Strategies for Environmental Monitoring of Marine Carbon Capture and Storage

STEMM-CCS

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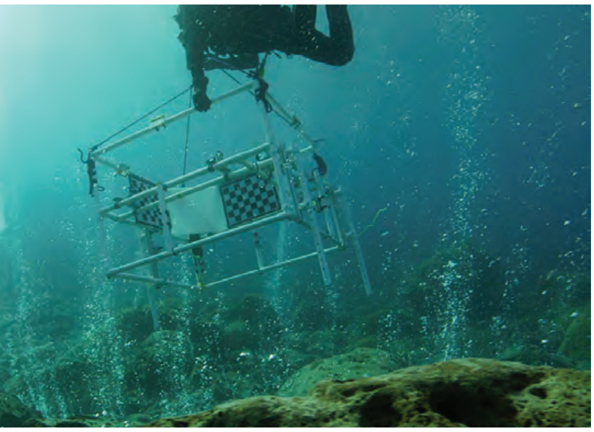

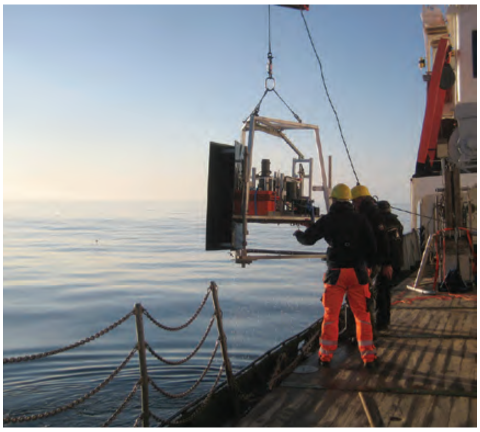

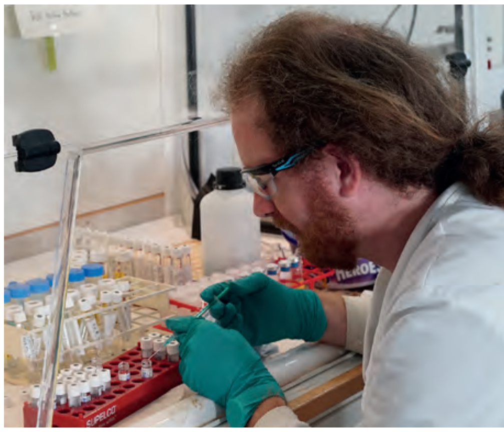

Research Highlights

The STEMM-CCS Consortium

The National Oceanography Centre, UK (Coordinator)

Shell Global Solutions international B.V., Netherlands

Helmholtz Zentrum fur Ozeanforschung Kiel, Germany

Universitetet i Bergen, Norway

NORCE Norwegian Research Centre AS, Norway

Technische Universitaet Graz, Austria

Max Planck Gesellschaft zur Foerderung der Wissenschaten E.V., Germany

University of Southampton, UK

Universitetet i Tromsø, Norway

Norsk Institutt for Vannforskning, Norway

Heriot-Watt University, UK

Plymouth Marine Laboratory, UK

Seascape Consultants Ltd, UK

Associated partner: Alfred Wegener Institute, Germany

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This report was written and compiled by the following team on behalf of the STEMM-CCS consortium: C. Berndt, J.C. Blackford, D.P. Connelly, V.K. Gunn, V.A.I. Huvenne, R. James, S. Loucaides, M. Mowlem, C. Sands and K. Saw, with additional contributions from D. Koopmans, A. Omar, T. Dixon and K. Romanak. Layout and design by V. Gunn.

Front cover images (clockwise from top left): Using natural CO_2 seeps at Panarea for testing visual and acoustic bubble detection methods (image courtesy R. Rinaldi); Recovery of lander and sensors onto RV *Poseidon* after testing in the North Sea, August 2018 (image courtesy P. Linke); Working up samples in the lab on board RRS James Cook (image courtesy B. Roche/NOC); RRS *James Cook* at work in glorious weather in the North Sea in May 2019, with the Goldeneye platform in the background (image courtesy J. Strong/NOC).

www.stemm-ccs.eu   @STEMM_CCS_EU   STEMM-CCS@noc.ac.uk

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The STEMM-CCS project: Research Highlights

Contents

Executive Summary

The Strategies for Environmental Monitoring of Marine Carbon Capture and Storage (STEMM-CCS) project was funded under the European Union’s Horizon 2020 programme to address the current knowledge and capability gaps in approaches, methodologies and technology required for the effective environmental monitoring of offshore carbon capture and storage (CCS) sites. Drawing on a broad range of expertise from researchers in 14 institutions, including Shell as the principal industry partner, the project undertook extensive research into a range of CCS-relevant issues including: the establishment of accurate environmental baselines; better understanding of fluid flow pathways in the sub-seafloor and their implications for reservoir integrity; methodologies for detecting, tracing and quantifying CO_2 leakage in the marine environment, and the development and testing of new technologies to enable cost-effective monitoring of marine CCS operations.

Central to the project was the STEMM-CCS controlled release experiment – the first sub-seafloor release of CO_2 to be carried out under real life conditions. Implemented at a site near the Goldeneye platform in the North Sea, this experiment successfully simulated a CO_2 reservoir leak scenario and demonstrated that the leak could be successfully detected and quantified using the range of instruments, tools and techniques developed during the project.

In summary, STEMM-CCS has successfully developed and tested a robust methodology for establishing environmental and ecological baselines under ‘real life’ conditions. It has developed a suite of cost-effective tools to identify, detect and quantify CO_2 leakage from a sub-seafloor CCS reservoir, including an assessment of the utility of chemical tracers in the marine environment. Results have enabled the modelling and assessments of the local, regional and wider impacts of different reservoir CO_2 leak scenarios, including the potential role that fluid pathways in the shallow subsurface may play in reservoir integrity, and a decision support tool has been developed to assist operators in monitoring, mitigation and remediation actions. STEMM-CCS has delivered best practice for selection and operation of offshore CCS sites, and results have been shared with industrial and regulatory stakeholders in order to help increase confidence in the physical security of CCS, and to support the European Union’s progress towards a carbon neutral society.

The Goldeneye platform in the North Sea, as viewed from RV Poseidon. Image courtesy P. Linke.

Introduction

Carbon dioxide Capture and Storage (CCS) is an important strategy in mitigating anthropogenic CO_2 emissions. All credible climate change scenario models indicate that CCS will be essential to meeting the internationally agreed targets set by the UNFCCC Paris Agreement in 2015, which aims to limit global warming to 2° C relative to pre-industrial levels. The European Union's commitment to the Paris Agreement involves reducing carbon emissions by 85-95% by 2050[1], with the greater ambition of becoming carbon neutral by 2050 in order to limit global temperature rise to 1.5°C. The EU's "*Clean Energy for all Europeans*" package[2], published in 2019, clearly identifies CCS as a critical step towards achieving a climate-neutral economy.

The aim of CCS is to capture CO_2 from large emission sources, such as power stations and industrial facilities, transport it to a storage site and permanently lock it away so that it cannot be released into the atmosphere. CCS storage sites are usually geological formations deep underground, either onshore or offshore.

To date, CCS has mainly been developed using land-based storage reservoirs (for example, Shell's Quest CCS project in Canada). There are currently two operational marine CCS sites in Europe, located at Sleipner in the central North Sea and at Snøhvit in the Barents Sea. A third CCS storage site linked to the Northern Lights project in Norway, is planned in the northern North Sea. There is potential for many more marine CCS facilities to be developed and the process of identifying suitable locations is ongoing, but monitoring them during operation in a reliable, economic and accurate manner needs to be established. For offshore CCS, there are challenges in implementing accurate monitoring strategies in such a dynamic environment, and in developing robust and cost-effective technology to support these strategies.

The Strategies for Environmental Monitoring of Marine Carbon Capture and Storage (STEMM-CCS) project (2016-2020) was conceived to address the current knowledge and capability gaps in approaches, methodologies and technology required for the effective environmental monitoring of offshore CCS storage sites. Funded under the European Union's Horizon 2020 programme, a multidisciplinary team of researchers from 13 institutions across Europe worked in collaboration with industrial partner Shell to develop a set of tools, techniques and methods to enhance our understanding of CCS in the marine environment. The key project objectives were:

- Develop methods for assessing the ability of CO_2 to permeate through the overlying seafloor sediments at offshore CCS sites, in terms of both the natural system and where CO_2 has been artificially introduced.
- Build on best practice from previous research to develop robust methodology for establishing environmental and ecological baselines under 'real life' conditions.
- Develop cost-effective tools to identify, detect and quantify CO_2 leakage from a sub-seafloor CCS reservoir.
- Assess the suitability of artificial and natural chemical tracers for the detection, quantification and mapping of escaped CO_2 in the marine environment.
- Model and assess the local, regional and wider impacts of different reservoir CO_2 leak scenarios and provide decision support tools for monitoring, mitigation and remediation action.
- Deliver documented best practice for selection and operation of offshore CCS sites and to transfer knowledge to industrial and regulatory stakeholders through education and training programmes.
- Share knowledge and project results, and thus increase confidence in the physical security of CCS.

STEMM-CCS combined a unique set of field experiments alongside laboratory work and mathematical modelling. Over the course of four years, researchers used the results of eight offshore expeditions totalling more than 6 months' time at sea to identify new cost-effective ways to establish environmental and ecological baselines, advance understanding of how CO_2 can move through the subsurface, and develop new techniques for the efficient and accurate detection of any CO_2 escape. A key achievement is the development and enhancement of sensing technologies (chemical, optical and sonar), many of which have applications beyond the CCS arena.

This document serves as a concise summary of the main objectives, achievements and results from the STEMM-CCS project. It is intended to highlight the key outcomes of the project's research in an accessible format, and signpost where more detailed information on STEMM-CCS results can be found. The project's successes are the result of four years' hard work by a dedicated team of researchers, whose commitment, innovation and perseverance have considerably advanced our understanding and technical capability in the responsible environmental monitoring of marine carbon capture and storage operations.

Professor Douglas Connelly
STEMM-CCS Coordinator
National Oceanography Centre

The STEMM-CCS controlled release experiment

The keystone of STEMM-CCS was a novel experiment to simulate a sub-seafloor CO_2 leak under real-life conditions in the North Sea. Over a period of two weeks in spring 2019, CO_2 gas - augmented with inert chemical tracers - was injected into seafloor sediments at a carefully chosen experimental site near Shell's Goldeneye complex (a proposed CCS storage site), located approximately 100 km north-east of Peterhead (Fig. 1). The consequences of this CO_2 release were carefully monitored by a sophisticated array of chemical sensors, acoustic devices, visual observations and seismic surveys operated by scientists aboard research vessels RRS *James Cook* and RV *Poseidon*.

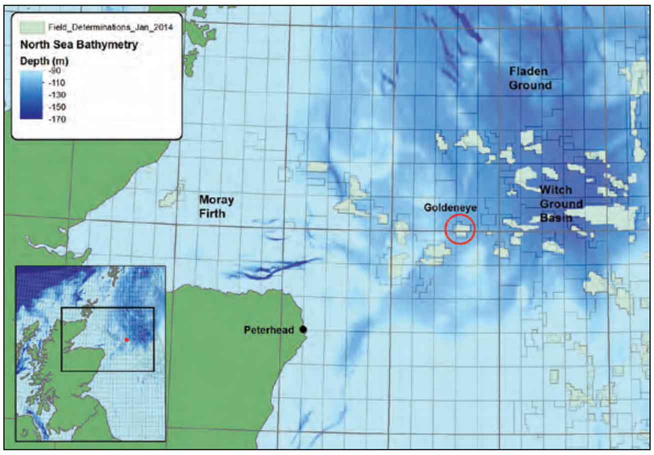


Figure 1: Map showing the location of the Goldeye experimental site in the North Sea.

The use of two research vessels was critical to the experiment's success. Whilst the main CO_2 release experiment was executed and monitored in the near-field by RRS *James Cook*, the German vessel RV *Poseidon* carried out parallel water column surveys in the far-field in order to determine the lateral spread of CO_2 away from the release site.

Preparations for this experiment took three years, not only in the development of new technology capable of detecting the smallest changes in marine conditions, but also in establishing a robust and reliable environmental baseline against which to monitor for CO_2 emissions during the experiment. This involved detailed bathymetric mapping of the experimental area, continuous monitoring of environmental conditions via deployment of seafloor landers, extensive water column and seafloor sediment sampling, and benthic ecology surveys. These in situ measurements were supported by the development of a comprehensive regional model to predict short-term seasonal and spatial changes in baseline conditions.

Innovation in sensing technology and measurement techniques was key to this experiment. As well as overcoming some significant engineering challenges, STEMM-CCS developed and tested a range of new techniques and instrumentation specifically oriented towards detecting very small physical and chemical changes that could indicate CO_2 escape. The experiment was highly ambitious, designed to test the effectiveness of existing and new technologies in detecting and tracing CO_2 leaks, and to inform cost-effective strategies for the long-term monitoring of marine CCS storage sites.

