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Energy Procedia 4 (2011) 4524–4531

**Energy
Procedia**

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GHGT-10

Mobilisation of organic compounds from reservoir rocks through the injection of CO₂ – Comparison of baseline characterization and laboratory experiments

Ann-Kathrin Scherf^{a,b,*}, Carsten Zetzl^b, Irina Smirnova^b, Michael Zettlitzer^c,
Andrea Vieth-Hillebrand^a and CO₂SINK-group

^a German Research Centre for Geosciences GFZ, Organic Geochemistry Section, Telegrafenberg, 14471 Potsdam, Germany

^b Institute for Thermal Separation Processes, Technical University Hamburg-Harburg, Eissendorfer Str. 38, 21073 Hamburg, Germany

^c RWE Dea AG, GeoSupportCentre, Laboratory Wietze, Industriestrasse 2, 29323 Wietze, Germany

Abstract

In the framework of CO₂ storage activities, the aim of our investigations is mainly to evaluate the effects of supercritical CO₂ (scCO₂) on the quantitative and qualitative extraction of organic compounds from reservoir rocks. Within the scope of the CO₂ storage project CO₂SINK the major task was to identify key mechanisms occurring in the reservoir as a result of the injection of CO₂ into a saline aquifer. Here, it is of special interest what types and amounts of organic matter will be extracted and mobilized from the reservoir rocks in conjunction with the injection of scCO₂. Thus, our investigations may help to evaluate the efficiency and reliability of the long-term storage of CO₂ in such a geological system.

Here, we present compound-specific results from laboratory scCO₂-extraction experiments on reservoir rock samples from the CO₂ storage site in Ketzin, Germany. Low molecular weight organic acids (LMWOA) as well as polar lipid fatty acids (PLFA) extracted by scCO₂ were analysed using ion chromatography and gas chromatography-mass spectrometry, respectively. Through the exposure to scCO₂ mainly formate and acetate, but also other LMWOA were released from the rock samples in varying amounts. PLFA profiles of scCO₂ extracts were dominated by saturated and unsaturated fatty acids with 16 and 18 carbon atoms of bacterial origin. The results of scCO₂ extraction are compared with the characterization of the organic inventory of pristine rock samples and fluid samples from observation wells of the Ketzin site to obtain information on quantitative and qualitative significance of the solvent potential of scCO₂.

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Keywords: CO₂ storage; Ketzin; organic compounds, supercritical CO₂ extraction

* Ann-Kathrin Scherf. Tel.: 0049-(0)331-2881906; fax: 0049-(0)331-1436.
E-mail address: scherf@gfz-potsdam.de.

1. Introduction

Carbon dioxide is one of the key compounds within the natural and also the anthropogenic green house effect. One strategy for future minimization is the carbon dioxide capture and storage (CCS) technology which includes the separation of carbon dioxide from industrial and energy related sources, transport to a storage location and long-term isolation from the atmosphere [1,2]. One option for the geological storage of carbon dioxide is the sequestration in deep saline aquifers [3]. The European project CO₂SINK has been the first research and development project on the on-shore underground storage of carbon dioxide in Europe [4,5]. For this purpose a geological formation of the younger Triassic (Stuttgart Formation) near the city Ketzin (north-east Germany) was chosen as a reservoir for the long-term storage of carbon dioxide (see [6]). Since June 2008 carbon dioxide is injected into the injection well Ktzi 201, and injection and propagation of CO₂ as well as changes in the reservoir are monitored via numerous geochemical, geophysical and microbiological techniques in the two observation wells Ktzi 200 and Ktzi 202 in 50 and 112m distance, respectively [5].

