Review: The potential impact of underground geological storage of carbon dioxide in deep saline aquifers on shallow groundwater resources

Jean-Michel Lemieux

Abstract Underground geological storage of CO_2 in deep saline aquifers is considered for reducing greenhouse gases emissions into the atmosphere. However, some issues were raised with regard to the potential hazards to shallow groundwater resources from CO_2 leakage, brine displacement and pressure build-up. An overview is provided of the current scientific knowledge pertaining to the potential impact on shallow groundwater resources of geological storage of CO_2 in deep saline aquifers, identifying knowledge gaps for which original research opportunities are proposed. Two main impacts are defined and discussed therein: the near-field impact due to the upward vertical migration of free-phase CO_2 to surficial aquifers, and the far-field impact caused by large-scale displacement of formation waters by the injected CO_2. For the near-field, it is found that numerical studies predict possible mobilization of trace elements but concentrations are rarely above the maximum limit for potable water. For the far-field, numerical studies predict only minor impacts except for some specific geological conditions such as high caprock permeability. Despite important knowledge gaps, the possible environmental impacts of geological storage of CO_2 in deep saline aquifers on shallow groundwater resources appears to be low, but much more work is required to evaluate site specific impacts.

Keywords Review · Groundwater protection · Contamination · Carbon sequestration · Saline aquifers

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Introduction

Carbon dioxide (CO_2) capture and storage is a process consisting of the separation of CO_2 from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere (IPCC 2005). Underground geological storage of carbon dioxide is considered as one of the possible options for reducing emissions of greenhouse gases into the atmosphere. Potential geological formations include oil and gas fields (depleted or for enhanced oil recovery), unminable coal beds and deep saline aquifers. For now, storage in deep saline aquifers is the most attractive option for several reasons (Hitchon et al. 1999): among all other geological reservoirs considered, mineral trapping is most efficient in saline aquifers, the volume of pore space available in deep saline aquifers is enormous, they are widely distributed and more importantly, they underlie most point sources of carbon dioxide emission. Carbon dioxide is a good candidate for saline aquifer disposal because of its high density and solubility in water at the relatively high pressures which exist in deeper aquifers (Hitchon et al. 1999).

Proper site selection and management of CO_2 storage projects are important considerations in order to ensure long-term storage and to ensure that risks to humans and the environment are low. There are, however, a number of issues that were raised with regard to the potential hazards to groundwater from CO_2 or formation fluid leakage, brine displacement and pressure build-up (Bergman and Winter 1995; Holloway and Savage 1993).

Upward CO_2 leakage into a surficial aquifer can occur as a result of the caprock failing to contain CO_2, the presence of faults or fractures, or through poorly cemented or abandoned boreholes (IPCC 2005). Dissolved CO_2 can modify the pH of natural groundwater which can become acidic. This, in turn, can mobilize trace elements such as lead and arsenic by the process of mineral dissolution or desorption and adversely impact groundwater quality (Wang and Jaffe 2004; Kharaka et al. 2010).

Co-transport of formation water with CO_2 is yet another adverse consequence of containment failure and leakage (Kharaka et al. 2009). Formation waters often have high total dissolved solids concentration and often

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carry other toxic compounds (Kharaka et al. 2009). Mobilization of natural organic compounds present in saline aquifers by supercritical CO_2, which is an efficient solvent for hydrocarbons (Kolak and Burruss 2006), is also a potential concern if it is transported to shallow freshwater aquifers (Kharaka et al. 2006). Pressure build-up in saline aquifers due to massive CO_2 injection can cause the displacement of formation waters and brines and increase their velocity. Brine migration can result in the contamination of freshwater aquifers, and higher velocities could modify discharge rates into lakes, streams (Bergman and Winter 1995) or springs.

While many scenarios have been suggested with respect to the potential environmental impact of underground geological storage in deep saline aquifers, little research has been conducted to support them. It is only very recently that quantitative studies have been completed. In this paper, these studies are reviewed with the objective to summarize the current scientific knowledge pertaining to the potential impact on shallow groundwater resources of geological storage of CO_2 in deep saline aquifers. First, background information is given on the important CO_2 properties controlling its migration, followed by a review of the transport processes and trapping mechanisms. Two main impacts are defined and discussed therein, the near-field impact due to the upward vertical migration of free-phase CO_2 to surficial aquifers, and the far-field impact caused by large-scale displacement of formation waters by the injected CO_2. Knowledge gaps are identified and research opportunities are proposed to improve our understanding of the potential environmental impact of underground geological storage of carbon dioxide.

Transport processes, storage mechanisms and escape pathways

Before discussing the behaviour of CO_2 in saline aquifers along with its potential escape pathways, the relevant CO_2 properties are reviewed. It is only intended to provide an overview of the fundamental transport processes and storage mechanisms and the reader is referred to Bachu and Adams (2003), Gaus (2010) and Holloway (1997), among others, for a more detailed description.

Selected carbon dioxide properties

The physical state of CO_2 is a function of temperature and pressure as shown in Fig. 1. At normal temperature and pressure encountered in the atmosphere, CO_2 is a gas. When the CO_2 is injected at pressures exceeding 73.9 bar (7.39 MPa) and at temperatures above 31.1°C, it forms a gas-type phase known as supercritical CO_2, with a liquid-like density. It is usually assumed that this pressure would be encountered below a depth of 739 m for hydrostatic pressure and freshwater density. For security reasons, the targeted injection formations are below 800 m.

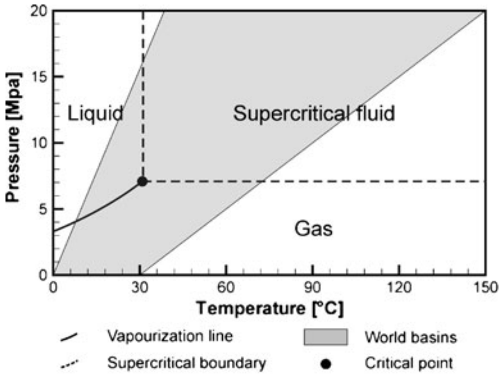

Fig. 1 Phase behaviour of CO_2 for conditions characteristic of worldwide sedimentary basins (Fig. 3 of Bachu (2003), with kind permission from Springer Science + Business Media)

Between temperatures of 31.1 and 100°C and below a pressure of 400 bar, supercritical CO_2 has a liquid-like density but its density is lower than that of water. For example, the density of supercritical CO_2 at an injection depth of about 1,500 m in a sedimentary basin at hydrostatic pressure, with a geothermal gradient of 25°C/km and a mean surface temperature of 10°C, is about 700 kg/m^3 (Fig. 2). It is therefore buoyant. Figure 2 shows the CO_2 density as a function of depth and surface temperature for a cold and warm geothermal gradient assuming hydrostatic conditions. These curves give a visual appraisal of the density of supercritical CO_2 with depth for the conditions relevant to a given sedimentary basin.

For typical freshwater aquifer conditions (depth<800 m and colder temperatures), CO_2 forms a gas phase and has a density that is much lower than water. It is therefore strongly buoyant. Solubility of CO_2 in water decreases as temperature and salinity increase (IPCC 2005), but increases with pressure. Hitchon et al. (1999) report that the solubility of CO_2 is high at the elevated pressures that exist in deep aquifers. For shallow aquifers, the solubility of CO_2 is usually described with partial pressure P(CO_2) and can vary

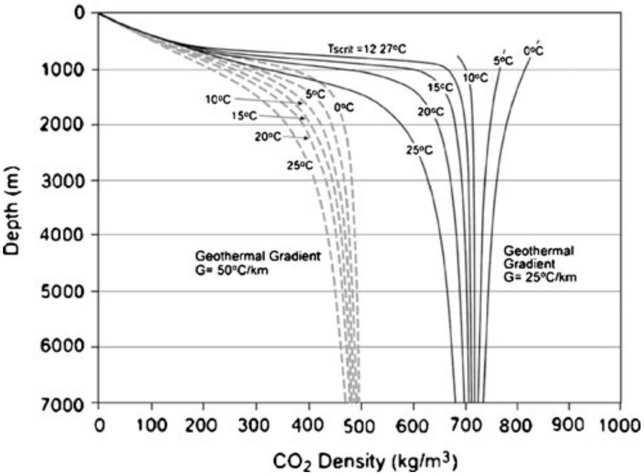

Fig. 2 Variation of CO_2 density with depth in sedimentary basins assuming hydrostatic pressure and various surface temperatures for geothermal gradients representative of "cold" and "warm" basins. From Bachu (2003), with kind permission from Springer Science + Business Media

between $log\ P(CO_2) = -4\ and + 1\ (in\ bars)$, which is the maximum range expected for hydrostatic conditions to depths of 100 m (Apps et al. 2010).

Dissolution of CO_2 in water can cause a decrease in pH according to the following simplified reaction:

$$CO_{2(g)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-.$$

Figure 3 shows the variation of pH with partial pressure of CO_2 under representative US aquifers conditions, at 25°C. However, the availability of buffering minerals like calcium and magnesium carbonates in the rock matrix (i.e., calcite, dolomite) can mitigate the pH decrease according to a dissolution reaction of this form (given for calcite, $CaCO_3$):

$$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-.$$

Transport processes of carbon dioxide in saline aquifers

Underground geological disposal of carbon dioxide in saline aquifers implies that CO_2 emissions are captured from major point sources and transported to the injection location. When CO_2 is injected into a deep saline formation in a liquid-like supercritical phase, it is immiscible in saline water and forms a nonwetting phase (Bachu 2008), although it is soluble and could dissolve in the formation waters. The density of supercritical CO_2 is less than brines for most of the targeted injection conditions and strong buoyant forces will drive CO_2 upward within the formation and a plume of CO_2 will form.

Along its migration path, some of the CO_2 will dissolve in the formation waters. On the short term (tens of years), numerical simulations have shown that a significant amount (up to 30%) of CO_2 can dissolve in the formation water (Doughty et al. 2001), while over a longer time frame, the entire plume of CO_2 could dissolve within a few centuries (McPherson and Cole 2000). The dissolved CO_2 will slowly migrate with the regional groundwater flow, knowing that for deep sedimentary basins with high salinity, groundwater flow velocities are very low (mm/a–cm/a; Bachu et al. 1994) and migration rates are much lower than those for free-phase CO_2 (IPCC 2005a).

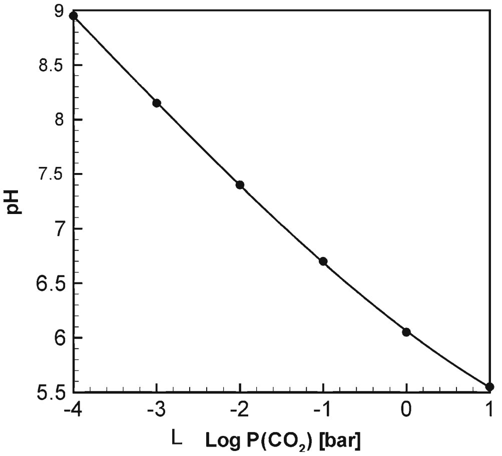

Fig. 3 Variation of pH with partial pressure of CO_2 under representative US aquifers conditions, at 25°C. Data from Apps et al. (2010)

Water saturated with CO_2 is slightly denser than formation water (Gasda et al. 2004) which may lead to free convection (convection cells) close to the injection locations, where the saturated fluid sinks toward the bottom of the formation (Ennis-King and Paterson 2003; Audigane et al. 2007). This process can contribute to a faster dissolution rate of CO_2 because it stimulates the contact between under-saturated formation water and the CO_2 plume. It also contributes to a longer residence time of the dissolved CO_2 in the subsurface because it flows toward the bottom of the aquifer instead of flowing upward toward the surface.

When CO_2 injection stops, the saturation at the tail of the CO_2 plume will decrease as the CO_2 migrates upward and CO_2 is no longer replenishing the bottom of the plume. When the saturation of the CO_2 reaches the residual saturation, the CO_2 no longer forms a continuous phase and it becomes immobile. The residual CO_2 could eventually dissolve into the formation water if it is not saturated with CO_2, but before then, it is immobile and trapped.

