Project acronym and title:
SECURe – Subsurface Evaluation of Carbon capture
and storage and Unconventional risks

Guidelines for next generation measurement and monitoring of Shale Gas/CCS with guidance for practitioners of the future

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D4.7

Disclaimer

This report is part of a project that has received funding by the *European Union's Horizon 2020 research and innovation programme* under grant agreement number 764531.

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Project funded by the European Commission within the Horizon 2020 Programme	
Dissemination Level	
PU	*Public*
CO	*Confidential, only for members of the consortium (incl. the Commission Services)*
CL	*Classified, as referred to in Commission decision 2001/844/EC*

Deliverable number:	**D4.7**
Deliverable name:	**Guidelines for next generation measurement and monitoring of Shale Gas/CCS with guidance for practitioners of the future**
Work package:	**WP 4 Advanced monitoring and sensor technologies**
Lead WP/deliverable beneficiary:	

Status of deliverable		
	By	**Date**
Submitted (Author(s))	**Tina B. Bech, Rasmus Jakobsen**	**10.03.2021**
Verified (WP leader)	Matteo Icardi	24.03.21
Approved (EB member)	Pierre Cerasi	25.03.21
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Public introduction

Subsurface Evaluation of CCS and Unconventional Risks (SECURe) is gathering unbiased, impartial scientific evidence for risk mitigation and monitoring for environmental protection to underpin subsurface geoenergy development. The main outputs of SECURe comprise recommendations for best practice for unconventional hydrocarbon production and geological CO_2 storage. The project is funded from June 2018–May 2021.

The project is developing monitoring and mitigation strategies for the full geoenergy project lifecycle; by assessing plausible hazards and monitoring associated environmental risks. This is achieved through a program of experimental research and advanced technology development that includes demonstration at commercial and research facilities to formulate best practice. We will meet stakeholder needs; from the design of monitoring and mitigation strategies relevant to operators and regulators, to developing communication strategies to provide a greater level of understanding of the potential impacts.

The SECURe partnership comprises major research and commercial organisations from countries that host shale gas and CCS industries at different stages of operation (from permitted to closed). We are forming a durable international partnership with non-European groups; providing international access to study sites, creating links between projects and increasing our collective capability through exchange of scientific staff.

Executive report summary

The potential advent of the unconventional gas industry and the probable introduction of large-scale CO_2 storage in Europe has generated public concern regarding contamination of groundwater and surface water resources. Like other technologies, the large-scale exploitation of the subsurface is not without risk of environmental impacts. Hence, the main objectives within WP4 have been to:

- Develop new technologies to improve the detection and monitoring of environmental impacts related to geo-energy projects.
- Apply, and test a range of pre-assessment methods, monitoring technologies, systems, and strategies to contribute to effective (best practice) risk evaluation, establishing baseline conditions, and monitoring and managing impacts.

WP4 consists of various topics related to CO_2 storage or fracturing of shale covering, for example, groundwater geochemistry (gas), molecular microbiology, (micro) seismicity, ground movement and atmospheric gas concentrations. Due to the experimental state of most of the methods, costs of devices as well as running costs are unknown, while parameters such as the physical scale covered by the method and to what extent automation is possible is known to some extent. The final section of this deliverable includes a table summarizing the principles of the different methods, the parameters measured, with indications of coverage, ease of use and to whether automation is, or could be, an option since this is a critical parameter for continuous monitoring at remote locations.

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1 Introduction

The main focus of the SECURe project has been to evaluate different aspects of shale gas exploration and CO_2 geological storage. Both are modern technologies with (or having the potential of) a large-scale deployment in the coming decades because they can play an important role towards a sustainable energy future. The recent expansion of the unconventional gas industry in North America and its potential advent in Europe has generated public concern regarding groundwater protection and surface water resources. This exploitation is not without the risk of environmental impacts.

When evaluating the environmental impacts and risks of geo-resource exploitation, it can be divided into three levels according to the spatial scale of the influence. Macro, Meso and Micro groups represent environmental impacts at global/continental, regional and local levels. The macro-level includes global warming potential, abiotic depletion potential and cumulative energy demand, etc. The meso level typically consists of the mid-point impact categories such as acidification potential, eutrophication potential, photochemical zone creation potential and ecotoxicity potential, etc. Human toxicity potential and water use are considered at the micro-level. The section on macro, meso and micro levels and below is commonly based on the review by Liu and Ramirez (2017).

The shale gas process releases and collects natural gas from shale formations. Horizontal drilling and fracturing are two key processes that make shale gas exploitation different from conventional gas. Here injection of fluids fractures the shale formation.

- At the macro level, methane migration to the atmosphere may contribute to climate change.
- At the meso level, changes in groundwater aquifers can result in elevated concentrations of cations and anions, including manganese, iron, bromide and chloride. Further, methane concentrations in drinking-water above 10 mg CH_4/L can be a potential explosion hazard.
- At the micro level, population exposure to toxic substances in the air related to shale gas exploitation activities could be a concern. This level has not been included in WP4.

Geological reservoirs considered for CO_2 storage are (nearly) depleted or abandoned oil and gas reservoirs, deep saline aquifers, and deep coal beds. The sources of CO_2 leakage are mostly related to operational failures such as inadequately constructed wells or geological failures such as caprock failure.

- At the macro level, the consequences of CO_2 leakage are an increase of CO_2 concentration in the atmosphere, and therefore linked to climate change.
- At the meso level, CO_2 leakage may cause negative impacts on the quality of groundwater, soil and surface water through, for example, 1) pH decrease, 2) increase in hazard trace elements such as lead and arsenic, and 3) concentration of Fe and Ca increases.
- At the micro-level, it is anticipated that there will be no health effects related to rapid CO_2 leakage. Again, the link to human health is not included in WP4.

Baseline monitoring is essential to characterize a site before CO_2 injection or hydraulic fracturing commences and should be considered as an integral part of the monitoring plan submitted at the time of storage/fracking permit application. It is also essential if a leakage event occurs to have a baseline to work towards if remediation is necessary. Hence, the main objectives of WP4 are:

- To develop new technologies to improve the detection and monitoring of environmental impacts related to geo-energy projects.
- Developing, applying and testing a range of monitoring technologies, systems and strategies to contribute to effective (best practice) risk evaluation, the establishment of baseline conditions and monitoring and management of impacts.

WP4 consists of various topics related to CO_2 storage or fracturing of shale covering, for example, groundwater geochemistry (gas), molecular microbiology, (micro) seismicity, ground movement and atmospheric gas concentrations covering both macro and meso investigations. WP4 aims to develop sensor and monitoring techniques and technology to mitigate risks and further de-risk unconventional gas exploitation and the sequestration of carbon dioxide in underground storage sites. New technologies have been tested to improve sensor measurement thresholds for toxic quantities below the current detection limit of state-of-the-art sensors to:

- Enhance the characterization of seals, fracture pathways, and their temporal change;
- Understand risk and create de-risking strategies by monitoring leakage pathways and rates;
- Improve detection threshold technology and provide a solution for the measurement of gases and toxic metals released during CCS and shale gas production;
- Carry out large temporal/spatial range seismic monitoring for microseismic activity detection to link with baseline monitoring and remediation WPs;
- Process, integrate and interpret large, multisource sensor data, and utilize data in the model calibration, allowing for sensor and monitoring data in a closed feedback loop to inform subsurface-to-surface parameters;
- Test new and improved technology to lower the sensor measurement thresholds to detect changes in parameters previously below detection limits of current state-of-the-art techniques.

Some of this work has been reported in detail in previous WP4 deliverables. Within this D4.7 deliverable, we provide background information and an evaluation of the applicability of the different methods in chapter 2. In chapter 3, the different methods are listed and grouped based on spatial scale of relevance.

2 Developed methodology

2.1 UAV TECHNOLOGY

Contact person: Dr Colm Jordan (BGS/UKRI)

2.1.1 Background

This section addresses the efficacy and development of Unmanned Aerial Vehicle (UAV) technology for large-scale greenhouse gas monitoring of shale gas and CCS sites. In particular, we address strategies to detect and monitor greenhouse gases (CO_2 and CH_4) directly with world-leading technology flown on rotary and fixed-wing small UAV platforms. The complete SECURe report on UAV technology can be found at https://www.securegeoenergy.eu/sites/default/files/SECURe_D4.1_Final.pdf (Jordan et al., 2021).

UAV data (and derived information such as orthophotographs, surface models and vegetation indices) are routinely collected and analyzed for a range of geoscience applications. However, UAV data are not routinely used for monitoring gases as these systems are still at research or prototype stages of development. We utilized the British Geological Survey (BGS) prototype fixed-wing UAV system and the TOTAL AUSEA rotary UAV system; both carry CO_2 and CH_4 sensors. We also consider systems to monitor gas emissions indirectly by detecting vegetation stress using UAV-based hyperspectral sensors and correlating those with in-situ gas sources; we utilized ground-based sensors as a proxy for what can be achieved with hyperspectral instruments mounted on UAVs.

Gas monitoring can be undertaken at various scales from the ground up using in-situ instruments, airborne sensors (on UAVs or conventional aircraft) and satellite-based methods. UAVs fill an essential gap between what is possible with in-situ surveys and traditional aircraft. Conventional survey aircraft can carry full-scale thermal, photographic and hyperspectral instruments along with gas sensors (e.g., Cavity Ring-Down Spectroscopy analyzer). Still, they are expensive to mobilize, and the raw data require significant processing time. In-situ (i.e., on the ground) surveys can be time-consuming and require full access to the field sites, which might not always be possible for a variety of reasons, including health and safety (e.g., rough terrain) or accessibility (e.g., dense scrub). UAVs cannot cover the same area as conventional aircraft, and the sensors are miniaturized and are often not as precise as their larger counterparts. However, we review what they can achieve and how they can be used to direct/focus ground-based surveys as part of an integrated monitoring operation.

2.1.2 Application

Within SECURe, TOTAL deployed their prototype TOTAL AUSEA rotary drone system to simultaneously detect both CH_4 and CO_2. BGS utilized their prototype fixed-wing UAV system mounted with CH_4 and CO_2 sensors (figure 1). BGS has also converted its system to operate on rotary drones, although the rotary system could not be tested before the publication of this report due to COVID travel restrictions. COVID-19 impacted the work schedules of all partners in this work package in several ways, including:

1. Travel restrictions meant that we were unable to undertake field testing from March 2020 onwards. For example, we had expected to fly the BGS gas sensing UAVs at the ERA GTB site where CO_2 injection was planned for 2020. The injection has been delayed until March 2021, at which point we plan to deploy the BGS UAV gas sensor.
2. Due to office closures, TOTAL could not access hyperspectral data from the October 2019 flights until May 2020, leaving less time for processing and analysis than originally planned.
3. Due to schedule re-prioritization at TOTAL, the October Alps UAV data could not be processed before October 2020, leaving less time for in-depth processing and analysis.

BGS undertook baseline test flights and surveys in the UK with the CO_2 fixed-wing UAV prototype in June and August 2019. The primary aim was to test the UAV and sensor in a field / operational environment. The survey determined baseline levels of CO_2 at the site; there was no controlled gas release. Fieldwork (comprising staff from BGS, BRGM and TOTAL) also took place from 20th to 25th October 2019 at Jonchiers and Molières-Glandaz. In October, the prototype TOTAL AUSEA gas sensor system was utilized alongside BRGM in-situ flux measurements (closed chamber system with external recirculation). The flux data collected at ground level were used to confirm the location and intensity of gas release detected by the UAV.

The BGS and TOTAL AUSEA UAV gas sensor systems' tests demonstrated that they are capable of monitoring and recording gas concentrations in flight. They record positional data and detect gas from surface emissions (albeit with caveats, see below). The datasets produced within SECURe contribute to the assessment of the advancement of the technology readiness level (TRL) for operational drone-based monitoring systems, moving the research from TRL 4 (i.e., technology validated in a laboratory) to TRL 5 (technology validated in a relevant environment). SECURe thus provided a research opportunity to demonstrate in the field that miniaturized monitoring systems can be successfully deployed by drone to detect emissions from ground level and at low emission rates.

Figure 1. BGS fixed-wing UAV CH_4 sensor prototype (left) with results plotted from a UK test flight (right)

Data processing of UAV-based datasets could not be addressed in depth during this work package due to COVID-19 limitations. Nevertheless, BGS has demonstrated some advances in identifying gas sources on the ground by modeling UAV in-flight data. Independently from SECURe, TOTAL has developed quantification proprietary algorithms along with its AUSEA technology development framework. This has already been assessed even at low emission rates against others and at controlled release sites simulating the industrial environment, though applying these methods to natural rough terrain exhibiting dispersed small intermittent sources is very challenging. This will be a necessary milestone to reach if environmental baselines are produced with UAV-based systems. Further study of hyperspectral acquisition by drone is a promising way of detecting CO_2/CH_4 leakage in vegetated areas through the detection and quantification of vegetation exposure.