To get insight into processes occurring in the reservoir in the presence of supercritical CO₂ (scCO₂) lab experiments using scCO₂ as solvent were performed on reservoir rocks from the Ketzin site under reservoir conditions. ScCO₂ is known as an excellent solvent of non- to moderately polar organic compounds depending on temperature and pressure [7]. Already in the 1980s several studies revealed that extraction of soluble organic matter from rock samples by scCO₂ is feasible for hydrocarbons with up to 30 carbon atoms and also some heteroatom-containing compounds [8]. In the context of geological CO₂ storage activities it is of special interest what types and amounts of the organic matter (OM) will be extracted and mobilized from the reservoir rocks in conjunction with the injection of scCO₂ into a saline aquifer and thus, may be transported by the formation fluids.

Increased concentrations of organic acids and high DOC (dissolved organic carbon) contents have been described in formation waters from the Frio Formation after the injection of carbon dioxide [9,10]. A potentially increased availability of those acids, which could serve as substrates for the present microbial community, may induce an increased microbial activity and thus, production of biomass. Lab experiments, simulating the geological storage of CO₂ have only been done until now in the framework of an ECBM study by Kolak and Burruss [11] on coals. They figured out, that the organic matter extracted by scCO₂ equated qualitatively to the organic matter present in the coals.

As a part of the CO₂SINK project, we investigate the composition of the organic carbon pools within the saline aquifer and the effect that the injection of carbon dioxide may have on the existing deep microbial ecosystem and reverse using biogeochemical methods. The results obtained by the scCO₂-extraction experiments will be combined with results from the organic-geochemical background characterization of the reservoir rocks and results from the fluid monitoring on the observation wells. In principle, the organic-geochemical characterization of rock samples using organic solvent extracts is used to describe the inhabiting microbial communities (e.g. [12], [13]) as certain organic compounds, so called biomarkers, are characteristic for certain organisms. Beside the characterization of the microbial community in rocks and sediments it allows also to conclude on the type of fossil organic matter as well as redox conditions prevailing during its deposition [14 and references therein]. Thus, the experiments described here give both, an insight into the composition of the present microbial community in the reservoir and information on the quantitative and qualitative significance of the solvent potential of scCO₂.

2. Materials and Methods

2.1 Sample description

Three boreholes, one injection (Ktzi 201) and two observation wells (Ktzi 200 and 202), each about 800 m deep, were drilled at the CO₂SINK site near Ketzin, Germany in 2007 and 2008 [15]. CO₂ is injected into the sandstone of the younger Triassic Stuttgart formation (approx. 620 to 650 m). For the scCO₂ extraction experiment we decided for a total of five different samples - one silt (B2-2) and four sandstone samples - taken from 627.45 m to 647.8 m depth (table 1). Ktzi 201 and 202 supplied two samples each and Ktzi 200 contributed one sample. The sandstone samples were not entirely consolidated. In-situ conditions in the reservoir prior to CO₂ injection were 62 bar and ca.

35°C [6,16]. Until end of June 2010, ca. 36,000 t of food grade CO₂ have been injected and since August 2009 pressure has stabilized at ~74 bars [6]. Thus, CO₂ is in supercritical state at the injection well and the near bore area.

Table 1 Sample overview

Abbr.	Well	Depth [m]		Lithology
		top	bottom	
A13-3	Ktzi 200	638.47	638.55	sandstone
C-7-3	Ktzi 201		638.55	sandstone
C-10-3	Ktzi 201		647.8	sandstone
B-2-2	Ktzi 202	627.45	627.58	siltstone
B-3-3a	Ktzi 202	631.15	631.22	sandstone

2.2 Bulk analyses

The total organic carbon (TOC) content of the rock samples was determined as the difference between the total carbon (TC) and total inorganic carbon (TIC). All carbon analyses were performed on lyophilised and ground samples in a carbon analyser (multi N/C 2100, Analytik Jena AG) by means of combustion with pure oxygen at high temperatures followed by infrared spectroscopic detection of the carbon dioxide that was formed (cf. [17]).