CO_2 was supplied from large-capacity gas tanks mounted on a bespoke frame, lowered into place from the RRS *James Cook* at about 100m from the injection site in order to minimise disturbance. A sophisticated gas flow control system and remote communications allowed full control from the ship. Also mounted on the frame were cylinders containing the tracer gases that were mixed with the CO_2 gas before delivery to the experiment. Overall, the experiment used less than a third of the 3 tonnes of CO_2 held in the gas tanks during the 2-week experiment.

A bespoke, innovative drill rig, designed and built by Cellula Robotics in Canada, was lowered into place from the ship onto the seafloor with the aid of downward-facing cameras. Once in position, the rig used hydraulic rollers to push a 8-metre long, rigid, pre-curved carbon steel pipe into the seafloor sediments. This is the first time this approach with a pre-curved pipe has been used. The end of the pipe was capped by a spear-like head to ease the pipe through the sediments, and a gas diffuser unit with backward-facing apertures to avoid sediment clogging during the pipe insertion process. Cameras on the rig fed real-time video footage through to a control panel operated on the ship. Once the pipe was in place, the drill rig was recovered back to the ship, the ROV connected the pipe to the CO_2 supply and the experiment began.

The CO_2 gas was pre-mixed with a cocktail of inert, non-toxic chemical tracers prior to its release: Kr, SF_6 and C_3F_8. CO_2 is quite a reactive compound in the marine environment, which makes it challenging to differentiate between natural variability and a leak, especially when the leak is small. The addition of chemically distinct tracers to the released gas provided a failsafe for detecting and tracing the fate of the CO_2 released during the experiment.

A range of sensing technology was deployed around the experimental site in order to monitor for any changes at the seafloor and in the water column, including chemical, optical

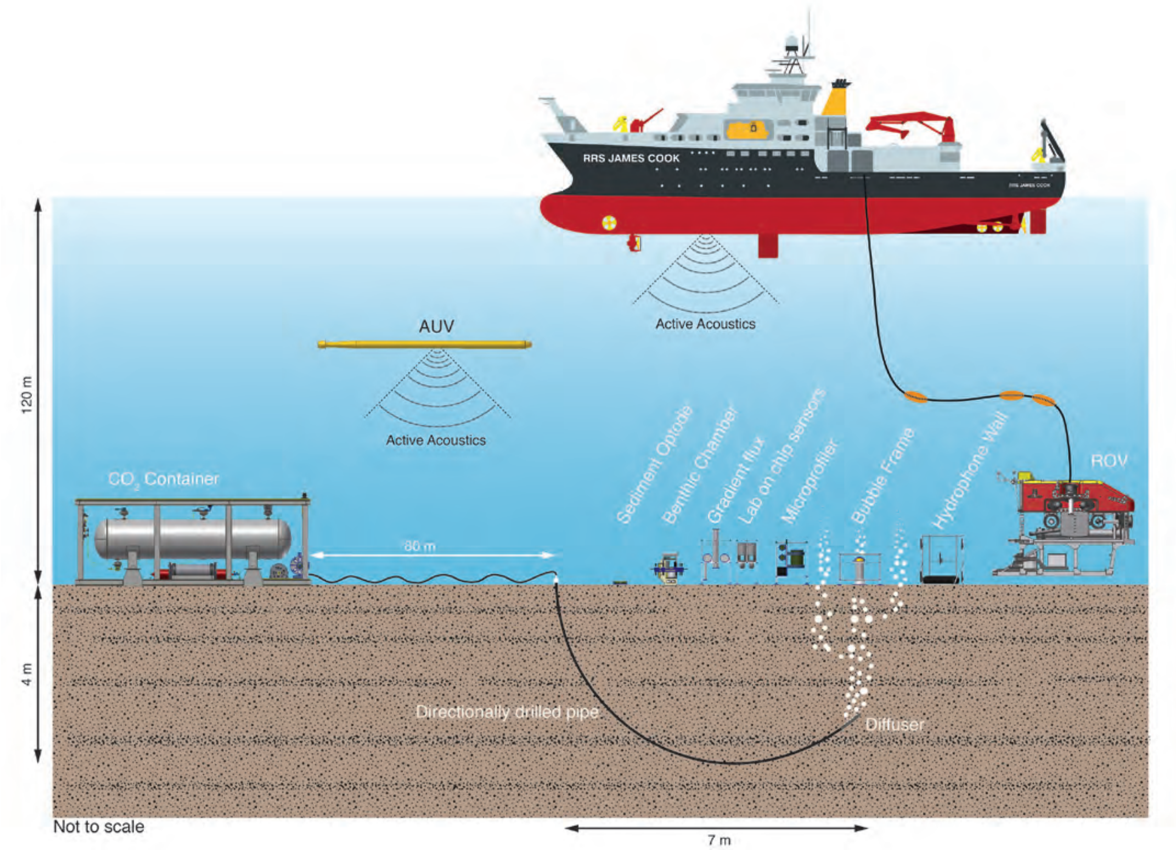


Figure 2: Schematic showing the STEMM-CCS controlled release experiment. Image courtesy C.Pearce, NOC.

and acoustic sensors (Fig. 2). These were deployed either in situ at the seabed or mounted on remotely operated (ROV) and autonomous underwater (AUV) vehicles. Hydrophones were placed on the seabed within 5m of the injection site before CO_2 release commenced to perform continuous listening for gas escape for the duration of the experiment. Gas bubbles emerging from the seabed were measured for bubble size and rising speed using optical techniques.

A suite of chemical sensors was used to measure biogeochemical and carbonate parameters before and during the experiment. These miniaturised sensors - known as lab-on-chip technology - measured nitrate, phosphate, pH, total alkalinity (TA) and dissolved inorganic carbon (DIC) in situ. Optodes measured pH and pCO_2 values in both the water column and seafloor sediment. These sensitive instruments process measurements very quickly with minimal power consumption, so are ideal for long-term deployments. In addition, a number of instruments focused on chemical measurements at the seafloor to determine how much CO_2 entered the water column in the dissolved phase. Benthic chambers measured sediment respiration rates during and after the experiment for comparison with baseline data. The Benthic Boundary Layer Lander was equipped with a suite of sensors to measure O_2, pH, temperature, H_2S and turbulence at the sediment-water interface, and the resulting data used in eddy covariance and mass balance techniques to determine CO_2 flux.

After an 11-day period, the gas supply was turned off, the ROV disconnected the supply line and the tanks and equipment were recovered.

At a distance from the experimental site, the research vessel RV *Poseidon* carried out parallel water column surveys in order to determine the lateral spread of CO_2 away from the release site. This involved in situ measurements of biogeochemical parameters throughout the water column using video-CTD, towed membrane inlet mass spectrometer (MIMS) surveys at 5-120m above the seafloor, and deployment of the Ocean Floor Observatory System (OFOS) at the seafloor. Once the CO_2 release experiment was completed and all seafloor installations removed, RV Poseidon undertook a comprehensive survey of the release site, encompassing water column, benthic and sediment sampling to complement measurements made by RRS *James Cook* during the period of CO_2 release.

The controlled release experiment represented an enormous research effort - both at sea during the experiment and in the years of preparation leading up to it. The following pages highlight some of the engineering challenges that were overcome to make the experiment happen, and the scientific results that followed. The success of the experiment is testament to the teamwork and dedication of all the scientists, engineers and technicians involved.

Engineering solutions for a ground-breaking experiment

Baseline data

To confidently differentiate signs of CO_2 escape from a CCS reservoir from the normal background variability in the local environment, it is essential to establish a baseline of what that normal variability looks like. To address this, the STEMM-CCS team deployed a suite of sensors to gather continuous physical and biogeochemical baseline data for a year prior to the release experiment.

A specialist seabed lander to gather these data was constructed by German company develogic GmbH. The lander carried sensors to measure and record pressure, temperature, salinity, pH, nitrate, phosphate, oxygen, water current profiles and acoustic data. All data were logged centrally on the lander and mirrored to a number of expendable pop-up data pods, pre-programmed to release to the surface every 3 months to relay the data back to base via the Iridium satellite network. The reason for this approach was twofold: i) to provide data to the science team at the earliest possible opportunity, and ii) to secure as much data as possible should the lander not be recoverable for any reason.

The lander was deployed from RV *Poseidon* in October 2017, approximately 200 m north-east of the experiment site in the North Sea, and recovered to the RRS *James Cook* in April 2019.

A backup lander (Fig. 4) was built at NOC and deployed for the duration of the release experiment at a location approximately 500 m south-east of the experiment site - far enough away to provide unperturbed background measurements. The sensor suite was similar to that deployed on the develogic lander with pressure, temperature, salinity, pH, nitrate, phosphate, total alkalinity, dissolved inorganic carbon, water currents and acoustics being measured.

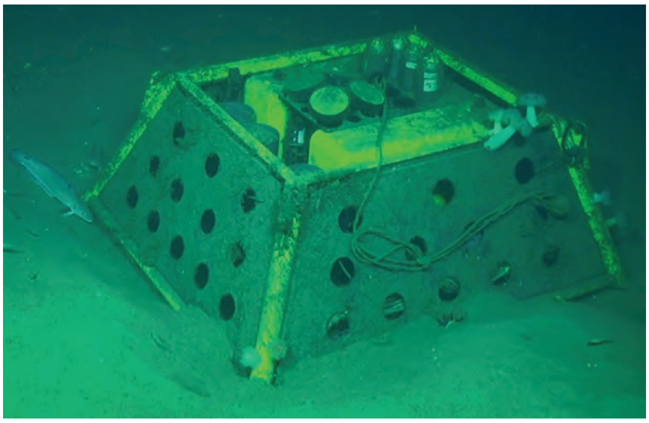


Figure 3: The baseline lander – as photographed by ROV ISIS in April 2019.

Figure 4: The backup baseline lander being deployed from RRS James Cook.

Drill rig

A fundamental requirement of the CO_2 release experiment was to release gas from a point within the sediments approximately 3m below the seabed surface. This presented a major engineering challenge. The QICS project undertook a similar approach in 2012[3] using directional drilling to create a U-shaped borehole under the seabed. However, the experiment was sited close to the shoreline of a Scottish loch so the drilling could be conducted from dry land. Carrying out directional drilling 100 km offshore in the North Sea was not an option.

The solution was to draw on well-known cone penetrometer techniques whereby an instrumented rod is pushed vertically downwards into the seabed using a subsea drive unit. This technique was adapted to push a pre-curved steel pipe downwards into the seabed such that it followed its own curvature to describe a U-shaped path with its leading end stopping 3m below the seabed with an upward attitude (Fig. 5). The upward attitude of the outlet end was important to prevent the gas from tracking back along the outside of the pipe rather than finding a natural pathway up through the sediment.

The design and manufacture of this equipment was contracted to a Canadian company, Cellula Robotics, who have a proven track record in designing and building cone penetrometers and were well-placed to design this equipment.

Within its 2.3 m cubic steel frame, the rig housed a hydraulic power pack to drive a set of clamp rollers that held the pipe firm and slowly rotated to drive the pipe along its own axis

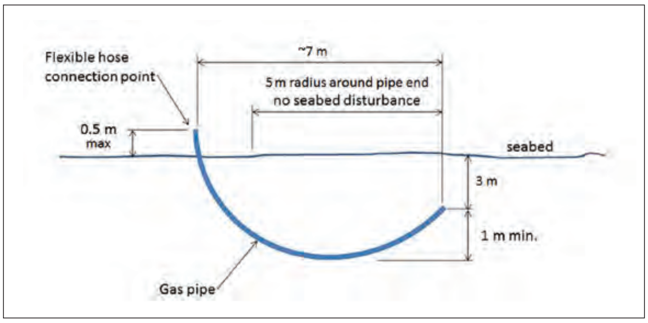


Figure 5: Illustration of gas release pipe geometry used in the experiment.

into the sediment. The carbon steel pipe was 38.1 mm OD with a 12.7 mm bore and 8 m in length, and pre-curved to a radius of 4.5 m. A retractable 'goose-neck' was included to support the pipe during deployment, and the outlet end of the pipe was closed with a pointed tip to aid penetration. Just behind the tip were a number of 12.7 mm diameter gas exit holes drilled through the pipe wall at a 45° backward slant to help prevent sediment clogging during insertion. Inside the drilled portion of pipe was a 460 mm long sintered stainless steel diffuser with a pore size of 9 μm, to ensure the gas flow was distributed evenly across the outlet holes. The inlet end of the pipe, which would remain above the seabed, was fitted with a quick-connect fitting for connection to the gas supply via a flexible hose.

Control and electrical power to the hydraulic unit was provided via an umbilical cable from the ship. The umbilical also carried live video back to the ship to a) verify the rig was landing on a suitable site and b) to monitor progress of the pipe as it was pushed into the sediment. The rig had sufficient push force to jack up its 6-tonne mass should the pipe encounter an impenetrable object; an inclinometer was included to provide early warning of any change of frame angle that would result from such an occurrence.

Figure 6: Deployment of the drill rig from RRS James Cook.

