Well-based, geochemical leakage monitoring of an aquifer immediately above a CO$_2$ storage reservoir by stable carbon isotopes at the Ketzin pilot site, Germany

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Abstract

We measured dissolved inorganic carbon (DIC) stable isotopes ($\delta^{13}$C$_{\text{DIC}}$ in ‰) of brine from an observation well within the first aquifer above the CO$_2$ reservoir at the Ketzin pilot site, to test whether these can detect potential CO$_2$ leakage. The monitoring revealed that DIC concentrations and $\delta^{13}$C$_{\text{DIC}}$ values were masked by the used high alkaline drilling mud, even eight months after well development. However, subsequent changes in $\delta^{13}$C$_{\text{DIC}}$ and DIC from of -27 ‰ and 165 mg L$^{-1}$ to -23.5 ‰ and 116 mg L$^{-1}$ reflect most likely a shift towards pristine values of the aquifer.

Keywords: CO$_2$ storage; leakage; well-based monitoring; stable isotopes; overlying aquifer

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1. Introduction

Carbon dioxide capture and storage (CCS) can be a substantial part within a greenhouse gas reduction portfolio in order to mitigate anthropogenic CO₂ emissions into the atmosphere [1]. However, its application also has to consider possible risks and public concerns regarding this technology. To ensure safety and health for environment and people in the vicinity of CO₂ storage sites and to prove the integrity of the injection processing, efficient complementary monitoring is important [2,1,3]. To achieve this, monitoring activities should comprise also other compartments than the target reservoir for CO₂ injection. This particularly includes overlying aquifers as well as soils and surface waters and the biosphere compartment [2]. Furthermore, appropriate baseline survey of all these compartments before injection is key for meaningful monitoring.

At many CCS pilot sites world-wide, several present and newly developed surface- as well as downhole geochemical and geophysical techniques have been applied for monitoring purposes [3-12]. Within the geochemical compartment, stable isotope investigations became an increasingly applied method and an overview is presented by [13]. Stable isotopes of carbon and oxygen can contribute in the investigation of gas-water-rock interactions via tracing of CO₂ migration in the reservoir and may detect leakage between aquifers in the subsurface [14,15]. Stable isotope investigations of the CO₂ are also able to quantify how much of the injected CO₂ is kept in solution by “ionic trapping” [16,4,17,18,8,19,20].

By convention, natural abundance stable isotope ratios are expressed in a per mille (‰) deviation from an internationally accepted standard according to the following equation:

\[
\delta^{13}C \ [\%o] = \left( \frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \right) \times 1000
\]  

(1)

The principle of stable isotope applications is that the naturally occurring variations of isotope abundances are useful tracers for phase changes, mobility and mixing of materials. In this manner, many chemical and physical processes that are accompanied with the injection of CO₂ can alter the oxygen and carbon isotope ratios of injected CO₂ and the already present dissolved inorganic carbon in reservoir fluids. For example, in many cases the injected CO₂ has another carbon isotope ratio than the dissolved inorganic carbon (DIC) of the reservoir brine and thus determination of \( \delta^{13}C \) values before and after injection can allow to quantify solubility trapping of the injected CO₂ with the aid of isotope mass balances [19,20]. In addition intensive exchange rates between oxygen of the CO₂ molecule and the water in the pore space are expected to equilibrate the oxygen isotope ratio of each phase and with that alter the isotope composition of the present water. This can constitute a secondary dynamic tracer for the interaction of CO₂ and H₂O.

Stable carbon isotopes may also provide a tool to detect possible leakages of injected CO₂ in overlying aquifers. That is, carbon isotope values of DIC can alter very quickly, if injected CO₂ dissolves in the present groundwater. Such advanced isotope indicators have been shown in studies at the Ketzin Site in Germany [19]. Here, the \( \delta^{13}C \) value of DIC in the reservoir shifted towards \( \delta^{13}C \) values of injected CO₂. This helped to anticipate the breakthrough of the CO₂ plume at observation wells. However, so far few studies are published about leakage monitoring in overlying aquifers, such as for instance for the Frio I experiment [21]. In this study, one observation well was sealed at the injection horizon and perforated in the overlying section six months after injection. Results obtained from this sampling campaign yielded new chemical and isotope markers that indicated migration of CO₂ into the overlying aquifer [21].