2.3 ScCO₂-extraction and sample preparation

For supercritical CO₂ extraction Ketzin rock samples were broken into gravel-size pieces and filled into a high pressure cell, which was placed into an oven, heated to 40°C. To simulate the conditions within the saline aquifer a supercritical fluid extractor (Spe-ed SFE 4, Applied Separations) was used. By a pump, pressure of food grade CO₂ was increased to 80 bars. This CO₂ then flowed through a capillary into the oven and through the high pressure cell. At the outlet of the oven, the CO₂ stream was heated, in order to avoid solidification (dry ice) due to the Joule Thomson effect, and in the same time depressed to atmospheric pressure while being released through a needle into a screw cap vial. As CO₂ returned to gaseous state, the extracted compounds were released in the collection vial, while the CO₂ could evaporate. The amount of evaporating CO₂ was measured by a flow meter. All experiments were performed using a CO₂ flow of 3 NL/min. Extraction time was 3 hours. Most experiments were performed as duplicate. From each sample one of the duplicates was used to analyse the extracts by gas chromatography-mass spectrometry and the other one via ion chromatography. Therefore, scCO₂-extracts were solved in dichloromethane-methanol (9:1 v/v) or water, respectively. The duplicates solved in organic solvent were ultrasonicated for 10 min. Then, the extracts were transferred into pre-weighed sample vials and solution-steps were done. Then, the solvent was evaporated under nitrogen and the extract weight determined.

2.4 Organic solvent extraction

Prior to extraction, fresh rock samples were lyophilized and ground. Lipids were extracted using a single-phase mixture of methanol/dichloromethane/ammonium acetate buffer (pH 7.6, 2:1:0.8 v/v; [18]) and a flow-blending system [19]. After centrifugation the supernatant was collected. Then, extraction was repeated twice using ultrasonication. Dichloromethane and distilled water were added to the combined extracts until a ratio of methanol/dichloromethane/ammonium acetate buffer of 1:1:0.9 (v/v) was obtained. The organic phase was removed and the methanol-water phase washed three times with dichloromethane. The combined dichloromethane phases containing the extracted lipids were evaporated to dryness and the residue stored at -20°C.

2.5 Gas chromatography-mass spectrometry of organic solvent soluble compounds

The scCO₂-extracts solved in dichloromethane-methanol as well as the organic solvent extracts were diluted in 500 µl of dichloromethane and an aliquot was taken for derivatisation. Erucic acid has been added as internal standard. First, samples were methylated using diazomethane to transfer free fatty acids into fatty acid methyl esters (FAMEs). The product was analysed using a Trace GC Ultra (Thermo Electron Corporation) linked to a Dual Storage Quadrupole (DSQ) mass spectrometer (Thermo Electron Corporation) using the method described by Kristen et al. [20]. After the analyses, trimethylsulfoniumhydroxid (TMSH) was added 1:1 to the sample for ester cleavage and methylation of ester-bound fatty acids. Sample-TMSH mixtures were heated for 2 h to 70°C in an oven. Afterwards the solvent was evaporated under nitrogen and the product resolved in the original amount of solvent. The samples were measured again as described above. Both derivatisation procedures yield fatty acid methyl esters. The amount of ester-bound FAMEs was determined as the difference between both measurements.

2.6 Ion chromatography of water soluble compounds

Extracts were analysed in replicate using ion chromatography with conductivity detection (ICS 3000, Dionex Corp.). An analytical column (AS 11 HC; Dionex Corp.) was used at 35°C. The sample was eluted with KOH solution of varying concentration over time. For a detailed description of the used method see [21].

