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Abstract

Geological storage of CO$_2$ in deep saline aquifers is one of the options considered for the mitigation of CO$_2$ emissions into the atmosphere. A deep geological CO$_2$ storage is not expected to leak but potential leakage monitoring is required by legislation, as *e.g.* the EU Directive relative to Geological Storage of CO$_2$. To ensure that the storage will be permanent and safe for the environment and human health, the legislation require that the CCS operators monitor the injection, the storage complex and if needed the environment to detect any CO$_2$ leakage and its hazardous effects on the environment. Various monitoring methods are available for the monitoring of CO$_2$ storage sites and the environment as listed by the IEA-GHG and the monitoring selection tool. Geophysical based methods have a greater area of investigation but may suffer from insufficient sensitivities to detect small leakages. At the opposite, geochemical monitoring methods may have insufficient investigation area but may be able to detect more subtle changes even if monitoring in deep environments is not straightforward. Leakage detection is not yet well constrained and research efforts and tests are required to gain confidence into monitoring strategies.
In the framework of the CIPRES project, funded by the French Research Agency, a shallow CO$_2$ release experiment has been performed in October 2013 in a chalk aquifer from the Paris basin. The Catenoy site has been characterised since March 2013 through several wells set on a straight line oriented along the local flow (see Gombert et al., this conference). Such an experiment is designed to gain confidence in leakage detection in subsurface environments by understanding processes and principles governing seepage occurrence. Contrary to other experiments such as ZERT

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or CO_2FieldLab ones, where gaseous CO_2 was injected directly in the water, the injection was done with water saturated with CO_2 at atmospheric pressure. 10 m^3 of water were pumped from the aquifer, then saturated with 20 kg of food-grade CO_2 and injected during 40 hours between 12 and 25 m depth. Daily monitoring of soil gases and water was performed during injection and post-injection phases (2 weeks duration) in the area previously delimited by a tracer test. The aim is to determine if geochemical methods are accurate enough to allow detecting small release in shallow environments. If successful, such an experiment can help to gain confidence in leakage detection.

As expected, no change was noticed in the unsaturated zone. The shape of gas concentrations distribution at the surface (CO_2, O_2, N_2, ^4He, ^{222}Rn) observed during the injection is strictly similar to the repartition of gas species observed since March 2013. The main process observed is respiration and no change linked to the injection was highlighted, only seasonal effects.

Slight changes were observed in the saturated zone. The water was collected at 15 m deep excepted for one stratified borehole where water was sampled at 15 and 18 m. The pH of the injected water was lower (mean value: 5.3±0.1) than the initial pH of the aquifer (7.1-7.2) due to CO_2 dissolution. Only two monitoring boreholes set 10 m and 20 m downstream from the injection well may be considered as influenced by the experiment. A probable enrichment in HCO_3 linked to interaction of the CO_2 saturated water with chalk was noticed, with an enrichment close to +8 to +10% of the initial value. For one borehole the pH value remained nearly stable in relation with pH buffering and in the other borehole a slight decrease was observed (-0.1 to -0.15 pH unit). However this decrease is significant as it is above the instrumental uncertainty of the electrodes. In addition, a slight increase of the electrical conductivity was noticed but it did not exceed +6% compared to baseline data.

Such slight changes in the physico-chemical parameters are related to small variations in dissolved elements. Apart from HCO_3, the other major ion affected by CO_2-water rock-interaction is Ca as the aquifer is mainly composed by calcite. Concentrations increases by +8 to +9% whose amplitude is in agreement with the increase of HCO_3. Trace elements were also little affected, the main change concerned Sr (+8 to +10% increase).

Modifications occurring during this CO_2 release experiment have small amplitude as expected but these results highlight that geochemical methods are able to detect small leakages. Consequently, effects were noticed only during a short period of time. It is not possible to determine if all the injected CO_2 has migrated downwards in the direction of flow or if partial lateral migration has occurred, but post-injection monitoring and boreholes logging 12 days after the stop of injection did not reveal any discrepancy in the water columns. On the other hand, the magnitude of the pH change is consistent with the behaviour of the co-injected tracer (dilution ratio ~30). In the perspective of getting more information on the remobilisation of trace metal elements, a push-pull test will be performed in 2014 on the basis of the learning of this first experiment.

