Two young scientists were recognized for their sustainable approach to the use of the Earth's resources at the Third Sustainable Earth Science Conference & Exhibition 2015 in Celle, Germany. The winner of the Young Scientist Prize is Ms Angeliki Baritantonaki from Rijksuniversiteit, Groningen. We would like to congratulate her for this achievement. Her paper, 'Dolomite Dissolution Rates at Conditions Relevant to CO_2 Sequestration in the Rotliegend Gas Fields in NE Netherlands' is under review elsewhere, so we were unable to publish the content of her paper in this article.

However we would also like to congratulate Mr Marton Berta of the Kiel University on being the runner-up for the Young Scientist Prize. His paper about 'No Short-term Attenuation of Methane Leaked into Shallow Aquifers – An Experimental Study' is available below. The SES jury would like to thank both winners for their submission.

Experiments showed no reactions coupled to methane leaked into shallow aquifers

Marton Berta[1], Anne Becker[1], Frank Dethlefsen[1], Markus Ebert[1], Saskia Koch[1] and Andreas Dahmke[1] experimentally characterize the geochemical effects of methane intrusion on shallow aquifers.

The need for subsurface energy storage to balance the fluctuations in power production using renewable sources already exists, and based on the current deployment rate of wind and solar power stations, scenarios with a renewable share of up to 80% of the German energy production were developed for the next decades (UBA, 2010). Owing to the fluctuating character of renewable energy production, storage of gases, including compressed air, methane, and hydrogen may play a deciding role in the geological energy storage mix (Bauer et al., 2013). In case of a methane storage concept, the gas is generated from surplus renewable electricity via the Sabatier process, stored underground in deep porous reservoirs or salt caverns, and retrieved and used in the existing energy system when needed. Any geological gas storage may result in leakages of the stored gas into shallow geological compartments due to various reasons such as well failure (Evans, 2009). Evaluating hydrogeochemical reactions following such a potential accidental methane leakage into shallow aquifers are of particular importance for ensuring good groundwater quality, especially if the overlying shallow aquifers are used for drinking water production.

Changes in groundwater chemistry following an intrusion of methane are probably controlled by the metabolic response of the subsurface microbial community. In aquifers not affected by leakage incidents, methane practically does not appear together with potential electron acceptors (e.g. McIntosh et al., 2014), therefore redox reactions, consuming biogenic or thermogenic methane intruding such aquifers, can be expected. In these processes, oxygen (Smith et al., 1991), nitrate (Raghoebarsing et al., 2006; Eisentraeger et al., 2001; Ettwig et al., 2010), ferric iron (Beal et al., 2009), and sulphate (Kelly et al., 1985; van Stempvoort et al., 2005) can serve as electron acceptors, while methane is oxidized to CO_2. Amongst these processes, sulphate reduction is the most influential on groundwater quality owing to comparatively high concentrations of dissolved sulphate (Dethlefsen et al., submitted) and the potential of sulfide production. However, the process is mostly known from marine environments in so-called 'sulphate-methane transition zones (SMTZ)', summarized for instance by Knittel and Boetius (1999). In such environments, microbial communities could establish on long, perhaps geological time scales. On the other hand, some groundwater environments, such as aquifers overlying hydrocarbon reservoirs that are being exploited for a comparatively short time span, suggest that a response may not take place if the encounter of methane and an electron acceptor is rather immediate (eg. Osborn et al., 2011, Ziemkiewicz and He, 2015).

As the reactions potentially triggered by methane have not been studied in laboratory experiments representing groundwater conditions so far, the goal of this work is to experimentally characterize geochemical effects of methane intrusion on shallow aquifers. These findings are supplemented by studies regarding the hydrochemical effects of compressed air (Berta et al., in prep A) as well as hydrogen (Berta et al., in prep B) potentially intruding shallow aquifers.