Gas release system

A total of 3 tonnes of CO_2 gas was required for the release experiment, which was mixed with a cocktail of non-toxic tracer gases (octafluoropropane (C_3F_8), sulphur hexafluoride (SF_6) and krypton (Kr)) in precise ratios before injection.

Delivering these gases to the seabed proved challenging. One option might have been to pipe the gases down from tanks on the research ship but this would not be possible as the ship needed to remain mobile and could not be constrained to one place. An anchored barge was also considered but its fixed anchor warps and the descending gas hose would present unacceptable hazards to ROV operations should the ROV umbilical become entangled with them. It was apparent that the gas tanks would need to be positioned directly on the seabed.

It was originally intended that the gases would be supplied in standard industrial cylinders and delivered to the seabed in palletised form, but this was also not feasible: commercial suppliers were not willing to supply cylinders for use in a subsea environment, and the number of cylinders required for the experiment presented too many leak risks. It was therefore necessary for us to design and build our own gas storage solution.

A pair of bespoke bulk storage tanks, connected to act as one single storage volume of 5.6 m^3, were procured from City Gas EOOD in Bulgaria. This storage volume was sufficient to accommodate 3 tonnes of liquid CO_2 with a 1.7 m^3 vapour headspace at 20°C. It is usual for bulk CO_2 to be stored cryogenically to reduce storage pressure to around 20 bar, however this requires insulated tanks and cooling plant to maintain the temperature at around -20°C, which was not viable in a subsea setting. The tanks were therefore uninsulated and designed for a maximum working pressure of 80 bar - sufficient to allow for an ambient temperature in excess of 30°C, which was unlikely to be encountered during springtime in the UK. Once on the seabed, ambient temperature would be around 8°C with an equivalent storage pressure of 42 bar(a).

The bulk storage tanks, along with the other equipment described below, were mounted in a steel deployment frame. With a gross weight of 13 tonnes, this frame was the heaviest single piece of equipment ever to be deployed from RRS *James Cook* (Fig. 7).

The trace gases were supplied in a gaseous state, pre-mixed with CO_2 (70.8% Kr, 25.1% CO_2, 3.8% SF_6 and 0.3% C_3F_8 by mass) and decanted into four manifolded bladder accumulators for deployment. The accumulators were kept charged to a constant pressure of 30 bar(a) via a regulated gas feed from the bulk CO_2 tanks. This was necessary to aid stability of flow and to ensure nearly all of the mixture could be extracted when submerged to 120 m with an external pressure of approximately 12 bar.

The trace gas mixture was fed into a bespoke battery-powered control unit where the flow was metered through a mass flow controller (MFC) and then mixed into the main CO_2 line. The mixed gas line then re-entered the control unit where a second MFC metered the overall flow rate. The MFCs worked as a master-slave pair whereby the mixed gas flow was user controlled and the trace gas mixture flow followed at a pre-set mass ratio, set at 10,000:1 for the experiment. The overall flow rate was adjustable from zero to 100 normal litres per minute ('normal' is defined as 0°C and 1.013 bar), equivalent to a mass flow range of zero to 198 grams per minute. Remote adjustment of the MFCs, and feedback of engineering data for flow rate, pressure and temperature, was achieved using an optical modem that enabled communication to the research ship via the ROV's umbilical cable.

From the control unit the mixed gas flowed to a valve panel where a number of outlets could be selected, including a sample port from which 'raw' samples could be collected to verify the correct gas mixture was being achieved. Gas was successfully delivered as planned to the release point, percolating up through the sediment and producing bubble streams into the water column. The flow rate was gradually increased during the experiment from 2 to 50 'normal' litres per minute (4 to 99 grams per minute; Fig. 8). A total of 675 kg of mixed gas was released during the 11-day experiment.

Through development of novel pipe placement and gas storage and handling equipment, the STEMM-CCS engineering team were able to successfully produce a controlled sub-seafloor CO_2 release event. This work was vital in enabling the subsequent CO_2 monitoring experiment.

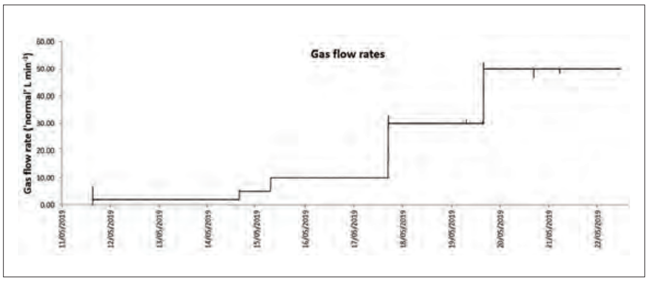


Figure 8: Plot showing gas flow rates during the release experiment.

Figure 7: Deployment of the bespoke gas storage and release system from the back deck of RRS James Cook.

Establishing the environmental baseline

Without a comprehensive understanding of its natural variability, both operational and environmental monitoring of a CCS site will be difficult and inefficient. An accurate assessment of pre-injection conditions and their variability over space and time are not only needed to distinguish between natural and operationally induced deviations, but also to evaluate potential CCS impacts against variability caused by other human activities in the area. However, the task is monumental: a wide range of biological, chemical and physical parameters may be needed to fully describe the baseline conditions of a site. In addition, while the spatial extent of storage complexes is expected to be large, impacts and unintended emissions may be very localised. Similarly, the signature of any potential emission will have to be distinguished from both short-term natural variability and long-term regional trends. In order to avoid the baseline data acquisition to become prohibitively expensive, a carefully designed, cost-effective observational programme is needed. This will then underpin further numerical modelling work that will allow extrapolation beyond the spatial and temporal framework for which actual observations can be obtained (see p24).

Whilst every marine CCS operation will be unique and require a bespoke baseline data acquisition plan, within STEMM-CCS we developed a generic framework for the establishment of an effective environmental baseline that can be adapted to individual offshore CCS projects. Combining more traditional approaches with novel technologies, this approach was applied at the Goldeneye site as an illustration of its implementation.

A generic framework for establishing an effective environmental baseline

Generally speaking, the baseline assessment process consists of three steps[4] (Fig. 9): (1) the initial site characterisation of the area that covers the CCS complex, which involves a desktop study to collect all existing environmental information together with a combination of broad-scale acoustic surveys, remote sensing observations and computer-based modelling, with the aim to define and map the different marine habitats, seabed features and water column characteristics in the area; (2) the dedicated collection of biological, physical and chemical data, using a sampling scheme informed by the data and modelling results obtained in the previous step, to fill knowledge gaps identified; (3) the development and optimisation of numerical models to hind-cast and forecast the environmental characteristics at the necessary spatial and temporal resolution over the desired study area and time frame.

To address the challenge of obtaining adequate observational information at the correct resolution over the extensive area that may influence the CCS storage site, a nested approach to baseline data collection is suggested. Four nested levels or 'tiers' were proposed[4] (Fig. 9):

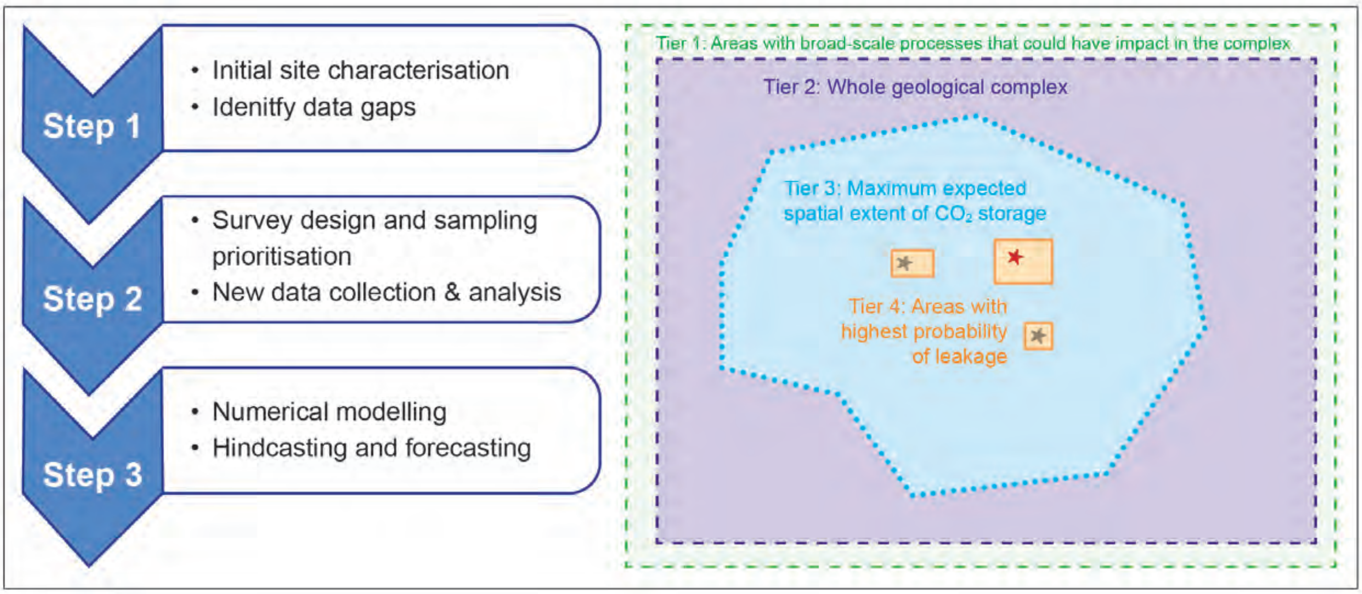


Figure 9: Three-step process of baseline evaluation (left) and schematic representation of 4 spatial scales for baseline establishment (right).

- **Tier 1**, the wider geographical context of the storage complex, within which environmental processes occur that can affect, or be impacted by, the CCS operation
- **Tier 2**, the entire geological complex within which the CCS operations are developed, and over which broad-scale marine environmental mapping (including seabed, water column and human activity) should be carried out
- **Tier 3**, the maximum expected spatial extent of CO_2 storage, over which finer-scale computer-based modelling should be carried out, validated by targeted field observations
- **Tier 4**, local sites considered at highest risk from leakage (highest probability of leakage, or greatest potential sensitivity to the impacts), which require spatially and temporally detailed surveys and models.

Applying the environmental baseline framework at the Goldeneye experimental site

Seasonality

An accessible and affordable approach to generate a wide-scale, spatially explicit environmental understanding

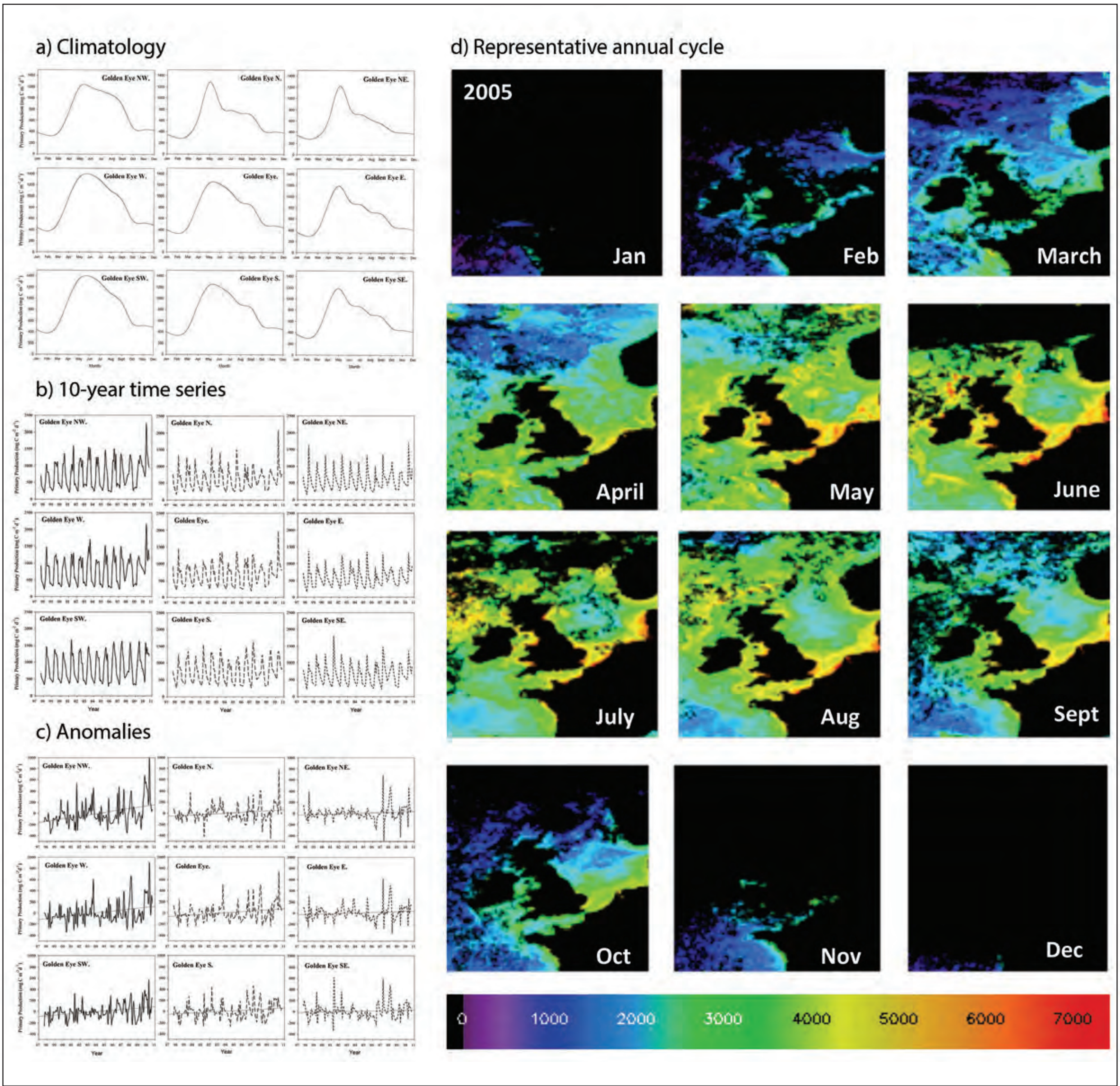


Figure 10: SeaWiFS derived Chlorophyll-a (mg m^{-3}) data illustrating the a) climatology, b) a 10 year time series, c) anomalies and d) a representative annual cycle at Goldeneye and in 1° x 1° boxes around the site.

of the variability of the marine ecosystem at the Tier 1 level, particularly in areas where only limited in-situ data is available, is the use of historical ocean colour data derived from satellites. By applying this method to the Goldeneye complex we could demonstrate that the storage complex sat below two contrasting water masses, each with their own seasonal characteristics and historical trends in terms of biogeochemical dynamics (Fig. 10). The seasonality information extracted from this analysis, together with targeted sampling information, informed coupled models that enabled us to predict and quantify natural variability and its heterogeneity over the Tier 1 area.

