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Abstract

Fresh groundwater protection is not explicitly taken into account in the European Directive on CO\textsubscript{2} storage, although it is indirectly covered by article 1.2: “prevent and, where this is not possible, eliminate as far as possible negative effects and any risks to the environment and human health”. In this context, the CIPRES project focuses on the characterization of potential impacts of CO\textsubscript{2} leakage on fresh groundwater quality. One of the objectives is to characterize the bio-geochemical mechanisms that may impair the quality of fresh groundwater resources in presence of CO\textsubscript{2}. The microbial composition, especially in deep aquifers, such as the Albian aquifer in the Paris Basin (France), but also in superficial aquifers, has yet little been explored and its role in controlling water quality is not well known. Another aspect already highlighted by previous studies is the role of sorption-desorption processes on the mobility of trace elements.

To reach the above mentioned objectives, this project proposes two complementary study contexts: (i) laboratory experiments to characterize biochemical and geochemical processes involved in deep Albian aquifer; (ii) field experiments to characterize in situ the mechanisms having an impact on water quality in shallow chalk groundwater (~20 m deep). The characterization of mechanisms in the laboratory and in situ will be based partly on the acquisition of experimental data and partly on the calibration of numerical models. This calibration is designed to improve the numerical modeling work carried out for predictive purposes during the site characterization, impact studies and design of monitoring networks.

One outcome of the CIPRES project will be to highlight mechanisms that can impact fresh groundwater quality when a CO\textsubscript{2} leak occurs and to propose recommendations to prevent or eliminate negative effects and any risks to the environment and human health.

Keywords: fresh groundwater quality, CO\textsubscript{2} leakage, Paris basin

1. Introduction

One of the questions related to the emerging technology for Carbon Dioxide Capture and Geological Storage (CCS) concerns the risk of CO\textsubscript{2} migration beyond the geological storage formation. In the event of leakage toward the surface, the CO\textsubscript{2} might affect resources in neighboring formations
(geothermal or mineral resources, groundwater) or even represent a hazard for human activities at the surface or in the subsurface. This project will focus on two major aquifers in the Paris Basin: the deep and strategic Albian sand aquifer, and the shallow and heavily tapped chalk aquifer. The Albian aquifer is the first one used for drinking water supply above the target reservoir formations of the Dogger and the Triassic.

This project aims to increase our knowledge of the mechanisms involved when CO$_2$ intrudes into freshwater aquifers and, therefore, to study the impact of potential CO$_2$ leakage into groundwater quality. The second objective of the project is to develop a reliable methodology for monitoring the groundwater in the aquifers above the future storage sites.

1. State of the Art

Leakage of CO$_2$ or brine coming from geological storage sites is often cited as a risk for overlying fresh groundwater resources, a risk that has not yet been sufficiently analysed. However, during the process to select and characterise suitable sites, the juxtaposition with groundwater resources must be considered at the regional scale (Birkholzer et al., 2007; IEA-GHG, 2011). In the scenario where CO$_2$ – or brine – escapes from the storage formation different independent mechanisms can have an impact on groundwater (IEA-GHG, 2011).

The potential impact of these processes on groundwater quality is enhanced by the modifications of factors such as pH and redox potential due to the inflow of CO$_2$ –or brine - in a system at equilibrium. In fact, changes in the physicochemical conditions (pH, redox potential) modify the water-rock interactions as well as, probably, microbiological activity in the aquifers. The drop in pH can lead to the dissolution of minerals such as carbonates and silicates (Lu et al. 2010; Little and Jackson, 2010; Smyth et al. 2009). These reactions will buffer the pH and increase the quantities of dissolved elements and the alkalinity, which are parameters to take into consideration when monitoring groundwater quality.