1. Introduction

Mitigation of CO_2 emissions into the atmosphere is a challenging question that has received strong interest worldwide since the beginning of the 90's. Among the ways that exist to mitigate such emissions, one option is to store CO_2 in the ground and specifically to store the CO_2 as a supercritical fluid in deep saline aquifers. Numerous works have been done on this topic either consisting in numerical simulations or in-situ experiments such as pilots existing in Germany or in the North Sea. One of the key questions concerning deep CO_2 storage is the safety of the process. As safety assessment is quite complex in deep environment, efforts have been put in designing smaller scale experiments to gain confidence in monitoring operations able to detect as early as possible undesired events. In that perspective, one of the experiment's designs consists in deliberately induce a leakage in near surface environment in order to detect the leakage, to monitor it and to study how it vanishes or how the environment accounts the changes consecutive to the leakage event.

One of the most documented release experiments is the ZERT one in Montana, USA [1]. Focusing on the geochemical aspects, effects on water and soil gas geochemistry have been reported as a consequence of such

experiments. Other experiments have also shown that, even in shallow environments, complex geological settings can quickly led to biases and, in the worst case, led to poor leakage detection [2]. Therefore it is crucial to increase the number of field experiments in order to increase the confidence level in monitoring methods and leakage detection.

The French research project CIPRES was designed in that perspective. The main monitoring site – that is extensively described by Gombert et al. [3] – was hence chosen in a chalky aquifer in the Paris basin. It has been designed to perform CO_2 injection as a dissolved phase, contrary to many other experiments that perform the injection of CO_2 as a pure gas phase. The heart of the project is to study undesirable effects on water quality by studying the remobilization of trace metal elements [4] but the project is obviously not restricted to that point and other chemical changes on dissolved and gas phases have also been taken into account.

Two CO_2 releases were performed at the experimental site (Catenoy, Oise, France), the first consisting of the injection of dissolved CO_2 in an injection well and subsequent monitoring of the aquifer downstream in several monitoring wells, and the second consisting of the injection of dissolved CO_2 in an injection well that serves as pumping well some days after the injection (push-pull test). Baseline acquisitions were performed during a six months period extending from March to early October 2013.

2. First release experiment – October 2013

This first experiment consisted in the injection of 10 m^3 of water pumped from the aquifer and saturated at atmospheric pressure with 20 kg of food-grade CO_2. The injection was performed along the screened part of the injection borehole and the water + CO_2 mixture was delivered continuously between 12 and 25 m below ground level (water table depth: 12m). The injection of the water saturated with CO_2 was done with a peristaltic pump, began the 08 October at 08:00 AM and lasted 40 hours. The migration of the injected plume was monitored at 10, 20, 30 and 60 m distance downstream using dedicated monitoring boreholes extending down to 25 m depth (PZ3, PZ4, PZ5 and PZ6 in Figure 1). An upstream monitoring borehole (PZ1 in Figure 1) and two lateral piezometers (PZ7 and PZ8 in Figure 1) were used as checking boreholes. The on-site monitoring period extended over two weeks and concerned both the saturated and the unsaturated zones.
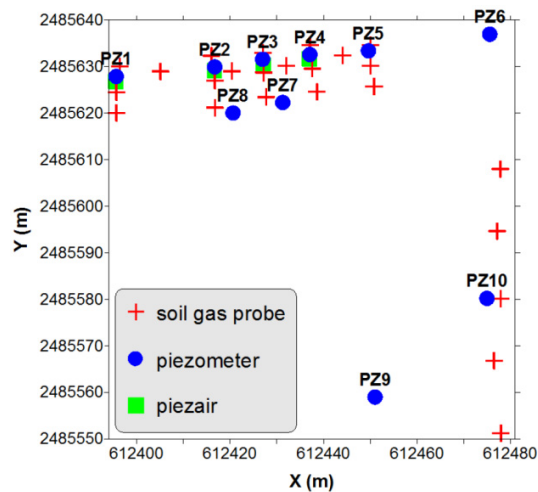

Fig. 1. Location of the monitoring points.

