Potential impacts of leakage from CO$_2$ geological storage on geochemical processes controlling fresh groundwater quality: a review

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Abstract

Leakage of CO₂ or brine coming from CO₂ geological storage sites constitutes a risk for overlying fresh groundwater resources. One of the main risks is the potential alteration of groundwater quality by the intrusion of contaminants such as trace elements. This paper reviews studies that address the potential impacts of CO₂ geological storage leakage on fresh groundwater quality. Leakage can directly modify the chemical properties of fresh water (pH, redox potential, chemical composition) and, as a result, indirectly modify the effect of biogeochemical processes controlling trace element availability. The ability of a CO₂ or brine leak to introduce or mobilize trace elements and potentially degrade the quality of water in an overlying aquifer depends on the composition and quantity of the leaking fluids, the nature of the solid phases making up the aquifer (buffering and scavenging capacity) and the concentrations of undesirable or toxic elements that can be mobilized following any such modification. Furthermore, hydrogeological conditions will control the potential dissemination into groundwater. To date, studies have shown that trace elements can be significantly mobilized without necessarily exceeding quality thresholds. In a few cases where aquifers are naturally rich in trace elements (i.e., whose natural concentrations in groundwater are already high), CO₂ is able to mobilize these trace elements (e.g. Fe, Mn, Ni, As, Ba, U) and increase concentrations up to or exceeding threshold values.

This literature review provides a return on experience essential for both assessing biogeochemical risks prior to the installation of future CO₂ geological storage sites and designing and installing fresh groundwater quality monitoring networks.

Keywords: CO₂ geological storage, groundwater quality, trace element, fresh groundwater, CO₂ leakage, microbial activity, CCS.
1. Introduction

One of the issues related to the emerging technology for Carbon Capture and Storage (CCS) is the risk that CO₂ or formation waters (e.g. brines) will move out of the deep geological storage formation. This is often cited as a risk for overlying fresh groundwater resources – a risk that has been insufficiently studied (Birkholzer et al., 2007, 2008; IEAGHG, 2011a). When selecting and characterizing sites suitable for CO₂ geological storage, we must ensure CCS viability and long term safety by correctly evaluating the sealing capacity and integrity of the cap rock (Song and Zhang, 2013). This evaluation must also consider the juxtaposition of storage reservoirs with groundwater resources at the regional scale and the assessed potential impacts (IEAGHG, 2011a).

To date, the geochemical impact of CO₂ storage on water composition has mainly been studied at the near-well and reservoir scales within the storage formation (e.g. André et al., 2007; Audigane et al., 2007; Gaus, 2010), whereas geochemical impacts in the larger context of regional shallow groundwater systems have yet to be assessed. Although there are several CO₂ injection and storage sites where the formation water is being monitored (Emberley et al., 2005; Shevalier et al., 2013; Caritat et al., 2013), no impacts have been observed in the shallow groundwater and therefore no effects can be directly studied above these storage sites. These effects have been monitored only during controlled release experiments (Kharaka et al., 2006; Assayag et al., 2009; Trautz et al., 2013; Cahill and Jakobsen, 2013; Kharaka et al., 2010) and on natural analogues (Keating et al. 2010; Lions et al., 2013). Until recently, the potential impact on drinking water quality has been the subject of few reviews (IEAGHG, 2011a; Lemieux 2011; Harvey et al., 2012). The difficulty in understanding the fate of chemical elements in the case of shallow aquifers is due mainly to the diversity of the biogeochemical mechanisms involved (Chapelle, 2000; McMahon, 2001; Flynn et al., 2012; Noble et al., 2012; Harvey et al., 2012). In fact, the movement of solutes in groundwater is affected by several factors: advection, dispersion, diffusion and biogeochemical reactions. In order to predict the impacts of CO₂ or brine leakage in groundwater it is therefore important to consider hydrogeology (for more details, see Lemieux, 2011 and IEAGHG, 2011) and water-rock-interactions i.e. the distribution of trace elements in solid, aqueous and gaseous phases and the biogeochemical processes such as adsorption/desorption, precipitation/dissolution and microbial metabolisms.

In this paper, we discuss the geochemical processes that must be considered if we wish to correctly evaluate the potential impacts of CO₂ geological storage leakage on fresh groundwater quality mainly by the mobilization of trace elements. We describe the direct effect of CO₂ leakage on the major chemical properties and the consequences on the variations in microbial diversity and activity (CO₂ fixation) and the geochemical processes controlling the mobilization of contaminants. We report results obtained using three methodological approaches: on-site observations of natural analogues, observations at the laboratory scale or field-scale controlled release experiments, and numerical modelling.

2. Leakage pathways and shallow groundwater

Geological storage of CO₂ is foreseen in deep geological formations (> 800 m), most of which are either depleted hydrocarbon reservoirs or deep saline aquifers. Deep saline aquifers are the most prevalent of the formations favourable for geological storage and they represent an enormous potential storage capacity. Saline aquifers are porous formations saturated with salt water unsuitable for human consumption. Depending on the degree of salinity, Kharaka and Hanor (2007) categorised aquifers as fresh (Total Dissolved solid (TDS) < 1 g/L), brackish (1 to 10 g/L), saline (10 to 35 g/L) and
brine (TDS > 35 g/L or 100 g/L). The US EPA considers that aquifers containing water with a salinity that exceeds 10 g/L are not drinking water resources.

During the injection phase, the compressed supercritical CO₂ fills the pore space in the reservoir rock by displacing part of the fluids present in situ, which results in an increase in pressure. In addition, because CO₂ is less dense than the saturated water in the medium, it has a tendency to migrate upwards. Therefore, CO₂ will move under buoyancy and hydraulic potential forces. The risk is that CO₂ could migrate up through wells, faults or the cap rock (Benson et al., 2002; IPCC, 2005; Lemieux, 2011; Wildenborg et al., 2005). The presence of an efficient cap rock overlying the storage reservoir is therefore important in order to ensure that the CO₂ will remain confined deep underground (Oldenburg and Rinaldi, 2011).

The changes in pressure caused by the injection of CO₂ can propagate away from the injection point ahead of the migrating CO₂ and can modify the hydrodynamic conditions of aquifers in both time and space. Therefore, if the pressure caused by the injection of CO₂ is not properly controlled in the storage formation, the propagation of this pressure within the basin can modify the hydraulic gradients and thus alter formation water movement. In turn, it can modify both vertical flow across aquitards and horizontal flow within the storage formation, possibly to the extent that the transition zone between brine and fresh water will shift (IEAGHG, 2011a; Birkholzer et al., 2007; Lemieux, 2011; Nicot, 2008; Birkholzer et al., 2009; Yamamoto et al., 2009a,b).