As concerns micro-organisms, in the aquifers, they float freely in the water or are attached to the surface of minerals and rock (Goldscheider et al., 2006), the latter being the predominant state in oligotrophic environments. The microbial bioenosis is represented mainly by Bacteria and Archaea, which play an essential role in biogeochemical reactions (Grieblers and Lueders, 2009). In aquifers, we encounter chemolithoheterotroph or chemolithoautotroph metabolising bacteria that use sources of carbon that are, respectively, organic or inorganic such as CO$_2$. The second of these is predominant in deep aquifers due to the very low dissolved organic carbon concentration. Several studies of the microbial communities in the deep biosphere have shown that the principal metabolic pathways are sulphate reduction, fermentation and methanogenesis. Thus, in Ketzin (Germany), a modification of the microbial community was observed following the injection of CO$_2$ (Morozova et al., 2010). Oligotrophic aquifers can therefore be particularly vulnerable to an intrusion of CO$_2$ that might modify the endogenic bacterial community and thus disrupt the ecological and geochemical equilibrium. However, there have been few studies of the effects of a CO$_2$ leakage on the biocenosis of aquifers in part because of the required specificity experimental set-up and analyses.

The impacts on water quality of CO$_2$ intrusion have also been studied by geochemical modelling and, occasionally, in the laboratory or on site. Modelling is limited by the complex mechanisms that are not systematically taken into account. They show impacts alternately negligible or significant, with in some cases, for example, the exceedance of water quality limits for Pb and As (Zheng et al. 2009; Apps et al., 2010; Viswanathan et al. 2012). Furthermore, these models are rarely calibrated due to the lack of experimental data. Indeed, only recently have experiments been carried out in the laboratory to determine the impact of CO$_2$ on water quality (Humez et al. 2012; Smyth et al., 2009; Little and Jackson, 2010; Lu et al., 2010). These studies consist in putting rocks in contact with water and CO$_2$ in order to characterise the evolution of the composition of the water and quantify the release of trace elements (undesirable or toxic). Few field studies have been carried out and those that have focused mainly on the storage formation itself. In the absence of any identified leak, the
impact on the groundwater has not been studied. Regarding the Frio pilot for which groundwater quality aspects were addressed, Kharaka et al. (2009) cite the dissolution of iron oxy-hydroxides as the engine of the dissolution of metals such as Fe, Mn, Zn and Pb, thus highlighting the potential impact that CO\textsubscript{2} might have on the degradation of the quality of water resources. Kharaka et al. (2010) have studied the effect of the injection of 300 kg of CO\textsubscript{2} /day for one month in a shallow aquifer and observed dissolution of carbonates the mobilisation of metals (Fe, Mn). Peter et al. (2012) performed a small scale and limited CO\textsubscript{2} injection test in a shallow aquifer. Associated with the pH decrease, major ions and trace elements were released.

In conclusion, the geochemical effects of CO\textsubscript{2} in an aquifer are complex, all the more so since some aquifers have naturally high concentrations of trace elements (Se, F, and Fe in the Paris Basin) and a modification of physicochemical conditions could result in the exceedance of maximum permissible concentrations. The impact of CO\textsubscript{2} leakage will depend largely on the nature of the water-rock interactions, which will be highly variable depending on the lithology of the aquifer formations (carbonates, sandstone, etc.). The study carried out for the IEA-GHG (2011) concludes that the underlying processes must first be well understood so that the risks for groundwater resources can be correctly assessed. The mechanisms must be better characterised and the impacts better defined, while a regional approach must be adopted in order to quantify the effects of potential leakage. Geochemical predictions of long term impacts, based on laboratory experiments and thermodynamic simulations must be supplemented and strengthened with data from natural analogues and field experiments. In order to characterize, and then to monitor a CO\textsubscript{2} injection site, it is essential, regardless of the target formation (deep aquifer, hydrocarbon deposit, coal veins, etc.), that suitable monitoring be done both in this target area and in the overlying horizons (Kharaka et al., 2010; Lewicki et al., 2010). Whether we are studying a storage site, an injection pilot, a leakage pilot or a natural analogue, it is essential that a common methodological and analytical corpus be used.

2. Laboratory experiments

This task is broken down into complementary approaches to characterize the microbiological and geochemical processes occurring in presence of CO\textsubscript{2}.