As the injected quantity of CO_2 is reduced when compared to other experiments [1, 2], the monitoring of soil gas species (CO_2, O_2, N_2, ^4He, ^{222}Rn) was only done to check that no degassing occurred. Twenty four soil gas probes were inserted in the soil and allowed the collection of gas at 1 m depth. CO_2 concentrations were directly monitored using infrared device and cross-checked in the field by gas chromatography measurements. Consequently, the shape of the CO_2 distribution in soils was not affected by the experiment as illustrated by Figure 2. Oxygen concentrations, measured using electrochemical methods, were found to reversely correlate with CO_2 concentrations, the relationship between the two species strongly suggesting the preponderant influence of respiration processes in soils onto the concentrations changes.

At longer time scale (months), it is possible to highlight the existence of concentrations changes linked to seasonal variations as a consequence of the temperature rise between March and summer months but this also correlates well with soil biological activity.
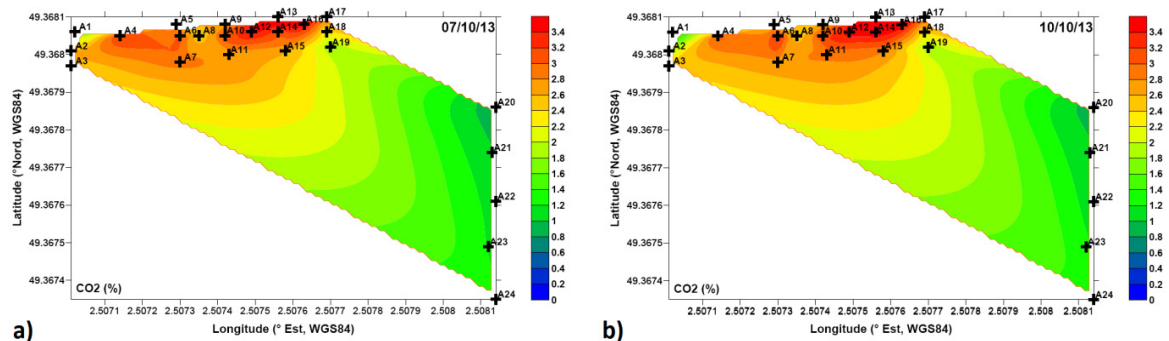

Fig. 2. a. CO_2 concentrations (% vol.) in the soil gas at 1 m depth prior to the injection; b. CO_2 concentrations during the release experiment.

The monitoring of the saturated zone was done by pumping at an intermediate level, *c.a.* 3 m under the water table level (around 15 m below ground level), except the PZ4 borehole that was also monitored at 6 m under water table level. These monitoring depths were not arbitrarily chosen and were deduced from the pumping tests and tracers experiments performed during the characterization phase of the experimental site. The injected water was characterized by a pH value consequently lower than the one of the aquifer, with values of 5.3 ± 0.1 and 7.15 ± 0.05 respectively. This is a direct consequence of the CO_2 dissolution in water and such a pH contrast can be easily monitored in natural conditions.

By reference to the last baseline acquisitions performed prior to the launch of the injection, only slight changes were noticed during the monitoring period and they only concerned PZ3 and PZ4 boreholes, the "strongest" changes being found in PZ4 as illustrated by Figures 3 and 4. The following statements can be made:

- pH values: as the natural variability of the site is very reduced, the decreases by 0.15 to 0.2 pH units do not result from measuring biases and can be considered as real decreases. Compared to the pH of the injected water, detecting the plume only referring to pH monitoring seems to be difficult. Nonetheless, this also suggests that the carbonated aquifer has a strong buffering capacity and that even quite large amounts of CO_2 may be quickly buffered – ingress of 20 kg of CO_2 in 10 m^3 of water near the surface in an aquifer will effectively constitute a strong leakage when considering a real CO_2 storage site.
- Electrical conductivity: slight increases of max. +6% are stated and may also be related to the remobilization of elements as dissolved phases as a consequence of the migration of the injected acidic water. Referring to the buffering capacity of a carbonated aquifer, such geochemical processes may have been restricted to the vicinity of the injection borehole and monitoring waters at 10 or 20 m distance may have led to signal dilution.

- Alkalinity: the bicarbonate concentration was monitored in the field quickly after water sampling. Increases of max. +10% were monitored, and they also argue for a reduced but existing influence of the acidic water onto the aquifer matrix.
- Dissolved CO_2 concentrations: slight increases are also monitored and again suggest weak influence of the CO_2-water injection.

