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Assessing drilling mud and technical fluid contamination in rock core and brine samples intended for microbiological monitoring at the CO_2 storage site in Ketzin using fluorescent dye tracers

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ABSTRACT

The CO_2SINK project in Ketzin represents a field laboratory for the storage of CO_2 in a 650-m deep saline aquifer. The project is accompanied by a microbiological monitoring programme to characterise the composition and activity of the autochthonous microbial community in rock and brine samples and their changes in response to CO_2 storage. A prerequisite of these studies is the acquisition of samples free of contamination from microorganisms and organic and inorganic components. Drilling mud and technical fluids are the main sources of contamination. This study describes the application of the fluorescent dye tracers fluorescein and rhodamine B as contamination controls for rock core and brine samples. Fluorescein was added to drilling mud that was used during the coring phase of the Ketzin wells Ktzi 200, 201 and 202. In addition, total organic carbon (TOC) concentrations, reflecting the carboxymethyl cellulose (CMC) component of the drilling mud, were determined to verify the tracer results. The fluorescence and TOC analyses revealed that drilling mud filtrate penetrated the outer 20 mm of mildly permeable sandstone cores. Rhodamine B was added to brines that were used to displace the drilling mud and to flush the wells after completion. The tracer monitoring during the discharge of drilling mud and displacement brines from the wells during hydraulic tests and nitrogen lifts enabled the quantification of reservoir fluid quality. After the production of 140-190 m^3 (16-21 borehole volumes) of fluid, the drilling mud concentration was reduced to about 0.05%. The use of fluorescein emerged as a field-capable, sensitive and reliable method during the sampling of rock core and formation brine samples.

Keywords: drilling mud, contamination, tracer, fluorescein, microbiological monitoring

1. Introduction

Carbon dioxide capture and storage (CCS) is being considered as an option for the mitigation of CO_2 emissions to stabilise greenhouse gas concentrations (Metz *et al.*, 2005). With the EU project CO_2SINK (www.co2sink.de), the first onshore storage site in Europe was established as a research facility in Ketzin, Germany in 2004 to examine the feasibility and effects of carbon dioxide storage in a natural saline aquifer at a depth of approximately 650 m (Schilling *et al.*, 2009; Würdemann *et al.*, 2010).

Saline aquifers are being investigated as possible storage sites for large volumes of anthropogenic CO_2 (Eccles *et al.*, 2009; White *et al.*, 2003). Sub-terrestrial regions such as saline aquifers also represent microbial habitats (Basso *et al.*, 2009; Pedersen, 2000). To track changes at the microbiological level, a monitoring programme was established using molecular biological methods.

As a consequence of the drilling process, rock and brine samples are contaminated with drilling mud and other technical fluids. Constituents of the drilling fluids, especially organic polymers, may promote bacterial growth in the bore hole (Ezzat *et al.*, 1997; Zettlitzer *et al.*, 2010). Microorganisms introduced by the technical fluids may affect the results of molecular biological studies. Thus, considerable care has to be taken to ensure the purity of rock and brine samples.

In the past, various tracers were applied to monitor the contamination of sediment and rock samples by drilling fluids. Chemical tracers (such as perfluorocarbons), particulate tracers (such as fluorescent microspheres) and hydrocarbon profiles of drilling fluid components have been used individually and in conjunction during microbiological investigations of marine sediments (House *et al.*, 2003; Kallmeyer *et al.*, 2006; Kimura *et al.*, 2003; McKinley, Colwell, 1996; Onstott *et al.*, 2003; Smith *et al.*, 2000; Smith *et al.*, 2000). Fluorescent dye tracers like fluorescein and rhodamine WT have been used as contamination markers to allow for calculations of the chemical and isotopic composition of formation water (Thordsen *et al.*, 2005).

This study describes the use of two fluorescent dye tracers, fluorescein and rhodamine B, to assess the contamination of rock core and formation fluid samples from the wells Ktzi 200, 201 and 202. These dyes were selected because they were approved by the mining authority due to their distinct absorption and emission characteristics, and their low cost and detection limits (Bäumle *et al.*, 2001). Drilling mud was labelled with sodium fluorescein. Rhodamine B was added to the brines that were used to displace the drilling mud and flush the cemented bore holes. In addition, total organic carbon concentrations were determined in rock and fluid samples, reflecting the organic polymer component of technical fluids.

2. Materials and Methods

2.1 Study site

The *in situ* CO_2SINK laboratory at Ketzin is located in the northeast German basin 40 km northwest of Berlin. CO_2 is injected into a saline aquifer of the Stuttgart Formation at a depth between 630-710 m below the surface. Three 750 to 800 m deep vertical wells, Ktzi 200, 201 and 202, were drilled from March to September of 2007. Core sections 89 mm in diameter composed mainly of clay and sandstone (Förster *et al.*, 2009) were recovered from the storage horizon using a wire-line coring system (Prevedel *et al.*, 2009). After well establishment, hydraulic tests (Wiese *et al.*, 2010) and nitrogen lifts (Zettlitzer *et al.*, 2010) were performed. Fluid samples were collected for tracer and organic carbon measurements.

