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High-resolution stable carbon isotope monitoring indicates variable flow dynamic patterns in a deep saline aquifer at the Ketzin pilot site (Germany)

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ABSTRACT

Stable isotopes of injected CO_2 act as useful tracers in carbon capture and storage (CCS) because the CO_2 itself is the carrier of the tracer signal and remains unaffected by sorption or partitioning effects. At the Ketzin pilot site (Germany), carbon stable isotope composition ($\delta^{13}C$) of injected CO_2 at the injection well was analyzed over a time period of 4 months. Occurring isotope variances resulted from the injection of CO_2 from two different sources (an oil refinery and a natural gas-reservoir). The two gases differed in their carbon isotope composition by more than 27‰. In order to find identifiable patterns of these variances in the reservoir, more than 250 CO_2-samples were collected and analyzed for their carbon isotope ratios at an observation well 100 m distant from the injection well. An isotope ratio mass spectrometer connected to a modified Thermo Gasbench system allowed quick and cost effective isotope analyses of a high number of CO_2 gas specimens. CO_2 gas from the oil refinery ($\delta^{13}C = -30.9$‰, source A) was most frequently injected and dominated the reservoir $\delta^{13}C$ values at the injection site. Sporadic injection of the CO_2 from the natural gas-reservoir ($\delta^{13}C = -3.5$‰, source B) caused isotope shifts of up to +5‰ at the injection well. These variances provided a potential ideal tracer for CO_2 migration behavior. Based on these findings, tracer input signals that were injected during the last 2 years of injection could be reconstructed with the aid of an isotope mixing model and CO_2 delivery schedules. However, in contrast to the injection well, $\delta^{13}C$ values at the observation well showed no variances and a constant value of −28.5‰ was measured at 600 m depth. This is in disagreement with signals that would be expected if the input signals from the injection would arrive at the observation well. The lack of isotope signals at the observation well suggests that parts of the reservoir are filled with CO_2 that is immobilized.

1. Introduction

Global emissions of carbon dioxide from energy consumption rose up to more than 30 Gt CO_2 a^{-1} in 2010. CO_2 concentrations exceeded 400 ppm in the earth's atmosphere at arctic stations in April 2012[1] and at Mauna Loa Observatory in May 2013[2] and will likely reach this value with global average in 2016 (NOAA 2012, 2013). The impact of elevated carbon dioxide concentrations on the global carbon cycle is a challenging scientific question related to climate change. Natural terrestrial and oceanic carbon sinks can mitigate these emissions (Le Quere et al., 2007; Piao et al., 2008; Zhao and Running, 2010). However, human activities in greenhouse gas reduction are still insufficient. Within this context, carbon capture and storage (CCS) technologies represent a considerable tool in a portfolio of different reduction methods to mitigate CO_2 emissions on a global and climate-relevant scale (Gunter et al., 1998; Haszeldine, 2009).

The application of CCS technologies also needs a clear understanding of potential risks and public concerns about gas-leakage and groundwater quality that might be affected by storage of large amounts of CO_2 in the subsurface (Kharaka et al., 2009; Zoback and Gorelick, 2012). To ensure safe storage of CO_2 over geological timescales and to minimize risks for local environments and populations, it is essential to characterize adequate sites, to monitor the injection process and to trace the fate of CO_2 in the subsurface (IPCC, 2005). Within the various efforts of monitoring,

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[1] http://research.noaa.gov/News/NewsArchive/LatestNews/TabId/684/ArtMID/1768/ArticleID/10187/NOAA-Carbon-dioxide-levels-reach-milestone-at-Arctic-sites.aspx (accessed 19 August 2013).

[2] http://research.noaa.gov/News/NewsArchive/LatestNews/TabId/684/ArtMID/1768/ArticleID/10061/Carbon-Dioxide-at-NOAA's-Mauna-Loa-Observatory-reaches-new-milestone-Tops-400-ppm.aspx (accessed 19 August 2013).

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stable isotope applications are a powerful tool to complement other geochemical or geophysical methods (Freifeld et al., 2009). The advantage of stable isotope analyses is that the carbon and oxygen isotope ratios of the injected CO_2 can be used as an already present, natural tracer. The direct measurement of isotope ratios of CO_2 can provide representative results as it traces the medium in question, whereas other tracers might have individual migration behavior (Myers et al., 2013).

At several CCS sites worldwide, isotope measurements were applied successfully and a comprehensive overview is given in Nowak et al. (2013a). Applications range from tracing the CO_2 plume (Emberley et al., 2005; Kharaka et al., 2006; Boreham et al., 2011), determination of amounts of CO_2 that arrive at enhanced oil recovery (EOR) production wells (Johnson et al., 2011b; Lu et al., 2012a), quantification of solubility and ionic trapping of CO_2 within the reservoir brine (Raistrick et al., 2006; Myrttinen et al., 2010) and assessment of porespace saturation of the reservoir with free phase CO_2 (Johnson et al., 2011a).

The Ketzin pilot site in Germany is the longest operating test injection site in Europe (Martens et al., 2012). Between June 2008 and June 2012 61,400 t of CO_2 have been injected into a deep saline aquifer that is monitored by several observation wells. A broad interdisciplinary monitoring program including geophysical, geoelectrical and geochemical investigations has been applied to ensure integrity of the reservoir and to trace the fate of injected CO_2 (Giese et al., 2009; Wiese et al., 2013). Within these monitoring campaigns, isotope techniques have already been applied to successfully monitor CO_2 dissolution and allowed early detection of the plume breakthrough at observation wells (Myrttinen et al., 2010). Additionally, a new well-based leakage-monitoring concept has been developed for the aquifer immediately above the reservoir, combining stable isotope, geochemical and hydraulic approaches (Wiese et al., 2013; Nowak et al., 2013b). These field observations and supplementary laboratory experiments helped to advance CO_2 isotope systematics under reservoir conditions and leakage monitoring (Becker et al., 2011; Myrttinen et al., 2012a; Wiese et al., 2013).