Once the CO_2 plume reaches a caprock or a sealing unit, it will stop its vertical migration due to the combined effect of permeability reduction and capillary barrier. Although CO_2 cannot enter the sealing units, saline water can, as it is displaced by the CO_2 plume under the increased pressure build-up due to continuous CO_2 injection.

Storage mechanisms

Four main mechanisms are usually recognized for CO_2 storage, namely, *stratigraphic/structural, hydrodynamic, residual* and *geochemical trapping*. No single storage mechanism can be thought of as independent. Rather, they act together, although their fractional contribution evolves with time (Fig. 4). The most effective storage sites are those where the CO_2 is immobile because it is trapped below a thick and impermeable caprock or is converted into solid minerals.

Stratigraphic and structural trapping (or hydrostratigraphic trapping) is a mechanism whereby the CO_2 is physically confined below a low-permeability seal like a shale or salt bed. In the structural trapping mechanism, traps are formed by folded and/or faulted rocks, similar to natural oil and gas reservoirs. These traps form a vertical and lateral barrier that limit CO_2 migration as a free phase. Stratigraphic traps, like structural traps, are composed of low-permeability seal units, but unlike structural traps, they are not confined laterally. Continuous and extensive seals are common in sedimentary basins and can prevent

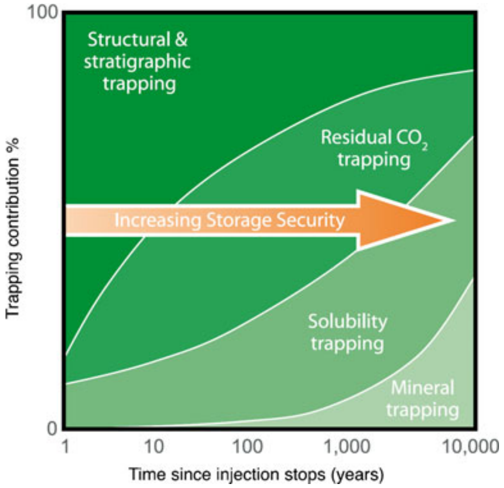

Fig. 4 The storage security of CO_2 is a function of the combination of various trapping mechanisms for which the proportion evolves with time. Early-on, the structural and stratigraphic traps are dominant but hydrodynamic (residual and solubility) and mineral trapping increase with time, which are more secure. Used with kind permission from IPCC (2005)

upward migration of CO_2 as a separate phase over great distances.

Hydrodynamic trapping (or solubility trapping) occurs when CO_2 dissolves completely or partially into formation fluids, below a stratigraphic trap and migrates slowly with them over great distances (Bachu et al. 1994). The time needed for dissolved CO_2 to reach the surface can be very long (e.g., millions of years; Bachu et al. 1994) and this time is considered long enough to ensure the safety of the stored CO_2.

Residual gas trapping (or phase trapping) occurs when the non-wetting fluid (CO_2) no longer forms a continuous phase. This occurs when the saturation of CO_2 reaches the residual saturation. The CO_2 then becomes immobile until it dissolves within the brines, if it does.

Injected CO_2 can react with the aquifer matrix and the formation water which will contribute to enhance the storage capacity and effectiveness. This process is called *geochemical or mineral trapping*. Mineral trapping is perceived as the most permanent form of geological storage. It is, however, a slow process that potentially needs many thousands of years, or longer (IPCC 2005). More details on CO_2-rock interactions can be found in Gaus (2010).

Escape pathways

Three main potential pathways for CO_2 release as a separate phase are usually recognized (e.g., IPCC 2005; Pruess 2008; Bachu and Celia 2009) including: leakage trough the caprock, migration along subvertical faults and fractures within the caprock and escape through boreholes.

Leakage through the caprock occurs when the capillary entry pressure threshold is reached. This can be prevented by limiting the injection pressure or by producing formation brines. While the caprock may have the proper hydrogeological conditions for free phase CO_2 containment, fractures and faults can modify its integrity. These features may naturally exist but geomechanical damages can also occur when the yield strength of the caprock is exceeded by the pressure build-up created through the injection of CO_2 (Rutqvist and Tsang 2002; Rutqvist et al. 2007).

Active and abandoned wells are recognized as one of the most probable escape pathways for free phase CO_2 due to the poor or unknown conditions of abandonment, cementing, alteration or plugging (Gasda et al. 2004; Carey et al. 2007) and extensive work has been dedicated to the prediction of leakage rates (e.g., Nordbotten et al. 2004; Celia and Nordbotten 2009). Moreover, deterioration of cement and metal casing can occur in the presence of CO_2 and further enhance the likelihood of CO_2 escape through abandoned wells.

A fourth escape pathway could be added for dissolved CO_2 which flows updip with regional groundwater flow. It is usually not discussed because it is believed that it will take hundreds of thousands of years before the CO_2 reaches the atmosphere and because it is expected that most CO_2 will precipitate before reaching the surface. This issue will be discussed in more detail in the knowledge gap section.

Near-field impact

The upward leakage of CO_2 as a free phase from the injection zone to overlying aquifers is defined here as the near-field impact of underground geological storage of carbon dioxide in deep saline aquifers. The near-field area is defined by the surface footprint of the leaking CO_2 plume. It is the result of a failure to contain injected CO_2 in the receiving formation and can be viewed as the direct impact of CO_2 leakage on shallow aquifers (Fig. 5).

Although we use the near-field terminology, the surficial aquifers and the injection zones are not necessarily nearby; they can be separated by a vertical and/or horizontal distance of a few hundreds of meters due to the buoyant vertical migration of CO_2 and lateral updip migration along the bottom of the caprock. It is named in relation to far-field impacts which are felt many kilometers away from the injection zone and are caused by the large-scale migration of displaced brines or elevated pressure (see next section and Fig. 5).

Potential leaks of free phase CO_2 exist along abandoned or active wells (Fig. 5) and through the caprock when the entry pressure is reached and when fractures or faults are open for flow (naturally or because of excessive injection pressure build-up). When the buoyant supercritical CO_2 migrates upward, it will undergo a phase change and will reach shallow aquifers as a gas.

The CO_2 as a gas phase can dissolve partially or completely within fresh groundwater. The CO_2 by itself is not a concern to the water quality of an underground source of drinking water, but it will change the geo-

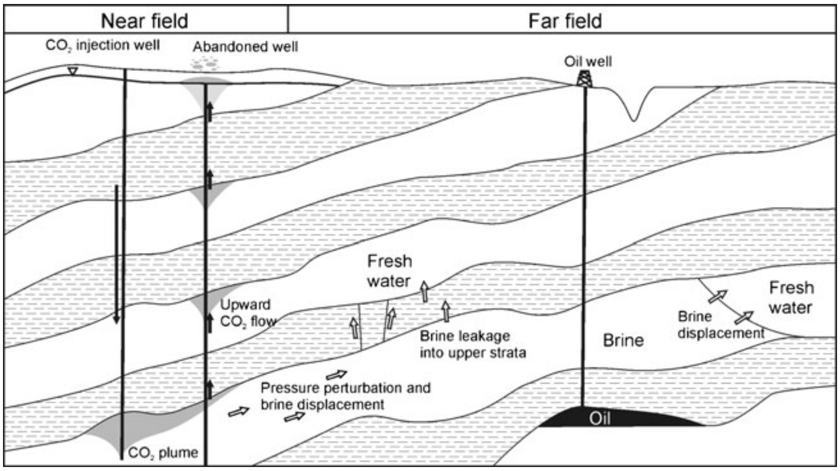

Fig. 5 Schematic showing different regions of influence related to CO_2 storage in saline aquifers. The footprint area of the CO_2 plume leaking in surficial aquifers is defined as the near-field and the footprint area of elevated pressure, updip formation water flow and brine leakage into shallow units across abandoned boreholes are defined as the far-field

chemical conditions in the aquifer. The dissolution of CO_2 in groundwater increases the total concentration of dissolved carbonate which in turn increases acidity and lowers the natural pH of groundwater (Langmuir 1997). Increased acidity can enhance the dissolution of minerals, including those containing hazardous trace elements (Zheng et al. 2009a; Apps et al. 2010). Decreased pH could also mobilize hazardous trace elements adsorbed on clays, iron oxyhydroxides or the surface of other rock-forming minerals (Kharaka et al. 2006; Kharaka et al. 2009; Zheng et al. 2009a; Apps et al. 2010). The resulting increase in concentration of hazardous trace elements can affect groundwater quality, possibly to the extent that safe drinking-water limits are exceeded. However, in highly buffered aquifers, the potential for a pH decrease can be compensated by the dissolution of alkaline minerals like calcite (if they are present; Bethke 2008).

It might be noteworthy to say that the impacts on groundwater are likely to be more important if the leaks enter a confined shallow aquifer rather than an unconfined aquifer. In this situation, the CO_2 as a free phase will accumulate at the top of the confined aquifer and impact a large volume of water. Conversely, if the CO_2 is leaking in an unconfined aquifer, it will flow upward and dissipate in the vadose zone, limiting its surface contact with freshwater.

This potential adverse environmental impact of CO_2 on shallow groundwater resources was recognized earlier by van der Meer (1992) but, at that time, he suggested that dissolved CO_2 in natural groundwaters due to CO_2 leakage could only lower the pH by one unit. This led to the conclusion that it was only of minor environmental significance. It took about 10–15 years before a detailed and quantitative assessment of the mobilization of hazardous elements in response to CO_2 intrusion in freshwater aquifers was undertaken. To date, this behaviour has been reported in a few laboratory experiments (Smyth et al. 2009; Carroll et al. 2009), one field experiment (Kharaka et al. 2010), many numerical studies (Apps et al. 2009; Audigane et al. 2009; Birkholzer et al. 2008a; Carroll et al. 2009; Jaffé and Wang 2003; Wang and Jaffe 2004; Zheng et al. 2009a, b, c) and from the observation of industrial or natural analogues (Keating et al. 2010; Lewicki et al. 2007; McGrath et al. 2007).

Laboratory and field observations

Few laboratory experiments and field observations are reported in the literature (see Table 1 for a summary of their key characteristics and findings). This is somehow surprising as they could be very helpful to quantify the possible environmental impacts. Smyth et al. (2009) report laboratory batch experiments that were conducted to investigate the extent to which injected CO_2 in contact with shallow aquifers could mobilize major and minor ions bound to aquifer host rocks. In most cases the pH dropped at the start of CO_2 injection with an average of 3 units and stayed more or less constant for the remainder of the test. Results also showed that cation concentrations were generally elevated at the end of the tests. However, these conclusions should be considered with caution because the same experiments conducted with a non-reactive gas instead of CO_2 yielded the same conclusions, rising doubts concerning the relation between pH decrease and CO_2 concentration.