Benthic habitats and human impacts

A baseline marine habitat map was created for the Goldeneye Tier 2 area, within the budget limitations of the STEMM-CCS project, illustrating what can be achieved within the framework of a wider programme in which habitat mapping is not the primary objective. Collation and interpretation of existing data was followed by strategic design of new data collection. Multibeam echosounder data were collected over the Tier 2 area, and point-based sediment grain size observations (from historical samples) were extrapolated to a full-coverage map using an ensemble of spatial distribution models (Random Forest and Generalised Additive Models). The bathymetry and substratum information were combined with available data on human activities in the area (seabed infrastructure, bottom trawling intensity) to create a broad-scale habitat map, which was then used to derive new sample locations for sediment characteristics and biological assessment, based on a stratified random sampling scheme.

The seafloor at the Goldeneye site is generally flat and featureless, ranging from c. 100 to 120m water depth. The Goldeneye seabed habitats are driven by sediment type, which changes gradually from sandy mud (>50% mud) in the NE to muddy sand (<50% mud) in the SW of the Tier 2 area. Pockmarks, the main seafloor geomorphological features, occur in the northern half of the area, and were mapped at Tier 3 level of detail. However, we found that their sediment characteristics did not differ significantly from the surrounding seafloor. Finally, high-resolution mapping using an Autonomous Underwater Vehicle (AUV, Fig. 11) at Tier 4 level captured the detailed effects of human activities, notably traces of seabed infrastructure and the marks of bottom trawl fishing.

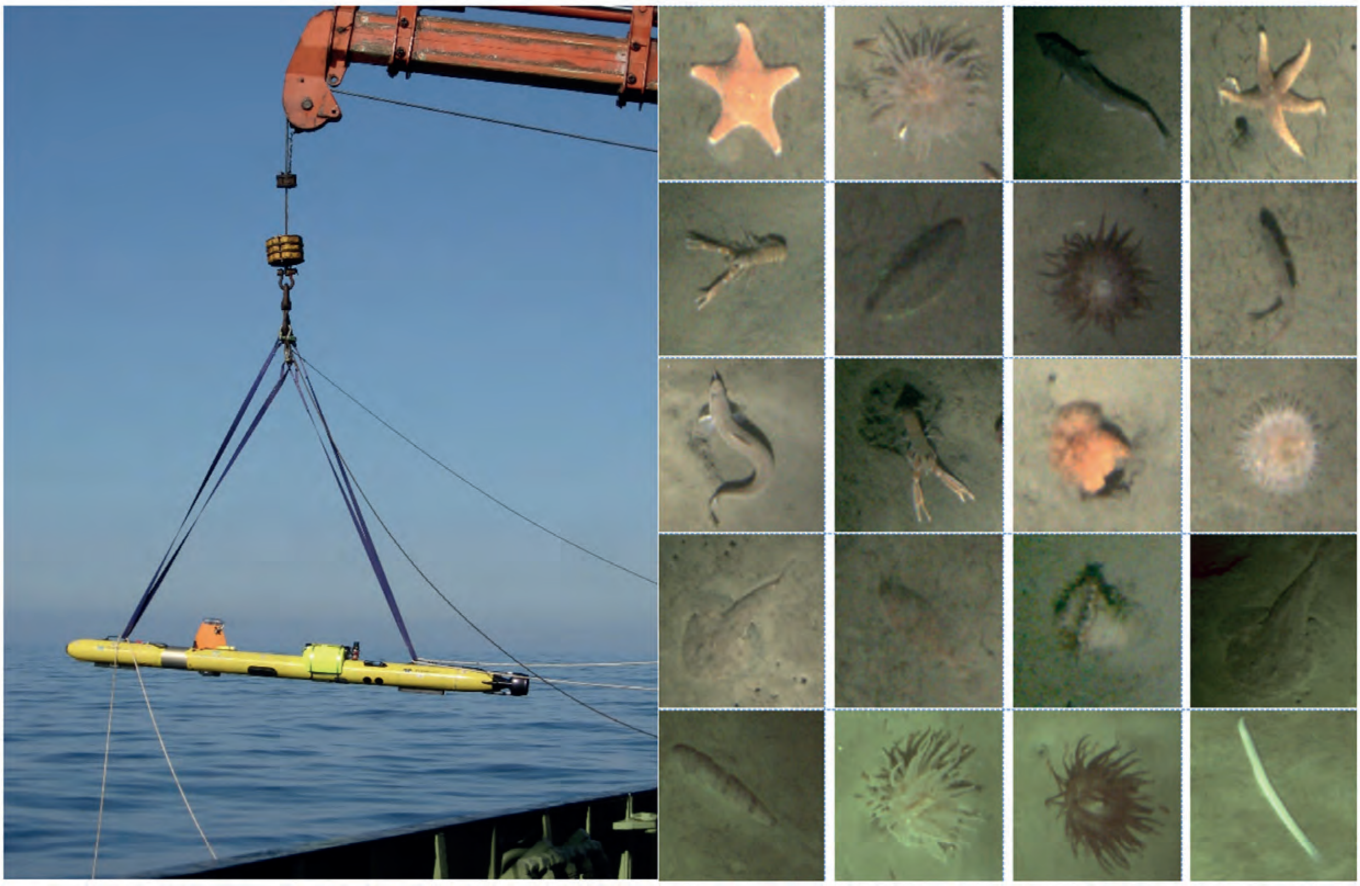


Figure 11: The Gavia Autonomous Underwater Vehicle deployed at the Goldeneye site (left), and a series of representative benthic megafauna specimens, photographed by the Gavia AUV (right)

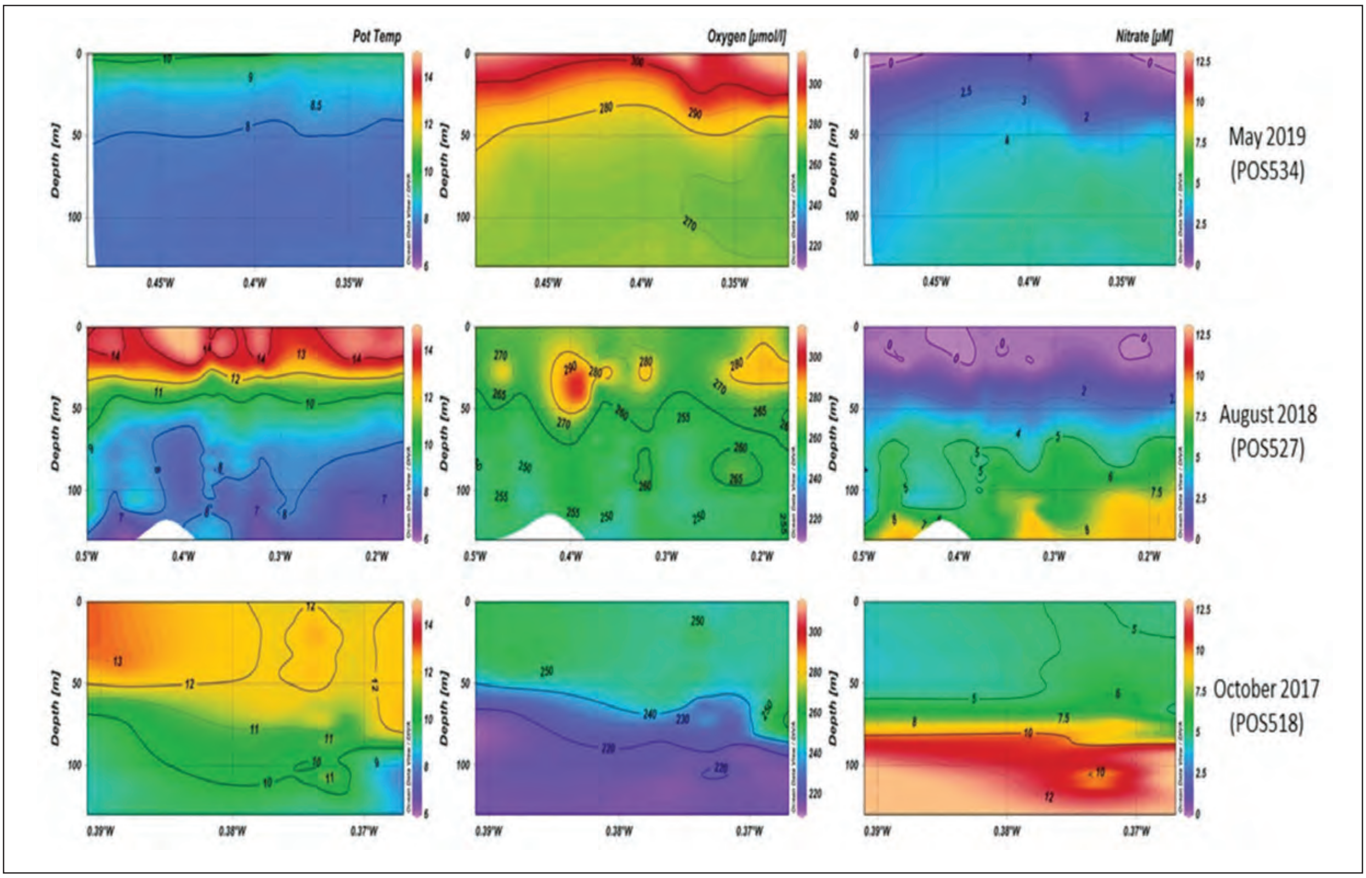


Figure 12: Water column structure at Goldeneye during spring 2019, summer 2018 and autumn 2017. Spatial variability in water column properties was quantified with a towed CTD system and illustrated that local signatures are also influenced by horizontal advection of water masses by the tidal current regime.

Faunal distribution

To characterise the fauna at the Goldeneye area, two techniques were used. The megafauna (animals >1cm) that mainly live on the seabed were observed in photographs taken with the Gavia AUV deployed during the STEMM-CCS expedition in the area. The system enabled us to take photographs at a rate of c. 6600 images per hour, providing much increased efficiency over traditional drop-down camera systems. Twenty-seven visually distinctive taxa ("morphospecies") were identified in the area, with some examples shown in Fig. 11. However, neither faunal density, diversity, nor community composition differed between the sites studied. This may be a result of the very homogeneous character of the seabed, with minimal morphological change, and very gradual changes in sediment characteristics.

Macrofauna (>1 mm) living in the sediment, however, did show changes over the Tier 2 area. Samples of the seabed were taken with a box corer and sieved to extract the specimens, which were then identified and counted under a binocular microscope – all together a more labour-intensive operation. Significantly different communities were found in the sandy muds compared to muddy sands, and the intensity of bottom trawl fishing activity impacted the macrofauna community composition.

Water column chemistry

Measuring CO_2 concentrations directly is not yet an efficient, automated process; instead marine scientists use either pH or pCO_2 (the partial pressure of CO_2 in the water) as indicators of CO_2 as these can be measured by off-the-shelf automated sensor technology and provide a reliable quantification of CO_2 concentrations.