Three main potential leakage pathways for CO₂ to aquifers are faults, wells and the cap rock and, in geological environments, leaking fluids can access them successively or simultaneously (Figure 1). Leakage by way of faults, fracture networks and wells can be rapid. Diffusive leakage through the pore space in the cap rock, on the other hand, is usually slow and very limited (Lewicki et al., 2007; Song and Zhang, 2013; IEAGHG, 2011b). While faults and fractures are among the principal potential fluid migration pathways to aquifers (IEAGHG, 2011a; Oldenburg et al., 2009; Song and Zhang, 2013), leakage through wells is often the main risk for CO₂ geological storage installations (Lemieux, 2011; Oldenburg and Lewicki, 2006). Leakage can occur through injection or monitoring wells, or through abandoned wells (e.g. Nordbotten et al., 2008; Humez et al., 2011) either at the interfaces between different completion materials or with the surrounding rock, or directly through the materials themselves if they are no longer impermeable (degraded cement, fissured or corroded casing, etc.) (e.g. Carey et al., 2007). Leakage by way of faults is particularly complex to predict because it involves the natural environment with complex properties. Furthermore, the presence of a fault does not necessarily mean that it is a potential leakage pathway because the fault might be impermeable and thus prohibit the migration of fluids to the aquifer.

There is a significant amount of research in the public domain describing how to predict and measure various leakage pathways out of the intended storage reservoir that will not be covered in this paper. We assume that if a leakage pathway could exist, this would enable either mobile CO₂ or CO₂ dissolved in formation water to enter shallow freshwater aquifer systems. This study covers the processes that would subsequently occur in the shallow system.
3. Changes in the chemical state of groundwater

In natural systems, the pH and redox potential are influenced by chemical reactions between the groundwater and aquifer materials or by mixing of different waters. These factors, in turn, control the chemical composition of the groundwater. The upward migration of CO$_2$ or CO$_2$-enriched brine to an overlying aquifer might directly impact the chemical state of the groundwater by directly modifying: (i) the pH, (ii) the chemical composition of the water, and (iii) the redox potential.

3.1. pH

Groundwater is in equilibrium with the gas (e.g. CO$_2$, O$_2$) that is naturally present, generally as dissolved gas (Appelo and Postma, 2005). The thermodynamic equilibrium between the gas and the groundwater depends on the pressure and temperature conditions in the system. In deep systems, the dissolution of CO$_2$ in the aqueous phase is notably enhanced due to higher pressure. Therefore, when CO$_2$ leaks or when CO$_2$-rich deep brines move upward, they mix with fresh water, causing an increase in dissolved CO$_2$ (CO$_2$(aq)), and hence in the carbonic acid (H$_2$CO$_3$) concentration in shallow groundwater. In neutral and alkaline aquifers, the introduction of H$_2$CO$_3$ is followed by its deprotonation, leading to a decrease in the pH in solution. An increase in the bicarbonate ion concentration (HCO$_3^-$) could lead to the oversaturation of water with respect to carbonate minerals and to the precipitation of secondary minerals (Druckemiller and Maroto-Valer, 2005; Kharaka et al., 2010).

Studies of the impacts of CO$_2$ leakage – several in situ and laboratory experiments, as well as modelling– have shown evidence of this drop in pH following CO$_2$ injection into a water-rock system (Trautz et al., 2013; Peter et al., 2012; Rillard, 2013; Kharaka et al., 2010; Lu et al., 2010; Little and Jackson 2010; Humez et al., 2013; Zheng et al., 2012; Zheng et al., 2009; Carroll et al., 2009; Birkholzer et al., 2008). Some examples of pH modifications are given in Table 1 to illustrate the very wide variety of cases that are obtained depending on the water-rock systems considered.
The protons introduced into the aquifer by CO\textsubscript{2} leakage might react with the various solid phases in the aquifer by precipitation/dissolution and adsorption/desorption that would consume them. As a consequence, the decrease in pH in the aquifer, i.e. increase in the H\textsuperscript{+} concentration in the aqueous phase, might be relatively moderate (Kharaka et al., 2010; Little and Jackson, 2010; Lu et al., 2010; Keating et al., 2010; Zheng et al., 2012; Rillard, 2013). For example, Lu et al. (2010) showed that the same CO\textsubscript{2} leak can cause various decreases in pH depending on the nature of the water-rock system involved. These authors reported a decrease in pH of around 1 unit in carbonate systems and up to 2 units in siliciclastic systems (Table 1). This shows that the protons introduced into the aquifer by CO\textsubscript{2} leakage can react with the mineral phases by dissolution or adsorption, instead of remaining in the aqueous phase.

The attenuation of the decrease in pH is particularly marked in aquifers that are rich in carbonate minerals. Indeed, in the presence of protons, carbonate mineral dissolution is thermodynamically very favourable and rapid. Carbonate dissolution also entails an increase in alkalinity by fostering an increase in the bicarbonate or carbonate ion concentrations. This increase in alkalinity leads to an increase in the intrinsic buffer capacity of the water in the aquifer (Kharaka et al., 2010). The decrease in pH caused by CO\textsubscript{2} leakage can also be buffered in siliciclastic aquifers. The protons introduced by CO\textsubscript{2} leakage can also be consumed by dissolution and/or precipitation involving oxides, sulphide minerals, feldspar or even clay and gibbsite (Kjoller et al., 2004).

Table 1: Evolution of pH measurements in the laboratory, observed in situ or modelled by geochemical calculations following CO\textsubscript{2} injection in fresh groundwater

<table>
<thead>
<tr>
<th>CO\textsubscript{2} experiments</th>
<th>Aquifer systems</th>
<th>pH drop</th>
<th>References</th>
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<tbody>
<tr>
<td><strong>In situ experiments</strong></td>
<td></td>
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<tr>
<td>5,700 ppm as dissolved CO\textsubscript{2} (30 days)</td>
<td>Confined sandy aquifer (Flow rate: 0.01 to 0.02 m/d)</td>
<td>~ 2.4-2.9 pH units</td>
<td>Trautz et al., 2012</td>
</tr>
<tr>
<td>787 kg of CO\textsubscript{2} (10 days)</td>
<td>Quaternary sandy, aquifer (Flow rate: &lt;0.1 m/d to 1 m/d)</td>
<td>~ 0.8-1.8 pH units</td>
<td>Peter et al., 2012</td>
</tr>
<tr>
<td>6 kg of CO\textsubscript{2} (0.5 day)</td>
<td>Shales and sandstone fissured aquifer</td>
<td>~ 1.3 pH units</td>
<td>Rillard, 2013</td>
</tr>
<tr>
<td>300 kg/d of CO\textsubscript{2} (30 days)</td>
<td>Alluvial deposits (Flow rate: ~ 2 m/d)</td>
<td>~ 1-1.3 pH units</td>
<td>Kharaka et al., 2010</td>
</tr>
<tr>
<td>45 kg of CO\textsubscript{2} (2 days)</td>
<td>Aeolian and glacial sands (0.04 to 0.08 m/d)</td>
<td>~ 1.5 pH unit</td>
<td>Cahill and Jakobsen, 2013</td>
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<td><strong>Laboratory experiments</strong></td>
<td></td>
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<tr>
<td>CO\textsubscript{2} bubbling (15 days)</td>
<td>9 sediment from carbonate and non-carbonate aquifers</td>
<td>~ 1.5-2.2 pH units (without carbonates) ~ 1.5-2.5 pH units (with carbonates)</td>
<td>Lu et al., 2010</td>
</tr>
<tr>
<td>pCO\textsubscript{2}=1 bar (300 days)</td>
<td>17 sediments from sandy aquifers</td>
<td>~ 1 to 2 pH units</td>
<td>Little and Jackson 2010</td>
</tr>
<tr>
<td>pCO\textsubscript{2}=2 bar (30 days)</td>
<td>1 sediment from sandy non-carbonate aquifer</td>
<td>~ 2.8 pH units</td>
<td>Humez et al., 2012</td>
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<tr>
<td><strong>Modelling</strong></td>
<td></td>
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<tr>
<td>Range of pCO\textsubscript{2}; from 0.2 to 1.4 bar</td>
<td>Unconfined sandy aquifer (ZERT field site)</td>
<td>~ 1.7 pH units (groundwater only) ~ 1 pH units (mineral interactions)</td>
<td>Zheng et al., 2012</td>
</tr>
<tr>
<td>2.36 tons of CO\textsubscript{2}/year (6.5 kg/d)</td>
<td>Confined carbonate, sedimentary aquifer (Flow rate: 0.03 m/d)</td>
<td>~ 1.5 pH units</td>
<td>Zheng et al., 2009</td>
</tr>
<tr>
<td>10\textsuperscript{10} to 10\textsuperscript{15} tons of CO\textsubscript{2}/year (3 \times 10\textsuperscript{10} to 3 \times 10\textsuperscript{15} kg/d)</td>
<td>Confined non-carbonate, sedimentary aquifer (Flow rate: 0.3 m/d)</td>
<td>~ 2 pH units</td>
<td>Carroll et al., 2009</td>
</tr>
<tr>
<td>2.36 tons of CO\textsubscript{2}/year (6.5 kg/d)</td>
<td>Carbonate, sedimentary aquifer (Flow rate: 0.03 m/d)</td>
<td>~ 2 pH units</td>
<td>Birkholzer et al., 2008</td>
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</table>
Consequently, CO₂ leakage might not modify much the pH of groundwater depending on: (i) the abundance of minerals whose dissolution might consume protons and (ii) the kinetics of these reactions. Dissolution and precipitation rates depend on both the intrinsic properties of the minerals (Gaus et al., 2008) and the water flux in the aquifer.