On a different scale, a field experiment was conducted at the Zero Emission Research and Technology Center (ZERT) field site in Bozeman, Montana, where food-grade CO_2 was injected into a shallow aquifer in order to evaluate near-surface CO_2 detection techniques, transport models and groundwater geochemistry, among many other objectives (Spangler et al. 2009). Approximately 300 kg/day of CO_2 was injected through a horizontal perforated pipe placed at a depth of 2–2.3 m in an unconsolidated aquifer, between July 9 and August 7, 2008. One objective of the experiment was to investigate the changes in the concentration of major, minor and trace inorganic and organic compounds during and following the CO_2 injection (Kharaka et al. 2010). A rapid and systematic change in chemical parameters was observed, including pH (from 7 to 5.6), alkalinity (from

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Table 1 Summary of experimental studies relevant to assess the potential changes in groundwater quality in response to CO_2 leakage from deep geological storage

Authors	Type of experiment	Location	Mobilized metals	Chemicals	Note
Smyth et al. (2009)	Laboratory (batch tests)	Various aquifers, Texas	Yes	pH Cations	
Smyth et al. (2009)	Field (monitoring)	SACROC oil field, Scurry county, Texas	No	pH Cations	Saline water observed
Kharaka et al. (2010)	Field (injection)	ZERT field site, Bozeman, Montana	Yes (below MCL)	pH, BTEX, Pb, As, Zn+other trace metals	BTEX was injected with CO_2

MCL maximum concentration limit

400–1,330 mg/L, HCO_3) and electrical conductance (from 600–1,800 μS/cm) following CO_2 injection. Laboratory analysis also showed major increases in the concentration of major and trace chemicals, including lead and arsenic. At the end of the experiment, all of the trace metals were significantly below the maximum contaminant levels specified by the United States Environmental Protection Agency (USEPA). BTEX compounds (an acronym for benzene, toluene, ethylbenzene and xylenes) were also detected but were later found to have been injected along with the CO_2. This is a reminder that the mobilization of organic compounds in saline aquifers (or other types of storage formations) by supercritical CO_2, which is an efficient solvent for hydrocarbons (Kolak and Burruss 2006), is a potential concern if it is transported to shallow freshwater aquifers (Kharaka et al. 2006).

Experimental data have also been collected to infer the changes in water geochemistry in the injection formations (e.g., Kharaka et al. 2009). This has important implications regarding the possible degradation of well casings and cement and provides some understanding on the leaching of trace metals and naturally occurring organic compounds (Gaus 2010). Geochemical conditions in freshwater aquifers are much different than those for saline aquifers—i.e., rocks or porous materials have generally been flushed by fresh water, CO_2 will be a gas rather than a supercritical fluid, and temperature, pressure and salinity are lower than in deep saline aquifers (Smyth et al. 2009). For this reason, it is dangerous to extrapolate results obtained from observations or modelling within the injection zone to shallow aquifers.

Although there are currently a few intermediate-scale research and/or commercial projects where CO_2 is injected in deep saline formations (e.g., Sleipner, Norway) or for EOR (e.g., Weyburn, Canada; Frio, USA), no groundwater quality changes have been reported so far (Michael et al. 2010). This is also the case for Scurry Area Canyon Reef Operators Committee (SACROC, a Texas petroleum joint venture) oilfield in Scurry County, Texas, USA where CO_2 has been injected since 1972 for enhanced oil recovery (Smyth et al. 2009).

Numerical experiments

As an alternative to laboratory and field experiments, several studies on the potential adverse effects of CO_2 release from deep reservoirs on the quality of freshwater aquifers have used numerical models (Apps et al. 2009; Audigane et al. 2009; Birkholzer et al. 2008a; Carroll et al. 2009; Jaffé and Wang 2003; Wang and Jaffe 2004; Zheng et al. 2009a, b, c). These models simulate one-, two- or three-dimensional (1D, 2D or 3D) groundwater and/or CO_2 flow within aquifers along with the advective-dispersive transport of solutes, including chemical reactions with the porous media (dissolution and/or sorption/desorption). They are used to predict pH evolution and solute concentration as well as for the design of monitoring networks to detect CO_2 leaks (e.g. Carroll et al. 2009). One of the main interests in using reactive transport models is that the origin of mobilized metals and other cations can be tracked because the dissolution and sorption/desorption reactions are specified in the model. Also, when the reaction rates are known, time estimates can be conducted to achieve a specific concentration. The reactions must be known a priori and are usually based on the mineralogy of minerals forming the porous media and the geochemistry of the natural waters under study. On the other hand, geochemical modelling is limited by the minerals defined in thermodynamic databases and the data available is usually based on pure phases that are well-crystallized, which can be different than what is found in natural systems. Chemical reactions can be described by reaction kinetics (reaction rates are specified based on laboratory experiments or field experiments), or assumed to be in equilibrium. Equilibrium models may be used for fast reactions, including carbonate, hydroxide and sulphate dissolution, or to assess the potential concentration of solutes at equilibrium. Kinetic reactions are best suited for slow reaction rates such as the dissolution of silicates. The main challenge in using kinetic models is to get representative and realistic reaction rates, which are often difficult to obtain.

Two main approaches can be distinguished that are either site specific or generic. Generic studies involve using the mineralogy and water quality data collected in a variety of aquifer types that could be impacted by CO_2 leakage, and to predict the possible impacts using known geochemical reactions. Site specific studies focus on one location where detailed mineralogical analyses are available, where the aquifers are well characterized and flow dynamics well understood. In either case, the findings cannot readily be applicable to other sites because the mineralogy and flow dynamics are different for every site. Table 2 summarizes the

Table 2 Summary of numerical studies conducted to assess the potential changes in groundwater quality in response to CO_2 leakage from deep geological storage

Authors	Name of model	CO_2 source	Dimensionality	Location	Chemicals	Potential impacts
Apps et al. (2010)	TOUHGHREACT[a]	Point source	3D	Generic	Lead Arsenic	Yes
Audigane et al. (2009)	TOUHGHREACT[a]	Point source	3D	Paris Basin (Albian aquifer)	Fe	Yes (aesthetic)
Birkholzer et al. (2008a)	TOUHGHREACT[a]	Point source	2D, 3D	Generic	Lead Arsenic	Yes
Carroll et al. (2009)	NUFT[b]	Point source	3D	High plains aquifer	pH	NA
Jaffé and Wang (2003)	In-house GW flow and solute transport model + MINTEQA2[c]	Point source	2D	Generic	Lead	Yes
Wang and Jaffe (2004)	Same as above	Point source	2D	Generic	Lead	Yes
Zheng et al. (2009a, b)	TOUHGHREACT[a]	Point source	2D	Generic	Lead Arsenic	Yes
Zheng et al. (2009c)	TOUHGHREACT[a]	NA	1D	ZERT field site	NA	NA

[a] Xu et al. (2004)

[b] Nitao (1998)

[c] Allison et al. (1991)

key parameters and findings of the numerical experiments discussed thereafter.

Jaffé and Wang (2003) and Wang and Jaffe (2004) conducted 2D reactive transport simulations, in a porous media containing a significant amount of galena (PbS), as an example of the potential effect of CO_2 intrusion into a freshwater aquifer from the dissolution of a mineral phase (galena) and the mobilization of a trace metal (Pb). No sorption/desorption of lead from the solid matrix was considered, which could have a more important effect on water quality than the dissolution of minerals (e.g., Birkholzer et al. 2008a). Their results, for a poorly buffered aquifer composed of quartz and galena only, suggest a strong increase of lead concentration that exceeds the action level defined by the USEPA after only 8 years of CO_2 intrusion. The action level is defined in the US as 10% of the maximum concentration limit. The lead concentration was found to be much lower for a well buffered aquifer composed of galena and calcite only.

As pointed out by Zheng et al. (2009a), Jaffé and Wang (2003) and Wang and Jaffe (2004) intended their study to only demonstrate the potential adverse effects of CO_2 intrusion on groundwater quality. Their geochemical system is greatly simplified and does not represent realistic conditions. They also used a 2D model while Zheng et al. (2009a) have raised questions regarding the limitations of the 2D assumption. Realistic predictions call for a more refined geochemical model in which many more minerals are to be found.

A more realistic and very extensive generic study using a refined geochemical model has been conducted by the Lawrence Berkeley National Laboratory (LBNL) on behalf of the USEPA to systematically evaluate the possible water quality changes in response to CO_2 intrusion into aquifers that are used as a source of drinking water in the United States (Apps et al. 2010; Apps et al. 2009; Birkholzer et al. 2008a; Zheng et al. 2009a, b). The study was composed of three steps and involved (1) identification of host minerals containing hazardous constituents that control their concentration in potable groundwater, (2) predicting the equilibrium concentrations of the hazardous constituents in groundwater in contact with leaked CO_2 and comparing them to maximum concentration limits (MCL), and (3) conducting a systematic reactive-transport modelling study to quantify the fate and migration of hazardous constituents in the groundwater and evaluate if their concentration can exceed water standards in a realistic but generic confined aquifer.

According to their analysis, the most likely solubility-controlling minerals hosts for hazardous constituents are given in Table 3. A preliminary assessment of water quality changes was conducted by calculating the expected equilibrium concentrations of hazardous constituents as a function of various pH values that would be observed where CO_2 leakage occurs in shallow aquifers. Results indicate that the concentrations of some of the studied constituents, for example barium, cadmium, antimony, and zinc, are sensitive to changes in pH, but that only arsenic, and to a lesser extent lead and zinc, have the potential for exceeding their respective maximum contaminant levels (as defined by the USEPA) at elevated CO_2 concentrations dissolved in freshwaters (Birkholzer et al. 2008a). For this reason, they only considered the fate and migration of lead and arsenic in their reactive transport simulations.

Simulation results with the TOUGHREACT simulator (Xu et al. 2004) show that the leakage of CO_2 into a confined freshwater aquifer can lead to significant mobilization of lead and arsenic and contaminate the water near and downstream (up to several hundred meters) of the CO_2 plume. While the simulated concentrations of aqueous lead and arsenic substantially increased with regard to background levels, the MCL for arsenic in groundwater was only reached in a few cases while it was never exceeded for lead. It was also found that the amount of mobilized trace metals was only a very small fraction of the contaminant mass available in the minerals, even after a time period of

Table 3 Potential mineral hosts for hazardous constituents under reducing conditions for typical potable water aquifers of the US. From Birkholzer et al. (2008a) and Apps et al. (2010)

Hazardous constituent	Potential mineral controls	
	Solid Solution Component	Discrete mineral
As	$(FeAsS)_{py}$	Arsenopyrite ($FeAsS$)
Ba	–	Barite ($BaSO_4$); Witherite ($BaCO_3$); Crandallite ($CaAl_3(PO_4)_2(OH)_5$)
Cd	$(CdS)_{sph}$	Greenockite(CdS); Cadmoselite ($CdSe$)
Hg	$(HgS)_{py}$	Cinnabar (HgS); Tiemannite ($HgSe$)
Pb	–	Galena (PbS); Clausthalite ($PbSe$)
Sb	$(FeSbS)_{py}$	Stibnite (Sb_2S_3); Kermesite (Sb_2S_2O); Antimonselite (Sb_2Se_3); Gudmundite ($FeSbS$)
Se	$(FeSe_2)_{py}$	Ferroselite ($FeSe_2$); Dzharkenite ($FeSe_2$); Antimonselite (Sb_2Se_3); Cadmoselite ($CdSe$); Clausthalite ($PbSe$); Tiemannite ($HgSe$)
U	–	Uraninite (UO_2); Coffinite ($USiO_4$); Brannerite (UTi_2O_6)
Zn	–	Sphalerite (ZnS); Hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$)

Note: *py* pyrite, *sp* sphalerite

100 years. Therefore, small amounts of available lead or arsenic in any minerals can provide a long lasting source of contamination (Birkholzer et al. 2008a). Finally, adsorption/desorption via surface complexation was found to be the most important process controlling the fate of hazardous constituents mobilized by CO_2 leakage when sorbing minerals are present (Birkholzer et al. 2008a).

As pointed out by Birkholzer et al. (2008a), although the potential impacts of CO_2 on groundwater quality can be estimated with generic studies, the processes leading to the mobilization of hazardous constituents and their aqueous concentrations must be determined by site-specific conditions. Field tests accompanied by the use geochemical models are necessary to confirm the validity of the postulated processes (Zheng et al. 2009a). The ZERT field site experiment described earlier provides such an opportunity. Zheng et al. (2009c) exploited this opportunity and tried to identify the geochemical processes which are responsible for the observed changes in chemical composition of the groundwater following the CO_2 injection with the use of a 1D reactive transport model (TOUGHREACT). While their model could explain some important reactions reasonably well (e.g., calcite dissolution), a detailed understanding of the key processes explaining the increase in the concentration in major cations and trace metals could not be achieved. This is attributed to a lack of knowledge of key parameters such as the cation exchange capacity as well as an unknown smectite and iron oxyhydroxide content. Therefore, their model interpretation depends only on hypothetical values for these critical parameters. More chemical characterization work is under way and should help to improve the model once available.