2.2 Tracer sorption tests

Although it is known that fluorescein and rhodamine show very little retardation (Bäumle, Behrens, 2001), the sorption behaviour of these tracers with drilling mud was tested. For this purpose, fluorescein and rhodamine B were added to a dilution series of drilling mud to final concentrations of 10 µg/l and 100 µg/l, respectively. Fluorescence intensities were determined first in turbid solutions and second in solutions clarified by centrifugation. Figure 1 shows that the fluorescence intensity was strongly affected by the turbidity of the solution. After the removal of drilling mud solids by centrifugation, the fluorescein and rhodamine B intensities were identical with those of the control samples containing no drilling mud (Fig. 1A and B).

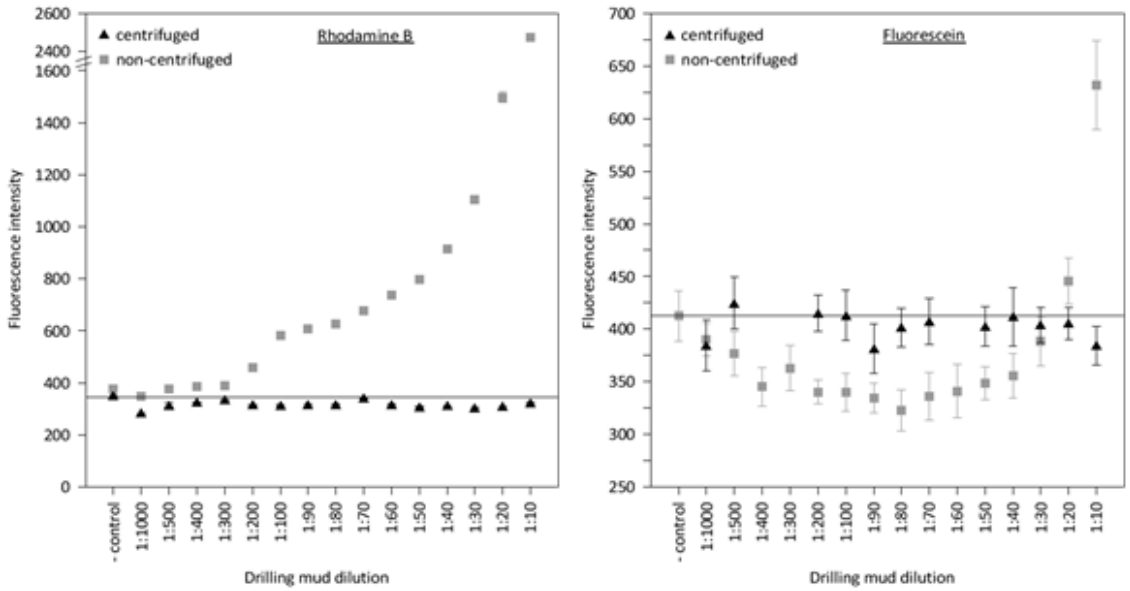

Figure 1. Testing the sorption of fluorescein (**A**) and rhodamine B (**B**) onto drilling mud.

2.3 Fluorescein labelling of drilling mud

During the coring operations in all three wells, KCl/$CaCO_3$/carboxymethyl cellulose (CMC) - based drilling mud was used (Prevedel *et al.*, 2008). To preserve the environment, the amount of tracer employed was kept to a low level that still enabled sensitive detection of the drilling mud (1 mg/l, personal communication Y. K. Kharaka, USGS). Sodium fluorescein (F6377, Sigma-Aldrich, Germany) suspended in water was added into a stirring tank of the circulating mud one day before core sampling. During the drilling of Ktzi 200, about 60 g of fluorescein was added to 66 m^3 of drilling mud in three portions distributed over one complete mud circulation (3.5 h). The following four days after tracer addition, the concentration fluctuated around the expected concentration of 0.9 mg/l (Fig. 2, circles). After coring, drilling, cementing and the installation of casings, unlabelled drilling mud units were intermixed with labelled mud, reducing the tracer concentration to 0.42 mg/l (Fig. 2, circles).

In contrast to Ktzi 200, the drilling mud used during the coring of Ktzi 201 and 202 was labelled by adding the complete amount of fluorescein (66 g) in one portion. The analysis of 11 samples taken from several hours to one day after tracer addition revealed varying fluorescein concentrations ranging from 0.8 to 1.6 mg/l (Fig. 2, squares). After three days, a concentration adjustment to the theoretical value of 1 mg/l was observed, and this remained stable during the testing period of three days (Fig. 2, squares). The fluorescein concentration after well establishment was 0.5 mg/l (calculated).

