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Results from twelve years of continuous monitoring of the soil CO_2 flux at the Ketzin CO_2 storage pilot site, Germany

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Abstract

The complete cycle of specific processes related to the geological storage of CO_2 is investigated in detail at Ketzin since 2004. The scientific monitoring program targets different depths of the involved area and addresses the safety and reliability of the storage. The surface monitoring comprises long-term soil CO_2 flux measurements and soil gas analyses. Annual mean values of soil CO_2 fluxes ranged from 2.4 to 3.4 µmol m^{-2} s^{-1} before the injection started (2005-2008) and from 2.3 to 3.5 µmol m^{-2} s^{-1} during and after CO_2 injection (2009-2016) and thus do not indicate an upward migration of the injected CO_2.

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Keywords: Ketzin pilot site; monitoring soil CO_2 flux; soil gas measurements

1. Introduction and motivation

Under the coordination of the GFZ German Research Centre for Geosciences the first European onshore CO_2 storage project was initiated in 2004 at Ketzin, approximately 25 km west of Berlin, Germany. About 67 kt of CO_2 (purity > 99.9%) were injected there into a saline aquifer from June 2008 until August 2013. All project stages were accompanied by a comprehensive monitoring and modelling program, focusing on the investigation of the processes involved and to assure leakage-free CO_2 injection and geological storage. Hence, methods from different geoscientific disciplines were applied, targeting the reservoir itself, the cap rock, the above-zone and the surface [1,2]. Here we report on the results of the long-term surface monitoring with continuous soil CO_2 flux measurements

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and complementary measurements of the soil gas composition and $\delta^{13}C_{CO2}$ isotopic ratios at selected locations. A profound and extensive database of measurements performed before injection started serves to interpret data during and after CO_2 injection [3]. As the CO_2 flux measurements reflect the specific site conditions, which can vary locally and over time, trends must be interpreted carefully.

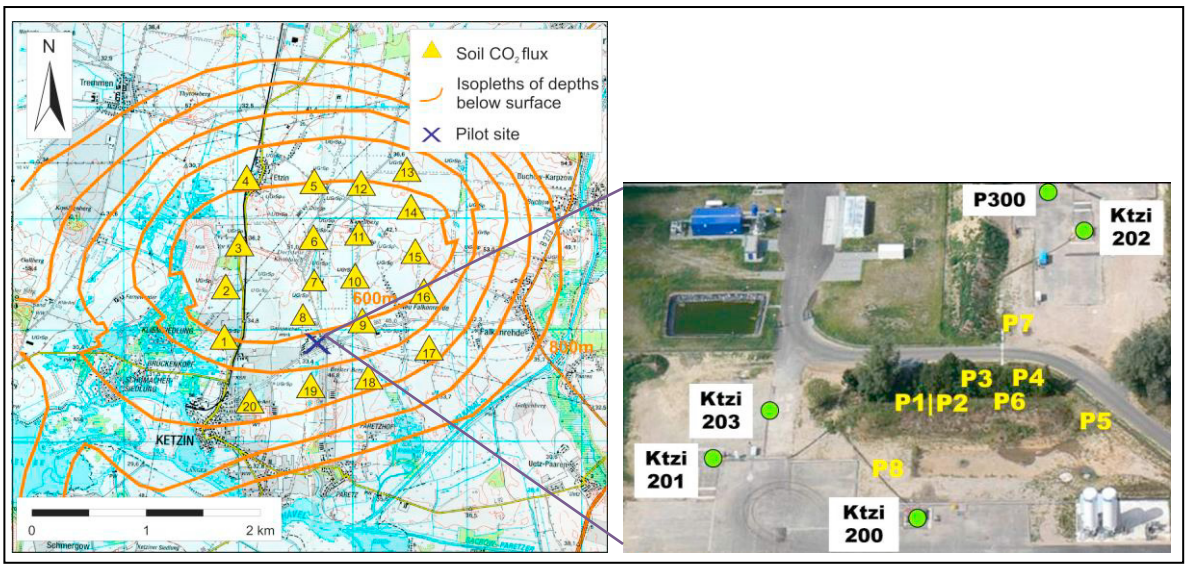

Fig. 1: Map of the Ketzin pilot site with 20 long-term surface sampling locations (triangles) and eight permanent locations at the injection site (blue cross and yellow squares on the photograph). Additionally, all five wells are depicted, with Ktzi 201 being the former injection well.