The results obtained by in situ and laboratory experiments showed that the ability of an aquifer to attenuate the decrease in pH does not depend on the clay or oxide concentrations but rather on the carbonate concentrations in the mineralogical assemblage (Assayag et al., 2009; Lu et al., 2010). Therefore, for siliciclastic aquifers with limited amounts of carbonate minerals, the protonation of the hydroxyl surface groups with variable charges at the surface of some minerals does not buffer the decrease in pH caused by CO₂ leakage as expected in a carbonated aquifer or in the presence of secondary calcite. Zheng et al. (2012) have shown, for example, that taking into account protonation alone results in an overestimation of the decrease in pH compared to values measured during an experimental CO₂ leak carried out at the aquifer scale. Their modelling showed that the weak capacity of protonation to buffer the decrease in pH in an aquifer is related to two characteristics: (i) the concentration of variable-charge adsorption sites that is relatively limited in aquifers and (ii) the electrostatic repulsion interactions associated with protons already adsorbed, in agreement with the diffuse double layer theory (Appelo and Postma, 2005). The more protonated the hydroxyl groups are, the less adsorption of new protons at the surface of the charged solid phases there is.

Therefore, as it is directly modified by CO₂ leakage, pH might initially be considered to be a parameter for monitoring purposes. However, beyond the technical issues related to the measurement of the pH in situ (Millero, 1995; French et al., 2002), pH must be used carefully. This parameter enables us to detect an intrusion of CO₂ or CO₂-brine, but its variation is controlled by the quantity of protons released (Zheng et al., 2012; Carroll et al., 2009). Depending on the geochemical system concerned and for small CO₂ release, the pH variation of might be not sufficient to be detected.

Alkalinity has also been used as a monitoring parameter (Gal et al., 2013). However, the alkalinity of a solution is not necessarily modified by CO₂ leakage since the deprotonation of the carbonic acid causes a simultaneous increase in the bicarbonate- or carbonate-ion and proton concentrations. In this case, the water-rock interactions, rather than the CO₂ itself, will induce a modification of the alkalinity.

Several equations have been developed to better characterize the drop in pH caused by CO₂ leakage. For example, Appelo and Postma’s equation (2005) makes it possible to correlate the CO₂ partial pressure, bicarbonate ion concentration and pH in shallow groundwater. However, these equations do not take into account the buffering capacity of the aquifer to attenuate this variation.

3.2. Mixing with deep brines

The potential upwelling of deep brine into fresh water could be one consequence of CO₂ storage (Figure 1). The mixing of these waters can have direct consequences on the chemical composition and associated salinity of the fresh water (IEAGHG 2011a; Bonnesen et al., 2009).

Deep brines alter the quality of fresh groundwater by introducing the contaminants that they naturally contain. Formation water in deep sedimentary aquifers usually contains large quantities of halides (F, Cl, Br, I). These brines also naturally contain trace elements such as Al, Fe, Mn, Pb, Zn, Cu, U and As (Hem, 1985; Yardley et al., 2003; Kharaka and Hanor, 2007; Birkholzer et al., 2008; Keating et al., 2010). In these highly mineralized environments, trace elements can exist in high concentrations as free ions or as complexes formed with dissolved organic matter, bicarbonate, chloride and fluoride, which increases their mobility. Several studies modelled saline water
displacement from CO₂ geological storage into overlying aquifers (Bandilla et al., 2012; Birkholzer et al., 2009; Jung et al., 2013; Walter et al., 2012; Carey et al., 2010).

Supercritical CO₂ (SC-CO₂) is known to be an excellent solvent of non- to moderately-polar organic compounds depending on temperature and pressure (Burat et al., 2012; Scherf et al., 2011). Therefore, in the context of CO₂ geological storage, knowledge of the types and amounts of organic matter that will be extracted and mobilized from the reservoir rocks and that might be transported by the formation fluids following the injection of SC-CO₂ into a saline aquifer is particularly important. Increased concentrations of organic acids and dissolved organic carbon (DOC) have been described in formation waters from the Frio Formation after the injection of CO₂ (Kharaka et al., 2006; 2009) and during Enhanced Oil Recovery (EOR) operations (Shiraki and Dumm, 2006). Therefore, the mobilization of organics, including BTEX and other toxic organics from non-oil-bearing saline aquifers, could have major implications for the environmental aspects of CO₂ storage and containment.

Any mixing with saline waters induces an increase in the TDS in groundwater. The TDS of natural waters can be measured using standard gravimetric techniques or conductivity/TDS meters. The specific conductance (electrical conductivity) of groundwater is directly related to the TDS based on the assumption that TDS in the water consist mainly of ionic constituents that conduct electricity. This is easy to measure, even in deep wells. This parameter should therefore be measured, and studying its vertical distribution could help to identify any saline intrusion as long as the brine is not diluted downstream when mixing.

### 3.3. Oxidation Reduction Potential

The redox status of the groundwater controls the chemical speciation of many chemical elements (e.g. Fe, Mn, As) and also influences the microbial ecology and metabolism. Redox reactions are almost always facilitated by bacteria that are able to gain energy from the reactions (e.g. sulphide oxidation). The redox potential can be correlated with the amount of dissolved oxygen. As the oxygen content drops, the environment becomes more reducing (the redox potential drops).