Audigane et al. (2009) also used the TOUGHREACT simulator to infer the potential impact of a leaky injection borehole on the quality of groundwater in the Paris Basin, France. They focused only on the mobilization of trace metals which dissolve from minerals due to the acidification of groundwater in which leaking CO_2 dissolves. The aquifer under study is composed of quartz, calcite, kaolinite, glauconite, siderite and pyrite, in decreasing volume proportions. Specific attention was paid to iron, which already has a high concentration in the aquifer. Although the iron is not a concern for health, high concentrations can adversely affect the taste and appearance of the water. The simulation results suggest significant mobilization of iron is possible as a result of a 2.4 pH unit decrease and pyrite dissolution. Pyrite often contains arsenic, which could also be mobilized if present in this aquifer.

Carroll et al. (2009) also simulated pH breakthrough curves showing a significant pH decrease that could easily be measured in the field and up to 500 m away from the leakage source. Depending on the scenario (undeveloped or developed aquifer, low or high leakage rates, distance from the leak source), the pH could be lowered by as much as 2.1 units within a few months, for this very specific aquifer.

Natural and industrial analogs

Natural and industrial analogs have been investigated as an alternative to experiments in order to directly observe the CO_2 impacts on shallow groundwater aquifers. While there are important limitations to this approach, insightful characteristics of CO_2 leakage to surface aquifers as well as real impacts on groundwater quality can be gained.

Leakage of CO_2 has occurred naturally from geologic reservoirs in many volcanic, geothermal and sedimentary basins (Lewicki et al. 2007). According to Keating et al. (2010), there are two major categories of natural analogs: (1) analogs where diffuse CO_2 is rising and flowing through an aquifer, and (2) analogs where CO_2 is rising along a discrete feature such as a fault or other conduit, and is released as a point at the ground surface, like a spring or geyser (Fig. 6).

Keating et al. (2010) have observed that although dissolved CO_2 content is high in an unconfined groundwater aquifer located in Chimayó, New Mexico, pH depression and trace elements mobilization are relatively minor. This is attributed to the buffering capacity of the aquifer that can naturally mitigate pH decreases due to CO_2 influx from the dissolution of high alkalinity and carbonate minerals. This is in accordance with the conclusions of Lewicki et al. (2007) that have conducted an extensive literature review in order to identify the

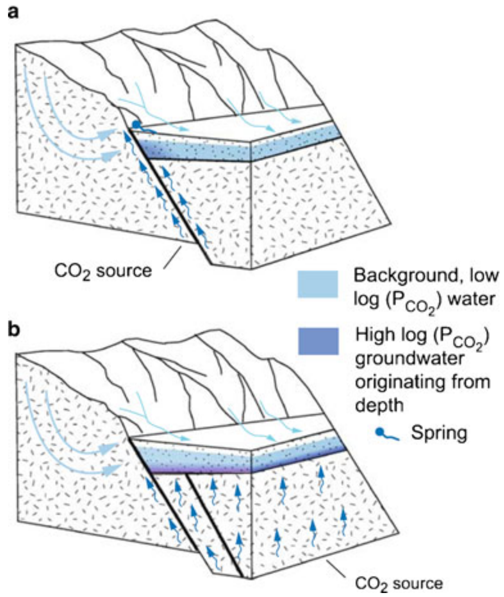

Fig. 6 The two main categories of natural analogs **a** CO_2 rises with deep water along a fault and forms a CO_2-rich spring, **b** CO_2 rises with deep water and diffuses into shallow aquifer water. From Keating et al. (2010), with kind permission from Springer Science + Business Media

features, events and processes that can be identified in natural and industrial analogues. They have found that chemical changes due to CO_2 leakage were sometimes observed where groundwater chemistry was monitored, but, in most cases, the groundwater remained potable. They also concluded that the style of CO_2 release at the surface varies widely between and within different sites. This conclusion may provide some important background for the definition of leakage scenarios considered in modelling studies, which are rather simplistic.

From their work, Keating et al. (2010) have proposed favourable natural conditions to mitigate the impact of CO_2 leakage on groundwater quality. These include (1) dilution and mixing of CO_2 impacted groundwater with ambient groundwater; (2) pH buffering reactions such as calcite dissolution and silicate mineral weathering; (3) limited trace metal availability in aquifer minerals; and (4) trace metal scavenging by secondary mineral precipitation.

Finally, the study of McGrath et al. (2007) on the mobilization of cadmium within an aquifer impacted by municipal solid waste landfill gas is often cited as an industrial analog for the potential impact of CO_2 on shallow groundwater resources. In their study, McGrath et al. (2007) conducted soil leaching experiments and geochemical modelling with native soils and concluded that the concentration of aqueous cadmium observed close to a municipal solid waste landfill (which was above the MCL) was likely caused by CO_2 dissolution into the groundwater. They suggested that the cadmium would have been mobilized from naturally occurring otavite (cadmium carbonate) in the soils due to the CO_2 related increase of acidity. In response to these findings, soil vapor extraction was initiated at the site to decrease the partial pressure of CO_2 in the groundwater. Since then, the concentration of cadmium has decreased below the detection limit, supporting the conclusions that CO_2 was responsible for the mobilization of cadmium.

Discussion

Most studies predict possible mobilization of trace metals through various mechanisms (dissolution, desorption, etc.) as a consequence of pH reduction due to CO_2 leakage, although many studies are too simple to support general conclusions. On the other hand, the reported impacts appear to be limited and the most realistic simulations (Birkholzer et al. 2008a; Apps et al. 2010) seldom report concentrations above MCL, while field observations at the ZERT site report metal concentrations much below MCLs. The observation of natural analogs also suggests that the CO_2 impact on groundwater quality is minor. On the other hand, the observation of industrial analogs provide an example where CO_2 leaking from a landfill site could mobilize cadmium, but it also shows that traditional remediation techniques such as soil vapour extraction could be used to restore the site. This is very encouraging if leaking CO_2 ever reach a confined aquifer because it means that this adverse impact can be mediated.

Clearly, the mobilization of trace metals and their impact on groundwater quality is site specific and very much related to the aquifer mineralogy, suggesting that general conclusions cannot be made. Site specific studies are needed to assess whether or not environmental impacts are likely to occur. Nevertheless, Birkholzer et al. (2008a) and Apps et al. (2010) have shown, through a theoretical study that the most likely constituents that can exceed their respective maximum limits in most U.S. aquifers are arsenic, lead and zinc, although numerical simulations have shown that only arsenic sometimes reached the MCL.

In the light of these conclusions, what may be more important than the mobilization of trace metals is the transport of co-injected H_2S and organic compounds mobilized by supercritical CO_2. Very few quantitative assessments are available, but preliminary simulations have shown that volatile organic carbon can easily be dissolved within supercritical CO_2 and mobilized to be transported into shallow aquifer (Birkholzer et al. 2010). More quantitative studies are needed to infer possible concentration levels in shallow aquifers.

Far-field impacts

Even if the injected CO_2 is safely trapped, large-scale injection of CO_2 into deep saline aquifers that are not compartmentalized may impact subsurface volumes much larger than that of the CO_2 plume (Birkholzer et al. 2009). Bergman and Winter (1995) have suggested that the injected CO_2 could displace brines and may increase flow velocity, resulting in a potentially increased rate of discharge into a lake or a stream. They also envisioned that a higher velocity may cause the brine to discharge along new paths into different zones, potentially mixing into drinking water aquifers (Fig. 5). The far-field impacts are thus defined as the indirect impacts related to basin-scale migration of displaced brines in response to large scale CO_2 injection into saline aquifers. Basin-scale migration and far-field impacts may become especially important when multiple injection sites are used for full-scale deployment of underground geological storage within an individual basin (Zhou et al. 2010).

Because of the very long time scale required before any adverse impacts can be observed, quantitative assessments of the large-scale impact of CO_2 storage in deep saline aquifers can only be conducted with predictive models. Again, simulations can be site specific, yielding insights for a given set of aquifer conditions, or generic, providing insights about relevant processes and potential impacts. Table 4 summarizes the key parameters and conclusions from the numerical studies addressing the far-field hydrogeological impacts of CO_2 storage presented in the following.

The first quantitative study on the far-field impact was conducted by Nicot (2008) for the Texas Gulf Coast Basin. He used a well calibrated 3D MODFLOW model to mimic the effect of injecting CO_2 into 50 wells over 50 years in a deep saline aquifer with wedge geometry (Fig. 7). The injection aquifer is located in the Simsboro Formation at the right-hand side of the cross-section shown in Fig. 7. They considered two CO_2 injection scenarios in which the injection rates were 1 and 5 million tonnes (Mt) CO_2/year/well. One of their assumptions is that multiphase flow processes are not important for describing the pressure anomaly created by CO_2 injection on the far-field aquifers. Therefore, they injected water instead of CO_2. Subsequent simulations with a multiphase flow simulator have shown that this assumption is sound and does not introduce much difference in the modelling results (Nicot et al. 2009). They also neglected the density of brines.

Their results show that the average water-level rise in the unconfined section of the injection aquifer is approximately 1 m at the end of the injection period but could reach a maximum value of 15 m when considering the large injection-rate scenario. The average value for the base-case scenario (1 Mt CO_2/year/well) is within the same order of magnitude as seasonal and inter-annual variations and therefore, is not considered to be a serious concern. They also found that baseflow to surface-water bodies did not increase noticeably in the base-case scenario, but could double for the large injection rate scenario. The increase in the water-table level causes an evapotranspiration flux increase by 50% in the base case scenario but can reach over 100% for the large-injection rate scenario. Finally, they found that the 3,000 ppm total dissolved solids boundary moved about 3–5 km up-dip, which was not considered an adverse impact on groundwater quality because the aquifers are located many kilometres away. Finally, one impact of CO_2 injection is the reversal of the flow system; the pre-injection regional groundwater flow direction was toward the bottom of the basin, but was reversed during CO_2 injection.

Birkholzer et al. (2009) studied the 3D region of influence of CO_2 injection on shallow groundwater aquifers in a stratified system with a particular focus on the interlayer communication through low permeability seals. Their conceptual model is shown in Fig. 8. They explicitly modelled the spatial CO_2 plume evolution with the multiphase flow simulator TOUGH2/ECO2N (Pruess et al. 1999; Pruess 2005). Their study differs from others

Table 4 Summary of the key parameters and conclusions from studies addressing the far-field hydrogeologic impacts of CO_2 storage

Authors	Model	Location	Injection rate	Duration	Predicted impacts
Birkholzer and Zhou (2009)	TOUGH2/ECO2N	Illinois Basin, USA	5 Mt CO_2/year/well (20 wells)	50 years	Same as Zhou et al. (2010)
Birkholzer et al. (2009)	TOUGH2/ECO2N	Generic	1.52 Mt CO_2/year	30 years	Unlikely vertical and lateral brine migration 0.7-bar lateral pressure build-up 100 km away from injection well
Dong et al. (2009)	TOUGH2/ECO2N	Songliao Basin, China	1 Mt CO_2/year (1 well)	100 years	Up to 2 bar vertical pressure build-up
Nicot (2008)	MODFLOW	Gulf Coast Basin, USA	1 Mt CO_2/year/well 5 Mt CO_2/year/well (50 wells)	50 years	Avg. 1-m lateral WT rise Max. 15-m lateral WT rise
Person et al. (2010)	Sharp interface in-house	Illinois Basin, USA	0.11 Mt CO_2/year/well (726 wells)	200 years	No lateral brine migration No lateral pressure build-up Vertical brine leakage
Yamamoto et al. (2009)	TOUGH2-MP/ ECO2N[a]	Tokyo Bay, Japan	1 Mt CO_2/year/well (10 wells)	100 years	Up to 1.5-bar vertical pressure build-up Marginal leakage in shallow aquifers
Zhou et al. (2010)	TOUGH2/ECO2N	Illinois Basin, USA	5 Mt CO_2/year/well (20 wells)	50 years	Up to 1-bar lateral pressure build-up Vertical brine leakage No lateral brine migration

[a] Zhang et al. (2008). *Mt* million tonnes

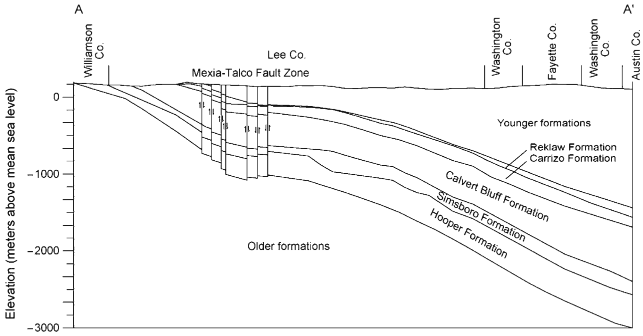

Fig. 7 Cross-section along the Carrizo-Wilcox system in the coastal plain of the Gulf of Mexico, Texas. The saline aquifers are the *Simsborro Formation* and the *Carizo Formation* which are confined by the *Calvert Bluff Formation* and the *Reklaw Formation*. The cross-section shows a typical up-dip configuration of a sedimentary basin considered for CO_2 storage. In this case, the targeted zone for injection is the Simsboro Formation at the eastern part of the cross-section. The length of the cross-section is about 80 km. From Nicot (2008) with kind permission from Elsevier

in that they considered intra-layer movement of brines as well as vertical interlayer migration. CO_2 was injected at a rate of 1.52 Mt/year over a 30-year period.