2. The Ketzin pilot site, the monitoring concept and methods

After an exploration phase in 2004 and drilling of the first wells in 2007, CO_2 was injected between 2008 and 2013 into Upper Triassic sandstones at a depth of 630 to 650 m. This reservoir is overlain by more than 165 m of shaley cap rocks. The site itself is located at the southern flank of the Roskow-Ketzin double-anticlinal structure [4,5,6] and the stored CO_2 mainly migrated in northern to western direction [2].

Monitoring at the surface started in 2005 with soil CO_2 flux measurements using a LI-8100 automated soil CO_2 flux system (LI-COR Biosciences) and a 10-cm survey accumulation chamber. The CO_2 concentration in the discharging soil air is measured with an integrated infrared gas analyzer. Twenty measuring locations were arranged in a 2.5 km x 2.5 km fixed sampling grid that covers (i) the potential area of subsurface CO_2 distribution and (ii) unaffected regions for comparison (Figure 1). The alignment of the sampling grid also considered geological and artificial structures e.g. faults, troughs [5,6] and wells. In order to obtain information on seasonal trends, measurements were performed once a month and since 2012 twice a month.

To refine the monitoring network grid, eight automated permanent 20-cm accumulation chambers (LI-COR) were additionally installed on site in 2011 in the direct vicinity of the injection and observation wells. Using this system, the CO_2 soil flux was measured on an hourly basis around the clock. Due to the automatic operation of the system without daily maintenance, technical problems (failure of sensors or clogging of the chamber by e.g. animals or leaves) have caused gaps in the data series. Simultaneously the soil temperature was recorded at all 28 stations with a thermocouple (Omega Engineering GmbH) and the weather conditions with a MWS 9-5 station (Reinhardt System- und Messelectronic GmbH).

Detailed soil gas analyses can give information about the origin of the CO_2. As natural soil CO_2 is produced via consumption of O_2 during biogenic reactions and/or methane oxidation, the ratio of both gases is used for evaluation of the CO_2 origin. Moreover, it is assumed that the addition of CO_2 from leakage results in a physical dilution of the

soil gas N_2, which is not involved in biological reactions [7,8,9]. Complementary soil gas composition analyses were performed at selected locations using a soil probe which was hammered to a depth of 70 cm. After 20 min the soil gas was pumped to a mass spectrometer (MS, Omnistar Pfeiffer Vacuum) for direct on site gas analysis. Additionally, gas samples were taken with gas collecting glass tubes for analysis with a gas chromatograph (GC, SRI Instrument's 8610C, equipped with a silical gel and a mol sieve column and HID and TC detectors) in the laboratory. The corresponding analytical error σ was calculated for the concentration of CO_2, O_2 and N_2 as ± 0.02, 0.01 and 0.05 vol %, respectively. The concentration error resulting from the sampling procedure (possible contamination with air) was estimated from comparison of the MS and GC data (σ = ± 0.02, 0.19 and 0.17%, respectively).

For analyzing the $\delta^{13}C$ isotopic composition of soil CO_2, gas samples were taken with 12 ml vials (Labco Limited) with a rubber septum. Analyses were performed at the GFZ using a GC-C-IRMS (gas chromatography /combustion /isotope ratio mass spectrometry). The system consists of a GC (6890N, Agilent Technology, USA) connected to a GC C/TC III combustion device coupled via open split to a MAT 253 mass spectrometer (ThermoFisher Scientific, Germany). The $\delta^{13}C$ of CO_2 is given relative to the VPDB standard (Vienna Pee Dee Belemnite) in the conventional delta notation. The standard deviation σ for the isotopic measurements was ±0.5‰.

Soil profiles of 70 cm depth were studied for their structure and carbon and nitrogen concentrations. The results very much helped to explain the spatial variations of the soil CO_2 fluxes at the different locations [3]. However, as most of the sampling positions are located next to agricultural roads and fields, an influence of used fertilizers and arable farming on the soil structure, chemical composition and the soil biology cannot be ruled out.

3. Results and discussion

3.1. Soil CO_2 flux measurements

The seasonal variations of the soil CO_2 flux and the soil temperature during 12 years are shown in Figure 2. The individual values represent averages of the measurements at the 20 sampling locations. Low fluxes were detected during the winter time (0.2 to 1 μmol m^{-2} s^{-1}), then increasing up to summer (about 5 to 9 μmol m^{-2} s^{-1}) and decreasing again during autumn. These trends show a good correlation with the soil temperature and consequently with the bioactivity and its natural CO_2 production in soil.