Analysis of the UAV results highlights that in-flight gas concentrations should be acquired simultaneously as ancillary data, including wind speed and 3D direction. With these ancillary data, we have shown that modeling can be undertaken to localize the emissions source on the ground. This modeling would help to focus ground investigations on pinpointing the gas source and determining the flux. This is an important demonstration, as it highlights the potential for a tiered monitoring program. For example:

1) UAVs deployed initially to cover large or poorly accessible areas, to highlight key areas of interest (or at the very least, rule out the vast majority of land);
2) Follow-up ground surveys directed by UAV-based data to pinpoint individual vents or vent clusters (e.g., if aligned along a fault/fracture);
3) Gas sampling at individual vents for specialized gas analysis (e.g., for tracers or noble gases) and/or deployment of automated equipment at fixed sites/vents to gather time-series data (e.g., to quantify how gas fluxes change under different meteorological conditions or seasonally).

Unfortunately, follow-up tests with controlled gas releases were not possible in SECURe due to COVID travel restrictions. Therefore, it has not been possible to quantify precisely what level of gas emissions can be detected from what altitude, given various weather conditions, including rainfall and wind speed/type. This is an important area that needs further study. In controlled gas releases, it is possible to know precisely how much gas has entered the air mass and for how long. It is, therefore, likely to draw a clear link with what is detected at altitude. Natural gas releases are very much harder to characterize accurately, and significant effort must define a reliable overall release rate.

As a consequence, we still need to demonstrate a quantitative link between UAV-based gas monitoring data over natural sites and monitoring with ground instruments at the same sites. Key to defining this will be well-characterized and instrumented sites (i.e., 'natural laboratories'), at a range of scales that can be used to test various gas monitoring technologies. This could include tower-based eddy-covariance monitoring (not applied during this study) that can indicate summarised emission rates over a large area and a closer link to UAV-based measurements.

Optimal flight patterns for gas monitoring were also qualitatively reviewed in this task. If the requirement of the drone survey is simply to determine if there are gas concentrations in the air that differ from the background/baseline, then a flight that traverses the area in a grid pattern at a single altitude is sufficient. Conducting automated flights at a constant altitude above ground or obstacles is thus a critical requirement for UAV systems. However, these data would not be appropriate to determine if high values originated from the site or were dispersed from further afield or if the size and shape of a plume of gas were required. The ideal flight pattern traverses the area at a range of altitudes and good coverage at 90° to the wind direction. It is also important to have simultaneous data on both wind speed and its direction in 3D (the vertical component being critical).

We have demonstrated that the partner UAV-based gas sensor systems (rotary and fixed-wing) can collect good CH_4 and CO_2 measurements. With further operational testing, they could be an additional practical tool for site monitoring, scaling up the ability to capture conventional/traditional ground-based measurements. UAVs can efficiently cover sites that would be time-consuming or even inaccessible for ground surveys. The in-flight gas measurements should be collected alongside ancillary data such as wind speed and direction to help locate ground sources of gas emissions. Furthermore, we recommend that the UAV data be collected in conjunction with ground measurements to validate these novel and cutting-edge systems.

2.2 DETERMINATION OF GEOCHEMICAL ELEMENT MOBILIZATION

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2.2.1 Background

Hydraulic fracturing is widely used to exploit unconventional hydrocarbon sources and enhance the exploitation of geothermal energy. The hydraulic fracturing fluids, which are commonly acidic, cause a dissolution of minerals and desorption of elements which can lead to groundwater contamination. A wide range of fluid acid concentrations, temperatures, and rock/fluid ratios have been tested to investigate element mobilization and gain insight into the chemical processes during hydraulic fracturing fluid-shale interaction. These data will provide a predictive tool for leaching, mobilization of elements, and potential contamination by mobilizing heavy metals. Our findings identify the chemical reaction pathways involved and evaluate the elemental mobilization from shale reservoirs with differing mineralogies. This method provides new knowledge that may help define strategies to mitigate risks regarding potential groundwater contamination related to hydraulic fracturing activities.

2.2.2 Application

Non-automated local monitoring (pre monitoring assessment)

After drying, grinding (using an agate mortar and pestle), sieving (<125 μm), and mixing, a uniform mineral content can be expected for powdered samples. The powdered samples were used in batch reactor experiments to investigate geochemical element mobilization by interaction with acidic fluids. Additionally, the powders were used for X-ray diffraction (XRD) analysis to determine their mineralogical composition (using DIFFRAC. EVA-XRD software to determine the mineralogical composition). Bench-scale batch reactor experiments were conducted to test the interaction of simulated fracturing fluids with the Bowland-Hodder shale at a variety of conditions, i.e., fluid acidity, temperature, and rock/fluid ratio, as well as two end-member mineralogical compositions from the Bowland shale (one with high calcite content, and one with high pyrite and clay content). Hydrochloric acid is the major constituent of fracturing fluid, and the solution in our experiments was prepared by Milli-Q water. The fluid pH was adapted by adding small amounts of concentrated or diluted HCl (trace metal grade). Each powdered sample was added to a 200 mL solution in a 250 mL closed batch reactor on a hotplate stirrer. The suspension was continuously stirred using a Teflon-coated magnetic stirrer bar. Each experiment was run for a total of 100 hours, and aliquots (2 mL) were sampled at 0, 1, 3, 7, 23, 27, 31, 54, 77, 100 h and filtered through 0.22 polyethersulfone (PES) membranes for further analysis. Hence, the change in pH and the change in geochemical composition of the fluids were recorded over ten-time steps in these batch reactor experiments. A total of 1 mL extracted fluid was used for pH analysis using a Fisher Scientific accumet benchtop pH meter. Another 1 mL extracted fluid was acidified and diluted ten times with ultrapure HNO_3 (2%) for elemental analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). The results enable quantification of the extent of geochemical element mobilization based on the experimental conditions. Hence, the data will determine the extent of leaching, mobilization of elements, and potential contamination by mobilizing heavy metals. Our results may lead to practitioners considering the amount of HCl used during hydraulic fracturing operations when a specific reservoir operation (formation temperature and rock/fluid ratio) is determined. To limit the environmental effects of element mobilization, this method can be used before a given operation.

Comparison to existing methods

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used for major element determination in the mg/L range. Given that inductively coupled plasma mass spectrometry (ICP-MS) is a technique to determine low-concentrations (range: ppb = parts per billion = μg/l), it was used for trace elemental analysis. The results of these experiments, obtained by measuring the elemental concentrations in the fluids, establish the impact of different variables (i.e., fluid acidity, temperature, and rock/fluid ratio) on the effect and rate of leaching, and thus potential contamination. Two non-milled pieces of solid shale samples were embedded in epoxy resin. The sections were finely polished and coated with carbon in preparation for Mineral Liberation Analysis (MLA) and SEM (scanning electron microscope) analysis. During automated MLA-SEM analysis, the Back-Scattered Electron (BSE) signals and Energy Dispersive X-ray spectra (EDS) of the grains are collected. The average BSE grey value of each measurement region relates to a mineral of unique average atomic number and different mineral components (the mineral identification is based on the chemical composition referenced to a database of minerals) and mineral boundaries can then be identified and established based on the BSE images. MLA measurements identify mineralogical components and mineral morphology of the two polished shale samples before and after interaction with the acidic fluid. The alteration in surface morphology of polished shale sample sections by the interaction of different minerals with fracturing fluids enables a better understanding of the kinetic dissolution of the main minerals.

Furthermore, the mineral-surface topography was investigated in these two reacted samples with 3D imaging using a Zeta-20 Optical Microscope. The focus of the objective lens is moved with Z-stage, and the 3D scanning microscopy of the shale surfaces can be observed by measuring the different vertical heights from the cross-section. This information is subsequently used to generate reconstructed 3D color images. The mineral topography demonstrates the preferential dissolution of calcite, related to the rapid mobilization of calcium. This can provide a fundamental understanding of pore generation and the kinetic dissolution of the main minerals during water-rock interaction.

Advantage/disadvantage

Several series of batch reactor experiments were carried out to determine elemental mobilization from simulated fracturing fluids over a range of fluid chemistries and other conditions. The underlying chemical mechanisms behind element mobilization involve mineral dissolution and element desorption at interfacial contacts and strongly dictate the chemistry of flowback water. Moreover, the morphology and topography of the altered zone in the shale matrix enable a better understanding of pore generation and the kinetic dissolution of the main minerals during water-rock interaction. Our results may lead to companies optimizing the amount of HCl used during fracturing activities under a specific reservoir condition. Moreover, understanding the transport of elements and the composition of fracturing fluids is critical to optimize the treatment and management of both flowback water and produced water and minimize the impact on the environment.

In terms of future work, reactive transport modelling will be used. We will establish more quantitative predictive rules on element mobilisation in porous and fractured shale samples, which link shale composition with fluid conditions.

How ready is the method to be applied commercially?

This method focuses on chemical reaction pathways. This technology could be further enhanced by investigating a larger diversity of shale sample compositions by conducting flow-through experiments and testing with real hydraulic fracturing fluids.

2.3 NOBLE GAS DOWNHOLE SAMPLING

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A specific downhole sampler (prototype) for noble gas content analysis determinations has been designed by IFPEN and constructed by the subcontractor ANTARES. This downhole sampler allows a complete measurement chain that offers downhole sampling, sample analysis and thermodynamic calculations. It has been designed for max. operating T 125°C, max. operating P: 350 bars, max. sample V: 600 ml. L: 2,5 m / Outside Diameter (OD): 63 mm (70 mm with stand-off). The single-phase homogeneous fluid is transferred into the measurement cell (designed by IFPEN) for further analysis, such as Bubble point measurement, GOR (Gas to Oil Ratio) or GWR (Gas to Water Ratio), composition analysis (GC) of the vapor phase (lab test). Knowing the bubble point, GWR/GOR (mass balance) and vapor phase composition, we can calculate the composition of the liquid phase in equilibrium to the vapor phase, the thermophysical properties of the system at different P & T (different reservoirs conditions) using Thermodynamic models (e.g., Soreide & Whitson approach (SW); Peng Robinson equation of state (PR Eos).

For this purpose, a thermodynamic calculation package has been developed to use the measured properties as the entry for the model to predict system properties / noble gas compositions at different conditions. IFPEN and Semm Logging (industrial partner) have also collaborated to propose an innovative mobile cabin. This collaboration was partly associated with the GECOSAMPA project funded by ADEME.

This cabin contains a sampling tool, a transfer cell to extract the gas phase, a micro gas chromatograph to analyse the gas composition and a thermodynamic model (pc installed package) to predict the dissolved gas composition at different conditions. It can combine the following steps directly on-site:

1) Fluid samplings in well at reservoir conditions, *i.e.,* pressure up to 350 bar and temperature up to 125°C,
2) Dissolved gas extraction and measurement of its composition and thermodynamic prediction of the dissolved gas composition in the aqueous phase.

2.3.1 Application

New applications linked to subsurface energy recovery, which can be described as geo-energies, includes CCS or geothermal energy. Their implementation can impact both surface and subsurface environments. Methodologies and technological tools for monitoring must be available to enable sustainable management of the subsurface. Synergies are possible between these new applications and traditional applications (hydrocarbons or gas storage) for the techniques to be implemented. Any fluid leaks (gas, water, oil) must be detected by monitoring and control systems adapted to each case's specificities to improve remediation.

Interest is also operational, allowing to inform the operator on the industrial production or storage process's performance and the environment, governed through continually evolving regulations. Monitoring is a methodological field and booming technology.

The sampler (Figure 2) was designed to collect any fluid (water/oil/gas) with a sufficient volume and without any contamination or leakage enabling the analysis of the geochemical composition of the gas/dissolved gas with high sensitivity, e.g., the possibility to use it for noble gas analysis. It also had to respect the following functional and operational specifications:

- the possibility of integrating the sampler as a module in an existing and already very complete toolset. This point was essential because it directly positioned the sampler as an additional element of a set already validated and recognized as a benchmark in the logging market;
- ease of use and maintenance;
- ease for transferring the sampled fluid to a transfer cell for gas analysis;
- ease of disassembly for cleaning after each use.