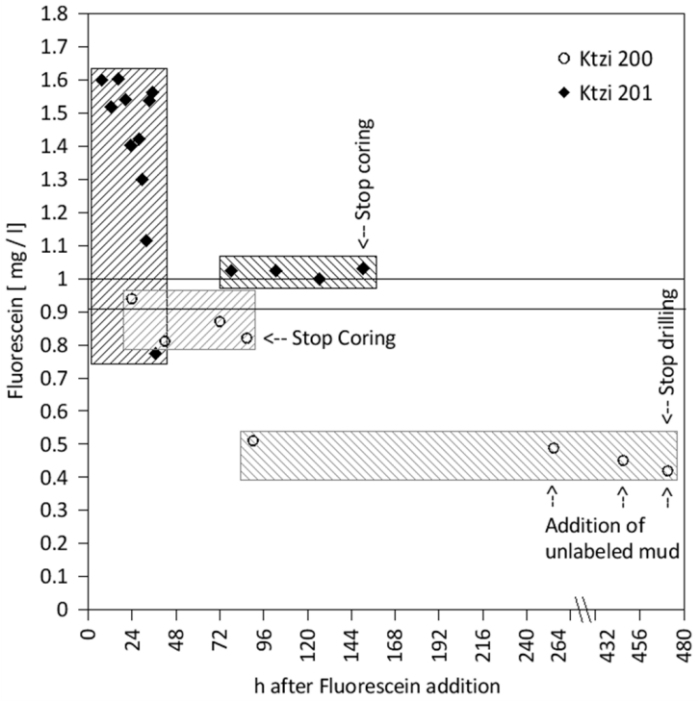

Figure 2. Fluorescein distribution and stability in the drilling mud during drilling operations in Ktzi 200 and 201.

2.4 Rhodamine B labelling of displacement brines

After cementation of the wells Ktzi 200 and Ktzi 201, the drilling mud was displaced with Staßfurt brine (Staßfurt, Germany, density 1.09 kg/l, 2.4 M NaCl) and shallow water, respectively. Because rhodamine B has a higher detection limit than fluorescein (Bäumle, Behrens, 2001), a concentration of about ten times higher was used. Thus, 200 g and 85 g of rhodamine B (T130, Roth, Germany) were added to 15 m^3 of Staßfurt brine and 12 m^3 of shallow water, resulting in final concentrations of 13 and 7 mg/l, respectively. To dissolve the tracer in the brine, the components were mixed in a stirred tank for about 16 h.

2.5 Determination of fluorescein and rhodamine B concentrations in fluid samples

Tracer fluorescence intensities in fluid samples such as drilling mud, displacement brine and formation brine were analysed using a mobile fibre-optic fluorimeter (Hermes Messtechnik, Stuttgart, Germany). Green and pink emissions were detected in the range of 528 ± 10 nm and 590 ± 10 nm, respectively. Because the fluorescence intensities are dependent on the chemical parameters of the medium (Liu *et al.*, 2005), calibration curves were prepared by adding sodium fluorescein and rhodamine B to the appropriate fluids. Because formation fluid from the reservoir horizon was not available, synthetic brine containing 3 M NaCl was used for the calibration. Fluorescein intensities were less affected by high salt concentrations. The slopes from the calibration curves prepared in Staßfurt brine (mass equivalent to 2.4 M NaCl) and synthetic formation brine differed only slightly (Fig. 3A). In contrast, the intensity of rhodamine B was strongly influenced by the brine used (Fig. 3B). Figure 3 also illustrates the higher sensitivity of fluorescein detection over that of rhodamine B.

Prior to the measurements, solids were removed by centrifugation. Fluorescein concentrations in drilling mud samples were determined at dilutions of 1:100. Samples were directly analysed in the field or stored for several days at 4 °C in the dark until being measured. A minimum of ten

measurements was performed automatically every two seconds for each sample. The standard deviations represent the technical errors of these measurements. The detection limit for fluorescein was found to be 0.03 µg/l, which means that drilling mud can be detected at a proportion of 0.005%. As expected, the detection limit for rhodamine B at 1 µg/l was found to be considerably higher (0.01% of displacement brine detectable).

2.6 Fluorescence microscopic detection of fluorescein

Drilling mud penetration into rock cores was examined microscopically using a stereo fluorescence microscope (MZ10F, Leica Microsystems, Wetzlar, Germany) with the GFP2 filter set from Leica Microsystems. The visual detection limit for fluorescein was found to be 50 µg/l, which corresponds to 5% of drilling mud. Core C11-1 was acquired directly after drilling and the drilling mud covering the core surface was wiped off. The sample was stored for seven days at 4 °C after which a 1-cm core section was separated into 5-mm layers from the outer rim to the inner core for microscopic analysis. Samples from the reservoir region of Ktzi 202 were examined in the field lab immediately after drilling.