3. Results and Discussion

3.1 TOC contents and extraction yields

The total organic carbon (TOC) contents of the rock samples were very low with less than 1 mg/g rock (0.1 %) except for sample A-13-3 which contains 0.3 % TOC (see table 2). The extraction yields after 3 hours of continuous extraction with scCO₂ are in a range of 7.3 to 50.7 mg/kg rock, 2.2 to 388.8 mg/g TOC or 0.23 to 1.4 mg/kg CO₂. Thus, using scCO₂ up to 39% of the TOC has been extracted. Regarding the extraction yields when calculated per kg CO₂ scCO₂-extraction of the siltstone sample B-2-2 yielded the highest amount of extract. Organic solvent extracts are in the range of 21.5 to 67.5 mg/kg rock or 6.5 to 540 mg/g TOC. Detailed results for extraction yields of both methods are listed in table 2. Comparison of the organic solvent extraction yields with scCO₂-extraction yields reveals higher concentrations for extraction of the sandstone samples probably due to the higher polarity of the methanol/dichloromethane/ammonium acetate buffer solution. Only for the silt stone sample B-2-2 scCO₂-extraction yields higher amounts.

Table 2 TOC values and extraction yields from scCO₂- and organic solvent extraction

Abbr.	TOC		scCO ₂ -extraction		Organic solvent extraction	
	mg/kg rock	mg/kg rock	mg/g TOC	mg/kg CO ₂	mg/kg rock	mg/g TOC
A-13-3	3316	7.3	2.2	0.23	21.5	6.5
C-7-3	911	n.d.	n.d.	0.33	61.2	67
C-10-3	613	n.d.	n.d.	0.25	67.5	110.6
B-2-2	649	50.7	78.2	1.43	25	38.5
B-3-3a	74	28.8	388.8	0.83	40.5	540

3.2 Comparison of scCO₂ and organic solvent extracts

Compound-specific analyses of organic solvent-soluble extracts of scCO₂-extraction revealed a quantitative dominance of free and ester-bound fatty acids. Among those, *n*-hexadecanoic acid as well *n*-octadecanoic, isomeric *n*-octadecenoic and *n*-octadecadienoic acids are dominant. The abundance of even numbered saturated fatty acids with 20 to 26 carbon atoms in most samples is also interesting. The patterns of polar lipid fatty acids (PLFA), which were produced via ester cleavage from intact polar lipids, allow conclusions on the composition of the microbial community [22]. In general, saturated straight-chain fatty acids (SFA) with 14 to 18 carbon atoms as well as terminally branched saturated fatty acids are considered typical constituents of microorganisms [13]. The even carbon numbered long chain fatty acids may also be attributed to bacterial origin as already Volkman and co-workers described their presence in lipid extracts from bacteria in low amounts compared to SFA with 14 to 20 carbon atoms [23].

Relative abundances of ester-bound fatty acids in scCO₂- and organic solvent extracts are displayed in Figure 1. The extracts from the Ketzin samples reveal a mixture of mostly even numbered straight chain fatty acids with 8 to 28 carbon atoms including *n*-hexadecenoic, *n*-octadecadienoic and two isomeric *n*-octadecenoic acids. Terminally branched saturated fatty acids have been detected in most samples only with 15 carbon atoms. The samples from Ktzi 202 contained also *i*-hexadecanoic as well as *i*- and *ai*-heptadecanoic acids. The branched saturated fatty acids (BSFA) extracted from the Ketzin samples relate to Gram-positive and sulphate-reducing bacteria (cf. [13,24]).

