geological complexity of the sites caused by diverse factors such as tectonic activities, variations in the pressure and temperature conditions, displacement, leakage and recharge history of $CO_2$, and changing groundwater flow regimes creates extreme difficulties in reconstructing $CO_2$ evolution in the host rock.

Moreover, although geochemical modeling has the advantage of covering a wide range of spatial and temporal scales (Song and Zhang 2012), most of the modeling studies are generally subject to considerable uncertainty inherent in the model parameters (e.g., effects of bacterial communities, mineralogy, chemical kinetics, and physicochemical heterogeneity in the subsurface environment). For these reasons, it has been very difficult to create simulations that can precisely predict the occurrence and the effects of $CO_2$ leakage in subsurface systems.

## Knowledge gaps and future challenges

Research on near-surface environments addresses not only the safety, but also the feasibility of a $CO_2$ storage system. In this context, the following topics can be identified.

- Most of the previous studies have focused on the impacts of $CO_2$ leakage on saturated soil or aquifer conditions; thus, a lack of knowledge exists on unsaturated or partially wet soil conditions. The impact of soil moisture content on the intrinsic effect of $CO_2$ leakage on the physicochemical properties of shallow soil needs to be addressed.
- Microbial influence and activities have not been completely understood. Because the effects of microbial activity on the mobility of metal(loid)s depend largely on the types and populations of the microbial community present in the local sediment or soil, investigations on the microbial processes associated with $CO_2$ leakage should be conducted.
- Previous studies have focused mainly on the $CO_2$-induced changes in pH, and only a few studies have addressed geochemical changes in the presence of redox-sensitive minerals or elements. For example, Carroll et al. (2009) recognized the potential changes of redox conditions and emphasized the need of coupling $CO_2$ plume modeling with laboratory experiments under a variety of redox conditions.
- Most of the previous studies investigated soil/water chemistry induced by $CO_2$ emission in a short period of time. For instance, Patil (2012) and Moonis et al. (2017) investigated soil mineralogy under an elevated $CO_2$ concentration for $< 3$ months. They have not been able to find any changes in soil mineralogy. However, results of a natural site (exposed to $CO_2$ for a considerable period of time) presented a change in soil mineralogy (Zhao et al. 2017). Hence, impacts of $CO_2$ leakage on the mineralogy of varieties of contaminated soils in a suitable period of time should be well estimated.

- There is a lack of information about soil–plant–groundwater interactions induced by $CO_2$ leakage. Previous studies individually investigated plant response, soil properties, and groundwater chemistry at an elevated $CO_2$ concentration. So, there is no comprehensive study which collectively addresses the soil–plant–groundwater relationships and the corresponding changes under elevated $CO_2$ conditions.
- Experimental data on how the rate of $CO_2$ leakage can impact the geochemical changes in groundwater or shallow soil are still limited. In this regard, only a few studies (e.g., Carroll et al. 2009; Zheng et al. 2009b; Vong et al. 2011) have investigated the impact of $CO_2$ intrusion rate on aquifer geochemistry using geochemical modeling programs as they emphasized the importance of $CO_2$ intrusion rate and its effect on pH.
- Most of the modeling studies are generally subject to considerable uncertainty inherent in the model parameters. Those uncertainties in the model parameters should be improved by accurate and reliable results obtained from well-controlled laboratory and field tests. Therefore, it is necessary to integrate and improve modeling approaches with laboratory and field experiments to benefit our understanding of the mechanisms that dominate the responses of $CO_2$-induced interactions in near-surface environments.

## Summary and conclusions

$CO_2$ intrusion in subsurface soil can affect the pH and may cause the migration and transfer of constituents of concern (e.g., soil nutrients or contaminants), leading to degradation of the surrounding environment (e.g., potable aquifers and near-surface soil). It is important to identify the geochemical processes related to $CO_2$ in subsurface soil, based on geochemical research approaches at both field and laboratory scales. The present study reviewed several important advantages and disadvantages of these approaches as well as geochemical changes induced by $CO_2$ intrusion in near-surface environments. The results are summarized in the following points.

1. When assessing the efficiency of CCS to mitigate climate change, evaluation of the possibility of any gas leakage from storage sites is crucial. Potential pathways of $CO_2$ leakage are attributed mainly to the cap rock properties, fracture networks, and faults in addition to wells or abandoned wells. Subsequently, $CO_2$ leakage would induce changes in pH and Eh and trigger a chain of geochemical reactions in near-surface soil.
2. For any risk assessment program associated with CCS, important issues include the reliability of single stations as well as comprehensiveness of the measured parameters. For the proper site selection and management in CCS studies, factors such as geological settings, aquifer features, soil and mineral compositions, and salinity should be considered.
3. Among the geochemical research approaches, laboratory studies are cost-effective and relatively easy to test to effectively identify the $CO_2$-induced geochemical reactions. Generally, experimental results can be applied as parameters in the geochemical modeling programs, which can mutually aid in properly designing experiments and analyzing the experimental results. Additionally, isotopic tracers can highlight the different processes occurring in natural or laboratory systems during $CO_2$ intrusion, and laboratory results can elucidate the characteristics of isotopic compositions in different geochemical processes. Therefore, a combination of these tools can be used as a reliable indicator for risk management associated with CCS.
4. Despite the numerous previous investigations, knowledge gaps still exist in this research area. Particularly, there is neither a clear definition of “acceptable” $CO_2$ concentrations or thresholds in typical ecosystems found in the near-surface areas surrounding storage reservoirs, nor have the criteria for suitable $CO_2$ concentrations for specific ecosystems been identified. For example, the emission scenarios including the worst and the most likely cases should be clearly defined and the effects of $CO_2$ on plant response varying with taxa and $CO_2$ level should be monitored. In addition, there is currently a lack of integration between the performance assessment of $CO_2$ sequestration through CCS and the assessment of the potential impacts of $CO_2$ leakage on terrestrial ecosystems. Thus, the CCS technology selected depending on site characterization (i.e., the integrity of the host

and cap rocks), assessment of geochemical interactions induced by $CO_2$ leakage, and research approaches must be well controlled to be able to certify that the site can harmlessly and securely store $CO_2$. Therefore, identifying the knowledge gaps and improving risk assessment associated with $CO_2$ leakage can aid scientists in making better decisions for CCS projects.

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