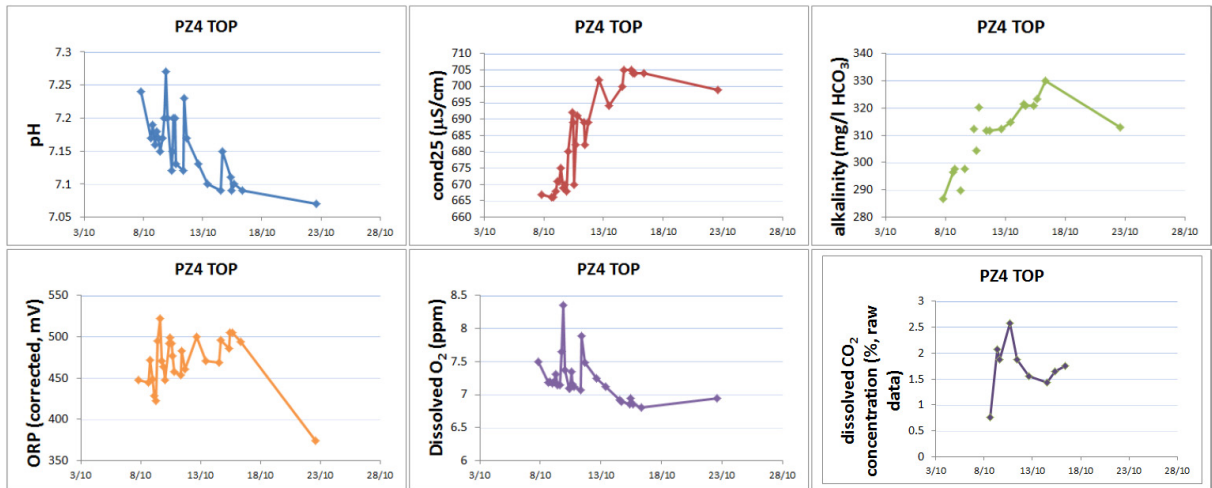Fig.3. Evolution of pH, electrical conductivity, alkalinity – expressed as bicarbonate content, redox potential (ORP), dissolved oxygen and raw dissolved CO_2 concentrations at 15 m depth in PZ4.
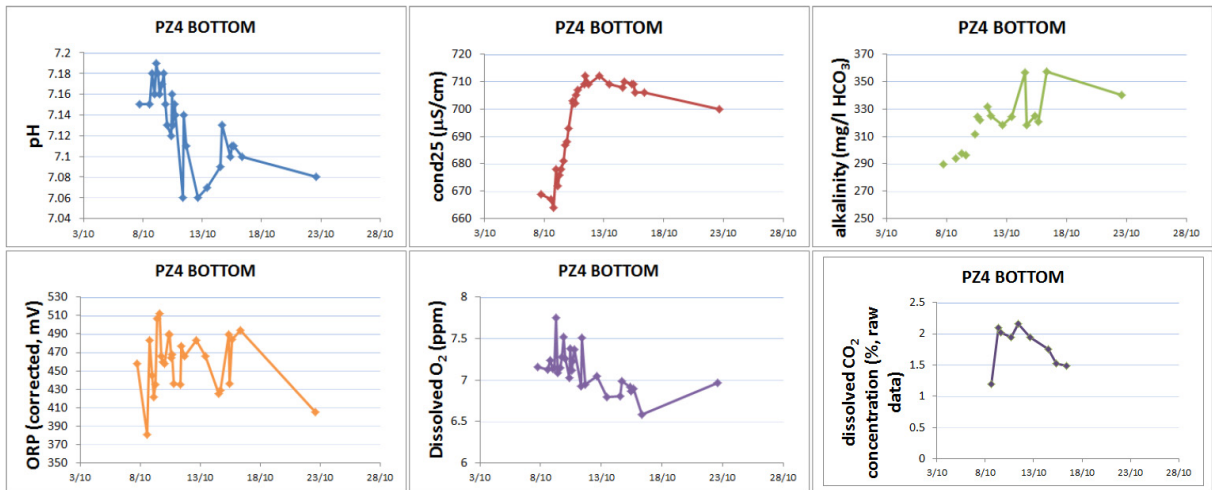

Fig. 4. Evolution of pH, electrical conductivity, alkalinity – expressed as bicarbonate content, redox potential (ORP), dissolved oxygen and raw dissolved CO_2 concentrations at 18 m depth in PZ4.