Their results show that considerable pressure build-up (0.7 bar; equivalent to 7 m of freshwater) in the storage formation is predicted more than 100 km away from the injection zone, while the lateral brine transport velocity and migration distance are less significant (Fig. 9). The pressure pulse travels fast and far within the injection formation, but the lateral brine flow velocities are quite small, and not much larger than natural velocities in deep basins. For this reason, large-scale pressure changes are likely to be of more concern to groundwater resources than changes in groundwater quality due to brine migration.

Results also indicate that the vertical interlayer pressure propagation through a succession of aquifers and aquitards is not very likely to affect shallow aquifers (Fig. 9). Moderate pressure increases are only predicted for large values of seal hydraulic conductivity (i.e., 10^{-16} – 10^{-17} m^2). However, whether the perturbations could cause environmental problems depends on the situation. For deep aquifers, a more significant change in pressure may be less important than for a shallow aquifer where river base flow and ecosystems are important. Vertical interlayer migration of brines toward surficial aquifers is also not a realistic concern, as indicated by the close-to-zero vertical transport velocity calculated along with a very low salt mass fraction observed in overlying aquifers. This, however, is for an ideal aquifer/aquitard system without leakage along wells and/or fractures.

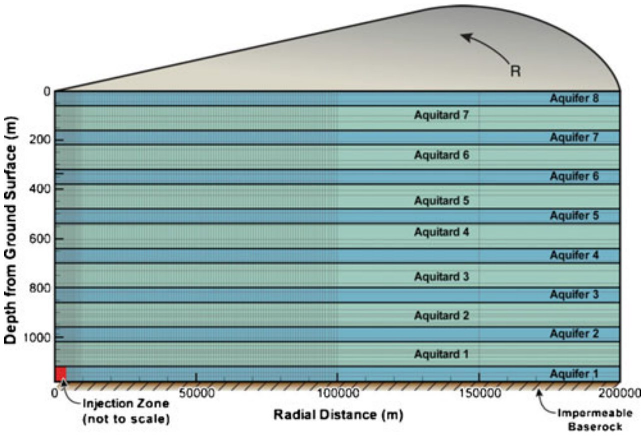

Fig. 8 Cross section showing the conceptual stratified and radial aquifer/aquitard system. *Aquifer 1* is the saline formation where CO_2 is injected (injection zone shown in red at the bottom left). The grid used in the simulation is also shown. From Birkholzer et al. (2009), with kind permission from Elsevier

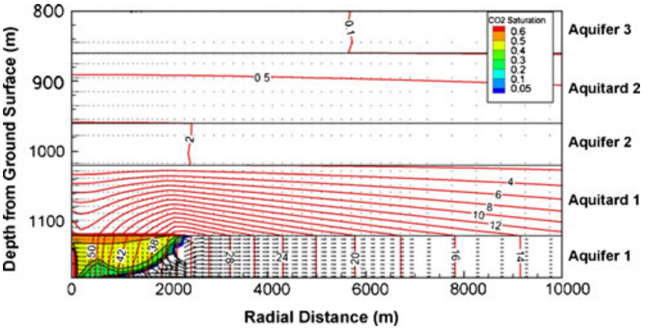

Fig. 9 Contours of CO_2 saturation (*colored areas*) and pressure build-up, given in bar (*red lines*), as well as water flux vectors in m/s at the end of the injection period (30 years), obtained for the base case with a seal permeability of 10^{-18} m^2. Only part of the simulation domain is shown. From Birkholzer et al. (2009), with kind permission from Elsevier

Through a sensitivity analysis of the caprock hydraulic conductivity, the authors show the intimate relations between lateral and vertical pressure build-up. The tighter the caprock, the more important the lateral pressure build-up, and the vertical build-up becomes less important. When the caprock is more permeable, more vertical pressure build-up can occur, although the lateral pressure build-up can decrease.

The same team of researchers also conducted a site specific basin-scale investigation with realistic multiple injection and storage sites in the Mt. Simon Aquifer in the Illinois Basin (Fig. 10; Birkholzer et al. 2008b; Birkholzer and Zhou 2009; Zhou et al. 2010). The Illinois Basin is well characterized and will host a CO_2 storage demonstration project named the Illinois Basin-Decatur project in 2010 at the Archer Daniels Midland site in Decatur, Illinois. They used the same approach as Birkholzer et al. (2009), which is the simultaneous modelling of basin and plume-scale processes with the TOUGH2/ECO2N simulator. The injection scenario considers multiple storage sites in the thick Mt. Simon aquifer (300–730 m) at a depth between 1,200–2,700 m which is confined by the Eau Claire caprock (see Figs. 10 and 11a). An array of 20 sites located in the center of the basin, separated by a distance of about 30 km from one another is included in the model, while the annual injection rate is 5 Mt/year CO_2 per site.

Their results show that injected CO_2 is contained below the low-permeability caprock and does not leak upward across the Eau Claire caprock (Fig. 11). The overall shape of the CO_2 plume at each site in the storage formation is attributed to the intrastorage layers of lower permeability

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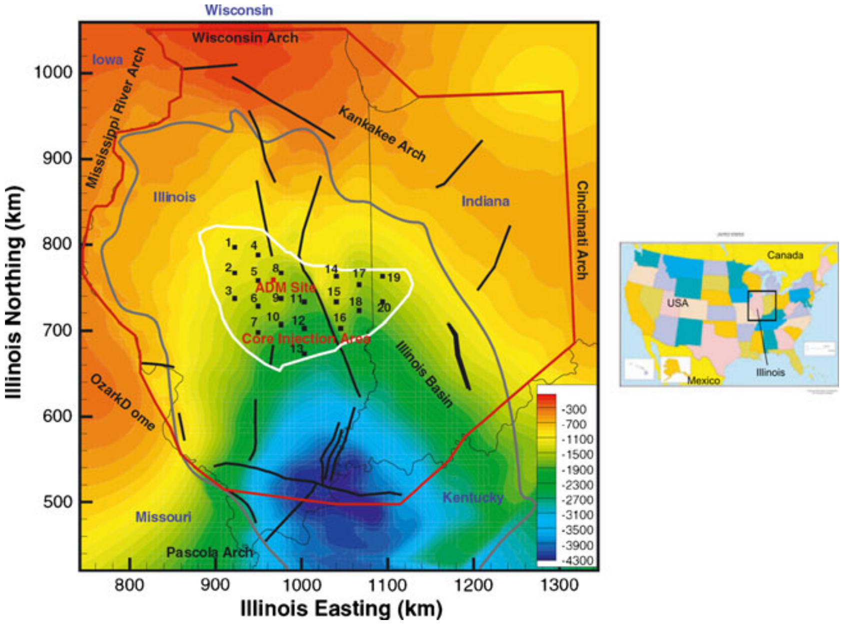

Fig. 10 Overview of the Illinois Basin and the model domain: the contoured area is the top elevation (m) of the injection formation (Mt. Simon Sandstone), state borders are shown as *thin black lines*, the Illinois basin boundary in *gray*, the model boundary in *red*, and faults or anticlines are *thick black lines*. The simulated domain is bounded by arches and domes. The injection area is shown in *white*, and the 20 injection sites in *numbered black squares*, as well as the Archer Daniels Midland (ADM) demonstration site as a *red square*. The ADM site will host a large-scale demonstration project called the Illinois Basin-Decatur Project for 3 years, starting in 2010. From Zhou et al. (2010), with kind permission from John Wiley and sons

which restrict vertical CO_2 migration and promotes lateral viscous fingering along the layers (Fig. 11). Lateral migration after 200 years of simulation becomes limited as the CO_2 plume becomes essentially immobile as a result of residual and solubility trapping (residual saturation of CO_2 is about 0.25 in this simulation).

Unlike the CO_2 plume, the pressure build-up in response to CO_2 injection travels fast and far. A pressure change of 1 bar and 0.1 bar (equivalent to 10 and 1 m of freshwater) are simulated as far as 150 and 300 km away from the injection area, respectively, where groundwater resources are important for water supply (Fig. 12). It has to be noted that these values are calculated for a confined aquifer. The water-table variation in an unconfined aquifer due to the same change in pressure would be much smaller. For example, Birkholzer et al. (2009) predicted a pressure change of 0.2–1.1 bars in a shallow confined aquifer that would correspond to water table rises of 0.1 and 0.5 mm for unconfined aquifers, which are negligibly small.

In any case, simulated values are less than the hydraulic drawdown induced by long-term extensive pumping in the aquifer. It was also predicted that the pressure build-up has the ability to push brines upward through the Eau Claire caprock and into overlying aquifers. Most of this leakage, however, occurs above the injection location, where the overlying aquifers are saline and shallow aquifers are not heavily used. On the other hand, a smaller fraction of the brine leakage occurs in northern Illinois, where the overlying aquifers contain freshwater, but the impact on the salinity would be smaller than that caused by the historic pumping of the freshwater aquifers in this area. Finally, up-dip migration of brines in the Mt. Simon aquifer outside the injection area is found to be limited, posing no threat to the freshwater portions of the Mt. Simon aquifer in southern Wisconsin.

An independent study conducted by Person et al. (2010) on the same basin yielded contradictory results. For instance, they predicted that pressure anomalies were restricted to a distance of about 25 km from injection wells while Zhou et al. (2010) simulated pressure anomalies reaching the limit of the basin. Person et al. (2010) also predicted a maximum pressure anomaly 6 times larger than Zhou et al. (2010). Person et al. (2010) suggest that most of the differences can be attributed to the choice of parameters, although some of the differences could also be due to differences in physical processes represented between the two codes. For instance, Person et al. (2010) model uses a sharp-interface approach while Zhou et al. (2010) used a multiphase flow model.

Another major effort reported in the literature was conducted in the Tokyo Bay area in order to predict the potential impact of CO_2 injection on the regional groundwater flow system (Yamamoto et al. 2009). The same approach as Zhou et al. (2010) was used, which involves simulating multiphase flow of CO_2 and brine in the injection area with the TOUGH2-MP/ECO2N simulator, which is a parallel version of the TOUGH2 code. The injection scenario selected for the study is an injection rate of 1 Mt CO_2/year in an array of 10 boreholes, for a duration of 100 years. The configuration of the basin is shown in Fig. 13 and the injection formation, located at a depth of about 1 km, is shown in the cross-sections of Fig. 14. Simulations have been carried for 1,000 years for a base case scenario, followed by a sensitivity analysis.