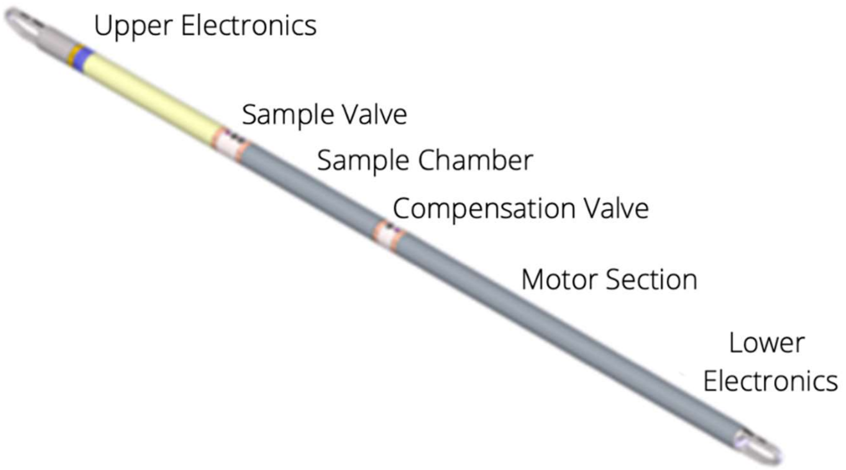
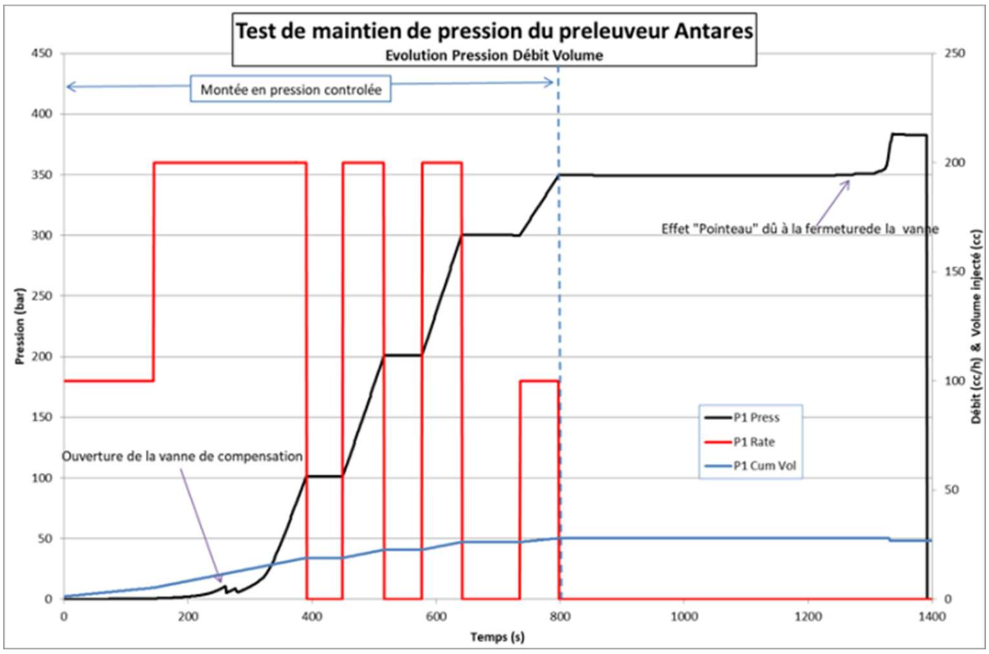


Figure 2. Sampler designed by ANTARES based on the specifications of Semm Logging and IFPEN

Also, with SEMM LOGGING subcontractor ANTARES, IFPEN has developed a re-usable tool for handling the cable head of the sampler. This allows proper operations for the handling of the sampler down into the well.

One of the major advantages of the presented measuring tool in comparison to the existing industrial tools is the capability of keeping, transferring and analyzing the sample while minimizing leaks and air contamination. The other main advantage is that the cabin with the analytical equipment makes it possible to deliver fluid composition analysis in a reduced time (0.5/1 day) and to optimize the experimental design of the fluid samplings in response to the fluid analysis results. This cabin can be easily transported by truck to different locations.



● pump rate ; ● sampling chamber volume ; ● sampling chamber pressure

Figure 3. Tightness test of pressure in the sampler @350bar (Max).

Two tests have been carried out to validate the functionalities of the sampler:

1) The first validation test was carried out at ANTARES facilities in their laboratory in Germany in order to predict the dissolved gas composition at different conditions (Figure. 3.).

A first sealing test was realized by injecting water in the sample chamber with a piston-pump to increase the pressure up to 350 bar at ambient temperature. The second sealing test was performed to verify the sampler's compatibility to conditions close to operational temperature and pressure using an autoclave. The tested temperature and pressure conditions were 95°C and 250 bar. These two tests demonstrated the conformity of the sampler to the set-point temperature and pressure since no leakage was observed during these operations.

2) The second validation test aimed to evaluate the equipment in real conditions in a deep (3000 m) aquifer located in Bonnefont, France. In addition, to test the tools, the main objective was to have feedback on the deployment of all the equipment, particularly on the ease of using the material and the time of each step.

Two further tests during the SECURe project were completed in February 2020 at SIG I and in October 2020 at SIG II in Switzerland. These two on-site tests allowed samples to be taken at -440 m down to -1500 m (refer to Table 2 below) for a potential client specialized in Geothermal activities.

Table 1. Measurements for the five samples: sampling depth (m), sampled fluid volume (mL), temperature (T°C) and pressure (bar) at sampling depth, measured dissolved gas volume (mL) at surface conditions (P=1 bar, T=10°C), gas volume ratio (GWR)

Samples	Depth (m)	Fluid volume (ml)	T (°C)	P (bar)	Gas volume (ml)	GWR (-)
1	1360	570	51.8	133.3	Gas traces	0.0003
2	880	570	39.0	86.1	9	0.15
3	996	570	42.2	97.5	No gas detected	---
4	880	570	39.1	86.1	9	0.15

5	800	570	37.6	78.3	12	0.2

The client's feedback is very positive and allows, at this stage, for possible future tests and development. However, it is too early to qualify for a potential commercial return, though it may be possible to assess the market readiness of the sampler during the 1st quarter of 2021.

One known drawback of the sampler is the degassing of samples during the transfer and analysis from geological formation to laboratories. The temperature and the pressure at the sampling depth are not maintained, but it is possible to re-compress the sample back to the reservoir pressure when the sampler is at the surface. The current design includes a variable volume sample chamber and a pressure compensation that allows us to control the surface pressure.

Potential redesign could be envisaged by ANTARES to upgrade the materials of the compensation chamber in order to increase and maintain pressure level resistance leading to competitive advantage at the commercial phase. Despite this pressure drop in the chamber evaluated at the design stage and deliberately put into evidence in the technical specification by the constructor ANTARES, an improvement on this lack of pressure in the sample chamber could be envisaged to redesign the sampler and thus improve the commercial development of the sampler at a later/future stage.

2.4 MONITORING OF INDUCED AND TRIGGERED SEISMICITY

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2.4.1 Background

Monitoring is fundamental to determine whether the injection of fluids in the subsurface is progressing as expected. Microseismic activity can reveal early signs of undesirable consequences of fluid/gas injection. Both induced and triggered seismicity are well-known side effects of subsurface activities across various fields such as hydrocarbon production, gas storage, waste disposal and geothermal energy production. Induced microseismicity is micro-events occurring in the vicinity of injection wells, whereas triggered earthquakes are typically larger events caused by stress changes on nearby faults (Ellsworth, 2013).

Microseismic events are typically too weak to be felt by the population but extremely useful for monitoring and mitigation strategies. Microseismic activity near a production site can act as a state-of-health indicator for the subsurface, where a rising level of microseismic activity can be a sign of stress perturbations or pore pressure changes (Ellsworth, 2013). Seismic monitoring cannot serve as the sole monitoring technology but should be part of a larger monitoring plan encompassing other geophysical, geological and geochemical technologies as outlined in (European_Communities, 2009).

For the ideal monitoring scenario, the natural seismicity in the area of interest is determined through a baseline monitoring campaign before the onset of subsurface activities. The purpose of the baseline monitoring is to establish natural seismicity in the undisturbed environment, making it possible to identify changes caused by anthropogenic activity. For more details see the SECURe deliverable D4.2.

2.4.2 Application

Microseismic monitoring has progressed to the point that extensive information on fracture development and geometry is detected. Furthermore, real-time signal processing facilitates real-time microseismic monitoring of hydraulic fracture treatments or other subsurface activities.

The monitoring of microseismicity can cover large areas/volumes, using relatively few installations, and the equipment can be deployed in remote locations from where the data can be transmitted automatically and wirelessly using the mobile phone network or other wireless systems. If needed, the system can be powered by solar panels and or windmills. The incoming data can be collected and monitored in real-time. It can be analyzed in more detail and compared with, e.g., data on injection, thunderstorms etc., to identify the source of specific events and determine detection levels.

Discriminating natural earthquakes and induced/triggered earthquakes is not trivial (Grigoli et al., 2017). Calculating a precise hypocenter and focal mechanism for each earthquake is very useful; however, it is often impossible for small events. High noise in part caused by production activities, insufficient seismograph coverage, and poor velocity models are common obstacles for a comprehensive physics-based analysis. A high-quality baseline is very helpful for discriminating between natural and anthropogenic seismicity.

The recommended best practice will always be to establish a baseline for natural seismicity before operations start, discussed in SECURe D3.1. In some cases, this is not possible because operations had started years or decades back in time before anyone realized a baseline would be useful. In other cases, there is not enough time to measure a proper robust baseline before operations are scheduled to commence. In these cases, is it necessary to establish the baseline post-operationally.

During the SECURe project, a monitoring network consisting of 6 monitoring locations was set up at the Stenlille gas storage site in Denmark. The Gas storage facility has been in operation since 1989, pumping up to 500 x 10^6 Nm^3 of gas in and out during an annual cycle. During 18 months of monitoring, there were no seismic events linked to the gas storage and retrieval. As no events larger than the detection level were detected at Stenlille, we cannot correlate these with pumping activity. However, the fact that no events were detected is a sign that the pumping is not causing any critical stress buildup despite the large volume of gas pumping. The detection level is estimated to be at or below ML 0.0, meaning that even tiny events are detected. In comparison, the detection level for the national monitoring network for onshore Denmark is around ML 2.0 (Dahl-Jensen et al., 2013; Voss et al., 2015).

Both the equipment and the processing tools are readily available, and the method has the advantage that it can be deployed remotely and function autonomously for extended periods. The area/volume covered is large, and the sensitivity is high.

2.5 GEOELECTRIC THRESHOLDING TECHNOLOGIES

Contact person: Oliver Kuras <oku@bgs.ac.uk>

2.5.1 Background

Geoelectrical monitoring and associated techniques in boreholes and at the surface can be used to address geoscience challenges related to energy (e.g., conventional and unconventional hydrocarbons; CO_2 capture, utilization and storage; geothermal) to assess subsurface fluid flow and monitoring of the near-surface environment. The British Geological Survey (BGS) Geophysical Tomography team provides leading-edge technology for non-invasive, geoelectrical imaging of the shallow subsurface.

The case study utilized for SECURe is the electrical resistivity tomography (ERT) system installed at the GeoEnergy Test Bed, which uses BGS-designed PRIME technology and can be operated remotely from the BGS offices while collecting ERT data in an unsupervised and automated fashion. Data transfer is by wireless internet, and processing and interpretation are undertaken at BGS.

Installation of the GTB boreholes, downhole sensor arrays have been undertaken over several years since 2016 and commissioning work is ongoing, with an experimental CO_2 injection program planned for 2021. The ERT arrays comprise two strings of electrodes in each deep monitoring well, a number of the electrodes in the deep aquifer into which CO_2 will be injected, have an experimental coating that is expected to improve longevity. The arrays are novel in that two strings of sensors were installed in each well. These arrays are deeper than previous arrays tested with the BGS system and electrode spacing is irregular, this was done to offer flexibility to accommodate uncertainty in the geology at the time of sensor design.

This section of the report will focus on the ERT method and review the planning, deployment and commissioning of the PRIME-ERT system and sensor arrays. At the point of writing this review (January 2021), the ERT system is fully deployed at GTB and commissioning trials are in progress. Figure 4 shows the arrangement of the ERT array and deep injection well at the GTB.