In view of a reliable CO_2 storage the average annual CO_2 fluxes detected during (2.9 μmol m^{-2} s^{-1}) and after the injection operation (3.1 μmol m^{-2} s^{-1}) are compared with the period before the injection started (2.9 μmol m^{-2} s^{-1}). The fluxes of the different periods cannot be distinguished by statistical tests and all yearly mean values are within a two sigma range of the pre-injection period. The slightly higher mean value for the last period is explained by the acquisition of more data at warmer temperatures (summer). The observed CO_2 fluxes during winter months always decrease to baseline values ≤ 1 μmol m^{-2} s^{-1} clearly precluding any input by upward migrating, leaking CO_2 from the storage complex, which would not show any seasonal or temperature dependent variability.

The permanent flux chambers in the direct vicinity of the injection and observation wells were set up in spring 2011 and monitored the active injection process until August 2013 and the post injection period until May 2017. The comparison of the soil CO_2 flux trends at the eight on-site sampling locations for these two periods reveals no statistical significant differences. However, diurnal and seasonal CO_2 flux variations were detected and it can be shown, that at similar temperatures the CO_2 flux in autumn is higher than in spring. This observation indicates a biological source of CO_2 as the metabolism of CO_2 producing microorganism after a colder winter period is less active than after a warm summer.

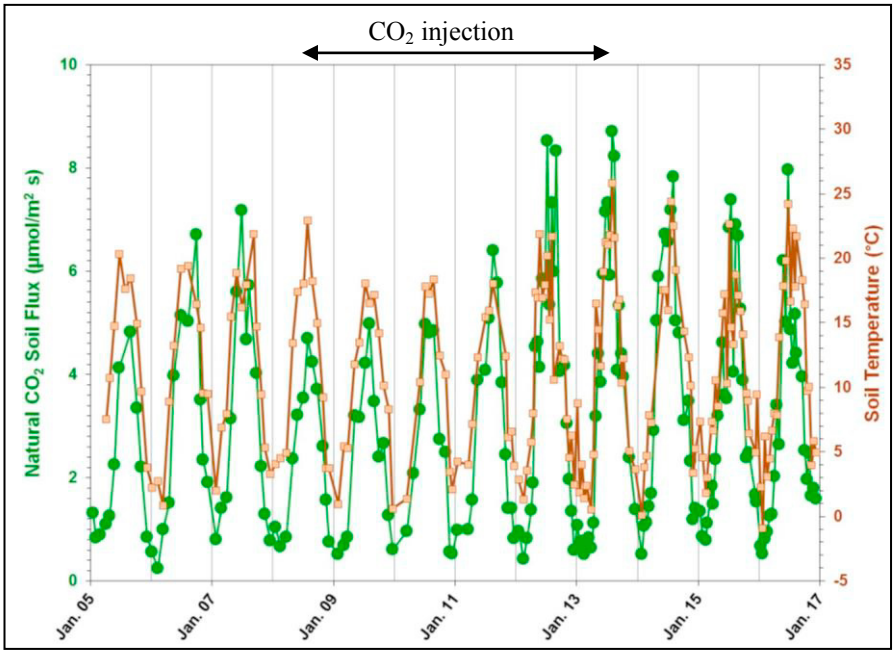

Fig. 2: Seasonal variations in soil CO_2 flux (green dots) and soil temperature (orange squares) averaged over 20 sampling locations from 2005 to 2016. CO_2 injection took place from June 2008 until August 2013.

3.2. Soil gas composition measurements

During March 2017, soil gas sampling was performed at three sampling locations in the northern part of the investigated area (locations 5, 13 and 14) and at two locations close at to the injection site (P3 and P4). Figure 3 shows the results of the gas chromatographic measurements with CO_2 concentrations ranging from 0.4 to 1 vol %. The O_2 versus CO_2 concentration ratios for the different samples follow a trend parallel to the theoretical biological respiration line. Only one sample (P4_2) distinctly plots to the left of this line, but with regard to the estimated error, no definite contribution of methane oxidation is inferable. In general, these observations suggest that CO_2 is produced mainly via biological respiration instead of methane oxidation. Co-measured N_2 concentrations range from 77.8 to 78.3 vol % and also do not provide any hint to dilution by leaking CO_2.