Major and trace elements have been analyzed in order to determine the impact of the CO_2 injection. Data are presented in Figure 5 for PZ4 at 18 m depth. There is no deviation from the Ca-Mg-HCO_3 water type during the experiment, but some subtle changes are noticed for Ca (increase by +9% of the concentration) and are synchronous with those established for HCO_3. The maximum of the increase is stated 3 days after the beginning of the injection and it also corresponds to the mean travel time between boreholes as established during tracer tests. Other major elements remained in the natural variability plus the uncertainty of the measurement (variation range of ±3%). Strontium was the main trace elements that had experienced some increases in concentration, again with a +10% rise three days after the initiation of the experiment.

These conclusions are well in agreement with the chemistry of the chalk that forms the aquifer matrix and the interaction of this matrix with CO_2 enriched water. The major component of the rock matrix is $CaCO_3$ with abundances ranging between 95.6 to 98.3 % (abundances determined at 10, 14 and 20 m depth in the injection borehole). The addition of acidic water has then changed equilibrium conditions and led to a weak but existing dissolution of carbonate and subsequently the rise in the Ca concentrations in water. Similarly, the Sr content of chalk has been determined between 950 to 1180 mg/kg whereas other trace elements were only present at low levels (less than 40 mg/kg). The increase in Sr concentrations just after the injection relies then on the same process that the one having led to rise in the Ca concentration *i.e.* calcite dissolution.
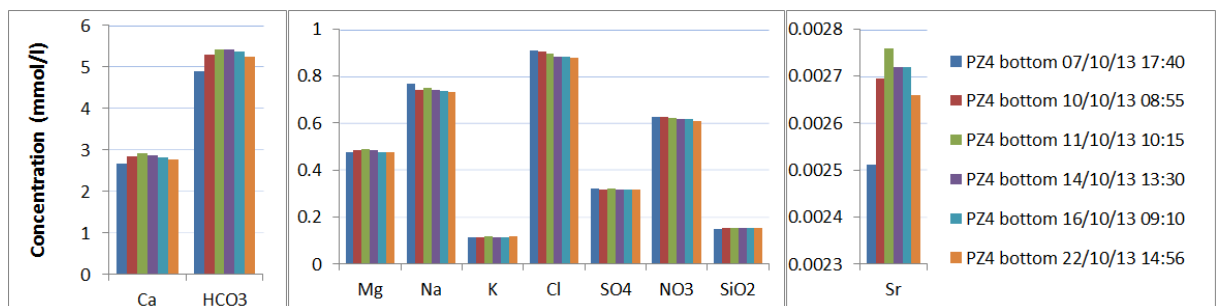

Fig. 5. Evolution of concentrations in dissolved elements at 18 m depth in PZ4.

Last measurements on site were performed on the 22 October, five days after the end of the regular site monitoring. For PZ4 (Figures 3, 4 and 5), most parameters did return to baseline levels or near baseline levels except the electrical conductivity and the bicarbonate content that were slightly higher. This led to the performing of new physico-chemical loggings in all the piezometers in order to check if no connate water was present. Apart from the bottom part of the injection well (Figure 6), no deviations of pH nor electrical conductivity nor other parameter that may be linked to the presence of residual waters enriched in CO_2 or dissolved elements were stated. As a consequence, it is thus believed that the buffering capacity of such carbonated aquifer is sufficiently strong to quickly attenuate CO_2 leakage events.
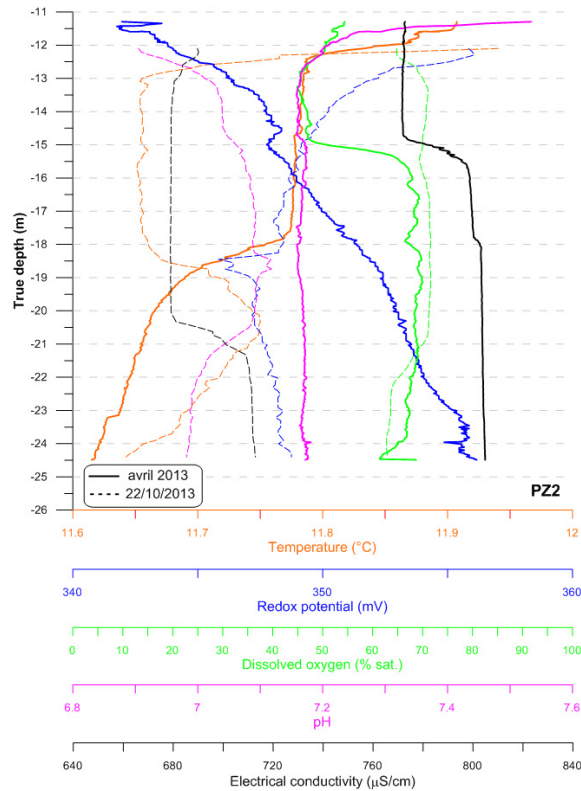
Fig. 6. Chemical logging in injection borehole PZ2; data from April 2013 (solid line) and October 2013 (dashed line) are presented.