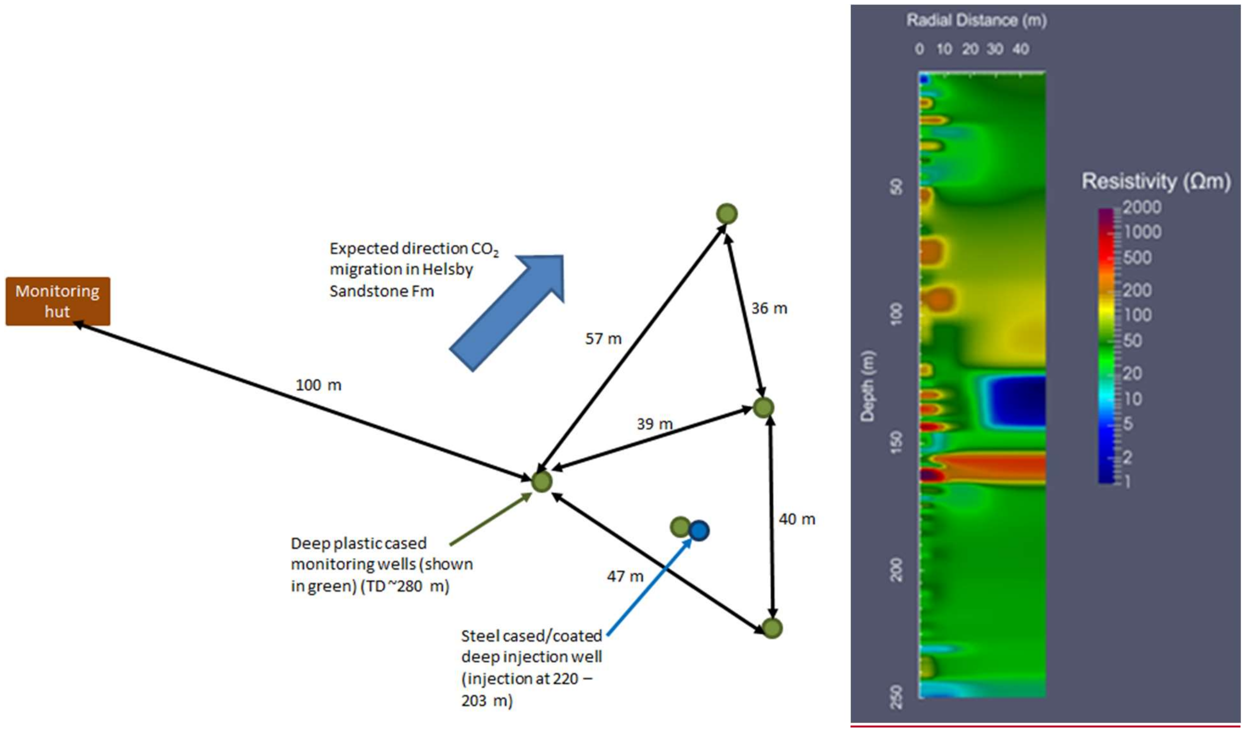

Figure 4. Array layout at the GTB (left), preliminary electrical resistivity tomography (ERT) image of one monitoring well using in-hole measurements only (right)

The review of the ERT concept at the Ketzin CCS research site in Germany (Schmidt-Hattenberger et al., 2011) had structured the learning points as follows:

- Preparation; Feasibility, design, installation of ERT
- Acquisition; Data acquisition, QC, transfer & conversion, archiving & mining
- Processing; Data processing, inversion, modelling, petrophysics (forward), geological a-priori information
- Evaluation; Parameter quantification, petrophysics (inverse), data integration

Table 2. Issues raised in the Ketzin review.

Issue raised at Ketzin	**Lessons applied at GTB**
Insulating steel casing with Ryt-Wrap	Similar coating applied to steel injection wells
Multicore cable issues	Less of a risk due to shallower depth of installation
Greater modelling effort pre-injection desirable	Modelling work underway
Matching ERT data with process data and well completion data essential	Ongoing
Bespoke pre-processing	Not thought to be required due to different measurement principle
Testing different inversion codes, develop bespoke constraints	Equivalent strategy planned
Separate investigation of 2D imaging panels	Used during GTB commissioning
2D time-lapse was critical for detecting CO_2	Ability to acquire and consider 1D, 2D and 3D time-lapse data
ERT cable take-out failures (brine entry)	Cable sealing tested, no aggressive brines expected

CO_2 dry-out in annular space	Noted
Difficulties matching data from different scales (e.g., surface-downhole)	Noted
3D time-lapse challenging	Noted
Detection of CO_2 in raw data vs delayed observation in inversions	Noted
Operating range limited to extended wellbore region	Borehole locations chosen for the ability to obtain meaningful crosshole ERT information away from wellbore

A similar review is being undertaken at the GTB, building on the lessons learned at Ketzin. As the GTB is at an earlier stage of operation compared with Ketzin, this review is not yet complete. Key lessons learned from the installation and early commissioning work of the GTB ERT system are as follows:

- ERT sensor deployment should be considered a critical deliverable for the entire borehole installation procedure – a borehole should not be a purpose in itself – rather, it should be regarded as a carrier and facilitator for sensors, sampling, and injection, which are the main scientific deliverables and therefore of overriding importance.
- Surface infrastructure (e.g., monitoring hut, ducting, shallow trenches, wellheads, communications, power) demands early planning (certainly before drilling) to fit for purpose and address the specific operational requirements of ERT and other sensor technology.
- Understanding site conditions, particularly water run-off, is critical during planning. Electrical connections need to remain dry and protected. Ephemeral flooding from surface run-off following seasonal rainfall led to significant additional engineering and further remedial work at GTB
- External factors influencing the array must be considered early in the project. Wellhead design and completion have proven to be an area that needed much more attention and resources than anticipated. The wellheads had to be below ground level to meet local planning requirements. Providing full environmental and mechanical protection to ERT connectors has proven difficult and time-consuming, given the need to bury all cabling, junctions and terminations. Heavy manhole covers mean that lifting equipment and two persons are needed to access wellheads and ERT cable connections
- During installation, installation details must be clear for the whole team. A large laminated working copy of the critical information was attached to the drill rig to instantly make the data available to the team on the drill pad and capture any changes or adaptions in real-time and under challenging conditions (darkness, cold, rain, mud). It was also invaluable to have an independent note-taker separate from the hands-on installation crew, who can record events and help coordinate the works in the background.
- It is good practice to establish a site datum referenced to Ordnance Datum to be used for all on-site drilling and downhole measurements. This is of great importance for later reconstruction of ERT sensor depths in the boreholes, which is critical for the accuracy and integrity of forward and inverse modelling, data interpretation and quality assurance.
- Design complexity within the downhole ERT arrays should be avoided to limit the effort required for data post-processing. This includes minimizing the need for non-uniform electrode spacings on ERT sensor cables and avoiding the interleaving of cables where possible (i.e., covering the same depth range with two identical cables but vertically offsetting one against the other). In particular, the combination of interleaving cables *and* non-uniform electrode spacings (as used at GTB) should be avoided as this adds significantly to the complexity of commissioning the system

2.5.2 Application

The application of electrical resistivity tomography requires sensor spacings that are sufficiently close to each other and to the process under observation, in order to offer added value. The BGS-designed PRIME system implements automated remote monitoring. At the GTB the wells carrying the sensor strings are 35 – 57 m apart and form a diamond-shaped array that has the potential to interrogate the volume of rock between the monitoring wells in 2D or 3D.

As an electrical geophysical technique, the ERT method has very specific requirements for optimal performance, and it is critically important to consider factors such as (1) proximity of ERT sensors to metallic infrastructure, (2) compatibility with other techniques and sensors, (3) compatibility with proposed methods for borehole grouting and stabilisation, and (4) electrical contact with the formation. Minimising the amount of metallic infrastructure in and near boreholes is an overarching goal for ensuring adequate ERT performance. Whilst parts of the borehole infrastructure at GTB are necessarily metallic (e.g. injector well casing), targeted measures such as applying a coating of non-conductive epoxy resin prior to casing installation appear to have been successful at the GTB (and a number of other sites, e.g. Ketzin).

In comparison to other methods, the sensitivity of the array is an improvement on electrical logging since the electrodes are on the outside of the well casing and therefore have better contact with the geological formations offering improved sensitivity and resolution, particularly post-completion. In addition, the fixed array enables continuous monitoring of the volume of rock between the wells, providing continuous data on an automated basis before, during and after induced changes in the pore fluids due to CO_2 injection.

Advantages of the BGS PRIME ERT system:

- Sensitive to changes in the subsurface due to good contact with the geological formation
- Applicable to multiple geo-energy subsurface uses
- Specified to suit the needs of the project

Disadvantages:

- A relatively small volume of rock interrogated compared with the overall volume of the scale of the industrial CO_2 storage site
- Relatively limited spatial resolution due to limitations of the physics of electrical techniques
- Requires significant time for planning and commissioning to get the system up and running
- Requires expert processing and interpretation of the data to produce results that can be understood and carry weight in the context of monitoring and verification

Commercial application

Each system is bespoke and designed around the geology and aims of the site. These arrays could be used to monitor regions highlighted during the risk assessment.

2.6 SEISMIC THRESHOLDING TECHNOLOGIES

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Time-lapse 3D seismic data has been the primary tool for imaging subsurface anomalies associated with injected CO_2 at Europe's large demonstration projects (Sleipner, Snøhvit, Ketzin). The seismic technique is well suited to detecting CO_2 in the subsurface as the fluid substitution (replacing brine with CO_2) has been shown to generate clear amplitude anomalies and significant pushdown effects. As commercial CO_2 storage in Europe continues to develop, there will be a requirement for cost-effective solutions in monitoring and verifying site performance. However, seismic data acquisition is still expected to play a major role in determining plume behaviour and demonstrating 'zero detectable leakage' within the overburden.

Within SECURe, we have advanced and tested a technique for establishing quantitative thresholds of detectability for leaking CO_2 (Chadwick et al., 2014). The approach requires two vintages of time-lapse seismic data (baseline and repeat) that allow an estimation of repeatability noise to be derived from extracted amplitude slices using a 2D discrete wavelet decomposition scheme. Then, following the addition of an ensemble of amplitude anomalies, the detection threshold for fluid related subsurface changes can be established using members of the ensemble where the anomaly exceeds the noise envelope (Figure 5).

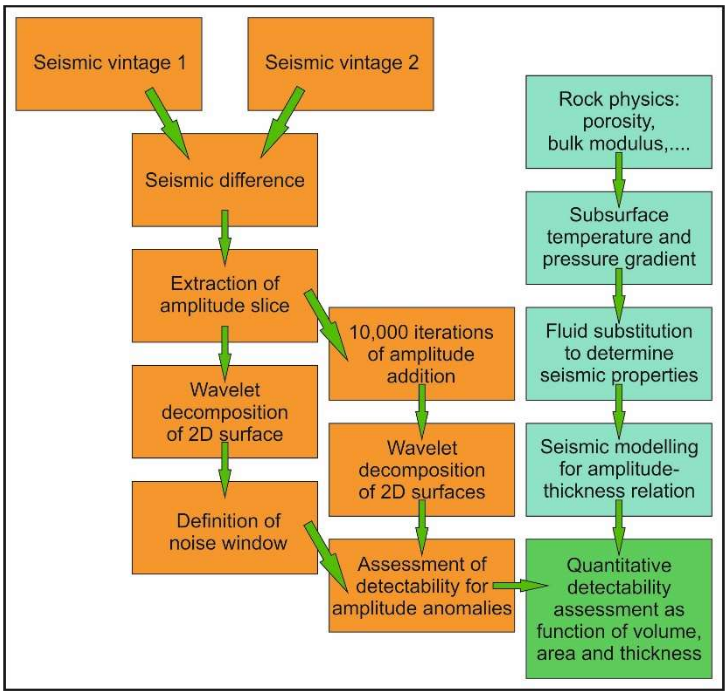

Figure 5. Flowchart highlighting required stages in quantitative detectability assessment tool.

To establish the correct site-specific subsurface properties and geophysical responses, a rock physics study was established that uses Gassmann`s fluid substitution equations and a synthetic seismic modelling scheme to accurately predict the relationship between amplitude and CO_2 layer thickness at the depth of interest. The output of the assessment is a quantitative estimate of the detection limit as a function of amplitude, area and thickness that can be related directly to CO_2 volume.