Within this study, geochemical monitoring, including measurements of pH, stable carbon isotope and concentration measurements of DIC were conducted at a newly drilled well at the Ketzin site. The primary purpose of this well and its monitoring was to gain baseline values from the aquifer above the reservoir. A novel U-tube sampling system was installed in order to allow frequent sampling of formation brine [22]. Based on these values, a possible impact of CO₂ from the reservoir on the Exter Formation brine was planned to be assessed. Subsequent baseline monitoring aimed to generate a data set that could
be compared to geochemical changes, caused by a potential leakage of CO₂ from the reservoir. To the authors’ knowledge, this is the first study that uses an observation well directly above the target reservoir for permanent geochemical leakage monitoring.

2. Methods

During a pumping test, which was carried out after drilling of the borehole, six fluid samples were collected at the producing wellhead (Fig. 1). Samples were collected in 500 mL gas-tight glass flasks for further subsampling in the laboratory.

Permanent baseline monitoring started about 7 weeks after the pumping test and 40 fluid samples were collected with a U-tube sampler for carbon isotope and dissolved inorganic carbon (DIC) analyses. The sampling apparatus consisted of a septum-capped 500 mL glass flask that was flushed and filled with the fluid gained at the U-tube outlet. Subsequently, 5 mL of the brine were extracted with a syringe and transferred into a septum-capped 5 mL glass vial that contained HgCl₂ for preservation. During this procedure, the sample was also filtered through 0.45 µm pore size nylon filter. This sampling procedure aimed to avoid particulate material and bacterial turnover of carbon in the sample and prevented contamination with air or degassing of the sample.

To determine DIC concentrations and its isotope ratios ($\delta^{13}C_{DIC}$) in the laboratory, field samples were subsampled and transferred to 12 mL helium flushed vials for analysis. Subsequently, the samples were treated with 100% phosphoric acid and left to degas for 24h. After this time period, all DIC was turned over into CO₂(g) and the headspace was analyzed for the carbon isotope ratio of the liberated CO₂ on an isotope ratio mass spectrometer (IRMS) that was connected to an auto-sampler with an extraction and transfer system (gasbench). DIC concentrations were determined from the area of the first sample peak in the CF-IRMS chromatogram and comparison to standards of known concentration. This method is described in detail in [23]. All DIC concentrations are reported in mg L⁻¹ as HCO₃⁻.

Geochemical batch and mixing calculations of the Exter-Formation fluid were carried out using the code PHREEQC. Concentrations of Na⁺, Mg²⁺, Ca²⁺, Fe²⁺, Mn²⁺, NH₄⁺, Cl⁻, SO₄⁻ and NO₃⁻ were obtained from literature data about typical fluids of the area [24, 28] and DIC as well as pH values were obtained from field measurements. PHREEQC was used to simulate the dissolution of an assumed 1400 mg L⁻¹ CO₂ that may represent a leakage scenario in the monitored Exter Formation brine, in order to evaluate the accompanying impact on DIC, pH and $\delta^{13}C_{DIC}$. Calculations were carried out with PHREEQC and the Pitzer database (Parkhurst et al., 1999).

3. Results

During the pumping test, DIC concentrations increased from 213 ± 19 mg L⁻¹ to 1147 ± 19 mg L⁻¹ after about 4 m³ of fluid were pumped from the well. After reaching this peak, concentrations decreased towards 433 ± 19 mg L⁻¹ after about 12 m³ fluid were pumped from the well (Fig. 1). Regular monitoring campaigns started six weeks after the pumping test and during the following 5 months, DIC concentrations further decreased and then remained constant at about 165 ± 12 mg L⁻¹.

$\delta^{13}C_{DIC}$ values of the pumping test correlated negatively with DIC concentrations. Lowest DIC concentrations showed the most $^{13}$C-enriched $\delta^{13}$C values (-27.1 ± 0.1 ‰), whereas the highest concentrations show the most $^{13}$C-depleted $\delta^{13}$C values (-30.2 ± 0.1 ‰). During the regular monitoring, $\delta^{13}$C values decreased slightly from -26.1 ± 0.1 ‰ at the first monitoring campaign to -27.4 ± 0.1 ‰ five months later (Fig. 1).
Figure 1: Observed DIC concentration and corresponding carbon isotopic composition from the pumping test and U-tube monitoring in well P300. During the pumping test both values are negatively correlated due to the variable ratio of high alkaline drilling fluid with a $\delta^{13}C$ value of -31.1 ‰ and a low $\delta^{13}C$ value (-31.1 ‰).