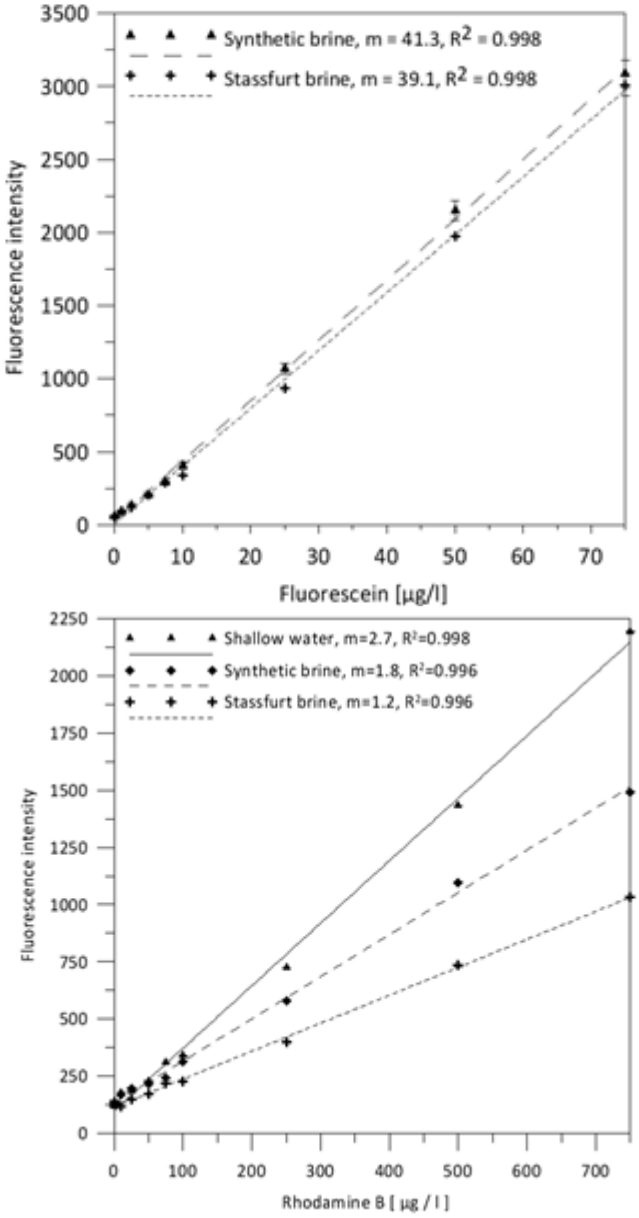

Figure 3. Fluorescein (**A**) and rhodamine B (**B**) calibration curves in displacement and synthetic formation brines.

2.7 Total inorganic and organic carbon concentrations

The total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations of the drilling mud, the xanthan-based viscose gel and the reservoir fluid samples were determined by Potsdamer Wasser- und Umweltlabor GmbH (PWU, Potsdam, Germany) using a carbon analyser (DIMATEC GmBH, Essen, Germany) according to DIN EN 1484-H3. The drilling mud and the xanthan solution showed TOC concentrations of 8 and 1 mg/l, respectively.
The carbon concentrations of a 1-cm cross section from core run C8-3 were analysed using a multi N/C 2100 carbon analyser (AnalytikJena, Germany). The core sample was frozen in liquid nitrogen immediately after drilling and stored at -80 °C until analysis. TOC was determined as the difference between total carbon (TC) and total inorganic carbon (TIC). Prior to the analysis, the core section was separated into six layers from the outer rim to the inner core. The divided samples were dried at 50 °C for 12 h and homogenised using a ball mill (MM400, Retsch, Haan,

Germany). All carbon analyses were performed by means of combustion with pure oxygen at high temperature followed by infrared spectroscopic detection of the carbon dioxide that was formed, modified according to DIN EN 1484. Error bars represent the standard deviations of the analysis of 3-4 samples.

3. Results

3.1 Penetration of drilling mud into rock core samples

Mud penetration was examined in six representative core sections with different permeabilities obtained from the reservoir regions of Ktzi 201 and 202. The permeability and porosity details, based on Norden et al. (2009), are shown in Table 1.

Table 1. Lithology, permeability and porosity (Norden *et al.*, 2008) of core samples used for the examination of drilling mud penetration.

Core run	Well / Depth	Lithology	Permeability / mD	Total porosity / %
C8-3	Ktzi 201 / 641.4 m	silty sandstone	2000	26
C11-1	Ktzi 201 / 648.1 m	fine sandstone	300	23
B1-3	Ktzi 202 / 626.9 m	silty claystone	<1	12
B2-3	Ktzi 202 / 628.6 m	siltstone	200	25
B3-3	Ktzi 202 / 631.4 m	fine sandstone	600-1000	30
B6-1	Ktzi 202 / 638. m	sandy claystone	2	20

The fluorescence microscopic analysis of a section from core C11-1 showed that the highest mud concentration was found in the outer 5 mm (Fig. 4B). The fluorescence intensity decreased from there to 20 mm deep (Fig. 4C-E). The inner core region (below 20 mm) did not show any tracer-originated fluorescence (Fig. 4E-4J). Yellowish fluorescence signals in the inner core (Fig. 4E-4J) are auto-fluorescence signals of the mineral background.
To verify the tracer-based results, TOC concentrations (reflecting the carboxymethyl cellulose component of the drilling mud) were analysed in C8-3.