SECURe has undertaken two studies utilizing this approach. Initially, SECURe researchers worked with partners in the STEMM-CCS project from University of Tromsø to test the developing scheme on high-resolution p-cable data from the Norwegian Barents Sea (Waage et al., 2019). Thick mudstones and thin sandstone layers dominated the overburden. Here, it was demonstrated that CO_2 detectability thresholds varied significantly within the overburden, as shown in Figure 6.Figure 6

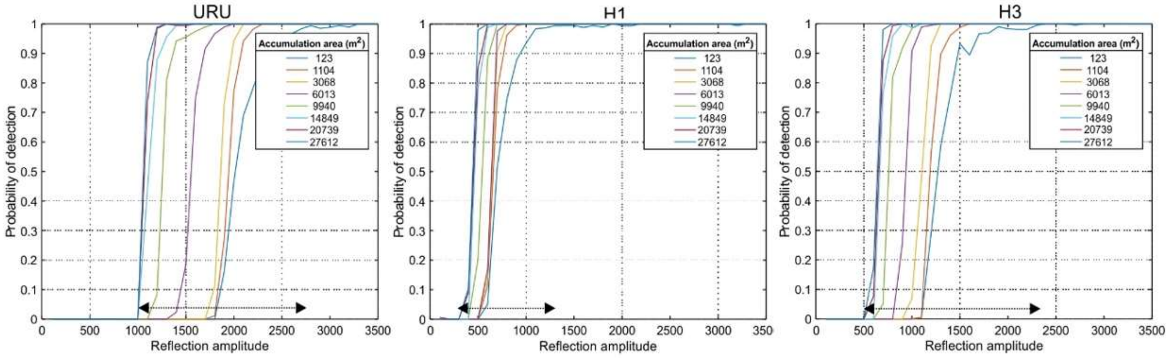

Figure 6. Probability of detection for anomalies of various sizes across interpreted horizons in the Norwegian Barents Sea.

Secondly, SECURe studied conventional onshore seismic data from the German Research Centre for Geosciences (GFZ) coordinated Ketzin project, the first onshore geological CO_2 storage project in Europe. Here, injection occurred into the Triassic Stuttgart Formation at between 625 and 700 m below mean sea level. Mudstones, claystones, sandstones and anhydrite overlay the reservoir, and limited information on the overburden was available for the assessment. Estimates of porosity and bulk modulus were used to provide forecasts of detection limits. Again, the quantitative detectability varied significantly within the overburden (Figure 7).

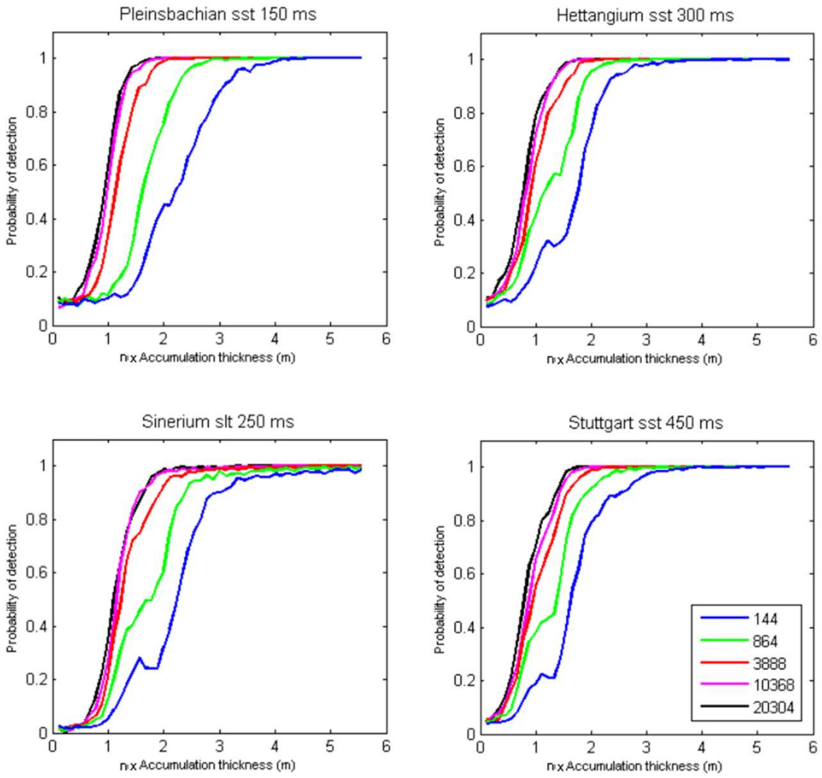

Figure 7. Quantitative detectability for synthetic CO_2 accumulations as a function of thickness from extracted timeslices in overburden.

In conclusion, SECURe has further developed a quantitative scheme to assess the detectability of CO_2 in the overburden. Most importantly, the necessary links with rock physics, fluid substitution and phase behaviour, and geophysical modelling have been established. This enables the approach to better constrain the expected seismic response of CO_2 at different intervals in the overburden. The scheme has been applied to two case studies highlighting the variability in detectability in different overburden strata. The technique is likely to be most useful in targeted detectability studies, where specific horizons have been identified as the most likely locations for the build-up of leaking CO_2.

2.7 GAS SOURCE BASED MONITORING SENSORS

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2.7.1 Background

Detection of present and past subsurface gas seepage and leakage (either natural origin or man-induced) is critical to apply mitigation processes to reduce such emissions (methane and/or CO_2). In this subtask, novel isotope-based methods were tested to 1) decipher the origin of gas seeping through the subsurface and 2) establishing long-term baseline monitoring of gas seepage. Short-term methods for in-situ determination of the origin of methane and/or CO_2 gas focused on determining its (subsurface) formation temperature. A second methodology investigated if and how local vegetation absorbs carbon from a CO_2 leak source and compared it to a long-term time-averaged reference baseline.

Established techniques for determining the gas origin and its subsurface migration utilize the gas' isotopic composition, in particular the $\delta^{13}C$ ($^{13}C/^{12}C$) and δD (D/H) ratios (Schoell, 1980; Whiticar, 1999; Hoefs, 2009). Differences in isotopic ratios are used to discriminate between methane gas from hydrocarbon source rocks (so called thermogenic gas) and methane gas formed in response to bacteriological processes in the shallow subsurface (so-called biogenic gas, (Schoell, 1980)). Post-generation processes (e.g., mixing, oxidation) may affect the isotopic composition in methane, making the distinction between thermogenic and biogenic sources challenging (Whiticar, 1999).

Expanding the suite of isotopic tracers for situations where deciphering the gas origin is ambiguous is therefore needed. Methane clumped isotopes have been suggested as a versatile tool for determining the gas formation temperature. "Clumped isotopes" refer to the bonding of two rare (heavier) isotopes in a molecule (Eiler, 2007). For CO_2, the clumping involves the bonding between the two heavy isotopes ^{13}C and ^{18}O in CO_2 (e.g., Eiler, 2007), whereas more recently also clumping in methane has been described (Stolper et al., 2014, 2015; Douglas et al., 2017). The clumping of the heavier isotopes in both methane and CO_2 gas is a direct proxy for the temperatures at which the gasses were formed.

Establishing a long-term, time-averaged baseline reference is useful for determining past gas seepages before routine gas monitoring. The application of tree-ring analyses has been postulated to serve as a monitoring tool for (past) CO_2 emissions (Donders et al., 2013). From an analytical point of view, Carbon-14 (C-14) dating is now routine and widely applied. In this subtask, its application for monitoring long-term CO_2 emissions is further explored.

2.7.2 Application

Clumped isotopes

A groundwater sampler was developed to collect large quantities (>> tens of liters) of water with dissolved gasses. Owing to the smaller molecular structure of methane (CH_4) compared to carbon dioxide (CO_2), methane is more prone to leakage from the groundwater sampling bag. Hence, initial testing of the water samplers' capability to preserve pristine isotopic compositions in gas dissolving from the groundwater was conducted. Isotopic compositions of gas extracted with the new groundwater sampling setup were compared to gas samples collected using established sampling techniques (e.g., Isoflasks). Isotopic data between the two systems are indistinguishable, indicating that the new setup may be readily used for a large volume of groundwater sampling and subsequent degassing.

To test the clumped isotope method for determining sources and origin of gas, several methane gas samples were collected from three different field locations: a natural gas seepage (the French Alps), a gas reservoir (Borzęcin, Poland) and a man-induced leakage site (Sleen, The Netherlands). The methane clumped isotope data was scrutinized against conventional $\delta^{13}C$ and δD isotope data to determine the origin of the gas. Bulk $\delta^{13}C$ and δD isotope measurements (specified using conventional isotope techniques) are comparable to the $\delta^{13}C$ and δD in the clumped isotope measurements (Figure 8), demonstrating the validity of the methane clumped isotope measurements.

Methane gas formation temperatures determined for the Borzęcin and Sleen samples range from ~50 to ~300°C (Figure 8). Clumped isotope $\Delta^{13}CD$ and ΔDD compositions for few samples deviate from the thermodynamic equilibrium curve (TEC, Figure 9), suggesting that the gas has no pure thermogenic composition but is a mixture with a biogenic or abiotic gas. For the sample from Sleen that falls on the TEC, the obtained methane gas formation temperature is in line with source rock maturity studies conducted in the eastern part of the Netherlands (Nelskamp, 2011).

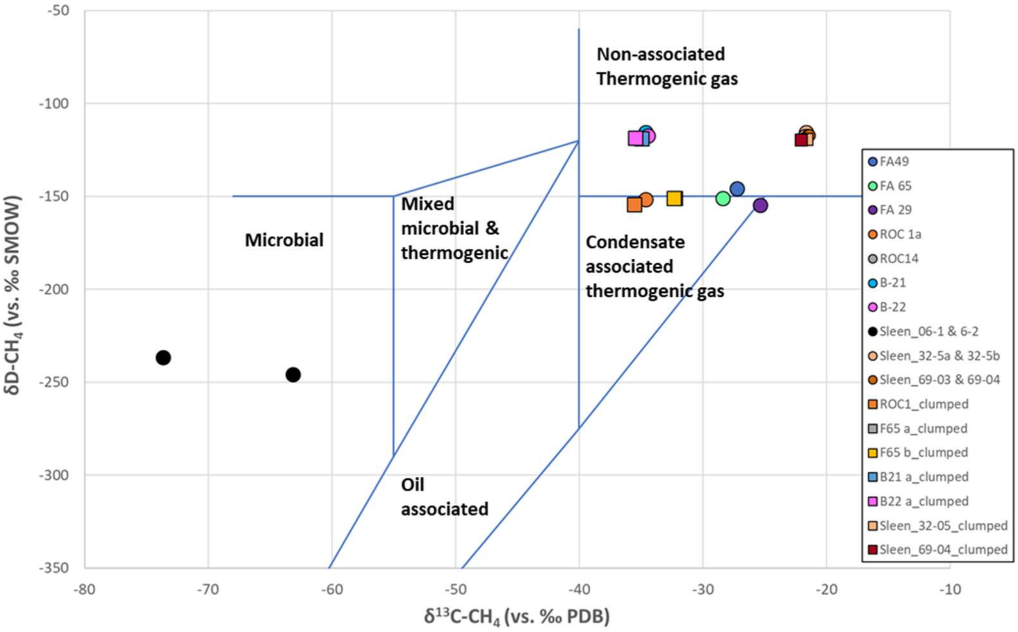

Figure 8. δ^{13}C and δD isotope data using routine techniques (circles) and methane clumped isotope measurements (squares) on the collected methane gas samples. Compositional fields modified from (Laughrey and Baldassare, 1995).

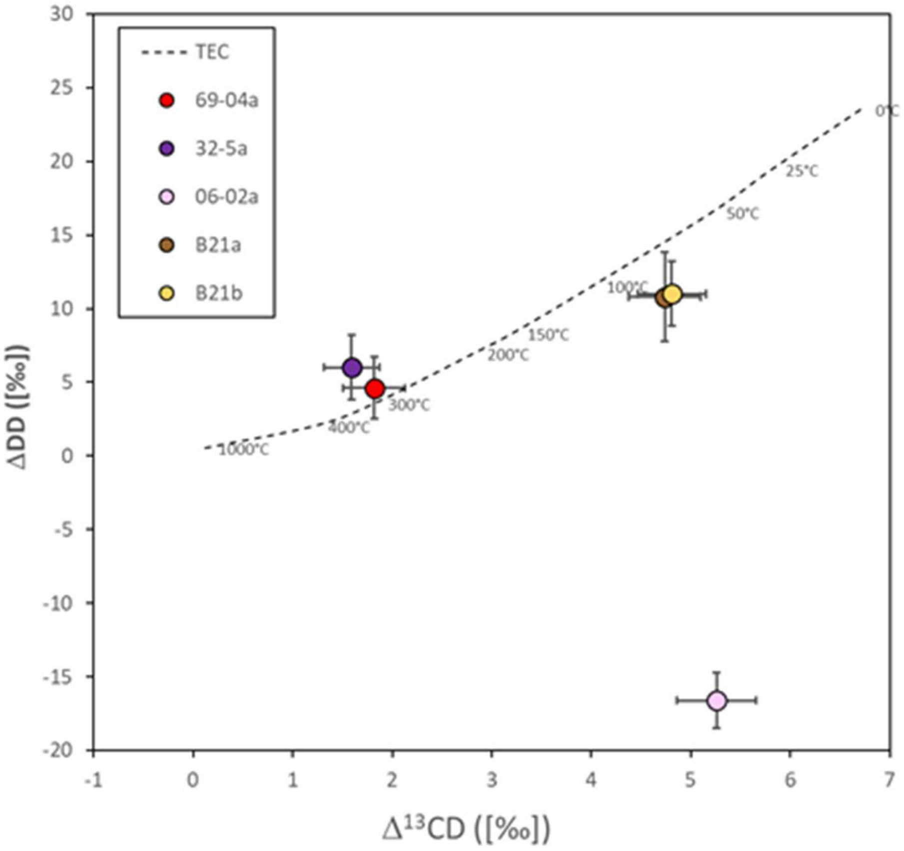

Figure 9. Clumped isotope data from methane gas samples collected from a natural gas reservoir (Borzęcin, Poland, samples B21 & B22) and a man-induced methane gas leakage site (Sleen, The Netherlands, samples 69-4, 32-5 & 06-02). Data from the natural gas seepage (French Alps, samples F65, F65, R1) are restricted and not reported here. TEC = thermal equilibrium line.