2.1. Biogeochemical reactions – batch experiments

The objectives are (i) to characterise the microbial community in the deep Albian aquifer, (ii) to identify the biochemical reactions that are taking place there, and (iii) to determine the CO\textsubscript{2} partial pressure beyond which an impact on the biogeochemistry is shown.

A global analysis of the microbial community of the oligotrophic aquifer will be done on the water. In a first stage, total and viable bacteria will be counted. The bacterial and archaean diversity in the water will be analysed by a culture-independent approach using molecular biology techniques available in the laboratory. In addition, the functional bacterial diversity will be studied by searching for the functional genes for the dissimilatory reduction of Fe(III), in the assimilation of CO\textsubscript{2}, in the denitrification process, in sulphate reduction. The search for functional genes in the groundwater will, along with physicochemical analyses, enable us to distinguish the metabolisms that occur and are potentially active in these aquifers.

Batch experiments will be done to determine the effect of various pCO\textsubscript{2} on the principal metabolisms occurring in the aquifer. The groundwater in the aquifer will serve as the basic medium to which will be added different electron sources (NO\textsubscript{3}, organic carbon, thiosulfates). Initially, the experiments will be carried out with natural pCO\textsubscript{2} (0.01 bar) in order to determine the predominant metabolic processes in the aquifer. The effect of pCO\textsubscript{2} (1 bar) will then be tested on NO\textsubscript{3} metabolic processes on the basis of predefined criteria (a dominant process or a process having a strong impact on the geochemistry). These tests will be done in a bioreactor. Experiment might be done at
atmospheric pressure (1 bar) and at high pressure (60 bar in Albian aquifer) in order to verify the effect of total pressure on the observed biogeochemical evolution.

### 2.2. Geochemical reactions – batch experiments

The principal objectives of this sub-task are to define the availability of pollutants in the Albian aquifer both in the aqueous and particulate fractions and to determine the pCO$_2$ threshold beyond which an impact on the adsorption-desorption mechanisms is observed by modelling the solid-solution exchanges. Previous study (Humez et al. 2012) has shown that three types of behavior: Type I concerns Ca, Si and Mg concentrations which increase during the experiment, Type II implies a major decrease in dissolved Fe immediately after CO$_2$ injection, Type III corresponds to Cl and SO$_4$ plateau. Regarding trace elements, As, Ni and Zn increased in solution with time without exceeding WHO and US EPA MCLs; U and Se remained below quantification limits; finally Pb, Co and Cr were not significantly released (Humez et al. 2012). In this project, interactions between clay minerals making up the Albian rock (for the most part glauconite and smectite) and metals (Ni, Zn) and As will be simulated in batches experiments and sorption isotherms for these trace elements will be determined.

### 2.3. Bio-geochemical processes – column experiments

The final objective is to understand and quantify the importance of processes that might take place during the intrusion of CO$_2$ in the Albian aquifer. The processes will have been identified and studied separately in the laboratory in the previous sub-tasks (acidification, bacterial activity, sorption/desorption, etc.). These processes will be implemented during an experiment with the percolation of a CO$_2$-enriched fluid in a column filled with Albian greensand. After injecting water acidified with CO$_2$, we expect to rather rapidly observe an evolution of the geochemistry related to desorption-resorption phenomena controlled by the pH and the dissolved CO$_2$ concentration. Over a longer term, any changes in bacterial activity might modify these geochemical processes. The interpretation of the results obtained in terms of processes will make it possible to model the system using reactive transport models. For this, we will also use the experimental results obtained during the batch experiments. The characterization of solid phases (XRD, SEM observations, etc.) before and after interaction with CO$_2$ will be done in order to evidence modifications in the rock induced by the CO$_2$ and bacterial activity (including the formation of a biofilm).