In addition, from May to July 2011, a field experiment was conducted at the Ketzin site, in which 1515 t of oxy-fuel CO_2 from the lignite-fired power plant "Schwarze Pumpe" were injected (Martens et al., 2012). The CO_2 derived from the oxy-fuel combustion process had a different carbon isotope value compared to the usually injected food grade CO_2 and caused a temporary shift of $\delta^{13}C$ values at an observation well at 50 m lateral distance from the injection site (Martens et al., 2012). Furthermore, the normally applied food-grade CO_2 strongly varied in its carbon isotope composition, because most of the injected CO_2 was supplied from two main sources. These are an oil refinery (source A) and a natural CO_2 reservoir (source B). In order to use all these variances as a natural tracer during injection, a high-resolution monitoring programme was established. It consisted of four one-week monitoring campaigns with up to three daily sampling events per day between March 2012 and May 2012 and subsequent monthly monitoring until October 2012.

The main objective of this study was to characterize the carbon isotope distribution of the input CO_2 and to quantify the amount and frequency of isotope tracer signals by a high resolved isotope monitoring at the injection well. These observations were compared to isotope data sampled with the same frequency at the observation well in the reservoir. Such high-resolution monitoring is important in order to test if variances of the input CO_2 can be characterized and predicted and if they are also transposed to the reservoir. This could reveal new insights into the migration behavior of injected CO_2 as well as help describe geochemical interactions in the subsurface. The setting at Ketzin is ideal for this purpose because CO_2 could be sampled and measured along every step of the CO_2-path from the source to the observation well of the reservoir. Furthermore, new sampling and analysis methods were developed in order to better handle large numbers of samples and to examine the extent to which sampling techniques may affect carbon stable isotope values.

2. Site description and geology

The Ketzin site is located 25 km west of Berlin, in the northeastern part of the German sedimentary basin. Injection was carried out into a deep saline aquifer, the Stuttgart Formation, at depths between 620 m and 710 m below ground level. Reservoir pressure and temperature range at 62 bar and 35 °C, respectively (Martens et al., 2012). The heterogeneous succession of the Stuttgart-Formation consists of fluvial flood-plain type silt and mudstones with occurrences of incised sandstones that represent channel facies deposits (Förster et al., 2006). These deposits represent the main target reservoir (Martens et al., 2012). This storage formation is overlain by an up to 150 m thick mudstone-dominated sealing formation that is known as the Weser Formation.

In the Ketzin area the gravitational doming of Permian salt deposits caused the formation of an ENE-WSW striking anticline structure, the Roskow–Ketzin double anticline. This structure serves as a structural trap for the storage site. The injection facility is located at the southern flank of the anticline structure. The injection well Ktzi 201 has two associated observation wells, Ktzi 200 and Ktzi 202 that are located at distances of 50 and 100 m (Fig. 1). All wells host a broad range of down-hole monitoring instrumentation including temperature, geoelectric and geophysical devices (Wuerdemann et al., 2010; Zimmer et al., 2011). The injection facility has operated since June 2008 with an average injection rate of 45 t CO_2 per day (Martens et al., 2012). CO_2 was usually delivered in 10–20 t loads by road tankers and was filled as a liquid phase into a pre-injection facility that consisted of two connected 50 t gas tanks, plunger pumps and electrical heaters (Fig. 1). In order to enable proper inflow into the reservoir against formation pressure and to avoid two-phase flow during injection, the CO_2 was injected in a near-supercritical state of 73.8 bar and 31.1 °C. Continuous injection into the reservoir via borehole Ktzi

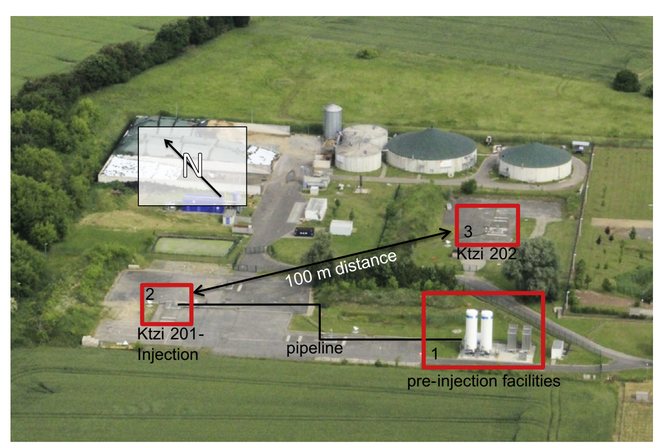

Fig. 1. Aerial view of the Ketzin pilot site. The experimental setting for this study was designed as follows: (1) The pre-injection facility comprises two 50 t storage tanks that are charged twice a day by road tankers. Samples of the charged CO_2 were taken directly from road tankers. (2) After passing the pre-injection facilities, the CO_2 is transported as a near supercritical phase through a pipeline to the injection well. Samples from Ktzi 201 were taken from the pipeline at the inlet to the well-head. (3) Samples from the reservoir were gained in 100 m distance from the injection point at well Ktzi 202. A rising tube allowed continuous sampling of the self-lifting CO_2 at this point.