Materials and methods

Flow-through column experiments were carried out to represent the hydrogeological conditions of a shallow aquifer, using four 30x6 cm glass columns that were filled with

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sediment and percolated with ground-water (Figure 1). Each column was equipped with five sampling ports along the flow path. The groundwater was equilibrated with methane at 1 bar partial pressure, resulting in methane concentrations of up to 1.2 mmol/L at 20±2°C, before being introduced to the columns. The residence times, determined using a LiBr tracer test, were between 13 and 16 hours. Sediments for two columns originated from a core drilled into a shallow (4-12 m below ground level, 10°C) Pleistocene aquifer near Neumünster (Germany) (NMS1 and NMS2 columns). For an additional column, marine sediment material was taken from the SMTZ in the Kieler Förde near Tirpitzhafen using the *RV Alkor*. This marine sediment had a share of one third, while two thirds of commercial quartz sand (0.3-0.8 mm) was added and the resulting mixture was homogenized under Ar atmosphere (MAR column). Finally, the fourth column was filled with quartz sand containing 0.5 wt% goethite (Bayferrox 920) (GOE column).

For the first 11 weeks, a near-surface aquifer environment was simulated in these four columns by percolation with tap water from a Pleistocene aquifer at Kiel University. Dissolved oxygen (up to 100 µmol/L), nitrate (20 µmol/L), and sulphate (500 µmol/L) were present in the columns' inflow. After this first aerobic period, sulphate-
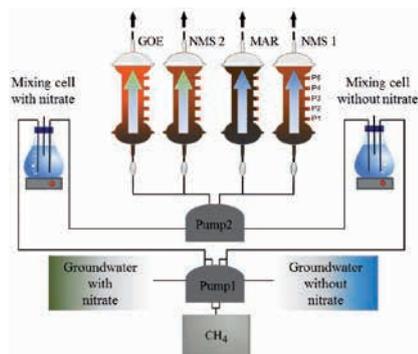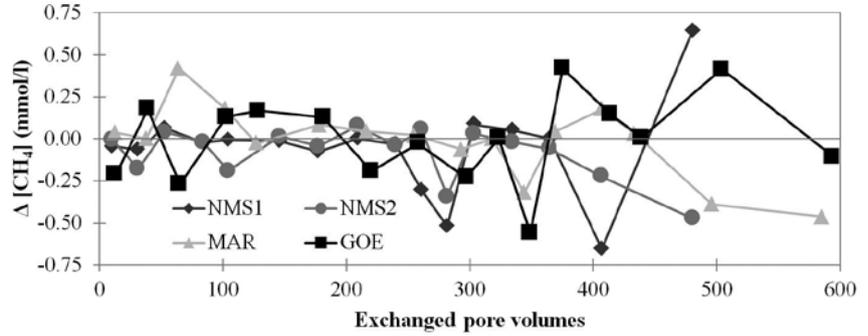

Figure 2 *The difference in concentration of dissolved methane in the groundwater flowing through the different experimental columns. One exchanged pore volume is completed in approx. 12 h. The electron acceptors (sulfate, iron, and nitrate) showed a similar behaviour (Berta et al., 2015).*

Figure 1 *Sketch showing the experimental setup. CH4 gas was used to bubble the groundwater in the mixing cells. From there, the CH4-saturated water is pumped into the columns. Samples were taken from the five ports along the flow path and from the inflows.*

containing (1000 µmol/L), nitrate- and oxygen-free (<8µmol/L) groundwater from the same NMS aquifer where the sediment was taken from was used to allow the development of a more anoxic environment in the columns NMS1 and MAR. In a further step after approx. 400 exchanged pore volumes, a pre-column filled with Fe^0 grains was added to reduce the redox potential of the inflowing waters of the NMS1 and MAR columns. However, for the two columns GOE and NMS2, up to 70 µmol/L of nitrate was added to the inflowing water. Further information regarding the sediments and groundwater used as well as the water analytics are provided in Koch (2014), Becker (2014) and Berta et al. (2015).