The physico-chemical characteristics of the water column at the Goldeneye site were measured with a combination of CTD casts, discrete water samples and benthic landers, equipped with novel sensors. Measurements were carried out over several expeditions, spread over the different seasons, and focussed particularly on the near-seabed conditions. Comparisons were also made with historical datasets of the region (e.g. from the GLODAP database or collected by CEFAS), and with the modelling data described later in this document. The results showed clear tidal, seasonal and inter-annual variability. Variations in pH and pCO_2 over a single tidal cycle were in the order of ±0.008 and ± 1.5 µatm respectively. The maximum annual variation in pCO_2 was closer to 166 µatm. The seasonal variability was strongly expressed in the water column stratification, while the influence of the phytoplankton spring bloom and the subsequent remineralisation processes at depth are clearly visible in the water column nutrient and oxygen concentrations (Fig. 12). Historical data showed similar values and trends, although in comparison with 2005, there was an average decrease in pH of 0.04 units. In terms of CCS monitoring, an inverse relationship between pCO_2 and dissolved O_2 was observed, which differed in strength over the seasons. Strong deviations from this natural pCO_2 – O_2 covariance relationship could be used as indications for a non-natural source of CO_2.

Sediment chemistry and fluxes

Biogeochemical characteristics of the sediments and pore waters at Goldeneye were determined from gravity cores (up to 5m long) and multicores (up to 30cm). Overall, the sediments at Goldeneye can be classified as low in organic carbon and depleted in organic nitrogen. Organic matter is respired in the pore waters, but the reactivity and content of organic carbon is too low to cause the formation of methane. Some reduction of sulphate and of iron (oxy) hydroxides does take place, resulting in the presence of FeS_2 in the upper 30cm of the cores.

The fluxes of key components such as dissolved oxygen, inorganic carbon and nitrogen through the sediment-water interface were measured using four different, complementary state-of-the-art techniques: in-situ benthic chambers, a sediment microprofiler, the novel eddy covariance technique, and ex-situ whole core incubations. The measured oxygen flux into the sediment was consistent between all four methods and was slightly higher in spring than in autumn. Also, the dissolved inorganic carbon (DIC) flux out of the sediments differed between seasons. Significantly increased DIC values could indicate potential CO_2 escape.

Summary

By combining existing information with a suite of newly gathered data and advanced numerical modelling (see p24), STEMM-CCS has constructed a comprehensive morphological, physico-geochemical and ecological description of the seabed above the Goldeneye storage complex. This information has been synthesised to create a comprehensive report and a seabed habitat map that also includes major human pressures such as fishing. Such documents are vital for determining the areas of seabed that potentially have the greatest sensitivity to CO_2 leakage, and therefore identify those areas around which to focus environmental monitoring.

Figure 13: The baseline lander and other instrumentation strapped down on the deck of RV Poseidon amid heavy swell in the North Sea in October 2017. Image courtesy P. Linke.

Understanding CO_2 pathways

Most CO_2 storage scenarios envisage storage in sedimentary basins in saline aquifers or abandoned hydrocarbon fields. Regardless of whether this occurs onshore or offshore it is important to determine whether the geological strata between the reservoir rock and the surface (the overburden) can act as a seal for the reservoir, keeping the CO_2 in place. Commonly, three layers of seals are required by regulators before a storage site may be considered safe. Whilst most effort is normally spent on analysing the integrity of the seal immediately above the reservoir unit, it is more difficult to assess the integrity of the rest of the overburden, simply because of its size and its frequently long and complex geological history.

As sedimentary basins compact, they continuously expel fluids from the pore spaces between grains. These formation waters find their way to the surface either through diffusive flow through the more permeable sediments close to the surface, or via focused flow pathways that penetrate through seals. Such seal bypass systems may take the form of geological structures such as faults, diapirs or permeable layers. They can also form as a result of fluid migration itself if the flow rate exceeds the permeability of the overburden materials. In this situation, pore pressure in the rock or sediment increases until hydrofracturing occurs and a focused fluid pathway is formed. Such systems are called pipe or chimney structures, and they are ubiquitous in sedimentary basins.

Within STEMM-CCS we spent considerable effort on constraining the nature of pipe structures in the central North Sea close to the Sleipner CCS site and the potential Goldeneye CCS site[5]. The objective was to understand if such systems can remain as open pathways for extended times after their formation and what their permeability is. The ultimate goal is the development of a more realistic parameterisation of pipe structures in hydrological models to provide robust input to CO_2 storage operation planning, i.e. to determine if pipe structures can be ignored during CCS planning or if they should be avoided - and if so, what exclusion distance would be required for safe CCS operations.

Geophysical experiments

During three research cruises to the Scanner pockmark in the central North Sea we collected all possible kinds of geophysical data to analyse the underlying pipe structure and to constrain its physical properties. Based on a large three-dimensional seismic cube made available by the

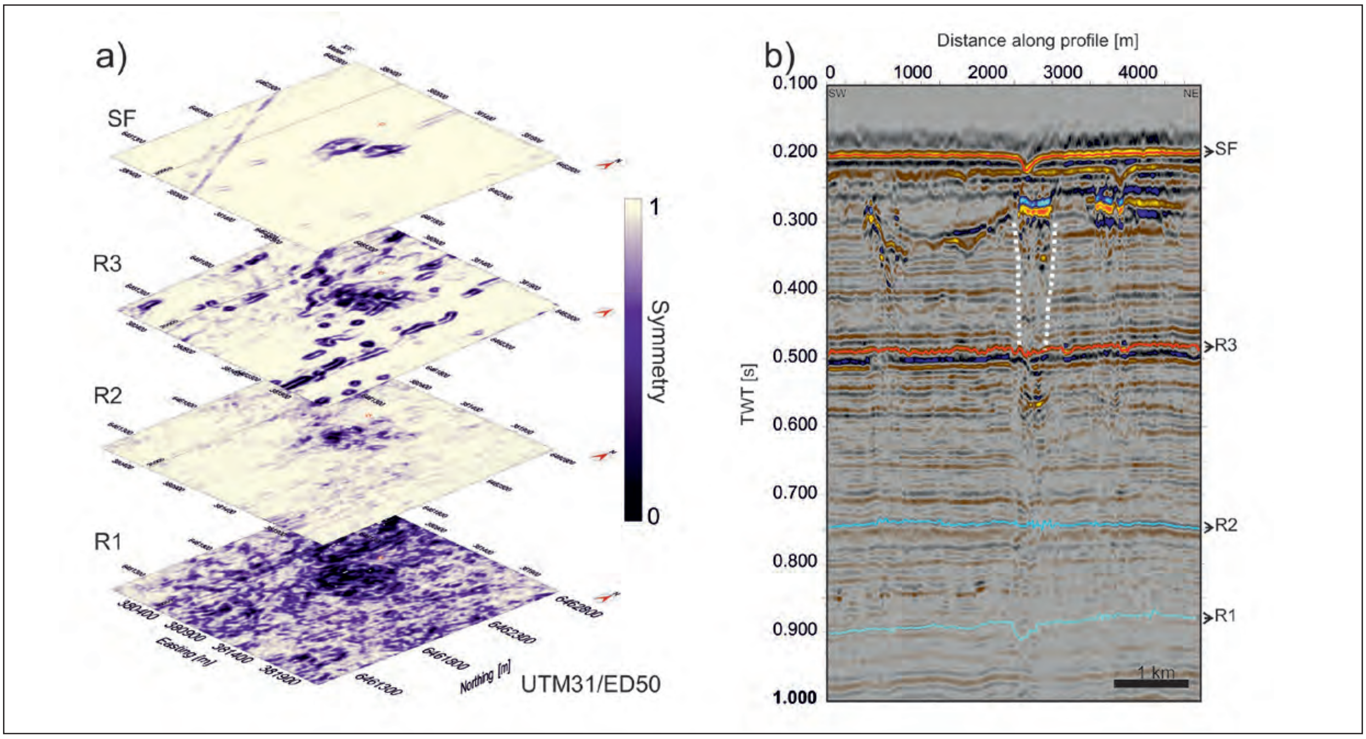


Figure 14: 3D seismic image of the pipe structure underneath the Scanner pockmark reaching down to about 0.7 s two way travel time (TWT) or approximately 600 m (right) and slices through a coherency cube (left) at the same location showing the three-dimensional geometry of the pipe depth at different depth (for depth see labels on the right figure). From Böttner et al., 2019 [5].

Norwegian geophysical service company PGS, we were able to identify a suitable site at which a pipe structure can be seen as a seismic anomaly reaching down to at least 800 m below the seabed (Fig. 14). At the top of this pipe there is a seafloor depression with a diameter of about 400 m and about 15 m in depth, known as the Scanner pockmark. This pockmark is one of a group of pockmarks in the Witchground Basin in the North Sea that are associated with pipe structures.

At the Scanner pockmark we collected high-resolution 2D seismic data with different seismic sources to obtain a more detailed image of the strata down to 500 m below the seafloor. The sources consisted of piezo-electric chirp systems (e.g. Parasound) with a resolution of 20 cm and a penetration of about 20 m, two different types of sparker systems with a resolution of about 1 m and a penetration of about 100 m and GI gun 2D seismic data with a resolution of about 6 m and a penetration of about 1000 m. The seismic data clearly detailed the stratification of the glacial and post-glacial stratigraphy, which enabled a complete reassessement of these strata.

Furthermore, we collected two sets of ocean bottom seismometer (OBS) data that were subsequently used to derive the three-dimensional velocity field below the Scanner pockmark using a method called tomographic inversion of the first arrivals. Preliminary results of this time-consuming and complicated data evaluation clearly show a low velocity anomaly below the Scanner pockmark, indicating that the sediments are disturbed and that gas is probably rising through fractures.

Another geophysical technique used, known as controlled source electromagnetic surveying, is sensitive to changes in the electrical conductivity of the sub-seafloor sediments. These sediments are saturated with conductive seawater, and survey results are therefore indicative of porosity and free gas content. An electromagnetic source was deep-towed above the seafloor and the electromagnetic field recorded by towed and ocean bottom receivers (Fig. 15). These data image the top ~150 m and down to ~1 km below the seafloor for the towed and ocean bottom receivers, respectively. Both electromagnetic datasets show a decrease in electric conductivity with depth, which is mainly due to the compaction of the sediments and the associated reduction in pore space. A local reduction in conductivity below the pockmark, co-located with a local decrease in velocity (OBS result), suggests the presence of free gas in the sediments.

Geological investigations

After these comprehensive geophysical investigations we drilled 10 m into the pockmark itself, and 50 m into the surface sediments at a reference site located about 4 km east of Scanner pockmark. We completed these boreholes with the RockDrill2 seafloor drill rig (Fig. 16), operated by

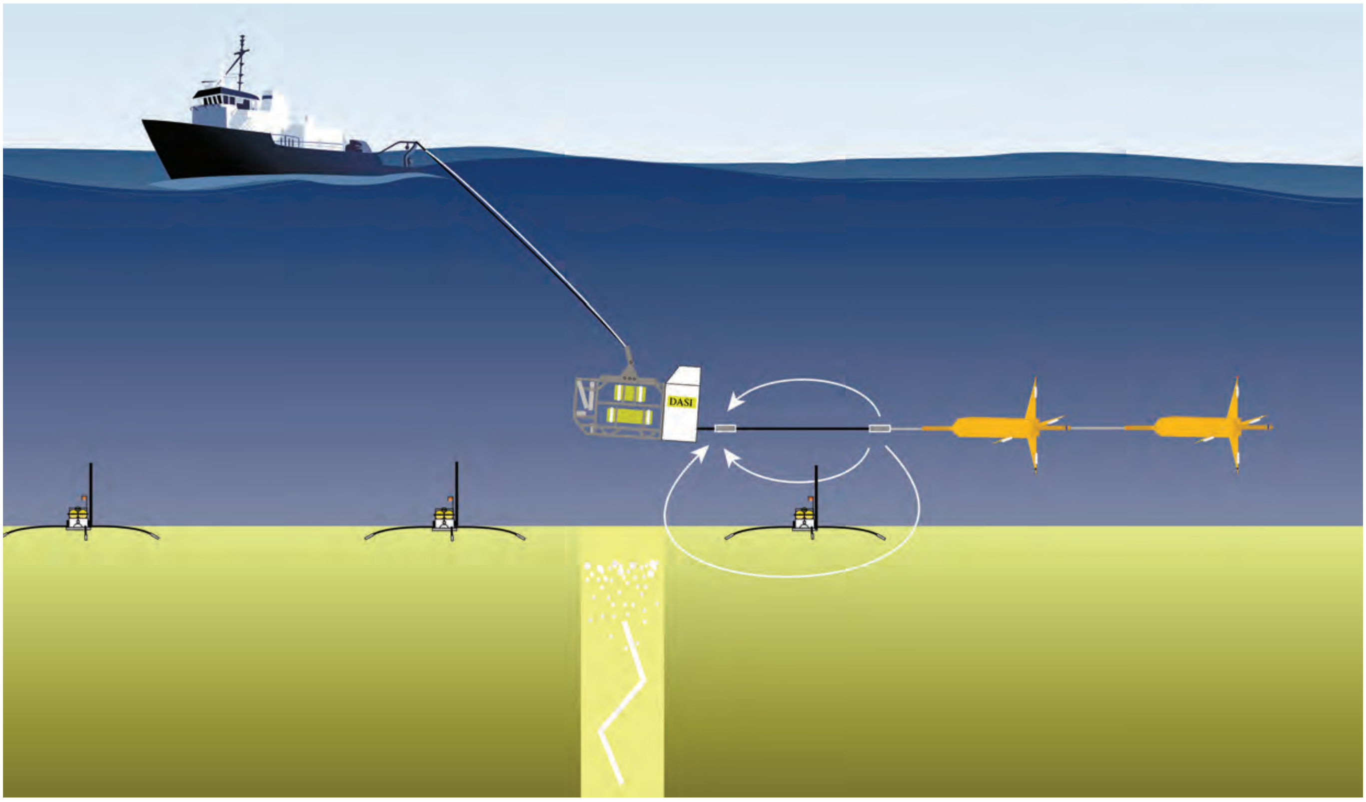


Figure 15: Deep-towed electromagnetic experiment sketch (not to scale) including a source that injects an electric current (white lines), towed receivers (orange tow bodies) and ocean-bottom receivers across a vertical fluid conduit (indicated by white arrow and bubbles). Image adapted from K. Weitemeyer and finalised by K. Davis.