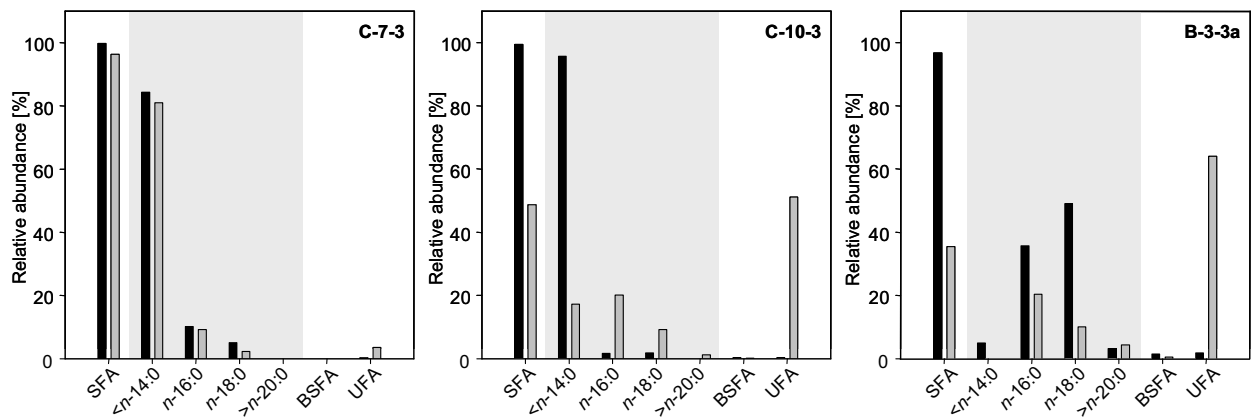


Figure 1 Relative abundances of ester-bound fatty acids in % from scCO₂- (grey bars) and organic solvent extraction (black bars) for sandstones from Ktzi 201 and 202. Bars on grey background indicate different groups of SFA. (SFA - saturated fatty acid; BSFA - branched saturated fatty acid; UFA - unsaturated fatty acid)

As scCO₂ has a different polarity than the applied organic solvent mixture, fatty acid patterns of both extracts may not resemble each other, neither qualitatively nor quantitatively. But extraction yields of individual higher molecular weight organic compounds in the scCO₂ extracts of the sandstone samples were found to make up to 71% of the extraction yield of the organic solvent extraction. The comparison of the relative abundances of ester-bound fatty acids in scCO₂- and the applied organic solvent extraction (Figure 1) shows quite similar patterns for sample C-7-3, whereas samples C-10-3 and B-3-3a show a dominance of unsaturated fatty acids compared to saturated fatty acids in scCO₂-extracts. This group of unsaturated fatty acids consists to more than 95% of isomeric *n*-hexa- and *n*-octadecenoic acids and *n*-octadecadienoic acid. Additionally, the proportion of the relative abundances of different SFA-groups varies between scCO₂- and organic solvent extraction.

3.3 Water soluble organic compounds in scCO₂-extracts and formation fluids

Ion chromatography was carried out on water-solved scCO₂-extracts. Among the organic acids, formate was the only one occurring in all scCO₂-extracts from the rock samples. Additionally, acetate, propionate, butanoic and pentanoic acid as well as lactic, pyruvic, glycolic and gluconic acid were detected in varying amounts in certain samples. The concentrations of formate, acetate and summed organic acids after 3 hours extraction with 3 NL/min CO₂ (equates in total to ca. 1 kg CO₂) are displayed in Figure 2. Overall, after 3 hours of continuous extraction summed organic acids amount to 0.9 to 538 µg/kg rock or 1.3 to 1877 µg/g TOC. Formate is the only LMWOA, which was detected in all sample extracts, but in most extracts acetate predominates. B-2-2, the siltstone, yielded the lowest concentrations of individual and summed LMWOA, both, when calculated per kg rock and per g TOC.

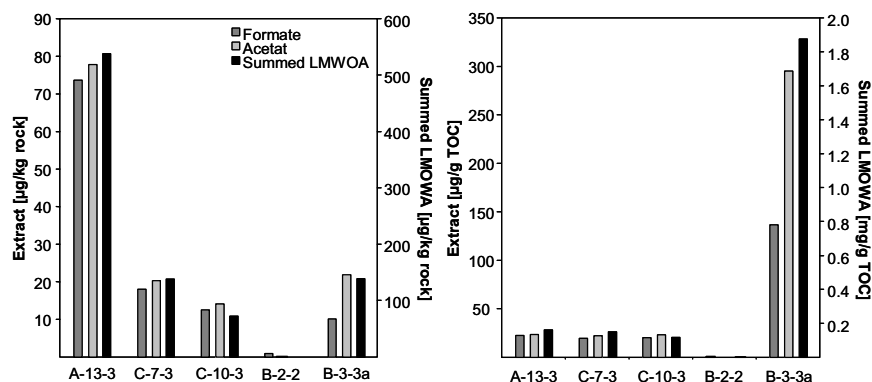


Figure 2 Compound-specific extraction yields for formate, acetate and summed LMWOA