Results

The column experiments showed no reproducible decrease in methane concentrations during percolation of the sediments (Figure 2) in the whole, one-year runtime. On the other hand, three of the four columns (MAR, NMS2, GOE) showed a slight consumption of electron acceptors. From the beginning, denitrification (0.6 and 1 µmol/L/h) was determined in the GOE and NMS2 columns, respectively (Figure 3). Nitrate reduction rates remained nearly constant over the experimental runtime measured over the flow path within the columns, regardless of the variation of the nitrate concentration between 13 and 72 µmol/L. However, the nitrate reduction rate was higher and increasing from 2 to 12 µmol/L/h and from 4 to 20 µmol/L/h, respectively, between

the inflow and first sampling port of both columns percolated with nitrate containing water (Figure 3). Ammonium concentrations showed no change versus the flow path based on a sampling event when it was also measured; and nitrite was detected in none of the samples.

The MAR column showed sulphate reduction (up to 3.8 µmol/L/h, Figure 3) after switching to the anaerobic groundwater. Smell of sulfide production in the MAR column was identified along with decreases of up to 150 mV in redox potential and 0.15 in pH. However, sulfide concentration stayed below the level of determination of 5 µmol/L.

Concentration of dissolved Fe^{2+} varied along the flow path increasing by up to 12.4 µmol/L in the NMS1 column and decreasing by up to 8.5 µmol/L in the MAR column, which were both percolated by nitrate-free groundwater. Mn^{2+} concentrations were increased in all columns by up to 1-1.5 µmol/L. Within the measured values no further changes were observed in electrical conductivity, pH, and redox potential; total dissolved organic carbon; dissolved ions (Na^+, K^+, Ca^{2+}, Mg^{2+} and Cl^-); furthermore no bromide, acetate, nitrite, or thiosulfate was detected in any of the samples. Thus, no methane oxidation by any electron acceptor could be detected in any of the columns.

Discussion

Effects of a potential methane leakage on groundwater composition

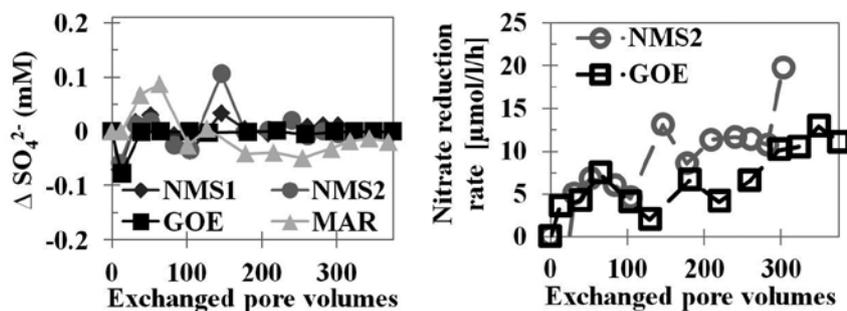Although the experimental conditions were considered suitable for the

Figure 3 The difference in concentration of dissolved sulfate (left) in the groundwater flowing through the different experimental columns. Nitrate reduction rates increase between the inflow and the first sampling port (right), but not within the columns (between first and fifth port; Koch (2014)).

expected methane oxidation, the series of results showed that significant aerobic or anaerobic methane oxidation did not take place in the represented hydrogeological conditions. Other works showed that the experimental setup is adequate for studying methanogenic (Jesußek et al., 2013) redox processes as well as reductive processes caused by dissolved hydrogen (Berta et al., in prep B). Anaerobic methane oxidation rates stoichiometrically corresponding to the observed sulphate reduction (up to 48 µmol/L during one pore volume exchange) and denitrification (up to 39 µmol/L) rates would balance to 48 and 24 µmol/L methane consumption, respectively. These changes supporting this calculated mass and electron balance were not identified in the experimental results. The reduction of sulphate and nitrate established in the experimental columns could also have been linked to oxidation of organic material that was potentially released from the sediments or possibly suspended in the inflow water, corresponding to up to 91 and 48 µmol/L C_{org}, respectively. Decreasing redox potential also could have been an indicator for anaerobic methane oxidation coupled to sulphate reduction as mentioned for instance by van Stempvoort et al. (2005), but our data suggests that the redox potential in the columns did not decrease below the typical level for nitrate reducing conditions (350 ±60 mV for NMS1-2 and GOE). Therefore, it is exemplified in the presented study that in the first year only a slow and uncertain response, if

any at all, can be expected following a methane introduction into an aquifer.