BGS during a second voyage with the German research vessel RV *Maria S. Merian*. The sediment core recovery of about 50% was a huge success and the cores showed a clear difference in sedimentary structure between the pockmark site above the pipe and at the reference site. Within STEMM-CCS we were able to develop a new indirect method to derive the permeability of sediments from sediment cores using computer-tomographic images and numerical simulations instead of laboratory tests [6]. Gas composition measured in sediment cores and in the water column show that the gas escaping from the scanner pockmark is predominantly methane.

In addition to studying the top of an active pipe structure in the marine environment we also conducted two terrestrial field campaigns to study fossil pipe structures and learn more about the geology of the deeper parts of pipes. The first campaign investigated fossil pipe structures in California; the second survey had an aerial component to investigate pipe structures near Varna in Bulgaria. In terms of lithology, both systems are fundamentally different to the pipe structure below the Scanner pockmarks and they are perhaps not optimal analogues. It is clear, however, that they can form in different types of lithologies and they can even transgress sandy intervals within the sediment sequence, which explains why the pipe structures in sedimentary basins can be vertically continuous for several hundred meters.

Numerical simulation of gas seepage through pipe structures

In order to assess the flow of CO_2 through pipe structures we developed several new numerical simulation schemes that are able to consider different transported species and in varying lithologies, linking the momentum equation with the mass continuity equation and the species transform equation. We parameterised the simulations with data derived from the geophysical experiments, the sediment cores and the field relationships from the outcrop analogues replacing methane for CO_2. First order observations show that the CO_2 is moving much faster through the high porosity sandy units and through fractures that are either pre-existing or generated by hydrofracturing in response to elevated pore pressures.

Summary

The ubiquitous nature of pipe structures requires their detailed understand to incorporate them into CCS site selection and CCS site assessment studies. Within STEMM-CCS we have made significant progress in understanding their nature and their role in fluid migration through sedimentary basins. The main study site for this investigation is a pipe structure underneath the Scanner pockmark in the central North Sea, which is an active seep site for methane. The geophysical data point to the presence of free gas at least in the top 80 m of sediments but is probably present down to several hundred metres below the seafloor, most likely hosted in a fracture network. Numerical simulations show that CO_2 can migrate much faster through such a structure than through the undisturbed host rock around it. However, apart from showing that pipe structures can transgress across different lithologies, the simulations also revealed the large variety of pipe structures, both in terms of size and formation mechanism. This clearly documents the demand for further studies of pipe structures in a range of sedimentary basins to put the findings on a more robust statistical footing.

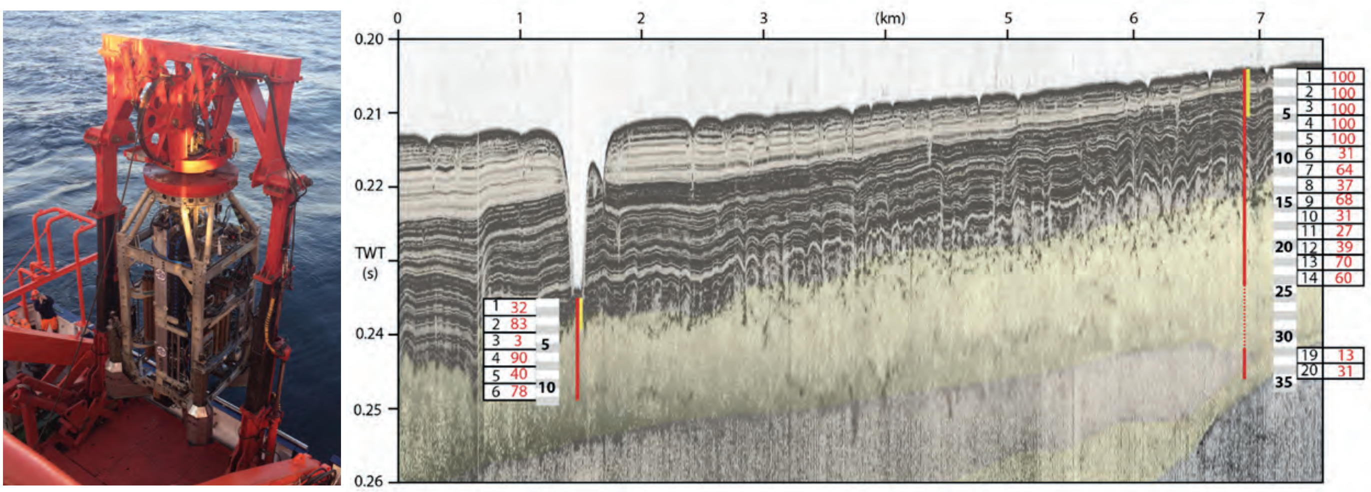


Figure 16: Left: RockDrill2 deployment during Maria S. Merian cruise MSM78 [7]. Image courtesy J.Karstens. Right: Sediment echosounder profile showing the relative location of the drill site in the Scanner pockmark and the reference site. Red lines show core recovery. The deep depression of the seafloor is the Scanner pockmark [7].

Detecting, tracing and quantifying CO_2 leakage

One of the key barriers to upscaling offshore CCS is the need to demonstrate capability in environmental monitoring to confirm safe CO_2 storage, and to detect, quantify and attribute fugitive CO_2 emissions in the unlikely event that leakage occurs. This capability is necessary for any type of Emissions Trading Scheme (ETS), for operators to guide mitigation/remediation actions in a CO_2 escape situation, and to alleviate public concern about CCS as a technology. A key objective of the STEMM-CCS controlled sub-seabed CO_2 release experiment was to assess this capability.

Challenges in detecting, quantifying and attributing fugitive CO_2 emissions

There are a number of challenges for detecting, quantifying and attributing the source of fugitive CO_2 emissions. While escape of gas bubbles across the seabed can be detected remotely (for example, from a ship's echosounder), the composition and source of the bubbles needs to be verified because gas may be seeping naturally from the seafloor, for example via methane seeps. Detection of fugitive CO_2 that has dissolved into sediment pore waters is complex because background concentrations of dissolved CO2 in seawater are naturally very variable, on daily, seasonal and decadal timescales. If the CO_2 leakage rate is low, then any CO_2 that escapes across the seabed will be particularly difficult to detect, because the CO_2 will be rapidly diluted as it mixes with overlying seawater.

Quantifying fugitive CO_2 emissions is especially difficult. Traditionally, leakage rates are determined from measurements made precisely at the spot from which the CO_2 escapes. However, at a CCS site, CO_2 escape may occur over a wide area and from multiple locations, so these traditional techniques are not practical. The best way to determine the source of CO_2 leakage is to 'label' the CO_2 that is injected into the storage reservoir using a chemical tracer. While this has been done for CO_2 stored on land, it has never been tested in the marine environment.

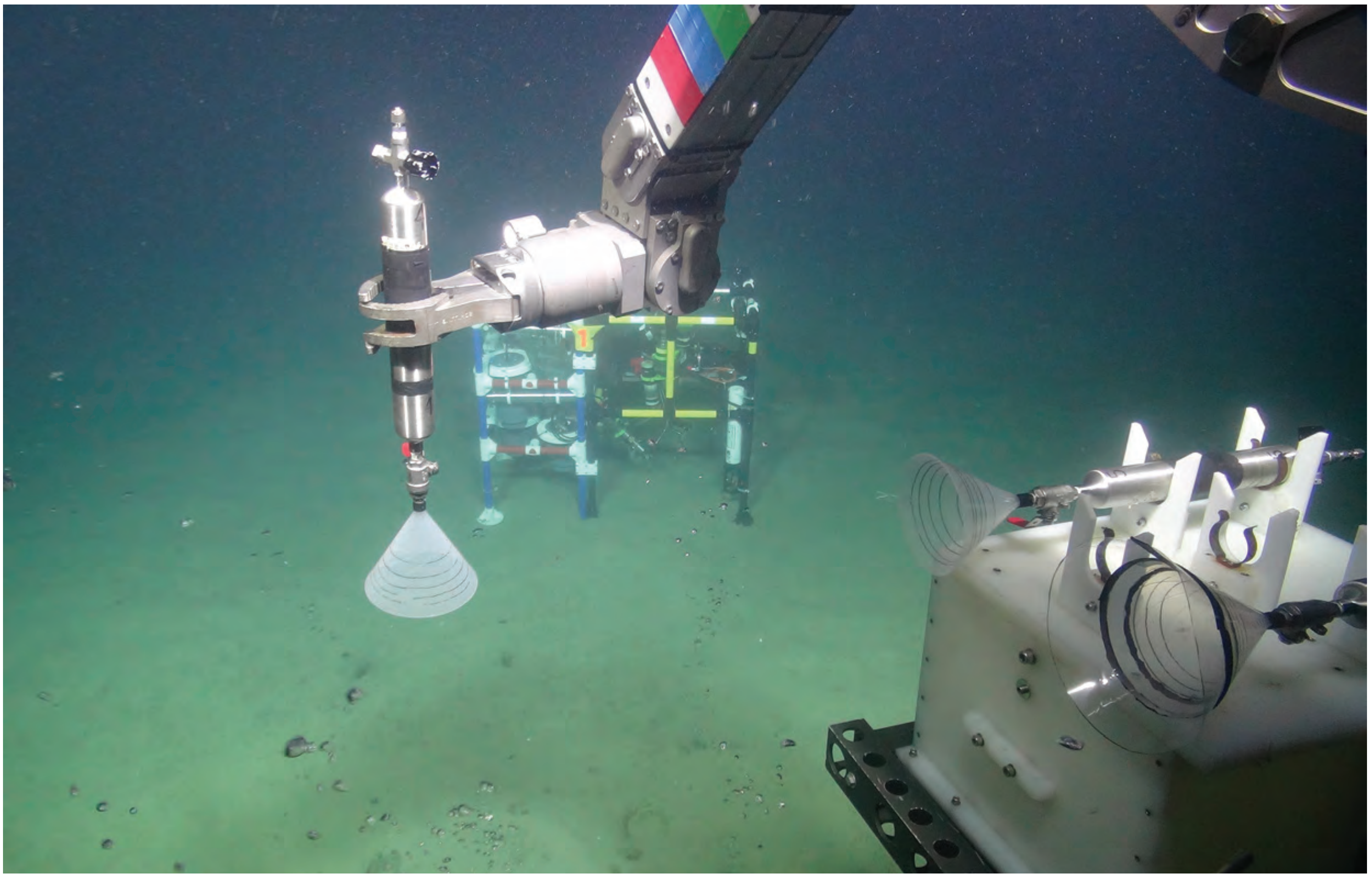


Figure 17: Collection of gas samples using a gas bubble sampler deployed from the remotely operated vehicle. The time taken to fill the funnel with gas was noted to derive an approximate estimate of the leakage rate. Image courtesy NOC/JC180.

In STEMM-CCS, we aimed to address these knowledge gaps by:

- Testing techniques for detecting and quantifying CO_2 leakage across the seabed at the proposed Goldeneye sub-seabed CO_2 storage site, using automated technologies where possible;
- Testing the efficacy of a variety of natural and artificial CO_2 tracers for CO_2 detection, quantification and source attribution in the marine environment;
- Developing a comprehensive model system for monitoring and predicting the impact of fugitive CO_2 emissions for a range of leakage scenarios.

Utility of natural and artificial tracers of released CO_2

A tracer is a non-toxic marker species that is either naturally present in CO_2 or can be added in tiny amounts to the injected CO_2. Tracers need to be detectable at very low concentrations and they need to occur at very low levels naturally in the environment. Tracers allow us to significantly improve the detection of CO_2 anomalies, and they are vital for showing that the leaking CO_2 comes from the CO_2 storage reservoir, rather than from a natural source. Different CO_2 reservoirs can be labelled with different tracers (or different proportions of the same tracers), allowing operators to be sure that any CO_2 leakage is coming from their storage site, rather than a neighbouring facility.

Methodologies for the detection, quantification and attribution of leaking CO_2 were tested during the STEMM-CCS controlled release experiment in May 2019. During this experiment, the injected CO_2 was labelled with natural tracers (CO_2 with distinctive $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios) and a set of artificial tracer gases (octafluoropropane (C_3F_8), sulphur hexafluoride (SF_6) and krypton (Kr)). Prior to STEMM-CCS, these tracers had never been tested in a marine setting, so their behaviour in the marine environment was unknown.