Within the same time period the measured pH values dropped from 8.3 to 7.2. In October 2012 DIC concentrations decreased to 116 ± 15 mg L$^{-1}$ and $\delta^{13}C_{DIC}$ values shifted about +4 ‰ towards more positive values to -23.5 ± 0.2 ‰ until November 2012 (Fig. 1).

4. Discussion

4.1. $\delta^{13}C$ and DIC concentration of pumping test samples

The rising of DIC concentrations and their subsequent decline after further pumping is most likely an indicator of contamination by drilling fluids. The drilling fluid used was mainly based on K$_2$CO$_3$, with several organic additives. This matches with drilling reports that indicated that the drilling mud had high alkalinity values of about 18000 mg L$^{-1}$ and ranged around pH values of about 10.5. Isotope measurements carried out for samples of the drilling fluid revealed negative $\delta^{13}C$ values of -31.1 ‰. Therefore, it is most likely that depleted $\delta^{13}C$ values coincide with higher DIC concentrations and drilling mud concentrations.

However, no linear relationship between drilling mud contaminations determined with fluorescine tracer data and the isotope and DIC data could be found. The reasons are most probably geochemical changes that affected the sample between sampling and analysis. When the samples arrived in the laboratory, large amounts of calcite had precipitated. It is known that Ca$^{2+}$ concentrations are generally high in the Exter-Formation and range around a value of 3000 mg L$^{-1}$ [28,26] and at the Ketzin area Pchalek [26] reported values of 715 to 1016 mg L$^{-1}$. Together with the high alkalinity of the pumping test samples, caused by the residual drilling mud, this led to rapid calcite precipitation. The geochemical batch and speciation calculations of the formation fluid gained after 12 m$^3$ pumping, i.e. at the end of the
pumping test showed, that the fluid was still oversaturated with respect to calcite (SI= 4.3). Therefore, calcite precipitation altered DIC concentrations and its $\delta^{13}$DIC of the samples and drilling mud contamination states cannot be quantified with these parameters [25-27,16]. Nevertheless, the data allow a semi-quantitative assessment of contamination states and pumping test processing.

4.2. Development of DIC and $\delta^{13}$C values during permanent monitoring

The drop of DIC concentrations in the timespan between the pumping test and beginning of the permanent monitoring, as well as the simultaneous shift of $\delta^{13}$DIC towards more positive values reflects the flushing of the formation fluid from drilling mud contamination. DIC concentrations of 165 mg L$^{-1}$ that were measured during the first five months of the permanent monitoring (March 2012 until September 2012) are comparable to HCO$_3^-$ concentrations of fluids from other wells in the Exter Formation (mean = 183 mg L$^{-1}$ HCO$_3^-$)[28]. According to batch and speciation calculations, the groundwater reached calcite equilibrium already 7 weeks after the pumping test. This should at least have partly caused the observed reduction in DIC concentrations between pumping test and start of the permanent monitoring. Another process that might have led to a reduction in DIC concentrations and also a reduction of residual drilling mud is groundwater flow that transported the mud away from the borehole and brought in fresh fluids with lower DIC concentrations.

The observed shift towards more depleted $\delta^{13}$DIC values between March 2012 and September 2012 from -26.1 ± 0.1 ‰ to -27.4 ± 0.1 ‰ may result from bacterial turnover of organic matter from the drilling fluid. Bacterial turnover of organic material from residual mud within the pores might have pushed the $\delta^{13}$DIC towards more depleted values. If so, only small amounts must have been turned over because within the same timespan, DIC concentrations showed no significant changes.

Although $\delta^{13}$C values shifted to more positive values after the pumping test, values between -26.1 ‰ and -27.4 ‰ that were measured between March 2012 and September 2012, appear still too negative for pristine values. This values may therefore still reflect residual drilling mud contamination and bacterial turnover.

Nevertheless, the quick changes in DIC concentration as well as $\delta^{13}$C after September 2012 might hint at decreasing influences of drilling mud contamination, because both parameters, DIC concentration and $\delta^{13}$DIC show a strong shift towards values that indicate drilling mud reduction. The reason for this reduction can be further groundwater flow, which have led the plume to pass the catchment area of the well.