Reasons for this slow response in sulphate reduction may include i) the high doubling of time to up to seven months of the microbial consortia (Knittel and Boetius, 2009), which is mainly caused by; ii) the low (only ca. 1%) rate of assimilation of the carbon consumed by the microorganisms carrying out anaerobic methane oxidations (Nauhaus et al., 2007); and iii) the low energy yield of the reaction, which is barely enough for synthesising a single ATP, the elementary energy transfer substance in cells (Wang et al., 2010). Regarding field experience on sulphate reduction coupled to methane oxidation, the reaction was not identified in shallow aquifers with thermogenic methane near unconventional hydrocarbon exploitation (Marcellus Shale, Pennsylvania, USA; Osborn et al., 2011). In a Canadian aquifer, more than seven years after a methane leakage from a gas well still high (up to 1.25 µmol/L) methane concentrations were observed, and seven more years were necessary to observe a decrease (up to 0.18 µmol/L) coupled to sulphate reduction (van Stempvoort, 2005). However, a response within less than a month was followed by a gas well blowout in Ohio, but efforts to experimentally reproduce the reactions were only partly successful (Kelly et al., 1985).

In the initial, aerobic period methane oxidation was also not observed, which is consistent with the conclusions of Smith et al. (1991), suggest-

ing that such a response is determined by the resident microbial population. This proposes that aerobic methane oxidation also needs the presence of a pre-existing community in an aquifer to show a prompt consumption of methane. Nitrate reduction took place in both experimental columns percolated with groundwater enriched with nitrate. This reduction apparently resulted in the production of N_2, as no ammonium or stop at nitrite were detected. This is in agreement with the results of Raghoebarsing et al. (2006).

Comparison of methane leakage effects to potential effects of compressed air and hydrogen leakages

Apart from the leakage of methane from a deep reservoir, potential effects of other gases, such as compressed air and hydrogen, were also evaluated. In contrast to the effects of a methane leakage in the presented study, prompt reactions took place following their introduction to various experimental aquifer systems. Compressed air leakage can result in the presence of oxygen in originally reduced aquifers. This oxygen can be lead to pyrite oxidation, increasing the sulphate concentration by up to 500 µmol/L at 1 bar of O_2 partial pressure and moderately decreasing the pH-level, as shown in laboratory experiments (Berta et al., in prep A). In these experiments, the oxidation kinetics is limited by a passivation layer precipitating at neutral pH from the ferric iron produced by the pyrite oxidation process. For further experiments, hydrogen concentrations in the order of millimoles per litre were used, as they may be created by a hydrogen leakage (Berta et al., in prep B). Such a set up can trigger a redox sequence with fast nitrate reduction (on the time scale of minutes) and iron^{III} reduction, followed by acetogenesis (up to 20 µmol/L/h) and sulphate reduction (up to 60 µmol/L/h) taking place together. Methanogenesis in these experiments seemed inhibited, probably owing to the considerable pH increase from 8 to 10.

Summary and conclusions

After a potential leakage of geologically stored methane into a shallow aquifer, no rapid oxidation of methane can be expected. A reason could be the slow metabolic response of the shallow subsurface biogeochemical system for a sudden methane intrusion, inhibiting methane oxidation within at least one year under the conditions described in the presented study. Therefore, we suggest that the response of the subsurface depends most probably on the initial density and the growing potential of the microbial community oxidizing methane and reducing the electron acceptors. This is in contrast to the leakage effects of other gases stored in the subsurface, such as hydrogen and compressed air, which are experimentally shown to cause rapid changes in groundwater composition.

From the quasi inert nature of methane that was identified in the presented study, results indicate that i) site vulnerability assessments should include experimental and also field studies. For the later, a push-pull redox tracer test is suggested using a site where anaerobic methane oxidation is already established. ii) Modelling efforts may consider methane as a conservative gas as a first approach. iii) Leakage monitoring efforts must focus on methane itself, instead of possible reaction products.

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