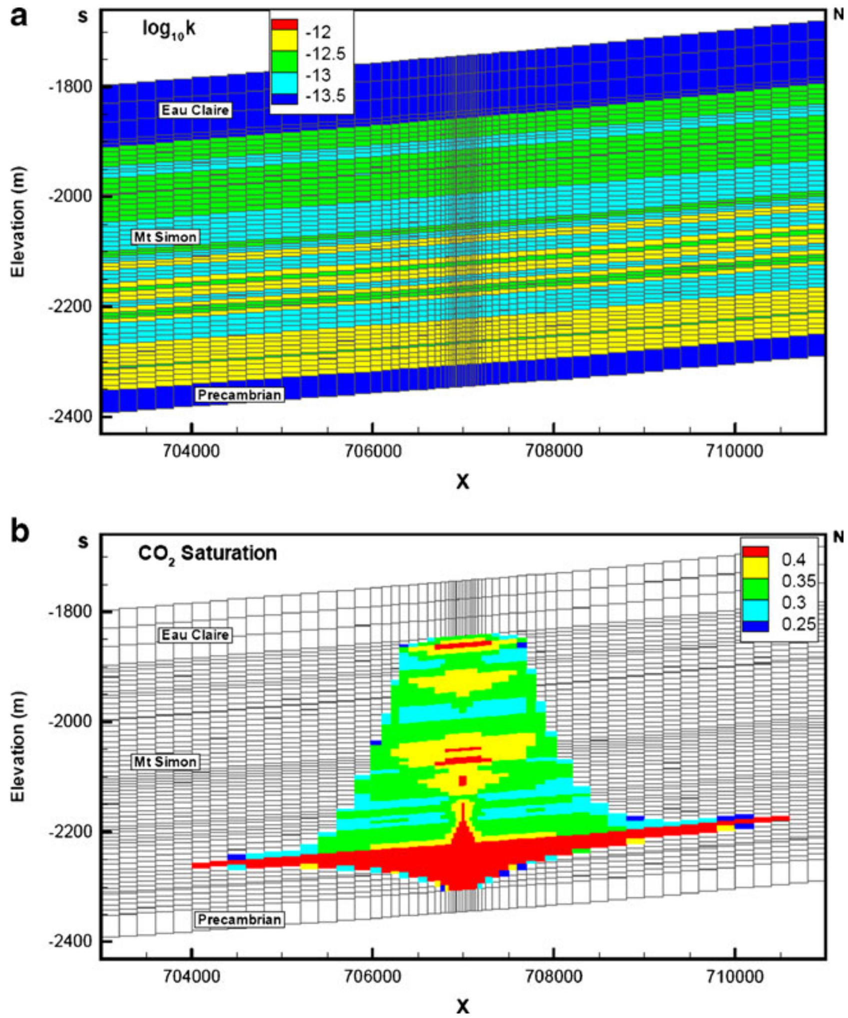

Fig. 11 Contours of simulated CO_2 saturation along a south–north cross-section at storage site 10 showing **a** the mesh and gridblock vertical permeability (in m^2), and **b** CO_2 saturation at 30 years of injection. From Birkholzer et al. (2008b), with kind permission from Lawrence Berkeley National Labs

Their simulations show that a pressure build-up of up to 1.5 bar (equivalent to 15 m of freshwater) can occur into overlying aquifers close to the injection area (Fig. 15). However, the sensitivity analyses have shown that these results rely heavily on parameters such as pore compressibility and hydraulic conductivity of the caprock, for which there are not many measurements and are highly uncertain. It was also found that groundwater discharge to the shallow aquifers can increase on the order of millimetres per year as a result of CO_2 injection and should not be a concern for brine migration.

Dong et al. (2009) conducted a quick evaluation of the potential impact of injecting CO_2 in the Songliao Basin in China on the overlying freshwater aquifers. They used the same approach as Zhou et al. (2010) and Yamamoto et al. (2009) who used the TOUGH2/ECO2N simulator to model both brine migration and the CO_2 plume development, although their conceptual model is much simpler. Their scenario involves the injection of 1 Mt of CO_2 per year in one injection well, at a depth of 1,800 m in a formation overlain by a thick sealing unit. Their primary objective was to evaluate the pressure build-up in the aquifers overlying the injection formation. Their main conclusion was that the pressure in the upper aquifer could increase from 0.5 bar up to 2 bar depending on the seal permeability.

Discussion

The far-field impact can be described as the consequence of brine migration and pressure buildup in freshwater aquifers. Brine migration can be updip, within the injected formation, or above the injection location due to vertical migration across the caprock. The most realistic simulations show that pressure build-up of 0.1–1 bar can usually be expected at a distance of 150–300 km depending on the injection volume and caprock properties. In most simulated cases, these values are in the same order of magnitude as annual variations of the water table, or to the drawdown caused by sustained historical pumping. As demonstrated by Birkholzer et al. (2009), the vertical and lateral pressure-buildup is tied to the permeability of the caprock. High permeability cap rocks (10^{-16}–10^{-17} m^2) promote vertical pressure-build-up against lateral pressure

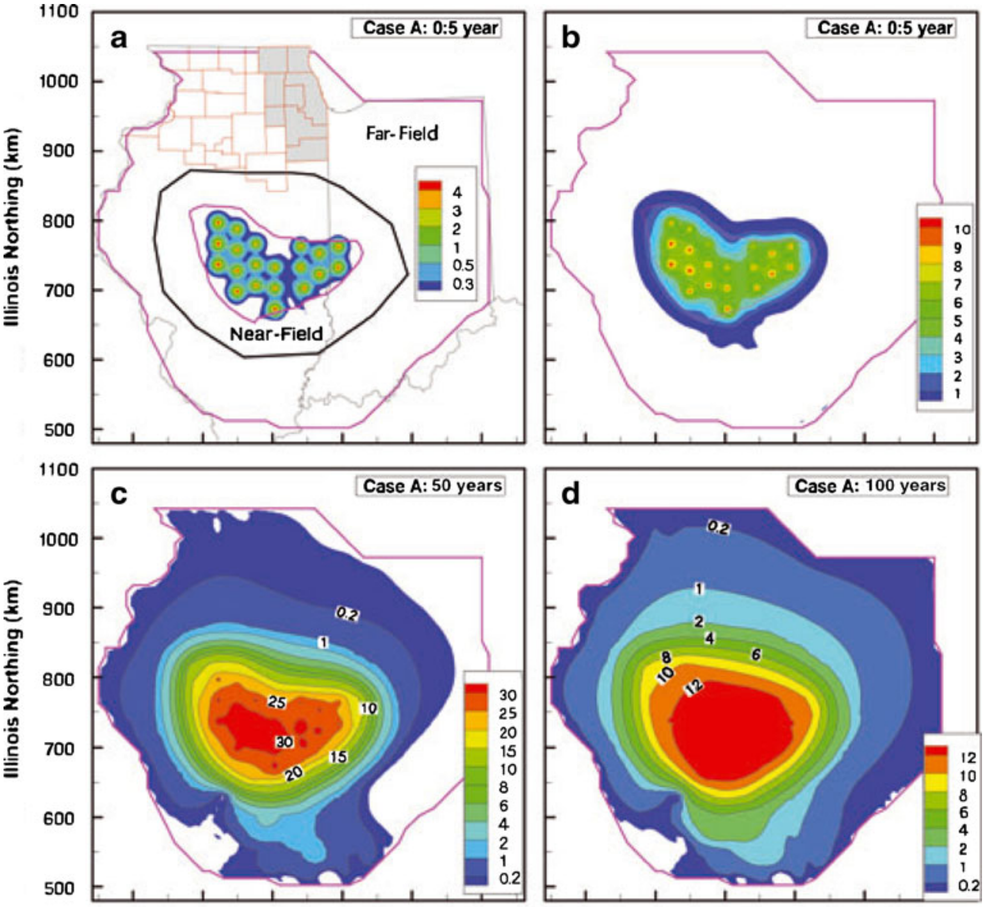

Fig. 12 Contours of pressure build-up (bar) at 0.5, 5, 50, and 100 years. From Zhou et al. (2010), with kind permission from John Wiley and sons

build-up. Conversely, tighter caprock (10^{-19} m^2) restrains vertical pressure build-up and favours lateral build-up.

Simulated pressure build-up is usually sufficient to displace brines. Simulation results show that the brine displacement in the injection formation is sometimes marginal (few hundred meters, Birkholzer et al. 2009) while in some other cases, it can reach up to 5 km over a 100-year time frame (Nicot 2008). Brine can also migrate vertically across the cap-rock and reach above formations, although the predicted volumes are usually low (e.g., the northern part of the Illinois Basin). If these formations are already saline, no environmental consequences can be expected, but if they are freshwater aquifers such as in the northern part of the Illinois Basin, the water quality can be slightly degraded (Zhou et al. 2010).

As discussed for the near-field impact, site-specific conditions are the key to realistic predictions. The choice of parameters is also very important, as shown by the different results obtained by two independent groups working on Illinois Basin (Person et al. 2010; Zhou et al. 2010). Nevertheless, scoping calculations with simple, yet realistic, models suggest that environmental impacts can be low in favourable geological environments. These favourable conditions are a tight caprock or the lack of aquifers in the formations immediately overlying the injection area.

Knowledge gaps

From the review of the published literature, some clear knowledge gap trends have emerged. These are described in the following.

Maturity of research

It is evident from this literature review that research into the potential impacts of underground geological storage of CO_2 on shallow groundwater resources has only recently been investigated and that more study is required to address the potential problems (Nicot 2008; Birkholzer and Zhou 2009; Birkholzer et al. 2009; Zheng et al. 2009a, among others). This is especially true for the far-field impact research for which the first quantitative study was published in 2008 (Nicot 2008) and for the transport of co-injected H_2S and organic compounds mobilized by supercritical CO_2, which has no quantitative predictions.

Moreover, most of the studies conducted to assess the near-field impact rely on theoretical reactive transport models and very little experimental laboratory work has been conducted so far. This clearly demonstrates that much more work needs to be conducted in order to build confidence in our understanding of the relevant processes