However, as DIC concentrations appeared to have almost remediated from the residual drilling fluid, the $\delta^{13}$C value of -23.5 ‰ that was measured after September 2012 is the one that could be closest to the pristine carbon isotope value and therefore the baseline of the Exter Formation.

Compared to baseline values from the Stuttgart Formation, which range at about 43 mg L$^{-1}$ DIC and -12 ± 0.4 ‰ $\delta^{13}$DIC [29], DIC in the Exter Formation appears at higher concentrations and more depleted carbon isotope values. This seems plausible, if one assumes organic contents within this formation that may have already been placed there during deposition [30]. Furthermore, findings of pyrite in drilling cores indicate activity of sulfate reducing bacteria. The decomposition of organic matter by sulfate reducing bacteria can generate high DIC concentrations with associated more negative (i.e. $^{13}$C-depleted) $\delta^{13}$C values [31,32,20].

4.3. Potential of stable carbon isotopes as a tool for on-going leakage monitoring

On-going stable carbon isotope monitoring can support detection of a potential leakage, because a value of about -23.5 ‰ is distinct from $\delta^{13}$C values of injected CO$_2$, which ranges around -30 ‰ [14]. In
case of CO₂ leakage, a shift in δ¹³C_DIC towards -30 ‰ accompanied with an increase in DIC concentration would be expected, although fractionation processes during dissolution and dissociation of CO₂ in the formation fluid have to be considered [16]. At pH and temperature conditions that are present in the Exter Formation, newly dissolved CO₂ from the storage reservoir (δ¹³C_CO₂ reservoir = -30 ‰) would contribute with about -23 ‰ to the DIC pool, because of fractionation between dissolved CO₂ and bicarbonate [26]. After dissolution of about 150 mg L⁻¹ CO₂ pH begins to drop to a value of 6 and the species CO₂(aq) becomes more prominent within the DIC pool. This changes the isotope difference between CO₂(g) and H₂CO₃ towards a value of -1 ‰ [27]. The overall isotopic composition of the DIC should then be the weighted average of HCO₃⁻ and CO₂(aq) in the DIC pool and their corresponding isotope values. Figure 2 shows the development in pH, DIC concentration and δ¹³C_DIC during the dissolution of the assumed 1400 mg L⁻¹ CO₂, with the assumption that 260 mg L⁻¹ calcite are present in the formation fluid due precipitation after drilling mud contamination and with a δ¹³C value of the CO₂ of -30 ‰.

Figure 2: Simulated evolution of pH, DIC and δ¹³C_DIC values during dissolution of 1400mg L⁻¹ CO₂ in the Exter Formation brine. DIC concentration curve is approximately exponential because it is plotted against pH, which has a logarithmic scale. The δ¹³C_DIC approaches a constant value of about -23.5 ‰ because of fractionation between CO₂(g) and HCO₃⁻. When pH drops and CO₂(aq) becomes the dominant species and fractionation between CO₂(g) and DIC (i.e. H₂CO₃ at this pH) becomes -1 ‰. Thus δ¹³C_DIC values shift towards a value -31 ‰.

5. Conclusions

Isotope baseline monitoring of the Exter aquifer above a CCS storage formation in Ketzin has been masked by influences of drilling fluids that were applied during the establishment of a new borehole for monitoring. Therefore it has not been possible to obtain pristine reservoir fluids at the beginning of the geochemical monitoring from this newly established borehole. The DIC and δ¹³C_DIC values of the Exter Formation were influenced by the highly alkaline drilling fluid, even several months after well development. However, a strong depletion in drilling mud contamination and a shift towards less contaminated δ¹³C values was observed eight months after well development. This suggests remediation of the drilling mud contamination by groundwater flow and adjustment by the formation fluid to geochemical equilibrium.
Ongoing isotope monitoring can contribute to leakage detection, because CO₂ that was injected into the reservoir (i.e. the Stuttgart Formation) has a distinct carbon isotope value when compared to $\delta^{13}\text{C}_{\text{DIC}}$ in the Exter formation and would cause detectable changes in both, DIC concentration and $\delta^{13}\text{C}_{\text{DIC}}$ in case of leakage.

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