The corresponding soil CO_2 ^{13}C isotopic ratios ranged from -17.7‰ to -23.5‰ and were thus in the isotopic range of CO_2 produced by plants (approx. -14‰ and -28‰, [10]). The majority of the injected CO_2 had a $\delta^{13}C$ of -28.3‰ [11] but fractionation processes on its way from the reservoir to the surface through the different geological layers may change the CO_2 isotopic composition to heavier values. In the injection well, the 440 m deep well P300 [12] and in the ground water in the direct vicinity of the injection site, CO_2 $\delta^{13}C$ values in a similar range were determined (-15.9‰, -23.5‰ and -12.9‰, respectively) [13,5]. Therefore, a definite interpretation of the Ketzin soil CO_2 isotopic data is still challenging.

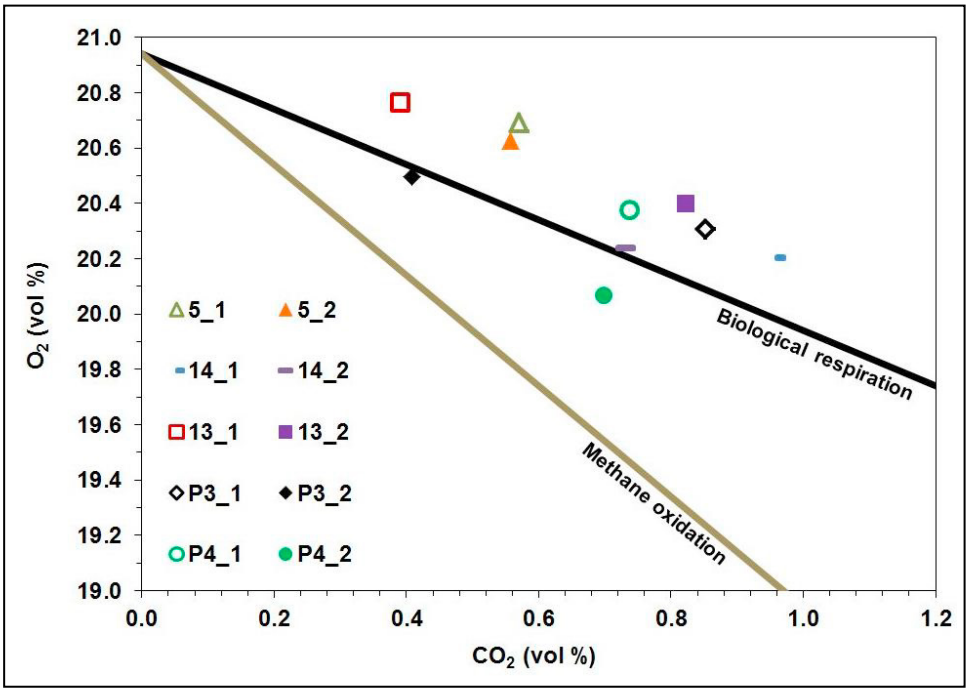

Fig. 3: Soil gas O_2 and CO_2 concentrations at two positions around location 5, 13 and 14 (Fig. 1, map) and at location P3 and P4 at the pilot site (Fig. 1, photograph), in March 2017. Trend lines represent theoretical gas ratios resulting from biological respiration or methane oxidation according to [7].

4. Conclusion

Using a fixed monitoring grid of 20 surface sampling locations covering the potential CO_2 underground distribution area as well as unaffected regions, soil CO_2 flux measurements were tested and applied as a monitoring tool during CO_2 storage. The position of the individual sampling locations considered natural geological features, i.e. faults and troughs as well as existing and abandoned wells. The soil temperature and the soil composition were identified to be the most relevant parameters inducing spatial and temporal flux variations. Therefore, baseline measurements prior to the injection process combined with meteorological parameters and soil analyses are essential for the reliable interpretation of soil CO_2 fluxes and to detect potential CO_2 leakages. Additional soil gas concentration analyses can give important hints on the origin of the detected soil CO_2. However, as the isotopic ranges of possible CO_2 sources at the Ketzin pilot site overlap, an interpretation of soil CO_2 isotope data gives no clear evidence on the origin of the CO_2. In conclusion, the gas monitoring concept applied for 12 years at Ketzin essentially contributes to the comprehensive monitoring program but the measurements can be applied only selectively and therefore, must be supported by and interact with other geochemical, geophysical and microbial disciplines and methods.

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