In unconfined aquifers, groundwater can be either oxic in the upper part of the aquifer where the redox potential is high and relatively constant, or anoxic at the bottom of the aquifer where the redox potential is lower and can change depending on the metabolic activity of microorganisms. It has been shown, however, that the redox potential in anoxic groundwater evolves very slowly because there is relatively little metabolic activity in these oligotrophic environments. Anthropic activities can modify the redox potential mainly by means of two mechanisms: (i) variation of the water table level and/or (ii) contamination by oxidizing or reducing components such as O₂, organic matter, CH₄, and HS⁻ (e.g. McMahon and Chapelle, 1991, 2008).

It seems to be generally accepted that the principal consequence of a rising water table on the redox potential of groundwater is observed where the unsaturated zone is flooded. In these newly saturated zones, the initial oxic conditions are replaced by anoxic conditions if the dissolution of O₂(g) in the water is not sufficient to compensate for O₂ consumption, leading to the decrease of the redox potential (Larsen and Postma, 1997; Appelo and Postma, 2005). It should be emphasized that the rising of the water table in overlying aquifers as a result of CO₂ geological storage seems limited, as shown by both industrial analogues such as natural gas storage sites and models, whereas the pressure can increase significantly in the storage formation (Kim et al., 2000; Yamamoto et al., 2009a,b; Nicot, 2008; Birkholzer et al., 2009; Mathias et al., 2009). Modelling has shown that the variations in the water table level that might occur during CO₂ injection into - or leakage from - the storage zone are similar in magnitude to natural variations and usually lower than those caused by groundwater withdrawal from aquifers (e.g. Birkholzer et al., 2007; Nicot, 2008). Monitoring
groundwater levels in two overlying aquifers above the Otway project site (Australia) has shown no effect of drilling, pumping and injection activities (Caritat et al., 2013).

The redox potential of the shallow groundwater could be probably modified by the introduction of oxidizing and/or reducing components in fresh water due to the leaking of deep brines or the formation waters of the units immediately adjacent to the shallow aquifer. Indeed, deep brines usually have a high concentration of dissolved organic compounds (acetate, formate) that can, once they have entered the fresh water, serve as energy sources for the endogenous microorganisms in these environments, which are, in most cases, oligotrophic. This increase in microbial metabolic activity results in a decrease in the concentration of electron acceptors such as oxygen in the aerobic zone. In anaerobic aquifers, increased concentrations of acetate and formate may lead to increased iron reduction, sulphate reduction and/or methanogenesis (McMahon and Chapelle, 1991, 2008), thereby affecting the existing redox state of the aquifer.

The redox potential can also be modified by the intrusion into fresh water of substances associated with the flux of migrating CO₂ in the event of gas leakage. In this case, co-injected substances can be strong oxidizing (i.e. O₂, SOx, NOx) or reducing (i.e. H₂S) agents. To the best of our knowledge, no studies have been carried out to characterize the impacts of the co-injected substances on redox potential in overlying aquifers.

Evaluating redox conditions in groundwater can be done for monitoring aquifer conditions because they are clearly disrupted when the chemical status changes. Eh is a summary parameter that characterizes the tendency, although not the capacity, of a system to oxidize or reduce. However, redox data are rarely reported. Electrometric measurement of redox potential (Eh) and redox couples could be used to calculate Eh values. The common redox couples useful for this purpose are Fe(III)/Fe(II), As(V)/As(III) and S²⁻/SO₄²⁻ (Holm and Curtiss, 1989; Ramesh Kumar and Riyazuddin, 2012).

However, no standardised or generally accepted approach exists due to slow transfer of electrons in some of the redox couples mentioned above. Because these features make direct electrochemical measurements and rigorous interpretation of redox potential dubious, Eh values must be used with care (Grenthe et al., 1992; Christensen et al., 2000).

4. Microbial metabolism

In oligotrophic aquifers, bacteria (eubacteria and archaea) are predominant and have a strong impact on biogeochemical processes. Most of the microbial biomass in the basement is associated with mineral surfaces and components of the solid phases that form the bedrock (Goldscheider et al., 2006). Nevertheless, few studies have been carried out to assess the biological impact of CO₂ in shallow aquifers. As a result, only comparative approaches can be used to assess the importance of the biosphere during a leakage event. Because microorganisms are in contact with the chemical compounds in their surrounding environment and whose mobility is sensitive to pH variations, increasing CO₂ concentrations could lead to toxic and/or beneficial effects for microbes. As a result, community structures and functions can change (Noble et al., 2012). Leakage of CO₂ to an aquifer is also expected to have a negative effect due to its toxicity. CO₂ bactericidal activity is well known in the food industry (Garcia-Gonzalez et al., 2007; Xu et al., 2011). Moreover, in deep saline aquifers at higher pressures, some changes have been reported in the composition of autotrophic communities (Morozova et al., 2010; Dupraz et al. 2013).

In shallow aquifers, CO₂ could affect microbial activity in two ways: (i) by changing environmental conditions due to CO₂ dissolution, and (ii) by penetrating cells and interfering with their metabolic
functions (Wu et al., 2010). Schulz et al. (2013) have studied the effects of various CO\(_2\) concentrations on the growth and viability of aerobic and anaerobic microorganisms present in soil and fresh water (\textit{Pseudomonas putida}, \textit{Bacillus subtilis}, \textit{Desulfovibrio vulgaris}, \textit{Thauera aromatica}). Under atmospheric pressure, the growth of microorganisms is already affected – some bacterial species being more affected than others. For CO\(_2\) concentrations greater than 60 %, a 51 % decrease in the growth rate was observed for \textit{B. subtilis} and a decrease of between 85 and 87 % was observed for \textit{D. vulgaris} and \textit{T. aromatica}. When the pressure (1-50 bar) was combined with the CO\(_2\) concentration, the viability decreased by around 99 % for \textit{P. putida} and \textit{B. subtilis} and by 100 % for \textit{T. aromatica} and \textit{D. vulgaris}. In addition to the pH effect, CO\(_2\) is also a stress factor for cells. Indeed, under high pressure, CO\(_2\) can diffuse through cell membranes and dissolve in the cell due to the membranes hydrophobic and liposoluble properties. This can increase membrane permeability, destroy cell integrity and modify the metabolic equilibrium (Wu et al., 2010; Garcia-Gonzalez et al., 2009).