Although the methane clumped isotopes show some promising results, the method is analytically challenging (complex sample preparation, gas analyses and data acquisition). To date, only three laboratories worldwide provide such analyses on non-commercial samples. Should the methane clumped isotope method become less of a research tool but gain more applied traction, methane clumped isotopes could be a viable addition to the suite of tools for routine gas leakage monitoring.

Carbon-14 for long-term baseline monitoring

There is evidence that the emission of ^{14}C –free CO_2 during volcanic emissions creates a bias for radiocarbon dating of volcanic events (Holdaway et al., 2018), showing that integration of "dead" carbon by vegetation can serve as an indicator of geogenic gas emissions. BRGM tested ^{14}C activities, and stable carbon isotope ratios of tree rings and herbal vegetation in the proximity of the natural gas seep at the Fontaine Ardente field site. Wood samples were taken from two alder trees at different distances and directions from the main gas vent. Grass leaves and roots (*Carex sp.*) were analyzed for two spots with different soil methane concentrations and fluxes within the zone of diffuse gas emanation around the main vent (Gal et al., 2019). Grass and wood samples show contrasting isotope compositions depending on their species, age, and position with respect to the gas seep, some with ^{14}C activities significantly lower than present-day values.

Figure 10 shows that the radiocarbon activities of the alder tree upwind of the Fontaine Ardente (alder 1) are mainly compatible with those measured on an old Fagus sylvatica on the northern hemisphere (Lardie Gaylord et al., 2019), whereas alder 2, situated downwind of the main vent has significantly lower ^{14}C-activities than would be expected for post-bomb atmospheric values. We interpret this as an integration of "dead" carbon from the CO_2 (direct emission or oxidized methane) transfer via the natural gas seep atmosphere.

The grass leaves and roots of *Carex sp.* growing within the diffuse methane emanation area around the primary gas vent are significantly depleted in ^{14}C. The conventional radiocarbon ages are abnormally old (330 to 550 y before present). For these samples, we also observe a depletion in ^{13}C (Figure 11). Carex can transfer methane from the root zone to the atmosphere. The strong ^{13}C-depletion of both leaves and roots analyzed in the diffuse methane emanation zone could be related to the assimilation of thermogenic methane. Other effects, notably methane oxidation, the influence of deep CO_2 from the geogenic gas seep and the associated carbon isotope fractionation processes, have to be taken into account to explain these values.

So far, it can be stated that vegetation around a gas seep, in our case a natural analogue, can act as an integrator of gas emanation over time and, if tree rings are used, as an archive of gas fluxes. This offers perspectives of using vegetation carbon isotopes as proxies for present and past gas emanations, including man-induced gas leaks, e.g., from gas storage or natural gas exploitation facilities.

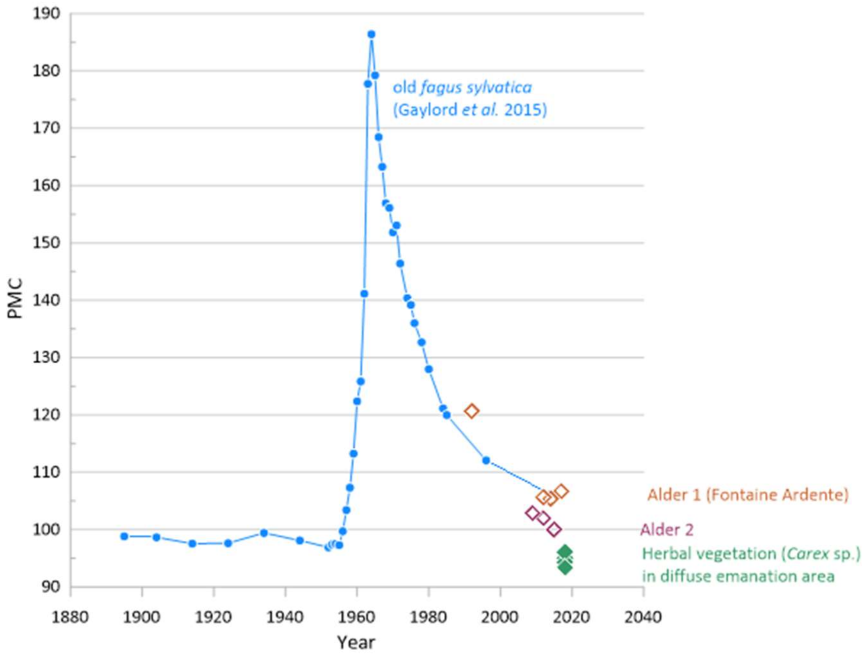

Figure 10. Preliminary data analysis of tree ring and herbal vegetation radiocarbon activities (tree ring counting to be confirmed).

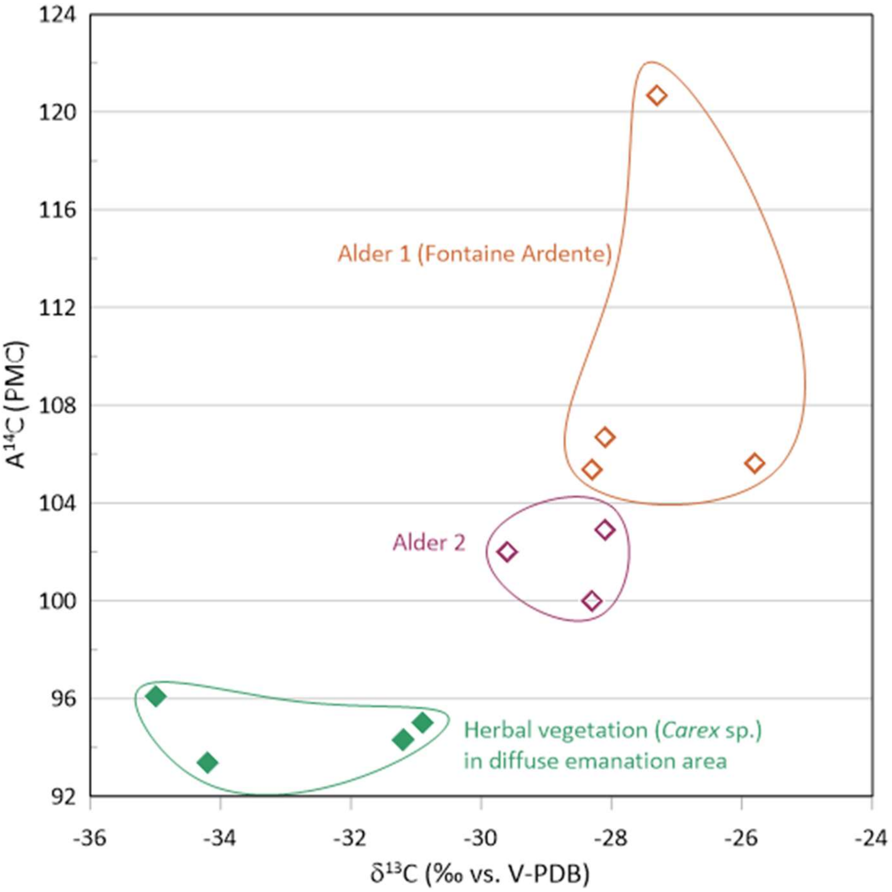

Figure 11. A^{14}C vs. δ^{13}C for vegetation samples around the Fontaine Ardente gas seep.

2.8 VIABLE MICROBIAL SENSORS

Contact person: Megan J. Barnett, megan@bgs.ac.uk

2.8.1 Background

Microbial monitoring for the detection of gas seeps is not new, and the oil and gas industry have used surveys of soil microorganisms to prospect for underlying hydrocarbon sources for decades using techniques such as Microbial Prospecting for Oil and Gas (MPOG) or Microbial Oil Survey Techniques (MOST) (Tucker and Hitzman, 1996; Manfred, Wagner and Smit, 2002). These methods rely upon detecting changes to soil microbial communities caused by gas seeping through microfractures that differs from atmospheric gas compositions. This results in detectable changes to the microbial communities. In particular, methane, ethane, propane and butane oxidisers, or the relationships between them, have all been used as indicators of gases leaking from hydrocarbon deposits (INC, 2017). Historically, industry application has used culture-based methods, where different headspace gases show differences in microbial communities. These techniques claim to have success rates of up to 90% (Manfred, Wagner and Smit, 2002). Compared to direct gas composition measurement, the microbial approach is reported to be more stable over time and indicates intermittent leakages for weeks or months (INC, 2017).

Of the microorganisms known to respond to gas leaks, methanotrophs (those organisms able to oxidize methane) are a subset of the broader group of methylotrophs (organisms that can oxidize single carbon molecules, such as methane and methanol). Microbial degradation of short-chain alkanes (SCA) is possible by a broad range of genera (Van Beilen and Funhoff, 2007). These alkane degraders might be particularly important to monitor as microbial methane generation in the subsurface might obscure a signal from thermogenic methane, and detecting organisms capable of growth on SCAs may help differentiate between sources. Microbial communities from gas seepage sites respond differently to non-seepage sites gas when exposed to butane, with Gammaproteobacteria and Betaproteobacteria showing increased abundance after exposure (Deng et al., 2018) with butane oxidation in key genera such as *Pseudomonas, Giesbergeria* and *Ramlibacte*r. Another study suggested that *Mycobacterium* and *Pseudomonas* could be indicators of hydrocarbon leakage (Deng et al., 2016).

2.8.2 Application

Culture-based methods have not been applied to monitor for methane leaks in groundwater. However, similar principles are behind MPOG and MOST as prospecting techniques using soil samples. After decades of development, MPOG has reported an accuracy of ~90%. The method developed here has an accuracy of ~70%, although this is limited to two field sites (28 samples) and needs validation in additional sites.

Advantages:

- Microbial communities are slower to react to changes in gas concentration; therefore, this technique is useful for the detection of intermittent leaks.
- Very low cap-ex costs, and only basic training required.

Disadvantages:

- Currently limited by accuracy for predicting gas source (~70%)
- Further development is required before commercial applications, currently TRL level 3. These developments focus on two primary goals: improved automation and improved reliability. Improving image analysis of results will drastically reduce the time required for data collection. This will help improve reliability by increasing the viability of repeat analyses from the same samples. Current commercial tests working on a similar principle have reported accuracy of ~90%; this method is currently 70%. Additional development is needed to apply to samples from different sites of interest and testing applicability on other water sources, i.e., natural springs and rivers in at-risk areas.

2.9 **MOLECULAR MICROBIAL SENSORS**

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2.9.1 Background

Historically, detectable changes of the microbial communities due to methane, ethane, propane, and butane oxidizers or the relationships between them have all been used as indicators of hydrocarbon deposits in industrial prospecting. Industries have applied culture-based methods (see section 2.8), but more recently, there have been attempts to apply DNA techniques to reduce culture-bias and improve accuracy and precision. All theoretical and conceptual models in community ecology can be explained by four processes: selection, dispersal, genetic drift, and speciation. Selection is the result of biotic and abiotic pressures causing variation in reproductive success across individuals and species. Genetic drift changes the frequency of gene variants and depends on population size and chance events. Dispersal governs the degree to which individuals move among communities, and speciation creates new species (Vellend, 2010).

Data from two geological formations revealed selection to dominate over genetic drift and dispersal in fine-grain sediments. Selection still exceeded genetic drift and dispersal in highly permeable sediments, while the latter increased in importance (Stegen et al., 2013). Therefore, the effect of highly variable methane and ethane concentrations is expected to reveal a large impact on the microbial community. Field-scale methane injection studies show that groundwater microbial communities remained disturbed after 253 days (Cahill et al., 2017), and laboratory microcosm studies show that methylotrophs may be suitable markers of methane contamination events, as they persisted for weeks after methane supply had stopped (Kuloyo et al., 2020). Methylotrophs not known to oxidize methane have also been suggested as possible indicator species in sediments and seawater (Redmond et al., 2010). The advantage of a microbial-based approach is that, compared to direct measurement of soil gas flux or concentration, microbial communities may be more stable over time and provide an indication of leakages in areas exposed to intermittent leakage for weeks or months (INC, 2017).