3. Second release experiment: push-pull test – March 2014

As the first injection test was successful but did not allow to monitor changes as strong as expected, and did not allow to easily determine if all the injected water flowed downstream as suggested by previous tracer tests, it was decided to perform another leakage experiment with another strategy. This second test consisted in injecting again water saturated with CO_2 at atmospheric pressure but only using 3 m³ of saturated water and in pumping it again in the injection well after 1 weekend of interaction within the aquifer. Both the injection process, performed this time only by gravimetric flow at the bottom of the borehole, and the pumping process were intensively monitored using physico-chemical characterization. In order to check that the injected water has been pumped back two tracers were added, namely uranin and lithium. Uranin is routinely used in hydrogeology and can be easily monitored in the field using spectrometric detection. Lithium is used as it is only present at trace levels in the water (less than 3 ppb) so that any increase will be related to the push-pull experiment. Prior to the use of lithium, tests were done at laboratory using the chalk and the water from the Catenoy site in order to check that no reactivity (*e.g.* adsorption onto mineral surfaces) can happen.

Soil gas monitoring was not carried out as the first experiment showed that no leakage occurred neither in the soil at 1 m depth nor deeper at 10 m depth above the water table level. Focus was on the water monitoring.

The 3 m³ of water were injected on the 21 March evening and the pull phase began on the 24 March at 11:00 AM. The pumping was first performed using one pump set at 17 m depth and a second pump was added at 16 m depth at the end of the 24 March in order to reach a global 4 m³ per hour pumping rate. This allows to sufficiently

drawdown the water table level and consequently to pump back the water that was injected before (Figure 7). Physico-chemical parameters experienced changes very comparable to those registered in October 2013:

- Water pH had a minimum value of 6.95 pH units that corresponds to a -0.2 unit decrease;
- Electrical conductivity rose up to 700 µS/cm and then decreased back to near pre-injection values at the end of the monitoring period (maximum increase of +6%);
- The alkalinity, expressed as the bicarbonate content, was also higher at the beginning of the pull phase (330 mg/l) and then decreased back to 295-300 mg/l, giving a maximum rise of +10%.
- Dissolved oxygen and redox potential values had some variations that are difficult to link with the experiment.