An increase in the CO\(_2\) concentration in groundwater might also stimulate the bacterial microflora in the aquifer. Indeed, in these environments, there is often little organic carbon. Since there is competition for the small quantities of organic carbon and rare energy sources, chemolithoautotrophy is one of the major metabolisms occurring in those environments. In this process, chemical species like H\(_2\), NH\(_4^+\), NO\(_2^-\), S\(_2\)O\(_3^{2-}\), H\(_2\)S, S\(_0\), Fe\(^{2+}\), Mn\(^{2+}\) act as electron donors. If present, they enable the growth of microorganisms while CO\(_2\) is the only source of carbon (Alfreider et al., 2003; Goldscheider et al., 2006; Berg, 2011). An increase in the CO\(_2\) concentration, without exceeding the toxic level of 10 % (Videmsek et al., 2009) and provided that electron donors are available, could cause a change in the biogeochemical equilibrium of elements such as oxygen, hydrogen, sulphur and carbon associated with the modification of the microbial community in groundwater. Microorganisms can develop CO\(_2\)-based metabolism using CO\(_2\) as a carbon source for biosynthesis and inorganic compound oxidation as an energy source. Ribulose-1,5-bisphosphate carboxylase/oxygenase (RubisCO), the enzyme responsible for CO\(_2\) fixation among certain hydrogenotrophic microbes, was detected in various groundwater systems. It has been shown that this metabolism is widespread in microorganisms living in groundwater systems (Alfreider et al., 2009). All these interactions across the carbon cycle (assimilation) and the scale of the cell (toxic) summarize the possible expected direct effects of the biosphere on the aquifer. Using a microbial energetic approach to evaluate the use of CO\(_2\) by lithoautotrophic bacteria following an increase in CO\(_2\) concentration in an aquifer, West et al. (2011) showed that the energy available for microbial methanogenesis from direct pyrite oxidation was not sufficient but some intermediate S and H\(_2\)S oxidation reactions could occur and provide sufficient energy for microorganisms.

According to Kirk (2011), a thermodynamic view of the physico-chemical data from the ZERT experiment, which focused on 3 microbial pathways: Fe(III) reduction, SO\(_4\) reduction, and methanogenesis, shows that a variation in the bulk chemical composition of groundwater due to CO\(_2\) leakage could benefit Fe(III) reduction more than to the 2 other microbial processes studied. This modification of microbial activity could have an impact on other biotic and abiotic pathways for trace elements mobility following CO\(_2\) injection. Kirk et al. (2013) have provided a measure of extent to which variation in CO\(_2\) abundance influenced chemistry and microbial activity. Iron reduction leads to increased dissolved CO\(_2\) trapping due to the corresponding increase in alkalinity compared to metabolic sulphate reduction. In contrast to the benefit of enhanced CO\(_2\) trapping, the elevated rate of Fe(III) reduction in the high-CO\(_2\) reactors negatively impacted water quality.

Deep biological monitoring would be difficult, even if it appears to be relatively feasible in shallow aquifers (Noble et al., 2012), and only a few biological monitoring tests have been done. The contribution of the biosphere to the impact of CO\(_2\) leakage needs to be assessed properly. Microbial characterization might reveal changes in microbial activities due to CO\(_2\) leakage, but baseline surveys must first be done to make these methods efficient owing to natural variability and seasonal or
climatic variations. The next critical stage for developing the biological monitoring of CO₂ geological storage is to determine the correlation between the modification in the expression of functional genes and dissolved CO₂ changes due to potential deep CO₂ geological storage leaks (Noble et al., 2012).

5. Impacts of CO₂ leakage on contaminant mobility in fresh groundwater

The principal risk to water quality associated with CO₂ geological storage is the transport into or mobilization of contaminants within fresh water aquifers and notably contaminants in quantities that exceed drinking water standards (DWS) (IEAGHG, 2011c; Harvey et al., 2012). According to the WHO (2011), these contaminants fall into two categories: (i) chemicals that are of health concern in drinking-water (e.g. As, Cd, Cr, Hg, Ni, Pb, Se) and (ii) those that are not of health concern although their presence might lead to complaints by consumers (e.g. colour, taste), but for which there is no proven risk or the probability of risk is zero (e.g. Al, Ba, B, Cu, Fe, Mn, F, Zn, Sb). Certain major elements such as chloride and sulphate can be included in this second category.

These risks are often related to the possible upward migration of deep saline formation water into fresh groundwater. However minor and trace elements can be mobilized in the fresh water aquifer itself or in the CO₂ reservoir via the intrusion of CO₂ and subsequent changes to pH.

Indeed, trace elements can be present naturally in groundwater (geochemical background) and their concentrations can, depending on conditions, naturally exceed regulatory thresholds (Little and Jackson, 2010). These contaminants are naturally present in the rocks that make up the aquifers and their concentrations vary depending on the lithology and the geological context under consideration. A broad description of natural occurrences of minor elements in rocks, and sea water for comparison, is given in Table 2 (Hem, 1985).

These contaminants are present both within the minerals and on the surface of the constituents that have adsorption surface sites such as oxy-hydroxides, organic matter or clays (Table 3). The chemical properties of water can be more important in controlling the concentrations of an element than the total content in the surrounding rocks.

5.1. Contaminant mobilization

Through its direct effects on the chemical properties of groundwater, CO₂ intrusion could modify the geochemical equilibrium, leading to the release of the trace elements present in the rock, depending on their potential mobility.

Concerning the mobilization of trace elements induced by the injection of CO₂ in shallow groundwater, several in situ laboratory and modelling studies have shown that elements such as Al, Fe, Mn, Ni, Zn, Co, Cd, Sr, Se, As, Ba, B and U can be significantly mobilized without necessarily exceeding quality thresholds (Birkholzer et al., 2008; Carroll et al., 2009; Apps et al., 2010; Kharaka et al., 2010; Little and Jackson, 2010; Lu et al., 2010; Humez et al., 2013; Peter et al., 2012; Viswanathan et al., 2012; Zheng et al., 2012; Trautz et al., 2013; Rillard, 2013; Cahill and Jakobsen, 2013). For each element, geochemical equilibrium could be modified by CO₂ intrusion. Indeed CO₂ could enhance the release of the initially sorbed element and/or the dissolution of mineral phases that contain it (Table 4).
Table 2: Average composition of igneous rocks and several types of sedimentary rocks and sea water (from Hem, 1985)