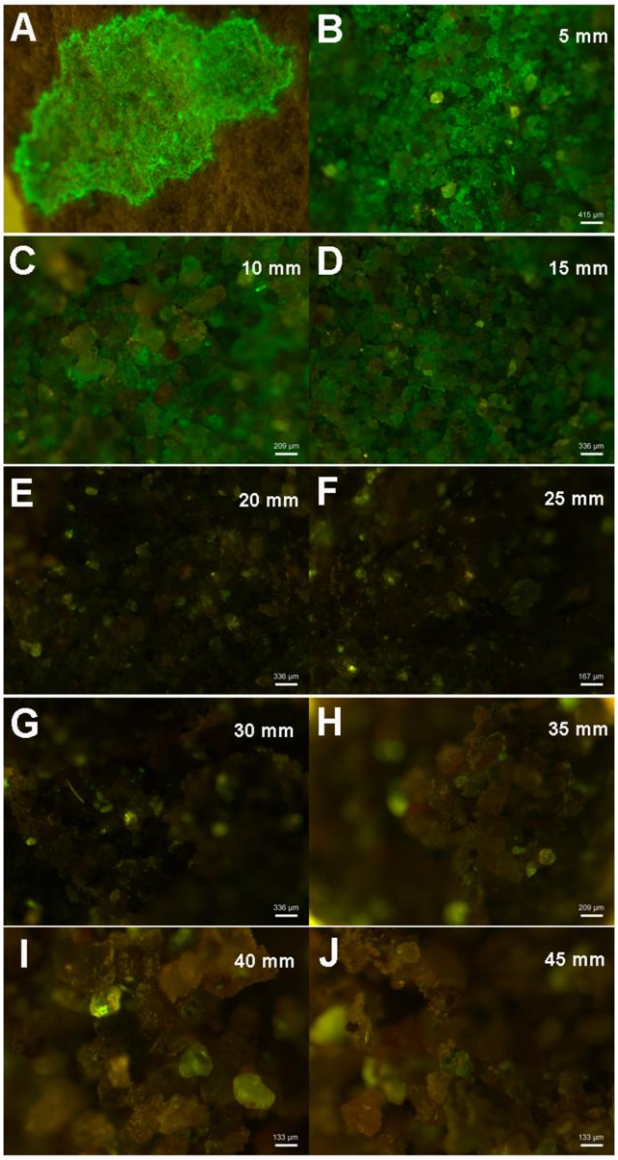

Figure 4. Detection of drilling mud infiltrate penetration into a core section from C11-1 by means of fluorescence microscopy. **A** shows a decline in fluorescein-labelled drilling mud. **B**-**J** show fluorescence signals in the outer rim of the core (**B**) and within the core (**C**, 5 mm; **D**, 10 mm; **E**, 15 mm; **F**, 20 mm; **G**, 25 mm; **H**, 30 mm; **I**, 35 mm; **J**, 40 mm).

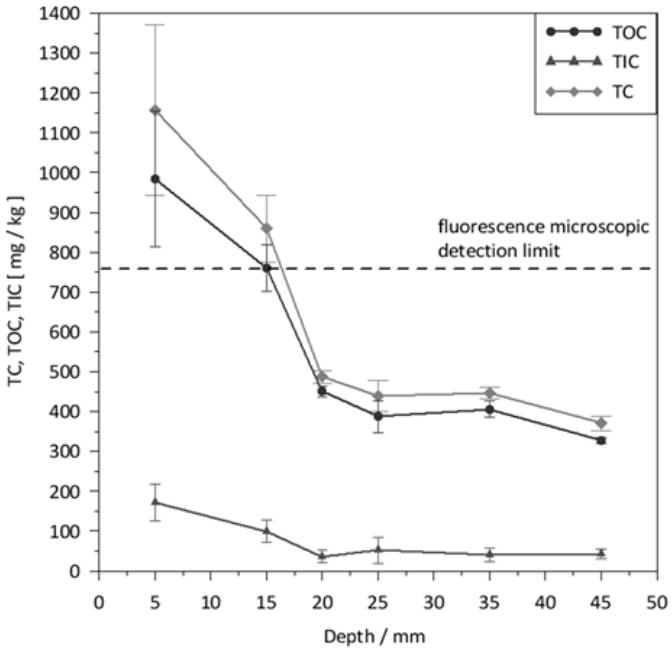

Figure 5. Detection of drilling mud infiltrate penetration into a core section from C8-3 by means of TIC and TOC analyses.