2.9.2 Application

Sampling DNA from groundwater wells can be complicated because you need a larger groundwater volume to extract sufficient DNA for downstream applications. Further, it has been shown from various low-energy aquifers that biogeochemical processes are primarily linked to the activity of microbes attached to the sediments and rocks rather than to bacteria suspended in groundwater. The cell abundance and activity of sediment microbial communities are typically one to four orders of magnitude higher than in groundwater (Baho et al., 2012). Due to these complications and the downstream applications, DNA-based methods are considered non-automated local monitoring.

The advantage of using molecular methods for potential methylotrophic indicator organisms is that methylotrophs can be hard to culture regardless of whether they are aerobic or anaerobic. When identifying potential candidates, it is important to consider the characteristics of the investigated environment because several interrelated parameters influence the microbial community. Hence, parameters such as oxic/anoxic conditions, pH, and temperature will affect the abundance of specific indicator organisms and may camouflage any abundance changes related to hydrocarbons.

Within the SECURe project, we analyzed microbial communities using 16S rRNA genes in methane and ethane impacted groundwater. Although some distinctions between wells were observed, the high number of other influences reduced the applicability of diversity of 16S rRNA gene as a sole indicator of methane or methane ethane ratio in groundwater. The diversity of functional genes involved in microbial methane oxidation may provide further insight.

Based on controlled laboratory experiments, selected microbial indicator organisms were selected, including, for example, *Terrimicrobium, Methylomonas, Crenothrix, Methylomonas and Methyloversatilis.* These indicators were used to interrogate the two 16S datasets from Sleen and VoP groundwater samples. Unfortunately, there was no clear trend between the abundance of selected groups and the methane concentration of the wells. To improve and validate these indicators, a larger dataset would be needed.

2.10 WELLBORE BASED MECHANICAL SENSORS

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2.10.1 Background

Cement nanocomposites have gained much attention in recent years. In addition to advantages gained in engineering the mechanical properties of the composites, their electrical properties have made these a versatile tool in making the cement electrically conductive and thereby also responsive to mechanical load (Ahmed et al., 2018; Hawreen and Bogas, 2019; Buasiri et al., 2019; Hawreen et al., 2019; Golewski, 2020; Zhou et al., 2020). It has been shown that cement materials with well dispersed electrically conductive fillers, such as metal fibers, graphite powder, carbon nanofibers (CNF) and carbon nanotubes (CNT), show conductive properties above a percolation threshold. The percolation threshold is a critical concentration of the dispersed material above which the dispersed particles form a continuous network able to conduct electric charge. Due to their conductive properties and sensitivity to stress (through the piezoelectric effect), the hybrid cement materials are considered excellent sensors in structural health monitoring of reinforced concrete structures and traffic monitoring. In these sensing applications, the hybrid cement materials function as signal transducers that translate changes in mechanical load or material failure into changes in electrical conductivity. The structural health monitoring of reinforced concrete structures relies on detecting and localizing failures in the concrete. When a fracture starts to propagate in the material, the effective resistivity of the sensors increases as the conductive network gets interrupted. In a traffic monitoring application, the strain sensitivity of hybrid cement materials is utilized. The strain sensitivity of conductive cement relies on changes in electrical resistivity upon the application of mechanical load.

The physical mechanism underpinning this phenomenon is associated with the connectivity between the conductive particles. When a uniaxial compression is applied to the material with embedded electrically conductive fillers, the inter-particle distance in the filler decreases, and new conductive paths are created. The closer the conductive particles are and the more interparticle connections made, the larger an electrical current can be established, leading to a decrease in resistivity of the material. It has been well established that increasing CNF content leads to a reduction in the bulk resistivity of CNF-filled materials, with the highest drop within the percolation threshold concentration range. More precisely, the bulk resistivity decreases most significantly in the concentration range at which nanofibers start forming a connected network. However, CNF concentration is not the only parameter that may affect the bulk resistivity values. Changes in other compositional parameters (e.g., water content or the concentration of different fillers and additives) and temperature may also affect the cement bulk resistivity at given CNF concentrations.

2.10.2 Application

Due to their stress sensitivity, piezoelectric cement materials are considered excellent sensors in the structural monitoring of reinforced concrete structures. Hence, an interesting application utilizes the stress sensitivity of cement composite materials containing carbon nanofibers in the sensing of stress changes that may occur in a permanently plugged well because of, e.g., subsidence, fracture reactivation etc. The monitoring of a well would rely on measurements of electrical resistivity of the sensor whose transducing material is made of stress-sensitive cement. It is expected that stress applied to the cement plug with an embedded sensor will result in changes in the electrical resistivity of the transducer. The well cement may undergo chemical degradation due to the long-time exposure to reservoir fluids. Downhole brines commonly contain carbonate and sulphate ions that tend to react with cement. The reactions are associated with density changes within the cement (Chavez Panduro et al., 2017). The density changes are therefore expected to affect the resistivity of cement/CNF composites. Hence, the carbonation process (as an example of degradation processes) may affect the signal response of the potential transducer material. Other relevant applications are where the sensing material is exposed to humidity and an environment that contains sour gases such as CO_2 and H_2S.

The EM method used in geophysical monitoring could be extended to monitor the state of permanent cement plugs containing CNF. As the EM method does not require wired contact with the cement material, it makes it a promising monitoring technique. However, more detailed studies are needed to understand the effect of CNF on EM signals and the sensitivities of various parameters (water content, temperature, stress amplitudes, fracture sizes, etc.) and how the signal response is affected by these.

3 Comparison of the developed methods and sensors and their applicability

In this chapter, the methods described in Chapter 2 are compared and grouped, to give an overview of the types of monitoring. The applicability of the methods in terms of scale and automation are evaluated. Both critical parameters for making observations with adequate density in time and space and possibly in remote locations. Key information for the different methods has been compiled in Table 3, forming a condensed overview of the described methods. Due to the experimental state of most of the methods, many of the parameters are not known or they are only known with a very high uncertainty. The methods developed and tested in this work package are a subset of the many methods available or being developed around the world; due to the large focus on monitoring in relation to the exploitation of the subsurface, a qualitative or quantitative comparison of the methods within this work package would not be fruitful.

3.1 PREASSESSMENT MONITORING

Some methods are applicable at a very early stage in the development of a site. This could be modelling applied using existing data, but it can also be used to evaluate the vulnerability of the system to possible impacts induced by the introduction of fracking fluids or CO_2 to the system. An example of this is found in Section 2.1.2, describing a method for predicting the release of elements from shales due to contact with acidic fracking fluids. The approach could be applied to other rock types as well as other fluids, including CO_2. Further, as described, the results could go into reactive transport modelling of the system to indicate possible issues in general and specific target volumes within the system for monitoring water chemistry, thereby optimizing the monitoring program. The scale of this approach will depend on the heterogeneity of the geology and of the materials tested. Because samples need to be obtained and handled manually, the level of automation obtained is limited. However, the lab tests of the materials can, to some extent, be automated if enough samples need to be tested.

3.2 WELL/SMALL SCALE MONITORING

A group of methods apply directly to wells or their surroundings. Four of these methods imply sampling of the well water. Either to obtain samples of gases in well water and analysing the gas on-site as described in Section 2.3, to sample the microbiology in water pumped from a well and analysing the microbial community by culturing or by molecular microbiological methods as described in Sections 2.8 and 2.9 or to measure the clumped isotopic composition of the CH_4 and CO_2(Section 2.7). The method described in Section 2.10 uses a material, namely the cement, that is part of the well itself to measure mechanical stress using cement amended with nano-carbon fibers. The microbial methods only apply to CH_4, while the other methods mentioned can also be used in relation to CO_2 storage. Though the coverage for the individual measurements is one well, the coverage can be scaled by merely including more wells. Likewise, the density of the monitoring can be increased by installing more wells, though each well comes at a cost that is highly dependent on the target depth of the monitoring. A given deep borehole intended for monitoring can be constructed with intakes at many depths and with stress sensors. Methods that rely on moving equipment from one borehole to the next to obtain water samples that need to be taken to the lab (including field labs) are difficult to automate. The reading of stress sensors embedded in cement may be automated, and results can be transmitted via mobile or dedicated data networks once they are installed.

3.3 MEDIUM SCALE MONITORING

The methods categorized here as medium scale methods comprise quite different methods. The measurement of carbon isotopes (stable ^{13}C and radioactive ^{14}C) in the vegetation described in Section 2.7 can give signals from historical and recent events related to both CH_4 and CO_2. The scale of individual trees is limited to 10's of m^2 but forests may cover large areas. The level of automation is currently low, but with advanced robotics, the sampling could be automated to some extent.

The development of UAV's (unmanned arial vehicles or drones) (Section 2.1) that can fly close to the ground at low velocities and have enough lift capacity to carry instrumentation implies that gases in the near-ground atmosphere can be monitored over large areas and over terrain or vegetation that would otherwise not be accessible. Current applications and presumably also legislation requires that personnel is on-site during the measurement campaign. Still, in principle, the UAV's could operate more autonomously and fly regular missions on their own, given docking and charging facilities as well as weather forecasts in the vicinity of the monitored area. The dock could also be used to transmit data for remote scrutiny.

Time-lapse ERT (electrical resistivity tomography) (Section 2.5) exploits the fact that changes in the porewater chemistry often lead to changes in the electrical resistivity of the water. The generated changes are high when CO_2 dissolves in water leading to an increase in the number of ions in the water, thereby decreasing resistivity. Bubbles formed by gases that are not dissolved in the water will increase resistivity. This effect is most probable in relation to a CH_4 leak due to the rather low solubility of CH_4 in water, but may also occur for CO_2. ERT can be made using electrodes in boreholes or on the surface, or in combination. The scale of the monitored area depends on how many kilometers of wire and electrodes, and boreholes are used. Realistically, covering more than ~1 km^2 would be challenging. Once installed, measurements can be collected and transmitted automatically.

Time-lapse seismics has been used at several sites. The study described in Section 2.6 specifically describes the sensitivity of the technology in terms of the detectable volume that can be seen related to the geophysical characteristics of the underground. This knowledge is important for informing and optimizing a given monitoring project. The scale covered by seismic surveys can be 100's of km^2. The level of automation that can be obtained in large scale seismic data acquisition is low as both energy sources and the signal collecting devices are moved during acquisition. On a smaller scale, where energy source and signal collecting can remain in place automation is possible.

3.4 LARGE SCALE MONITORING

In this work package, only the monitoring of induced and triggered seismicity can be considered a readily useable method for remote automated monitoring at large scales. Seismometers can register tiny events related to stress release in the underground. Because even weak seismic waves can be registered at a distance of several kilometers, large areas can be covered with relatively few seismic instruments. The seismicity is normally induced by the pressure changes caused by the injection and can be used to optimize injection rates in the injection phase. To what extent seismicity is induced post-injection while the injectate migrates and reacts is not known. The methodology is relevant for both CH_4 and CO_2 related operations, and the obtainable level of automation once installed is high as data can be transmitted via mobile or other data nets. To some extent also the analysis of the incoming data can be automated.