<table>
<thead>
<tr>
<th>Element</th>
<th>Igneous rocks</th>
<th>Sedimentary rocks</th>
<th>Sea-water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Resistates (sandstones)</td>
<td>Hydrolyzates (shales)</td>
<td>Precipitates (carbonates)</td>
</tr>
<tr>
<td>Cr</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
</tr>
<tr>
<td>Cu</td>
<td>97</td>
<td>1.5</td>
<td>45</td>
</tr>
<tr>
<td>Ni</td>
<td>94</td>
<td>2.6</td>
<td>29</td>
</tr>
<tr>
<td>Zn</td>
<td>80</td>
<td>16</td>
<td>130</td>
</tr>
<tr>
<td>Co</td>
<td>23</td>
<td>0.33</td>
<td>8.1</td>
</tr>
<tr>
<td>Pb</td>
<td>16</td>
<td>14</td>
<td>80</td>
</tr>
<tr>
<td>U</td>
<td>2.8</td>
<td>1</td>
<td>4.5</td>
</tr>
<tr>
<td>As</td>
<td>1.8</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>Cd</td>
<td>0.19</td>
<td>0.02</td>
<td>0.18</td>
</tr>
<tr>
<td>Hg</td>
<td>0.33</td>
<td>0.057</td>
<td>0.27</td>
</tr>
<tr>
<td>Se</td>
<td>0.05</td>
<td>0.52</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 3: Association of trace elements with the principal minerals (from Hem, 1985 and Wedepohl, 1978).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Minerals</th>
<th>Trace element-carrier phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>Chromite, silicate minerals and mafic rocks (pyroxene, amphibole, mica)</td>
<td>Fe oxi-hydroxides, clay minerals a</td>
</tr>
<tr>
<td>Cu</td>
<td>Carbonates, sulphides</td>
<td>Fe and Al hydroxides, organic matter, clay minerals b</td>
</tr>
<tr>
<td>Ni</td>
<td>Sulphides (pyrite, marcasite), Fe-Mg minerals (olivine, serpentine)</td>
<td>Fe and Mn hydroxides, clay minerals b</td>
</tr>
<tr>
<td>Zn</td>
<td>Carbonates (smithsonite), sulphides (sphalerite)</td>
<td>Fe and Mn hydroxides, clay minerals a</td>
</tr>
<tr>
<td>Co</td>
<td>Carbonates, cobaltite</td>
<td>Al hydroxide, clay minerals b</td>
</tr>
<tr>
<td>Pb</td>
<td>Orthophosphates, carbonates (cerussite), sulphides (galena), sulphates (anglesite)</td>
<td>Fe, Mn and Al hydroxides, clay minerals b, organic matter</td>
</tr>
<tr>
<td>U</td>
<td>Urannite, coffinite, brannerite</td>
<td>Fe hydroxides, clay minerals b</td>
</tr>
<tr>
<td>As</td>
<td>Sulphides (pyrite, arsenopyrite)</td>
<td>Fe and Al oxi-hydroxides, clay minerals</td>
</tr>
<tr>
<td>Cd</td>
<td>Sulphides (sphalerite, pyrite, galena)</td>
<td>Mn oxides, clay minerals b</td>
</tr>
<tr>
<td>Hg</td>
<td>Sulphides (cinnabar)</td>
<td>Fe oxy-hydroxides</td>
</tr>
<tr>
<td>Se</td>
<td>Selenites (ferroselite), sulphides</td>
<td>Fe oxy-hydroxides, organic matter</td>
</tr>
</tbody>
</table>

a 1:1 clay minerals: hydroxyl groups at the edge-surface of minerals are involved in adsorption reactions.
b 1:1 and 2:1 clay minerals: hydroxyl groups at the edge-surface of minerals and basal sites permanently-charged are involved in adsorption reactions.

Mn and Fe are the trace elements that are released in greatest abundance in the systems studied following the injection of CO₂ (Kharaka et al., 2010; Trautz et al., 2013; Lu et al., 2010; Little and Jackson, 2010; Humez et al., 2013). The mobilization of these elements is usually explained by the dissolution of the minerals that contain them. For example, Kharaka et al. (2010) showed that the increase in Fe concentration stems from the dissolution of carbonate minerals like siderite caused by acidification following CO₂ injection. In some field experiments, the increase in Fe and Mn could be explained by the creation of oxidative conditions in a reductive aquifer, leading to dissolution of Fe sulphides (Trautz et al., 2013; Rillard, 2013). This increase in the Fe and Mn concentrations occurs rapidly after the injection of CO₂ but it can decrease with time (see below), notably in oxidizing environments.
Laboratory and *in situ* tests, and modelling have shown that Ba and Sr are also strongly mobilized (Kharaka et al., 2010; Trautz et al., 2013; Lu et al., 2010; Viswanathan et al., 2012; Zheng et al., 2012). This is usually explained by the dissolution of carbonates after the pH decreases due to the injection of CO$_2$ because these elements are usually present in carbonate minerals. Since the dissolution kinetics of carbonate minerals are rapid, the increase in the Ba and Sr concentrations occurs shortly after CO$_2$ is introduced into the system.

Cd, Co, Cr and Ni are also mobilized in laboratory and *in situ* experiments (Little and Jackson, 2010; Humez et al., 2013; Kharaka et al., 2010). The concentrations of these contaminants increase just after CO$_2$ is introduced into the water-rock system. The mobilization of these contaminants seems to be explained by desorption from the Fe and Mn oxy-hydroxide phases and clay minerals. This desorption is caused by the decrease in pH as this change leads to (i) competition between protons and contaminants at the surface sites and (ii) a decrease in the affinity of the trace element-carrier phases for these positively-charged trace elements. After this initial increase, some tests have shown that the Cd, Co, Cr and Ni concentrations continue to increase steadily with time (Humez et al., 2013). This increase is controlled by the dissolution of the mineral phases containing the contaminants as a result of the decrease in pH (Table 3). The intensity and rate of this increase depends on the dissolution kinetics of the mineral phases involved.

Table 4: The main processes governing the mobilization or retention of trace elements after CO$_2$ intrusion in shallow aquifers

<table>
<thead>
<tr>
<th>Elements</th>
<th>Fe, Mn</th>
<th>Al</th>
<th>Se, As</th>
<th>Sb, Mo</th>
<th>Cr</th>
<th>Hg</th>
<th>Ba, Sr</th>
<th>Cd, Co, Ni</th>
<th>Pb, Cu, Zn</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolution of host mineral</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>(+)</td>
<td>++</td>
<td>+</td>
<td>+++</td>
<td>+</td>
<td>++</td>
<td></td>
</tr>
<tr>
<td>Desorption</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+++</td>
<td>+</td>
<td>+++</td>
<td>+++</td>
<td>++</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reduction</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Co)-precipitation</td>
<td>+</td>
<td>+++</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>(+)</td>
<td>++</td>
<td>++</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>+</td>
<td>+</td>
<td>+++</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td></td>
</tr>
<tr>
<td>Complexation with organic phases</td>
<td>++</td>
<td>(+)</td>
<td></td>
<td>(+)</td>
<td></td>
<td></td>
<td>++</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(+) not observed but could occur significantly

On the other hand, results obtained from laboratory and *in situ* experiments are contradictory for some trace metals – Pb, Cu, Zn, U – and for Al. Studies carried out under controlled conditions and the models that are associated with them have shown that these trace elements could be significantly mobilized (Little and Jackson, 2010; Lu et al., 2010; Humez et al., 2013; Viswanathan et al., 2012; Zheng et al., 2012). The mobilization of these trace metals might be mainly explained by the competition for surface sites by ion exchange (Montes-Hernandez et al., 2013). To a lesser extent, the dissolution of the trace metal-bearing mineral phases due to the decrease in pH might also contribute (Apps et al., 2010). In contrast, *in situ* studies have shown that Pb, Cu, Zn as well as Al are only weakly mobilized, if at all (Kharaka et al., 2010; Trautz et al., 2013; Cahill and Jakobsen,
In these studies, the low quantities remobilized can be explained by scavenging along the flowpath (see below) while both dissolution and desorption are artificially intensified under laboratory conditions.

Most of the field and laboratory experiments, as well as modelling, show very weak trace element mobility. Kharaka et al. (2010), for example, showed that Pb, Cd, Cu, Se, Al, As and Zn are mobilized in very small quantities, near the analytical detection limit. Trautz et al. (2013) have also shown that many trace elements (As, Pb, Se) remain below their detection limits, although the presence of As and Pb associated with pyrite in the rock is proven. These low quantities of remobilized elements can be explained by the complexity of the mechanisms that control the mobility of contaminants. Only one laboratory experiment (Little and Jackson, 2010), one modelling study (Apps et al, 2010) and one in situ injection (Rillard, 2013) have shown that CO₂ intrusion in shallow groundwater is able to mobilize some toxic trace elements with concentrations up to or exceeding WHO DWS (Ni, As and U in Little and Jackson, 2010; As and Zn in Apps et al., 2010; As in Rillard, 2013). This can be explained by the fact that these authors tested formations naturally rich in trace elements and therefore concentrations in groundwater are already very high (exceeding the WHO DWS).