The pumping was stopped at the end of the week after the extraction of 328 m^3 of water. Usually push-pull tests are performed by pumping a consequently lesser proportion of water. A recent test [5] performed also for CO_2 purposes in Mississippi injected 3285 l of water and pumped back 15142 l, giving a ratio of around 5 between pumped water and injected water. The present push-pull test pumped back approximately 110 times the volume that was injected notably as a consequence of the high transmissivity of the chalk aquifer where the experiment took place.
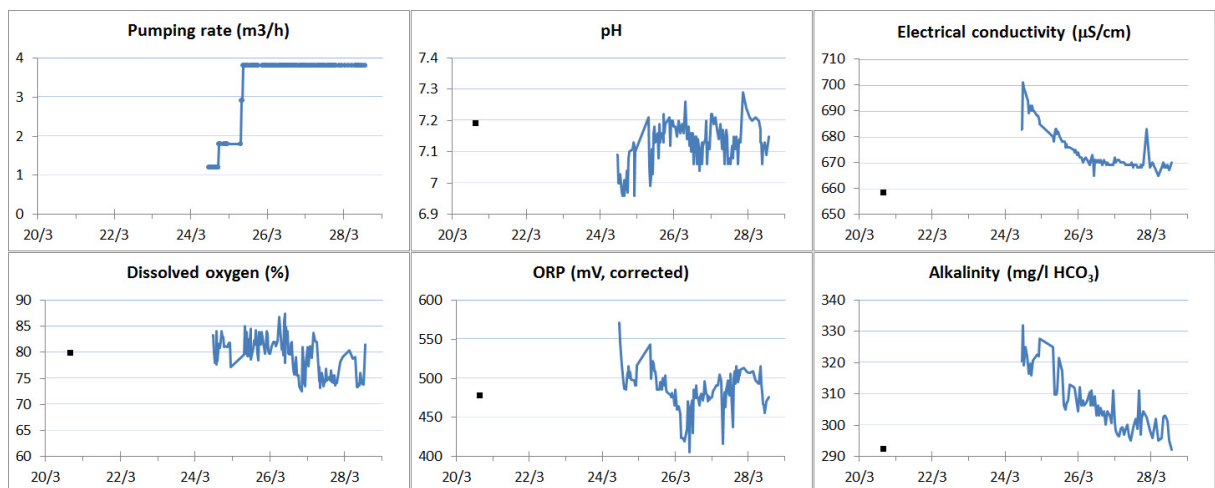

Fig. 7. Evolution of pumping rate, pH, electrical conductivity, dissolved oxygen, redox potential (ORP) and alkalinity – expressed as bicarbonate content in the water pumped from borehole PZ2 during the pull phase of the push-pull test, March 2014. Black dots represent the baseline data measured just before the injection of water + CO_2 mixture (push phase).

Such a volume is thought to be large enough to get a good tracer restitution curve. Hydrogeological tracer (uranin) indeed gives a good restitution curve (Figure 8). A pulse like rise of the tracer concentration was monitored just after the initiation of the pull phase and was followed by a decrease back to low concentration levels. This may be attributed to residual injection water present in the vicinity of the borehole that was not drained by hydrological flow. After two days of pumping, the real tracer peak appeared. At the stop of the pumping process, concentrations were back to low levels thus suggesting that most of the tracer was pumped. Such a restitution curve may suggest that the water was drained by the natural flow of the aquifer and that some time was necessary to pull back the water that may have travelled to some distance (typically of the order of few meters when referring to the hydrological characteristics of this aquifer).

The situation is different when considering lithium tracer. Apart from the first liters for which the concentration was high but not at its maximum, the shape of the restitution curve mimics the ones of electrical conductivity of

alkalinity (Figures 7 and 8). After 5 days of pumping, concentrations were not back to baseline levels. The lithium restitution curve can be approximated with a good confidence level by polynomial regression thus allowing to estimate the quantity of lithium that has been retrieved. Three grams of lithium standard were included in the 3 m^3 of injected water, laboratory checking leading to an amount of 2.92 g. Among these 3 grams, 2.28 grams have been pumped back to the surface. Such a restitution curve is similar to that obtained by Yang et al. [5] with bromide tracer. These authors attributed this shape to the occurrence of mixing processes between injection water and background aquifer water that progressively dilutes the tracer signal.

As a consequence, using two tracers allows to discriminate between distinct phenomena: the first is linked to hydrological settings. Uranin tracer indicates that a high proportion of the injection water has travelled in the aquifer thus highlighting the success of the injection experiment. Lithium tracer is a proxy that gives information on the reaction process that occurred in the aquifer. The reactional "paroxysm" is monitored few times after the initiation of the pumping as the proportion of injected water vs. background aquifer water is favorable. As the pumping took place, the proportion of injection water that had reacted with the aquifer matrix (*e.g.* Ca is solubilized) decreased. This gives an asymptotic-like curves for lithium, electrical conductivity or bicarbonate content.
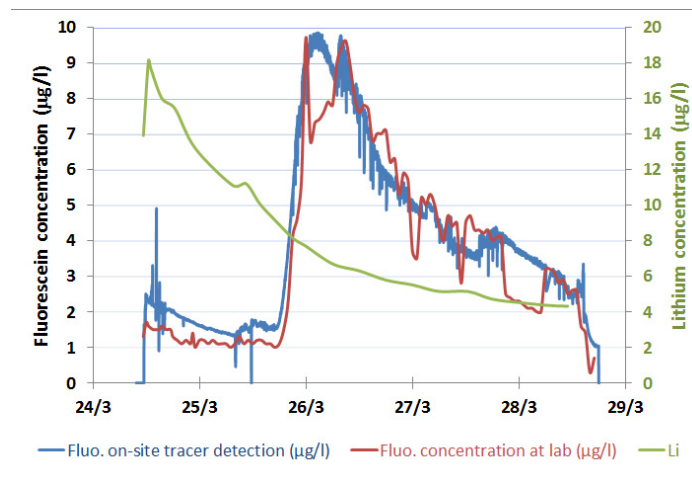