The TOC concentration was highest in the outer 5 mm of the core (985 mg/kg, Fig. 5). In accordance with the microscopic analysis, the drilling mud concentration declined significantly from there to the 20-mm region (451 mg TOC/kg). TOC concentrations were lowest in the inner core, showing slight variations between 328-406 mg/kg. These quantities probably represent background concentrations of the sandstone. Assuming the lowest TOC values as the background level (451, 387 and 406 mg/kg), the calculated drilling mud proportion in the outer 5 mm was found to be 8%, and it decreased to 1% in the 20-mm region. In agreement with the TOC results, the TIC concentration (reflecting the $CaCO_3$ component of the drilling mud) also declined from the outer rim to the 20 mm-region.

During the coring of Ktzi 202, differentially permeable samples (Tab. 1) from the reservoir region were acquired and analysed microscopically in the field immediately after drilling.

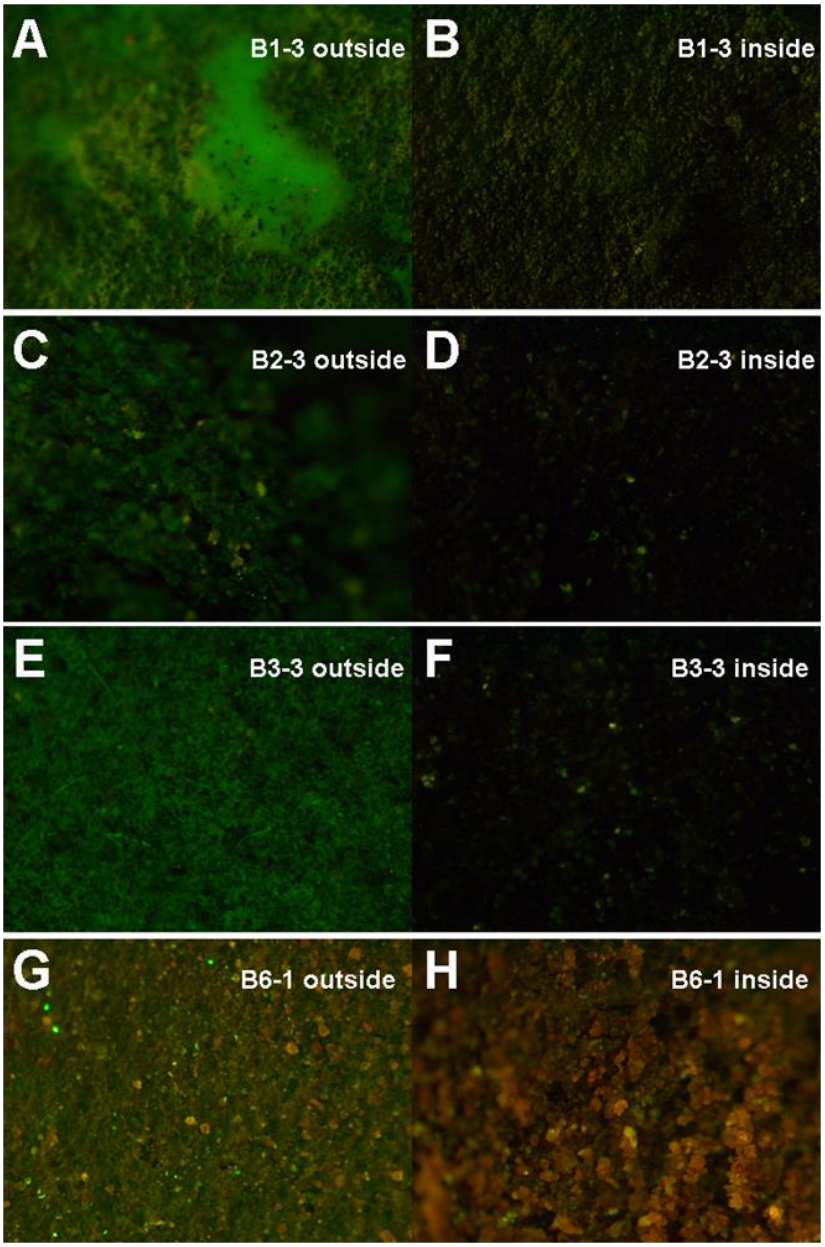

Figure 6. Detection of drilling mud infiltrate penetration into core sections from Ktzi 202 (B1-3, B2-3, B3-3, B6-1) by means of fluorescence microscopy.

Fluorescence micrographs are shown in Figure 6. Mud infiltration was not observed in the 20-mm region of the poorly permeable samples B1-3 and B6-1 (Fig. B and H), whereas the more permeable core sections showed weak fluorescence signals within the 20-mm region (Fig. 6D and F).