Generally, LMWOA, like formate, acetate, propionate, oxalate, lactic, pyruvic, citric and succinic acid can be seen as an indicator of microbial metabolism as they are produced by a huge diversity of microorganisms as part of their metabolic pathways ([25] and references therein). For example formate is amongst others microbially produced in the pathway of the formate fermentation. Additionally, it is used by methylotrophic bacteria and methanotrophic Archaea. Thus, its presence may on the one hand be explained as metabolic product from the active microbial community. On the other hand, it is important as a potential substrate for certain microorganisms and may induce an increased growth of the microbial community.

Since summer 2008, when CO₂ injection into the saline aquifer in Ketzin started, monitoring of downhole fluid samples has been carried out regularly [16]. Until now, the chemical composition of the fluid samples show no clear trend concerning the evaluation of the quantitative and qualitative composition of LMWOAs, but acetate was found to be always the major constituent of the LMWOA. Since injection started, LMWOA were detected in the downhole fluid samples from the two observation wells at total concentrations of up to 4.4 mg/l. Overall, formate, acetate, methyl succinic and malic acid have been detected in the samples.

4. Summary, Conclusions and Outlook

Extracting organic matter from rock samples using multiple extraction methods allows insight into the composition of the natural organic matter and the deep biosphere. Total organic carbon contents of the Ketzin samples are various, but polar lipid fatty acid profiles of the reservoir rock samples reflect a clear dominance of lipids of bacterial origin in all samples. The lipid composition does not provide more detailed information about the community structure as we did not detect any specific PLFA as major compounds.

Results from scCO₂-extracts illustrate that absolute TOC values of pristine rock samples have apparently no impact on the extraction yields as they do not correlate with the TOC values. The extraction yields of the scCO₂-extractions revealed total concentrations in the range of two orders of magnitude when calculated per kg rock and within three orders of magnitudes, when calculated per g TOC and had amounts of up to 39% of TOC. Regarding LMWOAs, the amounts extracted by scCO₂ seem to be very low compared to organic matter present in the reservoir

rock. But extraction and mobilization of organic compounds in a wide molecular mass range is of huge importance. ScCO₂-extraction of rock samples for longer time intervals revealed constant extraction rates for at least 8 hours (Scherf et al., unpubl. results). The differences in the extraction yields may be explained by differences in porosity and permeability, but although by mineralogical differences. Additionally, in the study presented, gravel size rock pieces have been used for scCO₂-extraction instead of intact core samples. Thus, surface areas of rock samples were increased artificially and also heterogeneities of the rock samples regarding porosity etc have to be taken into account.

Overall, information gained by the laboratory experiments has to be combined with models to determine how fast mobilized organic matter will be transported through the reservoir and how much of the mobilized organic acids and non organic material will occupy e.g. the pore space in the entire reservoir. Here, the increased availability of LMWOA as feedstock for the microbial community may induce an additional growth. Furthermore, when estimations are made on reservoir processes it has to be taken into account that food grade quality CO₂ was used in lab and field experiments. Compared to CO₂ that will be captured from power plants, food grade CO₂ lacks certain byproducts which may have additional effects on the reservoir.

Acknowledgements

The authors would like to thank Jenica Andersen for technical and Kristin Günther and Cornelia Karger for analytical support.

The CO₂SINK project received its funding from the European Commission (Sixth Framework Program, FP 6), the Federal Ministry of Economics and Technology, and the Federal Ministry of Education and Research.

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