Using tracers during the release experiment

During the experiment we carried out: (i) multiple in situ surveys using an AUV-mounted Chirp sonar system to detect and map out the distribution of CO_2 in the sub-seabed sediments and CO_2 escaping into the water column; (ii) multiple surveys and sample collection using a remotely operated vehicle (ROV), to detect, quantify and attribute the source of escaping CO_2; (iii) video footage of bubble release from the seafloor; (iv) deployment of bespoke instrumentation on the seafloor for fixed periods to quantify fluxes of CO_2. This included benthic boundary layer landers, a hydrophone 'wall' and benthic chambers. Data collected from the vicinity of the CO_2 release site were compared to 'background' data collected by instrumentation deployed on the baseline seafloor lander system located away from the release site for the duration of the release experiment.

Chirp sonar images of the upper few metres of the sub-seabed sediments, obtained from flying the AUV a few meters above the seabed, showed that at low CO_2 injection rates most of the released CO_2 dissolved into the sediment pore waters. At high flow rates CO_2 gas was trapped within the subsurface sediments as the rate at which the gas entered the system was faster than the rate at which it could escape. However, once the CO_2 injection was stopped, the CO_2 gas rapidly disappeared and it was as if the experiment had never taken place.

We used three different techniques to estimate the proportion of injected CO_2 that escaped as gas bubbles

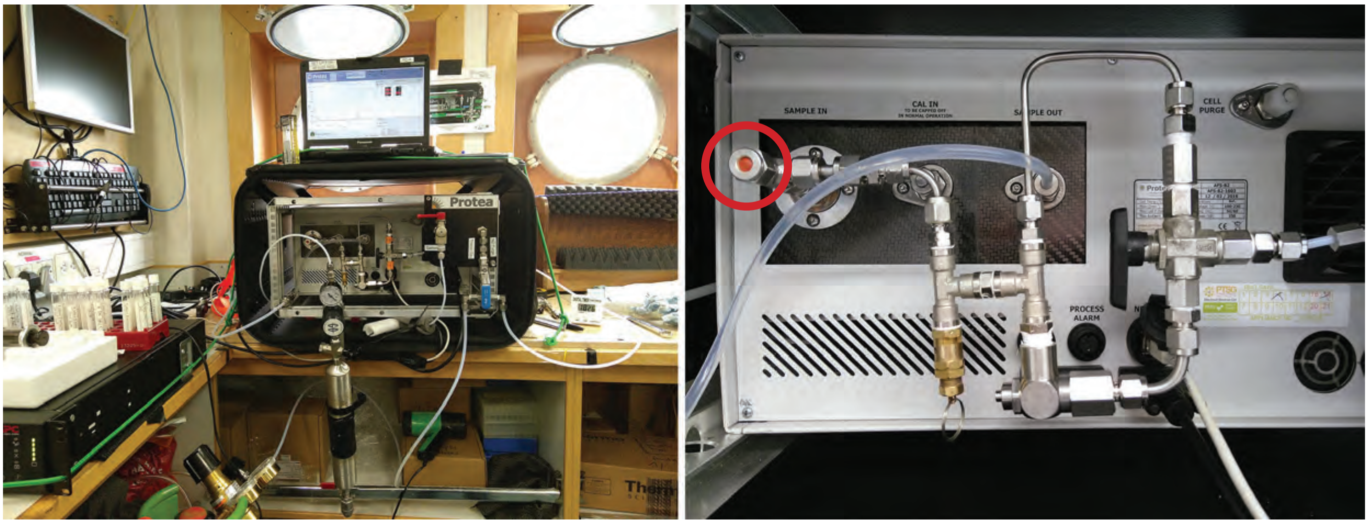


Figure 18: Gas analyser used for on board analysis of the gas composition. Red circle on the right-hand image indicates the sampling port used for retrieving discrete gas samples for Kr, $\delta^{13}C$ and $\delta^{18}O$ analysis. Images courtesy A. Flohr.

across the seabed. Agreement between these techniques was remarkably consistent, indicating that fluxes of gaseous CO_2 into the water column can be determined with a high degree of confidence:

- From active acoustic (hydrophone) detection of CO_2 bubbles at seeps
- From chemical analysis of CO_2 tracers in bubble gas samples
- From direct gas volume measurements made at bubble seeps by ROV (Fig. 17, 18).

Increased concentrations of dissolved CO_2 in the water column were detected using in situ sensors but these anomalies were restricted to within a few metres of seabed bubble seeps, even at the highest CO_2 injection rate of 50L/min (Fig. 20). Analysis of the seabed sediments showed that the injected CO_2 was not widely distributed, but rather confined to very narrow escape channels of less than ~5cm diameter.

Analysis of natural and artificial tracers showed unequivocally that CO_2 anomalies in the sediment pore waters and in the water column were due to the presence of injected CO_2. Even over the relatively short timescale of this release experiment, the seabed sediments were observed to react with the injected CO_2, with dissolution of both carbonate and silicate minerals. However, concentrations of heavy

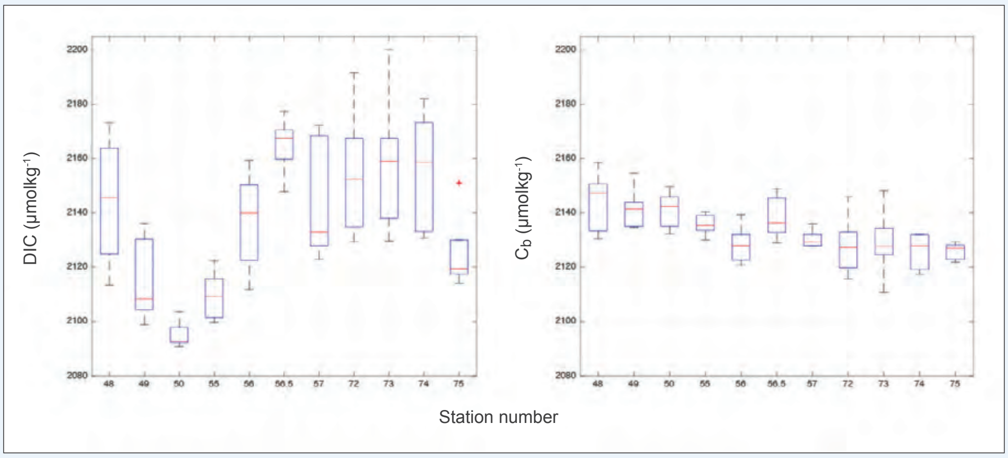
C_{seep} : a method for establishing baselines, detecting and quantifying CO_2 leakage in the ocean

The utility of a stoichiometric method called C_{seep} has been further developed and demonstrated during STEMM-CCS to estimate the quantities of CO_2 entering the water column during a leakage event. When CO_2 seeps through the seafloor and dissolves into the surrounding seawater a series of chemical reactions occur that ultimately increase the concentration of Dissolved Inorganic Carbon (DIC) and hydrogen ions in the seawater. Therefore, the extra carbon dissolved in the seawater (C_{seep}) should, in principle, be readily quantified from the resulting change in DIC (ΔC).

In practice, however, this is complicated by the fact that the dissolution of seepage CO_2 does not necessarily happen in isolation, but may occur in addition to natural DIC changes that result from processes such as formation/remineralisation of organic matter and/or calcium carbonate, mixing between water masses, and uptake of anthropogenic carbon.

The Cseep method addresses these challenges by employing process-based analyses to establish a baseline DIC concentration (C_b) with minimal dependency on spatial and temporal variations. The analyses are then repeated using monitoring data and the resulting concentrations (C'_b) are compared to C_b. The difference between these values is the C_{seep} concentration ($C_{seep}=C'_b-C_b$) and can be attributed to CO_2 seepage through the seafloor only when its values are greater than the uncertainty of the method - i.e. the detection threshold at a statistically significant level. Moreover, the values computed for C_{seep} directly quantify the extra carbon dissolved into the sampled seawater.

The C_{seep} method features process-based DIC analyses used to establish baseline values, detect the CO_2 seepage signal and simultaneously quantify the concentration of extra carbon dissolved in the sampled seawater. Therefore, used as a monitoring tool, this method can address several aspects of the current CCS monitoring requirements: background (baseline) measurements, assessment of CO_2 storage performance in the reservoir, detection of leakage, and (if leakage is detected, suspected or alleged) to quantify leakage and assess impacts[8].



Left: Box plot of measured background DIC (left) and computed baseline DIC (C_b) as a function of a sampling location i.e. station number. Based on historic (2001-2011) and new (2017) data acquired from a 2°x2° area around the depleted Goldeneye gas field in the North Sea. The plots demonstrate how the C_{seep} methodology minimises the spatio-temporal variability arising from natural processes.

metals in the pore waters did not increase significantly.

Fluxes of dissolved CO_2 across the seabed could not be determined from pore water profiles as these were chaotic, but remote eddy covariance techniques, tested for the first time by STEMM-CCS, were remarkably successful (see box, p22 for more detail).

Summary

All methodologies tested during the experiment were capable of detecting the leakage of injected CO_2, but only some were capable of detecting leakage at the lowest injection rates, or at distances of more than a metre or so above the seabed CO_2 seeps. Not all techniques were capable of quantifying the flux of CO_2 that escaped across the seabed.

The utility of different techniques for site operators can be summarised as follows. Gas migration through the seabed sediments can be detected remotely by sub-bottom profiler imaging (Chirp), but gas escape features need to be >~5cm in diameter. While ship-based echosounders readily detect the release of gas bubbles from the seabed, bubble fluxes are best quantified using hydrophones; however, they need to be located within ~10m of the gas seeps. As concentrations of dissolved CO_2 in the water column are highly variable, anomalies due to leakage are best demonstrated using stoichiometric techniques, such as C_{seep}. Suitable variables include the ratio of CO_2/O_2 both of which can be measured by in situ sensors with high precision. Fluxes of dissolved CO_2 across the seabed are best determined by analysis of artificial tracers that can be co-injected with CO_2 into the storage reservoir. Crucially, these tracers can also be used to unambiguously confirm the source of fugitive CO_2 emissions in the marine environment.

It is important to recognise that the CO_2 leakage rates tested by STEMM-CCS were relatively low (≤ 50 L/min). CO_2 leakage from a sub-seabed CO_2 storage reservoir is most likely to occur at the injection point, through faults or from abandoned exploration wells, which can be expected to have much higher gas flow rates (from ~100 L/min at abandoned wells, to ~50,000 L/min at the injection point). In these circumstances, the footprint of the CO_2 anomaly in both the seabed sediments and the water column can be expected to be significantly larger, which would greatly increase the utility of many of the methodologies tested by STEMM-CCS for leakage detection.

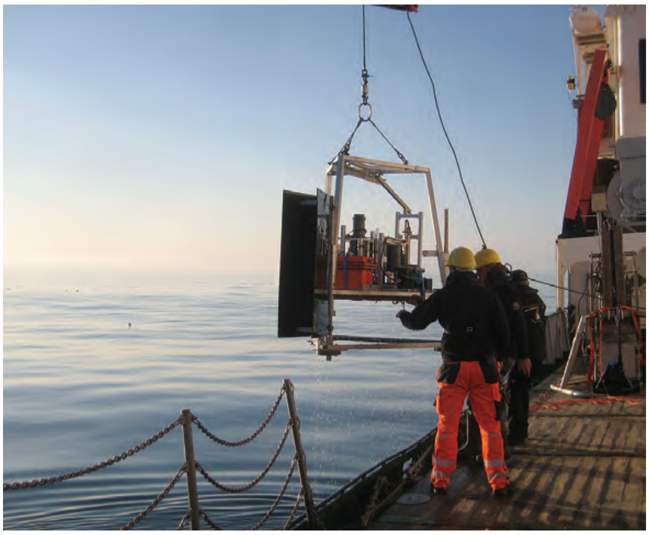


Figure 19 (right): Recovery of lander and sensors onto RV Poseidon after testing in the North Sea, August 2018. Image courtesy P. Linke.