3.2 Tracer and DOC concentrations during pump tests and N_2 lifts

After well completion, hydraulic tests (Wiese *et al*., 2009) and N_2 lifts (Zettlitzer *et al*., 2010) were carried out in all three wells. During these operations, tracer and organic carbon concentrations were measured in the fluids produced to monitor the discharge of drilling fluids from the bore holes (Fig. 7), and brine samples suitable for molecular biological investigations were obtained.

The majority of drilling mud and displacement brine was removed from the wells during the first 10-20 m^3 of produced fluid. Rhodamine B concentrations (Fig. 7A and B, pink) reached the detection limit after 20 m^3 or about 2.2 well volumes, reflecting the removal of displacement brine from the wells. By producing further fluid, more drilling mud was mobilised and removed continuously from the wells (Fig. 7, green). Mud proportions in the formation brine samples were reduced to 0.09 - 0.17% (0.46 - 0.81 µg fluorescein/l) at the end of the pump tests after the production of 70 - 90 m^3 fluid. During the nitrogen lifts, additional drilling mud volumes were mobilised and removed from the wells. The fluorescein concentration decreased further (down to 3.3 - 0.4 µg/l) after the pumping of 135 - 190 m^3 of fluid (19 - 21 borehole volumes), which corresponds to a 0.04 - 0.07% proportion of drilling mud.
A similar pattern of fluorescein and organic carbon concentrations (Fig. 7, brown) were found in the discharged drilling mud. However, peaks in the organic carbon concentration reflect the removal of the xanthan-based viscose gel that was used during the cementation to protect the filter regions (Fig. 7, data points labelled with *). In contrast to Ktzi 200 and 201, in Ktzi 202 most of the xanthan was removed from the well during the first 25 m^3 of fluid produced. This was probably due to the slightly different completion procedure of Ktzi 202.

4. Discussion

4.1 Tracer application

A uniform fluorescein distribution within the circulating mud was reached 24 hours after addition. Tracer concentrations in the drilling mud were found to be stable for at least three weeks during the entire testing period (Fig. 2). Furthermore, after dilution with unlabelled drilling mud, the theoretical concentration values were always in agreement with the measurements. In tests addressing the sorption behaviour of fluorescein with respect to drilling mud, no retention was observed (Fig. 1). The fluorescence microscopic detection of drilling mud in core material revealed non-sorptive behaviour as well, because the TOC concentrations (another mud indicator) were in good agreement with the decreasing fluorescence intensities (Fig. 4 and 5). During hydraulic tests and nitrogen lifts, about one year after drilling operations, the fluorescein concentrations in the produced fluid were still reliable. Currently, the sample quality of down-hole samples from the wells Ktzi 200, 201 and 202 can be addressed by means of fluorescein detection (Morozova *et al.*, 2010). Thus, the applied concentration of 1 mg/l was found to be sensitive enough to assess the sample quality of formation fluid samples.