Fig. 8. Tracers concentrations: uranin concentrations measured directly in the field (blue line) and at laboratory on samples (red line) – data courtesy of INERIS; lithium elementary concentrations measured at lab (green line) – natural lithium concentrations are less <3 µg/l.

Elementary concentrations in dissolved elements are also varying accordingly to that of physico-chemical parameters and lithium tracer at least for species that have been identified as changing ones during the first filed test (Figure 9). Calcium concentrations were slightly greater at the beginning of the pull phase (+10% enrichment) when compared to background levels. Strontium concentrations did not exactly follow the same evolution with time: maximum enrichment (+5%) was monitored twelve hours after the beginning of the pumping phase, a temporality that is neither congruent with that of physico-chemical parameters nor with that of uranin. All the other chemical species remained close to baseline concentrations.
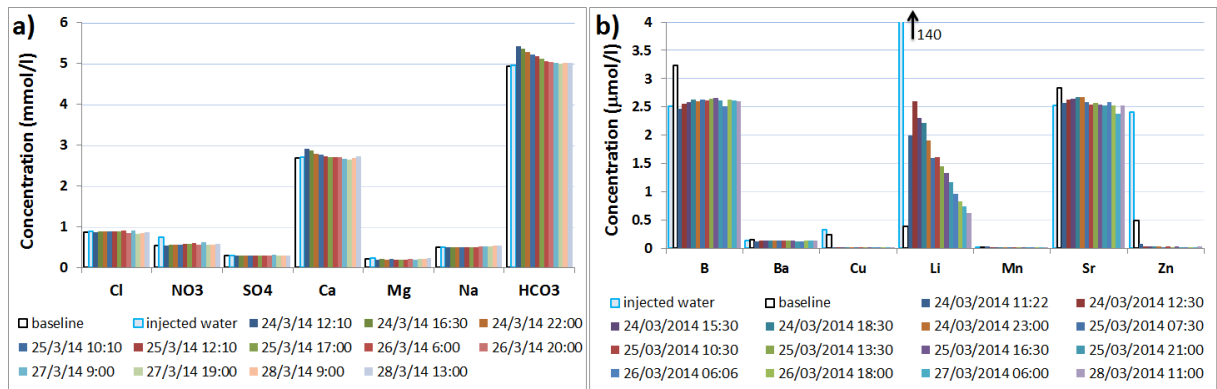
Fig. 9. (a) Major elements concentrations during the pull phase – data courtesy of IPGP; (b) Trace elements concentrations during the pull phase; baseline water and injected water compositions are indicated.

4. Conclusions

Two CO_2 release experiments were performed in a shallow chalky aquifer from the Paris basin. The first experiment consisted in the injection of 10 m^3 of water saturated with CO_2 in an injection well and to monitor plume migration under the sole action of the natural hydraulic gradient. The second experiment consisted in injecting 3m^3 of water saturated with CO_2 and containing uranin and lithium as tracers and to pull back the injected water by pumping in the same borehole.

The two experiments led to very similar conclusions: the buffering capacity of carbonated aquifers is strong and only allows to monitor slight changes of pH, electrical conductivity and bicarbonate concentration. Maximum deviation from baseline data was ±10% of the initial value. Only two chemical species, abundant in such geological context, were found to be affected by the presence of injected water, namely Ca and Sr. All the other monitored species or parameters remained close to baseline values. Especially, there was no strong release of trace metal elements in the water, as a result of i) the buffering capacity of the aquifer and ii) the relatively low content of the rock matrix in such elements. As a consequence, a third CO_2 release has been planned in more clayey environment and was accomplished in July 2014. Data interpretation is still under progress.

Acknowledgements

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