Modeling such an experiment using reactive transport models will enable us to quantify the relative importance of each of these processes and with regard to transport. The column experiment will involve different interdependent processes that must be taken into account in the model (mineral precipitation-dissolution kinetics, redox disequilibrium present naturally in the water, bacterial kinetics, sorption/desorption by surface complexation or cation exchange model). The injection of the fluid into the column will be modeled by 1D convective/diffusive transport whose hydrodynamic parameters will have been fitted with tracer tests. The results of the batch experiments will enable us to select the models and formulation best-suited to each of these mechanisms.

### 3. Experimental simulation and In Situ monitoring of CO$_2$ leak

A CO$_2$ leak will be simulated in a shallow aquifer (about 15 m deep) by a specific experiment in order to evaluate the impact on groundwater and to characterize the CO$_2$-water-rock interactions by means of a monitoring system set up.

The objectives of this task are (i) to identify, qualify and quantify the mechanisms of impact on groundwater quality, (ii) to identify the pertinent parameters to monitor to evaluate these impacts and (iii) to test monitoring sensitivity during a controlled leak.
3.1. Experimental site

The tests will be run on an experimental site in the chalk formation of the Paris Basin. The site will be equipped with an appropriate instrumentation and will have been previously characterized. The site consists of 11 wells (10 cm diameter): one injection well (25 m deep), 6 piezometers (25 m deep) and 4 piezairs of 12 m about deep. The conceptual model of this site is represented figure 1.

The injection tests will be preceded by the characterization of the site and 6 to 9 months of monitoring in order to characterize of the hydrodynamic and geochemical baselines of the site.

3.1. Monitoring of the leakage experiment

Leakage into groundwater will be simulated via the injection of a small quantity (approximately 100 kg) of CO$_2$ of food quality in the injection well. A plume of dissolved CO$_2$ will be formed and will move according to the direction of groundwater flow and eventually by degassing in part to the surface. The injected fluid will be pure CO$_2$ isotopically marked with a specific δ$^{13}$C signature. The CO$_2$ will be injected in the saturated zone at a depth of about 20 m. Monitoring the CO$_2$ leak will be provided by different systems in groundwater, unsaturated zone and soil by on-site measurements or laboratory analyzes. Gases (CO$_2$, He) will be monitored in the piezometers (gas dissolved in the groundwater) and the piezairs (free gas in the unsaturated zone).

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Figure 1: Conceptual cross section of the experimental site

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1 holes drilled only in the unsaturated zone
The parameters monitored in the groundwater will be the piezometric head, temperature, pH and electrical conductivity. Analysis on water samples will provide chemical elements (major, minor and trace metals), dissolved gases, microbiological diversity. The pH will also be monitored in situ using a new colorimetric method in order to monitor any perturbation caused by the injection of the CO$_2$. This sensor is based on a spectrometric technique that enables considerably greater stability and robustness than classical measuring systems using electrodes. The monitoring of the possible migration of gas into the unsaturated zone will be conducted through piezairs and by measurements of the gas flux to soil-atmosphere interface and the soil gas composition near surface.

3.2. Assessment of impacts on water quality

During the injection tests, hydrochemical monitoring of the aquifer will be done in situ and by sampling. The evolution of the composition of the groundwater in terms of major elements, possibly of trace elements and isotope signatures, will be interpreted in terms of geochemical mechanisms, and the water-rock-CO$_2$ interactions that might be evidenced will be characterised. Following the injection tests, post-injection monitoring will be done to evaluate the return of the disrupted parameters to the "environmental background" values as defined by the initial base line. Modification of the chemical composition of the water in the aquifer due to CO$_2$ injection will be assessed in term of groundwater quality i.e. metal element release and the possibility of exceeding references and quality of water for human consumption.

4. Outlook

The intended experiments will give insight into biogeochemical mechanisms due to CO$_2$ intrusion as a potential consequence of leakage from CO$_2$ geological storage sites. Particular interest will be given to the effect of CO$_2$ leakage on water quality and metal mobilization. On site, the implementation of various monitoring techniques will test tools efficiency to detect leaks, including groundwater, unsaturated zone, soils and microbial population. Moreover, one task of the project focuses also on the monitoring of deep aquifers (> 100 m deep).

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6. References