Table 3. Comparison of methods described in this report

Method	Principle	Parameters	Coverage	Detect. limits	Ease of use	Level of automation	On/off-site	Application limitations	TRL	Sect.:	Additional information
UAV monitoring	Airborne spectro-scopy	CO_2 and CH_4, other gases would be possible	Large scale monitoring 10's of km^2		Requires skilled operator	Can be high if UAV is developed to higher autonomous docking/charging	On-site	High winds and intense rain	TRL4	2.1	
Geochem. element mobiliza-tion	Measured release of elements due to fluid rock interactions	Element concentrations	Related to geochemical heterogeneity	n/a	Requires skilled operator	low	Off-site	Currently time intensive	TRL4	2.2	
Noble gas sampling	Downhole fluid sample	Soluble gases that do not react with sampler	Well tool	Related to parameter and analyte	Requires skilled operator	Low, the tool is inserted into one well at a time manually	On-site	Max. 125 °C/ 350 bar Well dia >80 mm	TRL 4	2.3	On-site when used with mobile gas analyser.
Seismicity	Detection of seismic waves	Amplitudes and time.	Large areas/vol. 100's of km^2	Indicated to be below an ML=0	Requires skilled operator	High	Both on-site and off site	Noise e.g., construction, heavy traffic	TRL 8	2.4	
3D- time-lapse ERT	Imaging of electrical properties associated with lithology and pore fluid	Changes in fluid chemistry and saturation levels resulting in changes in resistivity	Volume between the well array for this technique, with some limited sensitivity to the immediate vicinity	Spatial resolution limited to approx. fundamental electrode spacing; detectability of electrical changes dependent on geometry and noise conditions	Requires skilled interpreter	Medium, remote monitoring when system has been installed and commissioned, but some manual QC and largely manual interpretation of data required.	Off-site after commissioning	Requires closely spaced wells to maximise detectability of changes in the subsurface	TRL7 (TRL 9 for other applications)	2.5	
3D- time-lapse seismics	Seismic properties changes due to gas in porespace	Seismic	0.1 - 100 km^2	Not known	Requires skilled operator	Possible at small scale	On-site	Large scale on-shore time-lapse measurements are not feasible	TRL4	2.6	
Isotope tracers (clumped isotopes)	Formation temperature derived from isotopic composition of CH_4 or CO_2	Content of ^2H-^{13}C bonds in CH_4 or ^{13}C-^{18}O bonds in CO_2.	Clumped isotopes: borehole level	n/a	Requires skilled operator	Clumped isotopes: low. Manual sample preparation and data acquisition.	Off-site	labour intensive methods	TRL 3-4	2.7	
^{14}C dating	Long term CO_2 emissions from ^{14}C in trees	^{14}C variations in plant tissue	^{14}C: few m^2 around a gas leakage site		Requires skilled operator	Medium. Manual sampling and preparation but automated data acquisition	Off-site	labour intensive methods	TRL4	2.7	
Viable microbial sensors	Microbial communities reflect hydrocarbon content of groundwater	CH_4:C_2H_6 Microbial diversity. Identity of indicator organisms	Borehole / water sample level	n/a	Basic training needed	low	Off site	Low precision, currently time intensive	TRL3	2.8	
Molecular microbial sensors	Same as above	Same as above	Same as above	n/a.	Requires skilled operator	low	Off-site	Sensitivity, time intensive	TRL3	2.9	

Wellbore based mechanical sensors	Compression changes resistivity of cement with embedded carbon nanofibers	Resistivity	Well scale	Not known	Basic training needed	High	On-site		TRL3	2.10	

Glossary

DIFFRAC.EVA-XRD is a software and it provides tools for the quick analysis of one- and two-dimensional diffraction data. The EVA functionality covers a broad analytical spectrum from data reduction, basic scan evaluation and presentation, detailed peak analysis, phase identification and quantification, to the determination of crystallinity and crystallite size. (Web links: https://www.bruker.com/en/products-and-solutions/diffractometers-and-scattering-systems/x-ray-diffractometers/diffrac-suite-software/diffrac-eva.html)

ERT: electrical resistivity tomography

Genomic classification in descending order: Kingdom, phyla, class, order, family, genus, species

MOST: Microbial Oil Survey Techniques

MPOG: Microbial Prospecting for Oil and Gas

SCA: short chain alkanes

VoP: Vale of Pickering

4 References

Ahmed, H., J.A. Bogas, and M. Guedes. 2018. Mechanical Behavior and Transport Properties of Cementitious Composites Reinforced with Carbon Nanotubes. J. Mater. Civ. Eng. 30(10): 04018257. doi: 10.1061/(asce)mt.1943-5533.0002470.

Baho, D.L., H. Peter, and L.J. Tranvik. 2012. Resistance and resilience of microbial communities - temporal and spatial insurance against perturbations. Environ. Microbiol. 14(9): 2283–2292. doi: 10.1111/j.1462-2920.2012.02754.x.

Van Beilen, J.B., and E.G. Funhoff. 2007. Alkane hydroxylases involved in microbial alkane degradation. Appl. Microbiol. Biotechnol. 74(1): 13–21. doi: 10.1007/s00253-006-0748-0.

Buasiri, Habermehl-Cwirzen, Krzeminski, and Cwirzen. 2019. Piezoresistive Load Sensing and Percolation Phenomena in Portland Cement Composite Modified with In-Situ Synthesized Carbon Nanofibers. Nanomaterials 9(4): 594. doi: 10.3390/nano9040594.

Cahill, A.G., C.M. Steelman, O. Forde, O. Kuloyo, S. Emil Ruff, et al. 2017. Mobility and persistence of methane in groundwater in a controlled-release field experiment. Nat. Geosci. 10(4): 289–294. doi: 10.1038/ngeo2919.

Chadwick, R.A., B.P. Marchant, and G.A. Williams. 2014. CO2 storage monitoring: Leakage detection and measurement in subsurface volumes from 3D seismic data at Sleipner. Energy Procedia. Elsevier Ltd. p. 4224–4239

Chavez Panduro, E.A., M. Torsæter, K. Gawel, R. Bjørge, A. Gibaud, et al. 2017. In-Situ X-ray Tomography Study of Cement Exposed to CO2 Saturated Brine. Environ. Sci. Technol. 51(16): 9344–9351. doi: 10.1021/acs.est.6b06534.

Deng, Y., C. Deng, J. Yang, B. Li, E. Wang, et al. 2018. Novel Butane-Oxidizing Bacteria and Diversity of bmoX Genes in Puguang Gas Field. Front. Microbiol. 9(JUL): 1576. doi: 10.3389/fmicb.2018.01576.

Deng, C., X. Yu, J. Yang, B. Li, W. Sun, et al. 2016. Universal indicators for oil and gas prospecting based on bacterial communities shaped by light-hydrocarbon microseepage in China. J. Microbiol. Biotechnol. 26(7): 1320–1332. doi: 10.4014/jmb.1602.02045.

Donders, T.H., M. Decuyper, S.E. Beaubien, T.B. van Hoof, P. Cherubini, et al. 2013. Tree rings as biosensor to detect leakage of subsurface fossil CO2. Int. J. Greenh. Gas Control 19: 387–395. doi: https://doi.org/10.1016/j.ijggc.2013.09.017.

Douglas, P.M.J., D.A. Stolper, J.M. Eiler, A.L. Sessions, M. Lawson, et al. 2017. Methane clumped isotopes: Progress and potential for a new isotopic tracer. Org. Geochem. 113: 262–282. doi: https://doi.org/10.1016/j.orggeochem.2017.07.016.

Eiler, J.M. 2007. “Clumped-isotope” geochemistry—The study of naturally-occurring, multiply-substituted isotopologues. Earth Planet. Sci. Lett. 262(3–4): 309–327. doi: http://dx.doi.org/10.1016/j.epsl.2007.08.020.

Ellsworth, W.L. 2013. Injection-Induced Earthquakes. Science (80-.). 341(6142): 1225942–1225942. doi: 10.1126/science.1225942.

Gal, F., E. Proust, and W. Kloppmann. 2019. Towards a Better Knowledge of Natural Methane Releases in the French Alps: A Field Approach (G. Zheng, editor). Geofluids 2019: 6487162. doi: 10.1155/2019/6487162.

Golewski, G.L. 2020. Energy Savings Associated with the Use of Fly Ash and Nanoadditives in the Cement Composition. Energies 13(9): 2184. doi: 10.3390/en13092184.

Grigoli, F., S. Cesca, E. Priolo, A.P. Rinaldi, J.F. Clinton, et al. 2017. Current challenges in monitoring, discrimination, and management of induced seismicity related to underground industrial activities: A European perspective. Rev. Geophys. 55(2): 310–340. doi: 10.1002/2016RG000542.

Hawreen, A., and J.A. Bogas. 2019. Creep, shrinkage and mechanical properties of concrete reinforced with different types of carbon nanotubes. Constr. Build. Mater. 198: 70–81. doi:

10.1016/j.conbuildmat.2018.11.253.

Hawreen, A., J.A. Bogas, and R. Kurda. 2019. Mechanical Characterization of Concrete Reinforced with Different Types of Carbon Nanotubes. Arab. J. Sci. Eng. 44(10): 8361–8376. doi: 10.1007/s13369-019-04096-y.

Hoefs, J. 2009. Stable Isotope Geochemistry. Springer-Verlag Berlin Heidelberg.

Holdaway, R.N., B. Duffy, and B. Kennedy. 2018. Evidence for magmatic carbon bias in 14C dating of the Taupo and other major eruptions. Nat. Commun. 9: 4110.

INC. 2017. No Title. Microb. Tech. Hydrocarb. Explor. https://www.e-b-t.com/microbial-techniques.

Jordan, C., C. Rochelle, F. Gal, E. Proust, A. Maunoury, et al. 2021. Report on applicability of UAV technology for monitoring large-scale sites and the impact of remote sensing on decisions of baseline characterisations. SECURe project deliverable report D4.1.

Kuloyo, O., S.E. Ruff, A. Cahill, L. Connors, J.K. Zorz, et al. 2020. Methane oxidation and methylotroph population dynamics in groundwater mesocosms. Environ. Microbiol. 22(4): 1222–1237. doi: 10.1111/1462-2920.14929.

Lardie Gaylord, M.C., B.E. Longworth, K. Murphy, C. Cobb, and A.P. McNichol. 2019. Annual radiocarbon measurements in a century-old European beech tree (Fagus sylvatica) from coastal northeastern North America. Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms 456: 264–270.

Laughrey, C., and F. Baldassare. 1995. Geochemistry and origin of some natural gases in the Plateau Province, Central Appalachian Basin, Pennsylvania and Ohio. Aapg Bull. - AAPG BULL 79. doi: 10.1306/7834D8D2-1721-11D7-8645000102C1865D.

Liu, W., and A. Ramirez. 2017. State of the art review of the environmental assessment and risks of underground geo-energy resources exploitation. Renew. Sustain. Energy Rev. 76: 628–644. doi: 10.1016/j.rser.2017.03.087.

ManfredWagner, M.W.J.P., and R. Smit. 2002. AAPG Studies in Geology No. 48 / SEG Geophysical References Series No. 11, Chapter 19: Case Histories of Microbial Prospection for Oil and Gas, Onshore and Offshore in Northwest Europe. : 453–479. http://archives.datapages.com/data/specpubs/study48/st48ch19/st48ch19.htm (accessed 5 March 2021).

Nelskamp, S. 2011. Structural evolution, temperature and maturity of sedimentary rocks in the Netherlands: results of combined structural and thermal 2D modeling. PhD.

Redmond, M.C., D.L. Valentine, and A.L. Sessions. 2010. Identification of novel methane-, ethane-, and propane-oxidizing bacteria at marine hydrocarbon seeps by stable isotope probing. Appl. Environ. Microbiol. 76(19): 6412–6422. doi: 10.1128/AEM.00271-10.

Schoell, M. 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. Geochim. Cosmochim. Acta 44(5): 649–661. doi: https://doi.org/10.1016/0016-7037(80)90155-6.

Stegen, J.C., X. Lin, J.K. Fredrickson, X. Chen, D.W. Kennedy, et al. 2013. Quantifying community assembly processes and identifying features that impose them. ISME J. 7(11): 2069–2079. doi: 10.1038/ismej.2013.93.

Stolper, D.A., A.M. Martini, M. Clog, P.M. Douglas, S.S. Shusta, et al. 2015. Distinguishing and understanding thermogenic and biogenic sources of methane using multiply substituted isotopologues. Geochim. Cosmochim. Acta 161: 219–247. doi: https://doi.org/10.1016/j.gca.2015.04.015.

Stolper, D.A., A.L. Sessions, A.A. Ferreira, E. V Santos Neto, A. Schimmelmann, et al. 2014. Combined 13C–D and D–D clumping in methane: Methods and preliminary results. Geochim. Cosmochim. Acta 126: 169–191. doi: https://doi.org/10.1016/j.gca.2013.10.045.

Tucker, J., and D. Hitzman. 1996. Long-Term and Seasonal Trends in the Response of Hydrocarbon-Utilizing Microbes to Light Hydrocarbon Gases in Shallow Soils. : 353–357. http://archives.datapages.com/data/specpubs/memoir66/26/0353.htm (accessed 5 March 2021).

Vellend, M. 2010. Conceptual synthesis in community ecology. Q. Rev. Biol. 85(2): 183–206. doi: 10.1086/652373.

Waage, M., S. Bünz, M. Landrø, A. Plaza-Faverola, and K.A. Waghorn. 2019. Repeatability of high-resolution 3D seismic data. Geophysics 84(1): B75–B94. doi: 10.1190/geo2018-0099.1.

Whiticar, M.J. 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. Chem. Geol. 161(1): 291–314. doi: https://doi.org/10.1016/S0009-2541(99)00092-3.

Zhou, Z., N. Xie, X. Cheng, L. Feng, P. Hou, et al. 2020. Electrical properties of low dosage carbon nanofiber/cement composite: Percolation behavior and polarization effect. Cem. Concr. Compos. 109: 103539. doi: 10.1016/j.cemconcomp.2020.103539.