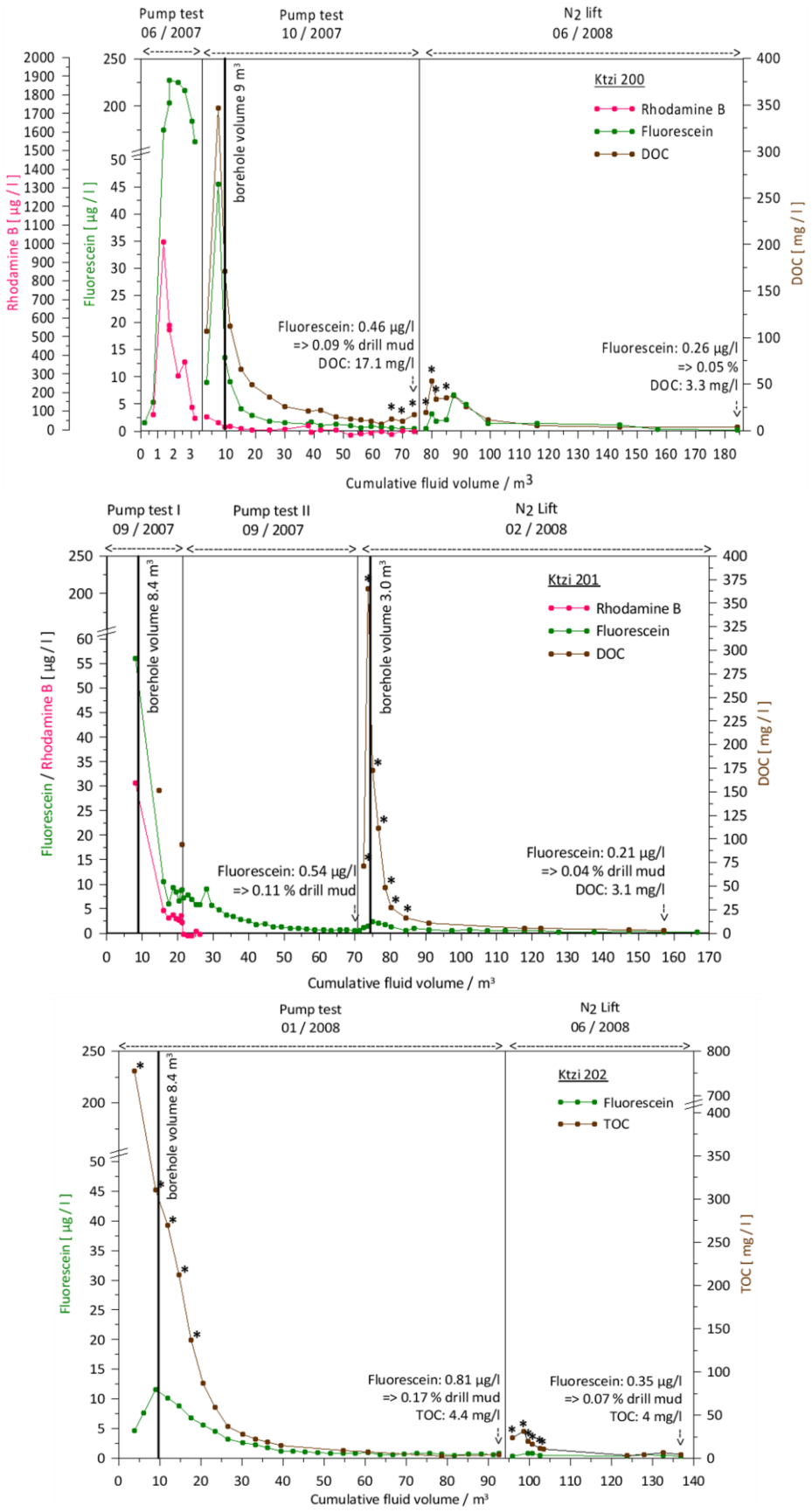

Figure 7. Detection of technical fluid discharge from the wells Ktzi 200 (**A**), 201 (**B**) and 202 (**C**) by means of tracer and organic carbon analyses during hydraulic tests and N_2 lifts.

Although the detection limit of rhodamine B (1 µg/l) was about 33 times higher than the detection limit of fluorescein (0,03 µg/l), the tracer was sufficient to monitor the discharge of displacement brines from wells. A disadvantage of rhodamine B is the relatively high concentration that has to be used, which may have an ecotoxic effect. The fluorescence intensity was strongly affected by the medium (Fig. 3), and concentration determinations in mixtures may not be reliable.

4.2 Penetration of drilling mud into core sections

The fluorescence microscopic analysis of core sections turned out to be a field-applicable method for the rapid screening of sample quality prior to the immediate preservation of samples intended for microbiological studies. The microscopic detection limit at the tracer concentration of 1 mg/l was found to be 5% (Fig. 4). TOC measurements were more sensitive and a mud proportion of 1% could be detected in the 20-mm region of core sections (Fig. 5). Although the TOC concentration profile implies that the inner core below 20 mm is not affected by drilling mud and inner TOC concentrations may represent background values from sandstone, the quantification of fluorescein in inner core samples is necessary to ensure that the analysed sample is not affected by drilling mud.
The microscopic analysis of rock samples with different permeabilities from Ktzi 202 showed that the depth of mud penetration depends on the permeability of the rock (Fig. 6). As expected, more permeable rocks showed deeper penetration than rocks with low permeability.

4.3 Contamination assessment in formation brine samples during pump tests and N_2 lifts

Application of the tracer allowed the technical fluids discharged from the wells during pumping and lifting to be monitored (Fig. 7). Whereas the displacement brines were removed very quickly with the production of 1-2 borehole volumes, the drilling mud was removed rather slowly. This may be due to the fact that the majority of the remaining drilling mud was located in the annular space (the non-cemented zone between casings). Nonetheless, after the production of about 20 well volumes, a small amount (0.05%) of drilling mud could be detected in the produced formation brine, which represents a tolerable amount for molecular biological studies. The high stability and sensitivity of fluorescein makes the sensitive assessment of sample quality possible even two years after its application.

5. Conclusions

This study describes the application of a reliable and sensitive tracer-based method for determining the infiltration of drilling mud and technical fluids into rock cores and fluid samples. This method allowed sample quality to be evaluated immediately in the field after drilling or pumping, which is a prerequisite for the adequate processing of samples intended for molecular biological studies. Tracers were detected using a mobile fibre-optic fluorimeter and a fluorescence stereomicroscope. We found that outer core regions of mildly permeable sandstone sections were significantly infiltrated with drilling mud. The tracer concentration in the inner core was below the visual detection limit. To make sure that inner core samples are not affected by drilling mud in the future, the fluorescein concentration of any sample used must be quantified. In addition, the removal of drilling mud and technical fluids from the wells should be monitored, which is of considerable importance for maintaining permeability and for the

purity of down-hole samples. Future work should address the question of how much drilling mud can be tolerated in core and brine samples intended for microbiological studies.

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