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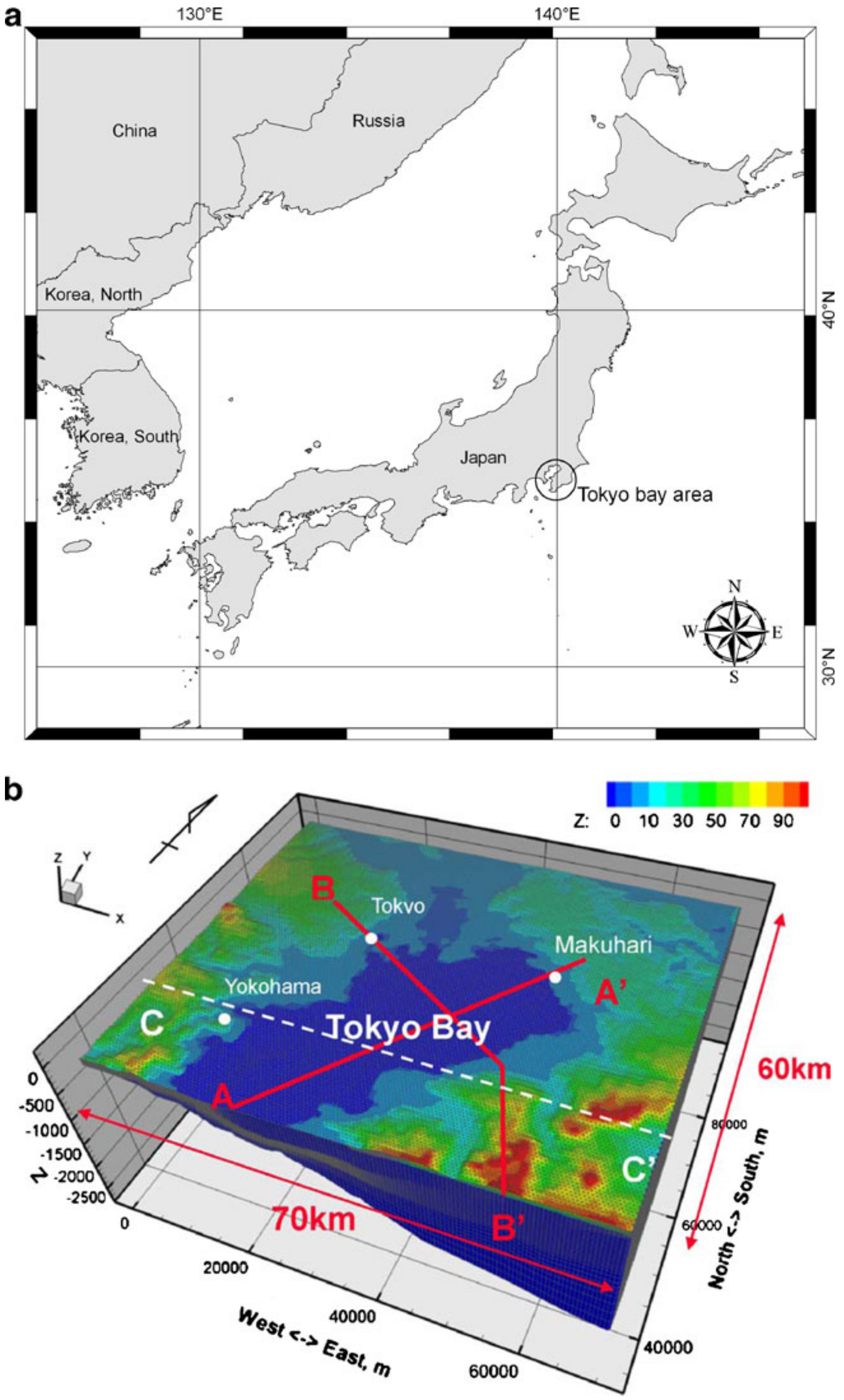

Fig. 13 **a** Location of study area. **b** Three-dimensional model domain. The color indicates the elevation *Z* in meters above sea level. From Yamamoto et al. (2009), with kind permission from Elsevier

which may be important to assess the potential impact of CO_2 storage on groundwater resources.

Lack of diversity in modelling approaches

Diversity of modelling approaches is desirable. Numerical models rely on many assumptions which can greatly influence their outcome. Defining a conceptual model, selecting the relevant modelling processes, defining boundary conditions, selecting parameters and picking a simulator are choices that can have various impacts on the modelling results.

Among the numerical studies reviewed, it was found that many strong assumptions were made which may weaken their conclusions. For instance, all of the studies focusing on the far-field impact have neglected the presence of faults and/or fractures in the caprock, while they have been observed in a few cases (e.g., Nicot 2008),

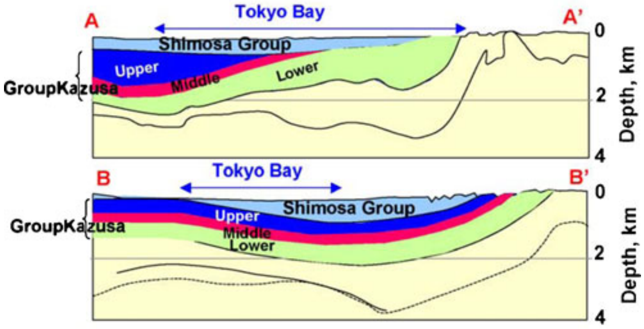

Fig. 14 Geologic cross-sections around Tokyo Bay. The storage formation is the *middle Kazuza Group*. From Yamamoto et al. (2009), with kind permission from Elsevier

or at least there are no studies demonstrating their absence. Density-dependent flow was not considered for most of the studies, while the density of brines can be up to 25% higher than fresh water. For shield environments and in the context of underground geological storage of nuclear wastes, Park et al. (2009) have shown that the upward vertical velocity can be significantly reduced by the dense brine under flushing conditions when the buoyancy becomes large. In one case (Yamamoto et al. 2009) it was also found that a fixed pressure boundary had been used at the model domain boundary, which was somehow limited (60 km×70 km). Fixing the pressure on the boundary strongly dampens the pressure build-up in the far field and introduces some bias in their predictions. The choice of parameters is also very important, as shown by the opposite results obtained by two independent groups working on the Illinois Basin (Person et al. 2010; Zhou et al. 2010).

Few of the numerical studies have considered heterogeneity within the aquifer. Heterogeneity can have many impacts on groundwater flow. For instance, Simmons et al. (2001) have found that, for certain hydrogeological conditions with fluid density variations, flow instabilities can grow and decay due to the structure and variance of a permeability field. These instabilities promote free convection that highly perturbs the flow field. This might be relevant to the far-field simulations. Spatial variability of hydraulic conductivity also contributes to the dispersion of contaminants (Sudicky 1986). For the near-field simulations, this may be important, considering that the heterogeneity of the hydraulic conductivity field will promote trace metal dispersion along the flow path and will affect the shape of the leaking CO_2 plume that migrates upward in the shallow aquifers.

Leakage scenarios for the simulation of the near-field impact were often simplified and relatively uniform. More work is needed with regard to the CO_2 leakage scenarios to surficial aquifers that could be used as boundary conditions for the reactive transport models. To this end, there might be some clues to be found in the observation of natural analogs, as described by Keating et al. (2010).

With regard to the near-field impact, it is found that some studies have completely or partially neglected adsorption/desorption (e.g., Wang and Jaffe 2004) while it is suggested that this is one of the most important process controlling the mobility of trace metals into shallow aquifers due to CO_2 leakage (Zheng et al. 2009a). The mineralogy is also often too simplistic (e.g., Wang and Jaffe 2004). The dimensionality of the models is another issue, which has been discussed, for example, by Zheng et al. (2009a), who suggested that a 2D model may not be appropriate for accurately capturing potential pH variations and trace-metal mobilization. However, many studies have been conducted in 2D only (see Table 3). In the end, the scarcity in thermodynamic data, kinetic rates, surface complexation, available mineralogy and water composition impose some serious limitations on prediction capacity of geochemical models.

A demonstration of the impact of these choices on the modelling results is critical. While sensitivity analyses were conducted by all authors, the exercise was limited to the input parameter values, and was not extended to the conceptual model. Hence, sensitivity of the results to the modelling approaches should be assessed as well.

Long-term predictions

Large-scale predictions were conducted with the underlying assumption that the major impact of CO_2 injection in deep formations would be related to the pressure build-up and saline displacement. These impacts are found to be important for the duration of the injection, and some time afterwards. If nothing important happens during that time, it is considered that future adverse impacts are unlikely because the CO_2 is contained in the hydrodynamic trap. However, what happens when the dissolved CO_2 in the formation water reaches a depth above 800 m after long-term lateral migration within the injection formation? CO_2 will likely degas. Will this indeed happen, and if so, how long will it take before this happens? Bachu et al. (1994) originally suggested that the time scale would be on the order of thousands to a million years. Using a simple numerical model, McPherson and Cole (2000) predicted a migration distance of dissolved CO_2 of only 23 km away from the injection location within 1 ka. Long-term simulations could provide an answer to this question.

Moreover, if the storage is desired for a very long time, it is important to address the potential changes in driving forces as they may impact groundwater dynamics in sedimentary basins (e.g., Jost et al. 2007; Lemieux et al. 2008c). For instance, glaciations have occurred periodically approximately every 100 ka during the Pleistocene. Even if the current interglacial period may be longer than previous periods due to global warming (Berger and Loutre 2004), it is not unlikely that another glaciation will occur within the next 100 ka. It is now fairly well accepted that glaciation periods can severely impact regional groundwater flow and reverse flow directions (e.g., Grasby et al. 2000). Subglacial meltwater infiltration can penetrate to great depths and provide a driving force that increases the groundwater velocity in deep sedimentary formations (Bense and Person 2008; Lemieux et al. 2008a, b, c; Person et al. 2007). Researchers in the field of radioactive waste disposal have

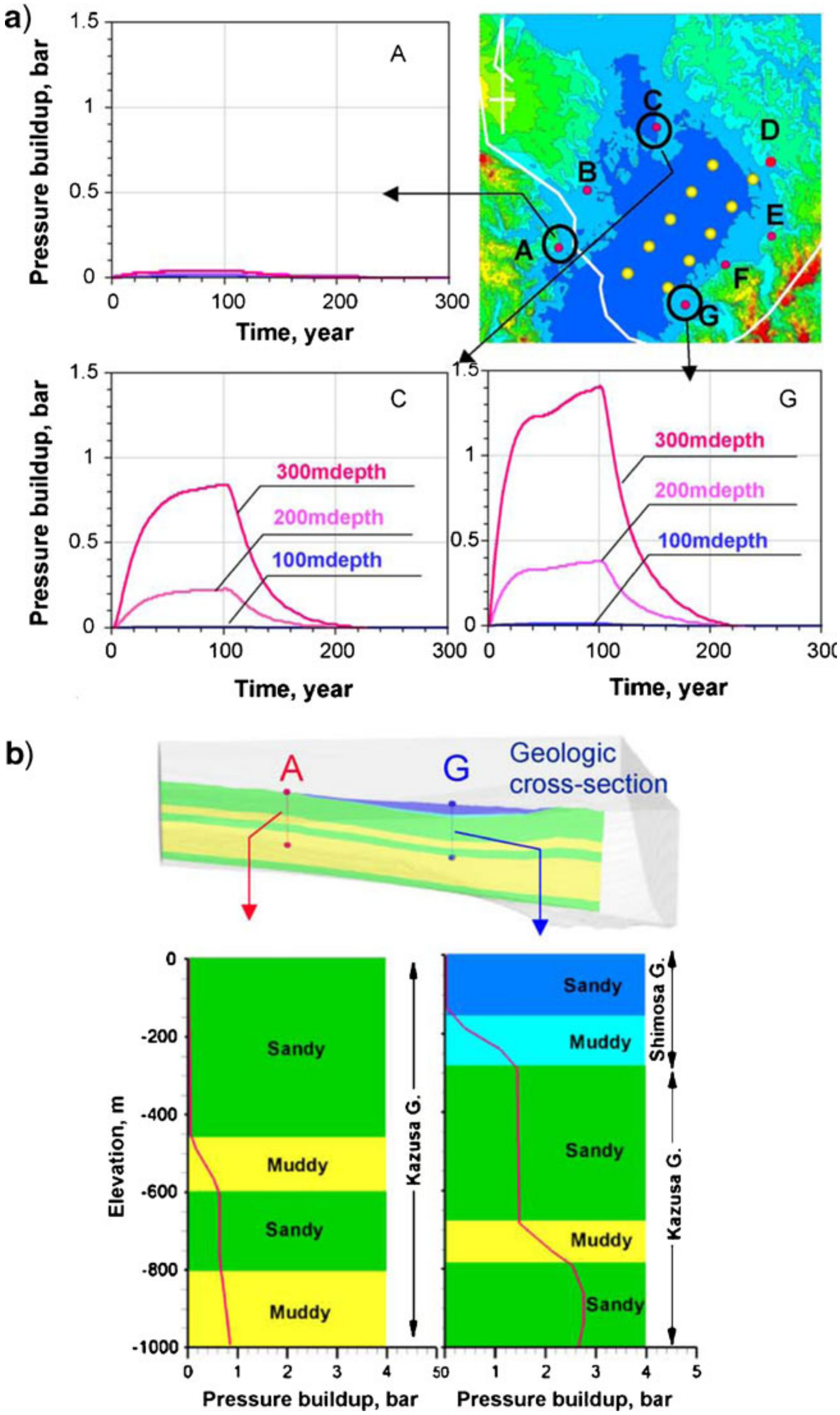

Fig. 15 Pressure build-up following CO_2 injection. **a** Transient pressure build-up at various locations and depths. **b** Vertical pressure buildup profiles at observation points *A* and *G* after 100 years. From Yamamoto et al. (2009), with kind permission from Elsevier

long recognized this issue which remains the subject of active research.