Most studies of the impact of CO₂ leakage on the mobilization of contaminants focus mainly on the effect of pH. However, modifications in the redox potential and the intrusion of brines can also lead to the mobilization of trace elements. In spite of the limited number of studies available concerning shallow groundwater overlying CO₂ storage sites, we can extrapolate the consequences of redox potential on the mobilization of contaminants.

The decrease in the redox potential in zones that are initially oxidizing caused, for instance, by transient water table elevation or intrusion of reducing reagents/waters, can lead to the mobilization of trace metals (e.g. Ni, As) sorbed or co-precipitated on the Fe and Mn oxy-hydroxides surfaces due to the reductive dissolution of these carrier phases as observed by Larsen and Postma (1997). This decrease in the redox potential implies that the As, initially present mainly as As(V), changes, due to oxidizing conditions, into As(III), which also increases its mobility (Apps et al., 2010; Sharif et al., 2008). To date, the modification of the redox status by CCS has not been observed in aquifers overlying CO₂ storage sites and potential water table elevations are expected to be insignificant compared to natural variations (see above).

Oxidizing conditions could, however, appear in an aquifer in the event of leakage by the introduction of the oxidizing impurities that are associated with the stored CO₂, notably O₂ and SOx (Zheng et al., 2013; IEAGHG, 2011c). This increase in the redox potential in anoxic zones can lead to the oxidation of reduced minerals like sulphides (pyrite, arsenopyrite, etc.) and hence the mobilization of sulphates and associated trace elements (Table 3). The oxidation of sulphides would, in turn, lead to the precipitation of secondary phases, notably Fe-oxy-hydroxides that might scavenge dissolved elements. The composition of the intruding fluid will therefore influence the modification of the redox potential. Many experimental studies use food-grade CO₂ to assess the impacts of CO₂ leakage, but impurities could significantly impact the geochemistry of the system (Jacquemet et al., 2011; Zheng et al., 2013).

To the best of our knowledge, the evolution of dissolution and desorption reactions following a modification of the salinity of fresh groundwater by the upward migration of brines or saline water enriched with CO₂ has not been studied. It is widely accepted, however, that desorption and dissolution can be strongly affected by a modification of the chemical composition of the aqueous phase (Appelo and Postma, 2005). For example, an increase in the cation concentration (e.g. Ca) in the aqueous phase might foster desorption of cations initially adsorbed on surface sites due to competition (Lions et al., 2007). We might therefore presume that the intrusion of sodium-rich brines or saline water will enhance cation-exchange reactions and lead to desorption of the metallic trace
elements initially adsorbed. It is also important to note that any modification of the chemical composition induced by the dissolution of mineral phases can strongly affect desorption (Apps et al., 2011; Zheng et al., 2012). For example, simulations by Zheng et al. (2012) have shown that the dissolution of carbonate minerals and the release into solution of calcium results in desorption of various trace metals due to competition by Ca$^{2+}$ ions for surface sites. However, the quantity of metal released will depend directly on the quantity sorbed. The quantity released could be significant in sediments previously contaminated and negligible in natural systems.

5.2. CONTAMINANT SCAVENGING

The intrusion of CO$_2$ does not result systematically in the release of trace metals into the aqueous phase even when these are present in the solid phase (see Table 3).

In the case of negatively charged metalloid oxyanions (of As, Se, Cr, Mo and Sb), their concentrations usually decrease following the injection of CO$_2$ due to the decrease in pH (Little and Jackson, 2010; Viswanathan et al., 2012; Humez et al., 2013; Montes-Hernandez et al., 2013). These elements are known to be less mobile in oxic or slightly acidic water (Appelo and Postma, 2005). Moreover, the scavenging of these elements can also be fostered following the injection of CO$_2$. Indeed, by causing an increase in the protonation of surface sites, the decrease in pH means that the surrounding electrostatic field, notably for oxy-hydroxides under oxidizing conditions, will facilitate the adsorption of anions (Apps et al., 2010; Zheng et al., 2012). However, studies show that the scavenging of metalloids in response to CO$_2$ leakage cannot be generalized, but depends on the metalloid under consideration and on the availability of minerals to promote adsorption (Zheng et al., 2009; Montes-Hernandez et al., 2013). Zheng et al. (2009) observed an increase in As and Se concentrations in situ following the injection of CO$_2$ and found that the release of As was caused by the dissolution of the mineral phase containing the As induced by the decrease in pH (or by the increase in redox potential). However, As could not be entirely adsorbed on the surface of the oxy-hydroxides in spite of the increase in the affinity between the mineral phases and this contaminant under acidic conditions. For Se, these authors showed that HCO$_3^-$ or CO$_3^{2-}$ ions compete with Se and can result in the release into solution of the Se from the surface sites of the oxy-hydroxides. For As, this competition with HCO$_3^-$ or CO$_3^{2-}$ ions seems to have been shown not only by modelling (Apps et al., 2011) but also by laboratory and in situ experiments (Anawar et al., 2003; Saafield and Bostick, 2010). However, these results were obtained under alkaline pH conditions.

Studies have shown that the concentrations of some trace elements such as Ni, Cu, Cr, Fe, Mn and Al increased following CO$_2$ injection and subsequently decreased with time (Lu et al., 2010; Little and Jackson, 2010; Humez et al., 2013). This complex evolution might be explained by the fact that, in some water-rock systems, these contaminants are scavenged. These authors consider that the influx of CO$_2$ entails, first of all, a rapid increase in the contaminant concentration in the water due to the rapid dissolution of some mineral phases containing trace metals or a desorption of the trace metals initially adsorbed. Thereafter, the modification of the water composition results in the formation of secondary minerals that might scavenge the trace metals in solution or foster surface reactions. This decrease in trace metal concentrations is, in some instances, kinetically controlled by the precipitation rates of these secondary minerals.