Lack of laboratory and field observations

Only limited laboratory or field experiments have addressed the potential mobilization of trace elements by acidic water due to CO_2 dissolution. These observations are very important in order to test numerical models and ensure that their predictions are realistic. Kinetic rates for dissolution and precipitation are some of the most important input parameters for reactive transport models but are also the most incompletely characterized (Wang and Jaffe 2004; Gaus et al. 2008). It has further been found that models are moderately to strongly sensitive to these rates (Zheng et al. 2009a). This means that, with our current knowledge, predictions are highly uncertain.

The conclusions obtained by Smyth et al. (2009) suggest that mobilized cations could be self-mediated by the system and be a limited risk to water quality in closed systems. However, natural aquifers are not closed systems and there is always active flow. Such conclusions need to be verified in open systems such as in column or field experiments.

Detection of carbon dioxide in freshwater aquifers

While the potential near-field impacts of leaking CO_2 on shallow groundwater resources are at some point understood, it is not yet clear how the monitoring systems to detect leaks should be designed. Some relevant questions in this regard include: Where and at what depth should the monitoring boreholes be placed? How many boreholes are needed and what should the distance between them be? At what frequency should groundwater quality and physicochemical parameters be measured?

Carroll et al. (2009) provide some answers to these questions. They suggest that occasional chemical testing for pH and alkalinity in water wells would indicate if leaking CO_2 is entering the aquifer. They also suggest that more than one monitoring well is needed to detect leaks and that one of the best places to put them is at the top of the confined aquifer, since the CO_2 will accumulate there and yield a large signal.

Research opportunities

The previous section highlighted many knowledge gaps for which new research would be beneficial. In this section, original research opportunities are proposed to fill these gaps and which would contribute to building our confidence in understanding the potential environmental impacts of underground geological storage of CO_2.

Post-auditing models

Numerical models have been used extensively as predictive tools for the assessment of near-field impacts on freshwater aquifers. While the conclusions obtained with the aid of models may provide a wide range of possible impacts, they need to be tested against field or laboratory data to assess their performance. Post-auditing consists of comparing the predictions of a model with field or laboratory observations after they have been collected.

Most of the time, numerical models are used as a tool to better understand observed processes. In this approach, a numerical model may be calibrated with observations until a good fit is obtained (inverse model). Once the fit is good, the model is used in a predictive mode to test various “what if” scenarios. However, this approach does not provide an assessment of the predictive ability of the model. To do so, it has to be compared with another set of data, different from the one used for the calibration. Ideally, predictive simulations are conducted before the field or laboratory experiments, and a post-audit is conducted afterwards. The post-audit should reveal a lot about the validity of the modelling approach for predicting the potential environmental impact of CO_2 storage.

Inter-comparison projects

Inter-comparison projects are a very good way to ensure that various models provide the same solution to a similar problem. A typical inter-comparison project involves the selection of a set of benchmark problems (or test problems) that are solved by different teams using the same precise model domain descriptions, boundary conditions, etc. The discrepancy between the model results originates from the simulator’s characteristics including time and space discretization techniques.

Such projects have been conducted in order to test the different simulators for CO_2 injection in storage formations because very complex processes are taking place. The conclusions for one of these projects are that substantial agreement was found between the results obtained from the different groups, although some discrepancies where found (Pruess et al. 2004). Nevertheless, it was concluded from the participants that the exercise has shown that models are rather robust and can be used to efficiently model the complex processes related to CO_2 storage in saline aquifers.

Another inter-comparison project, including a test problem on CO_2 leakage along a borehole, showed that a fairly good agreement of model predictions could be achieved in all cases (Class et al. 2009). The discrepancy between the modelling teams came mostly from different interpretations of the problem descriptions, for example, leading to a different assignment of boundary conditions (Class et al. 2009). A similar inter-comparison project could be conducted for the reactive transport models used for the prediction of trace element mobilization in shallow aquifers.

While inter-comparison projects build confidence in numerical models, they provide no information on how the models are used. Various approaches to the same problem can lead to significant discrepancies in modelling results. Moreover, wrong or incomplete conceptual models can usually be adequately calibrated (Bredehoeft 2003). Therefore, projects involving various conceptual models for a given problem ought to be conducted as well.

Such projects have existed for a long time for the performance assessment of radioactive waste repositories in geological formations. For instance, the DECOVALEX[1] project is an international research collaboration, initiated in 1992, for advancing the understanding and mathematical modelling of coupled thermo-hydro-mechanical (THM) and thermohydro-mechanical-chemical (THMC) processes in geological systems (Tsang et al. 2009). One of the primary

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[1] Acronym for DEvelopment of COupled (THM) models and their VALidation against EXperiments in nuclear waste isolation.

objectives is to compare model calculations with results from field and laboratory experiments (Tsang et al. 2009).

One of the key features of the project was that while model geometry and boundary conditions were specified, the conceptual model and representation of parameters were selected by the modelling team. This resulted in a wide variety of conceptual approaches addressing important topics such as the representation of heterogeneity. A similar approach was adopted by the Äspö Task force, which is a forum for the international organizations supporting the Äspö Hard Rock Laboratory to interact in the area of conceptual and numerical modelling of groundwater flow and solute transport in fractured rock (Gustafson et al. 2009). There is a need for diversity in the modelling approaches and projects like DECOVALEX and the Äspö Task Force are very efficient methods to promote this.

Field experiments

One of the major breakthroughs in contaminant hydrogeology was made in the 1980s and early 1990s through the detailed observation and description of contaminated sites located in relatively simple and well-known geological environments such as the Borden site in Ontario (Cherry 1983) and Cape Cod, Massachusetts (Leblanc et al. 1991). Artificial injections of contaminants to observe their behaviour have also been conducted many times and yielded invaluable insight into the mechanisms operating in the field. For instance, in October 1989, a dense non-aqueous phase-liquid source was emplaced in a sandy aquifer at the Canadian Forces Base Borden, Ontario, to provide a basis of investigating the effectiveness of various remediation techniques (Rivett et al. 1992). The source contained a total of 22.8 kg of chlorinated solvent composed of chloroform (TCM), trichloroethylene (TCE), and perchloroethylene (PCE).

The ZERT field experiment in Montana (Spangler et al. 2009) is the first large-scale field experiment conducted to evaluate the impact of CO_2 dissolution on the mobilization of trace elements in freshwater aquifers. The observations during the experiment shows that the processes occurring in the field are much more complex than what is usually modelled or observed in simple laboratory experiments. Many more of these experiments are required in order to gain insight into various geological environments where different minerals may be present.

Site specific studies

Generic studies are a very good way to understand the processes and to obtain a theoretical understanding of the potential impacts of CO_2 storage in deep saline aquifers. However, the systematic simulations conducted at generic sites should be translated to site-specific modelling of CO_2 storage for candidate sites, representing the local hydrogeological conditions (Birkholzer et al. 2009). These studies are likely to give a better and more relevant appraisal of the potential impacts of CO_2 storage in deep aquifers.

Conclusion

Underground geological storage of carbon dioxide in saline aquifers is considered one of the most attractive options to mitigate global warming due to anthropogenic CO_2 emissions. However, potential environmental impacts on shallow groundwater resources used for drinking water have arisen as a consequence of CO_2 or formation fluid leakage, brine displacement and pressure build-up (Bergman and Winter 1995; Holloway and Savage 1993). An extensive literature review has been conducted with the objective to summarize the current scientific knowledge pertaining to the potential impact of geological storage of carbon dioxide in deep saline aquifers on shallow groundwater resources.

Two main impact categories have been recognized: the near-field impact due to the upward vertical migration of free-phase CO_2 to the surficial aquifers, and the far-field impact caused by large-scale displacement of formation waters caused by the injected CO_2. Vertical CO_2 migration in shallow aquifers can occur along abandoned or active wells and through the caprock, when the entry pressure is reached and when fractures or faults are open for flow (naturally or because of excessive injection pressure build-up). At shallow depths, the CO_2 is a gas and can dissolve partially or completely within fresh groundwater. The CO_2 by itself is not a concern to the water quality of an underground source of drinking water, but it will change the geochemical conditions in the aquifer. The dissolution of CO_2 in groundwater increases the total concentration of dissolved carbonate which in turn increases acidity and lowers the natural pH of groundwaters.

An increased acidity can enhance the dissolution of minerals, including those containing hazardous trace elements (Zheng et al. 2009a, b, c; Apps et al. 2010). Adsorption/desorption via surface complexation is also found to be an important process controlling the fate of hazardous constituents mobilized by CO_2 leakage when sorbing minerals are present. Birkholzer et al. (2008a) have identified, based on an extensive compilation and geochemical study, that lead and arsenic are the two hazardous trace elements that are the most likely to be mobilized by CO_2 in many typical potable water aquifers of the US. Other trace metals can also be mobilized, depending on the composition of the aquifers.

Most numerical studies predict possible mobilization of trace metals as a consequence of pH reduction due to CO_2 leakage, although the reported impacts are limited and the most realistic simulations (Birkholzer et al. 2008a; Apps et al. 2010) seldom report concentrations above MCL, while field observations at the ZERT site report metal concentrations much below MCLs. The observation of natural analogs also suggests that the CO_2 impact on groundwater quality has a minor impact on groundwater quality. On the other hand, the observation of industrial analogs provide an example where CO_2 leaking from a landfill site could mobilize cadmium, but it also shows that traditional remediation techniques (soil vapour extraction) could be used to restore the site.

Even if the injected CO_2 is safely trapped, large-scale injection of CO_2 into deep saline aquifers may impact subsurface volumes much larger than that of the CO_2 plume (Birkholzer et al. 2009). Far-field impacts are defined as the indirect impact related to basin-scale migration of displaced brines in response to large-scale CO_2 injection into saline aquifers. Simulations conducted with numerical models suggest that lateral brine displacement due to CO_2 injection is in most cases minor. Vertical brine migration across the caprock into aquifers overlying the injection area is observed in most simulations, but the volume is rather small. Realistic simulations predict marginal vertical pressure build-up in the aquifers overlying the injection area but greatly depend on the permeability of the caprock. The same simulations show that pressure build-up of 0.1–1 bar can usually be expected in the injection formation at a distance of 150–300 km from the injection area depending on the injection volume and cap-rock properties. These pressure perturbations in shallow freshwater aquifers are usually in the same order of magnitude or lower than the seasonal variations of the water table or to the variations due to historical pumping.

While insightful knowledge has been gained on the potential environmental impact of CO_2 storage in deep saline aquifers, there are still many knowledge gaps. First and foremost, the state of research is very immature. It was found that quantitative assessments have only been published since 2003 and since 2008 for the far-field impact. Most of the consulted references argue that, up to now, there are few studies that have addressed environmental concerns. Most of the studies are based on numerical models, for which there are insufficient data to support firm conclusions. There is a clear lack of laboratory measurements, especially on the reaction kinetics of many minerals, and field experiments. Finally, numerical models are often used simplistically and many strong assumptions can restrict the breadth of their conclusions.

It is proposed that many of these gaps could be fulfilled by initiating inter-comparison projects in which various conceptual models are tested by different teams of researchers. This approach has been used for a long time in the nuclear-waste-disposal community. Since most of the studies have been conducted with models in a predictive mode, it is imperative that these models be post-audited once data become available. This will enable auditors to judge the quality of the predictions. More laboratory, and most importantly, more field experiments are needed to capture what will actually happen in the field. More site-specific numerical investigations are desired as they can lead to conclusions much different than generic studies. In conclusion, the possible environmental impacts of geological storage of CO_2 in deep saline aquifers on shallow groundwater resources appear to be low, but much more work is required to evaluate site specific impacts.

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