Aside from any pH variation, the modification of the redox potential can also foster the scavenging of contaminants like Fe, Mn and As because the oxidized forms of these contaminants are less mobile than the reduced forms. Indeed, the increase in the redox potential in zones of an aquifer that were initially anoxic by the introduction of impurities associated with the stored CO$_2$, notably O$_2$ and SO$_x$, fosters the precipitation of oxic phases such as Fe and Mn oxy-hydroxides (IEAGHG 2011c). These phases offer surface sites that also enable the scavenging of metals and As (Appelo and Postma,
No clear correlations have been determined between Fe, Mn and Sr concentrations and bicarbonate concentrations in CO₂ injection studies (Zheng et al. 2012). However, results obtained in aquifers naturally rich in CO₂ seem to indicate that the increase in bicarbonate concentration promotes Fe, Mn and Sr scavenging by leading to the oversaturation of the water in carbonate minerals and the precipitation of secondary minerals that contain these contaminants (Pentecost, 2005). These results from natural analogues suggest that trace metal scavenging depends on the quantity of carbonate minerals that precipitate, which can vary from several concretions at the source to deposits up to several meters thick over large areas in the case of travertine precipitation (Matsuoka et al., 2001; Crossey et al., 2006; Brogi and Capezzuoli, 2009; Golubic et al., 2008; Zentmyer et al., 2008). The precipitation of these carbonate minerals in these systems can be caused by two mechanisms (Golubic et al., 2008). The first of these is the decrease in the partial pressure of the water when it reaches the surface and/or the increase in the velocity and turbulence of the water flux at the outlet of the aquifer (i.e. springs) compared to conditions within the aquifer, which implies a decrease in the solubility constant of the carbonate minerals. In high-temperature groundwater (T > 60 °C), the decrease in temperature as the water rises to the surface also fosters the decrease in solubility of the carbonate minerals, facilitating their precipitation. The second mechanism is the production of carbonate deposits by endogenous autotrophic microorganisms near the spring. These results suggest that the decrease in the concentration of contaminants associated with the precipitation of secondary carbonate minerals in aquifers impacted by CO₂ leakage depends on the state of saturation of these waters with respect to these minerals. Therefore, a natural attenuation associated with the precipitation of secondary minerals is expected as the pH is being buffered.

6. Gaps and future perspectives

The potential degradation of groundwater quality has been shown to be related to a diversity of changes that can occur in shallow aquifers impacted by CO₂ leakage and co-injected substances or brines. Indeed, CO₂ or brine leakage can, on the one hand, directly modify the chemical properties of fresh water (pH, redox potential, salinity), and on the other hand, induce an indirect evolution of biogeochemical processes as a result of the modification of the chemical properties of the aqueous phase, which can lead to both the mobilization and the scavenging of trace elements.

Laboratory studies have shown that, depending on the pH and the buffer capacity of the solid phase, elements such as Al, Fe, Mn, Ni, Zn, Co, Cd, Sr, Se, As, Ba and U can be significantly mobilized without necessarily exceeding drinking water standards. To date, it has been demonstrated that CO₂ leakage is able to mobilize Fe, Mn, Ni, As, Ba and U with concentrations up to or exceeding WHO DWS for sediments that are naturally rich in trace elements whose natural concentrations in groundwater are already high. In situ tests, however, show very weak trace element mobility although the presence of trace elements (As, Pb) associated with rock minerals is proven. These low quantities of remobilized elements can be explained by the complexity of the mechanisms that control the mobility of contaminants. In fact, the mobility of trace elements is reversible, influenced by the evolution of the physicochemical properties of the solution during and after leakage. It is therefore necessary, when considering the mobility of contaminants, to take into account reaction kinetics (pH buffer effect, mineral dissolution and precipitation of secondary phases) in time and space along the flowpath of the potential plume.

Most of the laboratory studies of water-rock-CO₂ interactions have been done over short time periods of between 15 days and 1 month (Lu et al., 2010; Humez et al., 2013) or, at best, 300 days (Little et Jackson, 2010). In addition, the reactivity of water-rock interactions measured in the
laboratory following the injection of CO$_2$ is usually much greater than what is observed at the experimental site scale. Indeed, the dissolution of minerals, including carbonates, is amplified at the laboratory scale because laboratory conditions (grinding, stirring, etc.) foster water-rock interactions. Batch experiments do not take into account reactive transport as it occurs in an open system like a column experiment within which there is flow. Therefore, batch experiments do not make it possible to evaluate the mechanisms that occur in the aquifer along the flow path, downstream from the CO$_2$ injection point. The water-rock interactions that occur downstream from a leak will, for example, buffer the pH, which can then result in the precipitation of secondary minerals and the scavenging of trace elements.

In the laboratory, the use of natural solid samples makes it possible to create more realistic conditions (Lu et al., 2010). However, rock samples collected deep underground are sometimes contaminated by drilling fluids, which limits their use in the laboratory. Interactions with the atmosphere also make it difficult to study reducing systems not only in the laboratory, but also in situ during drilling. Any subsequent modification of redox conditions can give a bias to the results obtained for the behavior of trace elements, notably for elements such as Fe, Mn and As, by attributing to CO$_2$ consequences that are, in fact, caused by unsuitable experimental conditions (e.g. sulphides oxidation and oxides precipitation). Finally, the results obtained are strongly case specific, which limits their generalization. In spite of this, these mechanisms are well understood and it is possible to identify the potential impacts of CO$_2$ on groundwater quality provided one has a good knowledge of the aquifer system, its hydrodynamics, its mineralogical composition and trace element content and the physicochemical conditions of the groundwater.

We have been able to clearly identify the bio-geochemical processes associated with CO$_2$ or brine leakages that could impact fresh groundwater. However, to quantify the potential impact of CO$_2$ or brine leakage on a shallow freshwater aquifer, some gaps remain. The evaluations of the impacts of leakage on fresh groundwater reported in the literature are based mainly on laboratory or field experiments and modelling studies and are biased as described above. All of the impacts of CO$_2$ storage and leakage have not been well defined because it has been shown that impacts are site specific. In addition to the type of leaking fluid (gas or brine), its chemical composition and the leakage rate, it is necessary to consider all of the entire system’s biogeochemical processes that control groundwater quality (from the reservoir to the fresh groundwater). Numerical modelling could be useful for assessing the impacts of CO$_2$ geological storage on groundwater, but developing large scale models that take into account reactive transport is difficult (IEAGHG, 2011a). In fact, large scale basin studies are required to correctly assess the hydrodynamic impact of storage sites (pressure build up, brine or CO$_2$ migration) and powerful computing is increasingly being used to improve the assessment of CO$_2$ storage by numerical modelling.

To ensure the safety of CO$_2$ geological storage and preserve our fresh water resources, we need to study the impact of CO$_2$ or brine leakage on water quality. We must consider the possible presence of trace elements in fresh water aquifers or in leaking fluids and the abiotic and biotic mechanisms that control their mobility in fresh groundwater in the presence of CO$_2$. This characterization will have two objectives: (i) determine whether or not there is a risk of alteration of groundwater quality in the event of leakage and (ii) adapt the monitoring program and baseline data acquisition to the identified risk (i.e. to the presence of specific trace elements). To do this, we need to (i) identify the biogeochemical phenomena that occur during injection in the reservoir (transport, chemical reactions, etc.) in order to determine the nature and composition of the fluids that might migrate out of the reservoir, (ii) study the natural geochemical background of the fresh groundwater in order to identify the trace elements that are naturally present, (iii) know the carrier phases of these elements based on e.g. geological framework, solid phase characterization (e.g. mineralogy, surface properties, selective extraction...) or hydrogeochemistry (e.g. geochemical speciation calculations), (iv) identify
the specific mechanisms that control the trace element’s mobility based on general knowledge, experimental data and models, and (v) determine the natural state of the groundwater (pH, redox, salinity, chemical composition) over a period of time that is long enough to be able to overcome natural variability (baseline acquisition). In addition, the study of the hydrogeology of the shallow aquifer (regional flow, confined or unconfined) is important for predicting the potential migration of leaking fluid. This studying program should, of course, be adapted to the initial knowledge on the investigated area, the issues and the cost of the required investigations.

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