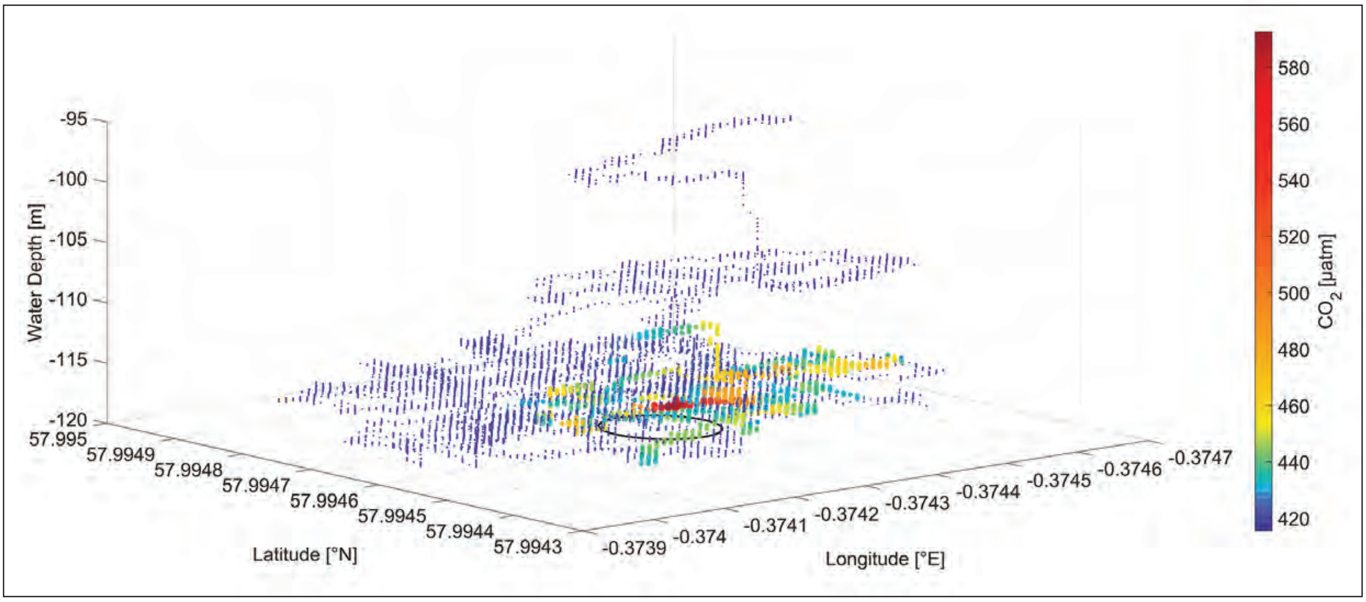


Figure 20: Map of the distribution of dissolved carbon dioxide measured in the water column above the sub-seabed CO_2 injection point (black ellipse) at the Goldeneye experimental site. Rate of CO_2 injection = 50 L/min. Image courtesy J. Gros (GEOMAR).

New sensing technology

Carbon storage in sub-seabed reservoirs requires assurance that the stored CO_2 gas remains contained, and that any leakage during and post injection is quickly detected, quantified and its impacts on the ecosystem evaluated. As part of its mission, STEMM-CCS addressed capability gaps in the instrumentation, sensors, observational systems and techniques required to reduce the cost and uncertainty in measurements of the environment at proposed and operational CCS sites for 1) site characterisation and selection, 2) baseline survey, 3) leak detection, 4) leak quantification, 5) environmental impact assessment and 6) mitigation/remediation decisions and efficacy assessment.

The principal technological innovations made during the STEMM-CCS project focused on the advancement of autonomous measurement technologies, including sensors and systems that use them, and their integration on autonomous and remotely operated landers and vehicles. In order to synthesise and process data produced by these measurement systems, the project also developed software tools to assist with decision support in monitoring system design, offshore CCS operation, and emission detection and quantification. Although there have been increasing efforts to reduce the cost of offshore data acquisition, the current state-of-the-art for marine observations remains dominated by physical sampling followed by laboratory analysis as part of ship-based surveys. STEMM-CCS developed chemical sensors to enable measurements of CO_2 leaks within the range of natural environmental variability, systems for measuring CO_2 (gaseous or dissolved) flux along the sediment water interface, and imaging systems with associated machine learning processing algorithms for biological mapping of the seafloor.

STEMM-CCS developed multifunctional sensor suites (carbonate system, nutrients, and dissolved oxygen) to enable accurate baseline biogeochemical surveys, measurement of pore water and reservoir water movement, and to provide contextual data improving observations of biological activity. New sensor technology included Lab-On-Chip (LOC) based wet chemical sensors for the determination of total alkalinity (TA), dissolved inorganic carbon (DIC), pH, nitrate and phosphate, and optical sensors (optodes) for the determination of dissolved oxygen and pH.

Quantification of emissions of CO_2 from a sub-seafloor reservoir that have transferred into the dissolved phase is a considerable challenge. In particular, measurements of fluxes from permeable sediments, such as those that cover much of the North Sea, are often inadequate because it is difficult to quantify pore water advection and hydrodynamic effects are excluded. To address this challenge, we have developed and integrated sensors with benthic lander systems for simultaneous, in situ analysis of the carbonate system (pH, TA, DIC), dissolved oxygen (DO), temperature and salinity directly above the seabed, and sediment microprofiling systems for high-resolution analysis of sediment chemistry that allow 3D fully automated determination of benthic fluxes.

Figure 21: Novel Lab-on-Chip (LOC) sensors (left) and dissolved oxygen (DO) optodes for autonomous in situ measurement of pH, TA and DIC integrated into landers and ROVs. Images courtesy NOC.

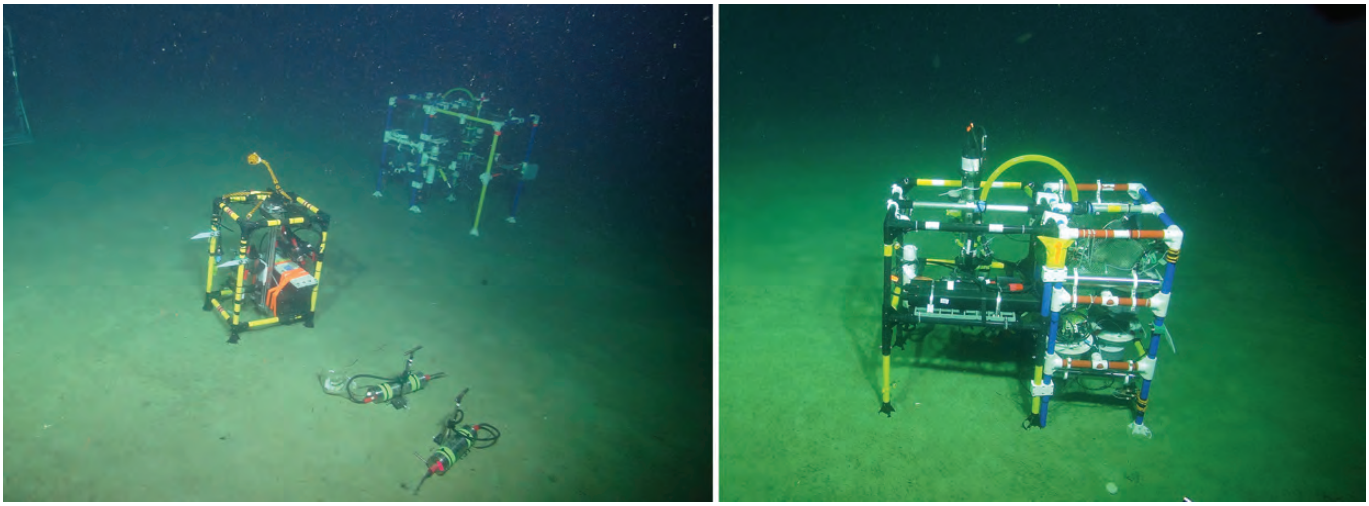
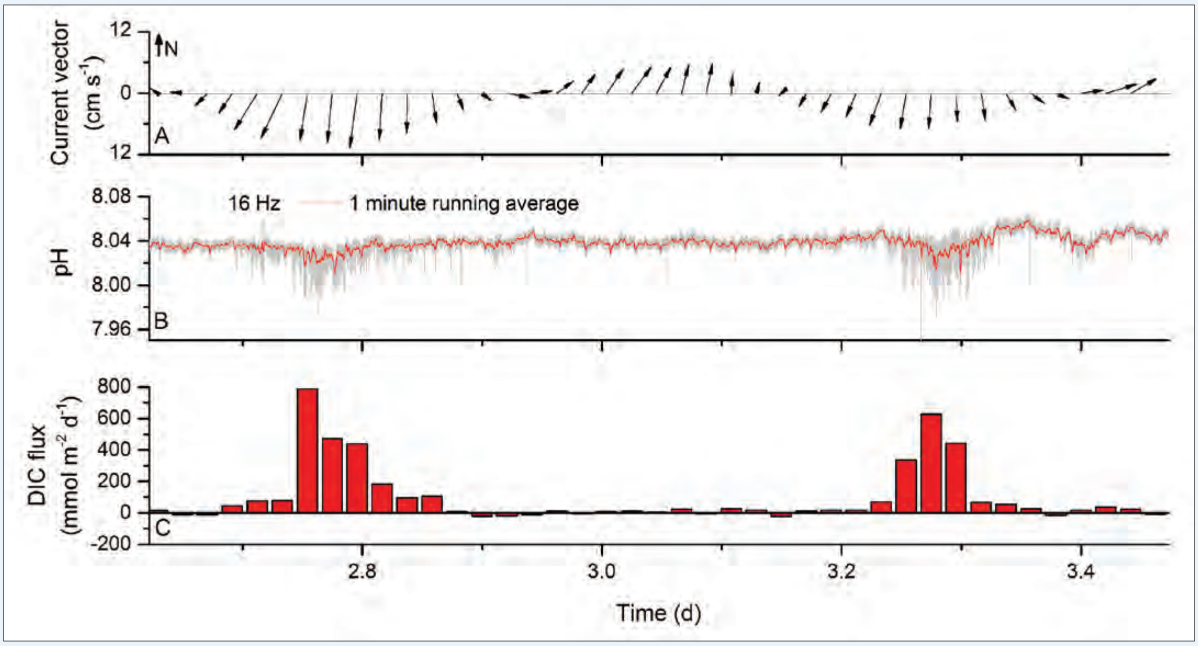


Figure 22: Sediment microprofiler (left) and benthic boundary layer lander (right) with integrated novel electrochemical, optical, and LOC wet chemical sensors for the determination of fluxes across the sediment-water interface. Images courtesy NOC/JC180.

Eddy covariance: A robust and sensitive tool for identifying CO_2 leaks at the seafloor

During a sub-seafloor CO_2 storage operation, a low pH anomaly at the seafloor is a geochemical signal that there may be a CO_2 leak. However, the risk of false positives is high. Low pH anomalies can also be generated by the natural production of CO_2 due to organic matter mineralisation. A useful geochemical tool could detect seafloor CO_2 sources, instead of the resulting anomaly in seawater pH.

Among the successes of STEMM-CCS is evidence that pH eddy covariance is highly effective at identifying a seafloor source of CO_2. At our lowest rate of experimental CO_2 release, the excess CO_2 in the water column created a subtle pH anomaly (Figure B). Viewed as eddy covariance flux, however, a clear seafloor source of DIC is seen to the north (Figure C). Natural production is observed in surrounding sediments and was confirmed with eddy covariance oxygen uptake. The source of DIC far exceeds natural DIC production. Therefore, the DIC source was abiotic. Based on these results, we suggest that pH eddy covariance would be a useful tool for detecting and attributing the source of a pH anomaly at the seafloor.



Above: Detection and quantification of the CO_2 bubble stream at the lowest release rate (5.7 kg d^{-1}) by pH eddy covariance. A) Current vector of water velocity and direction relative to north; B) pH time series with anomalies due to the CO_2 bubble stream; C) DIC flux calculated with pH eddy covariance.

Carbon dioxide flux from isolated leaks can be estimated by computation of mass balance with water column profiles and hydrological data (i.e. tidal flow, local turbulence) using a variation of techniques previously used to study oxygen flux. Sensors developed in STEMM-CCS were integrated with AUV (GAVIA) and ROV (ISIS) technology to enable proof of concept water column concentration profile and hydrological monitoring. Data generated by these techniques was used in models to enable CO_2 flux estimations.

We have used and further developed image annotation tools to annotate images collected during AUV surveys of the seafloor around CCS reservoirs, allowing automated detection of seafloor fauna and other features. An 'end to end' workflow by which images collected can be stored, pre-processed, and a set of training images can feed into the machine learning algorithms, the bulk of the images automatically annotated, and indicator analytics provided with graphics. This system maximises the effectiveness of pre-treatment and machine learning decision support vectors (i.e. decision trees) and can process photography-only indicators, as well as those that take in other inputs such as acoustic imagery, water chemistry, or seabed sampling. The combination of these tools and efficiencies for large-scale surveys mark a major innovation for marine mapping generally, as well as for capability in understanding the possible impacts of leakage from storage reservoirs.

To help future users to select the most appropriate methods for monitoring an offshore CCS storage complex before, during and after injection of CO_2 we developed an online monitoring and decision support tool to assist with the identification and prioritisation of appropriate monitoring techniques that could form part of a monitoring programme. This tool particular emphasis on (i) environmental baseline monitoring required to select an appropriate injection site, (ii) methods of detection and quantification that are appropriate during leakage and (iii) available sensors and platforms tested for CCS monitoring. It draws together results generated during the demonstration phase of the project and includes illustrations, indications of suitability and a cost-benefit analysis of each monitoring technique. This tool can assist with key operational decisions, principally: a) whether to continue injection at the current site or not; b) whether injection at an alternative site within the same complex is possible; or c) whether mitigation actions (e.g. well capping and other actions collated from literature and operational experience of our partners Shell and other stakeholders) are advisable. The tool can be accessed online at www.stemm-ccs.eu/monitoring-tool.

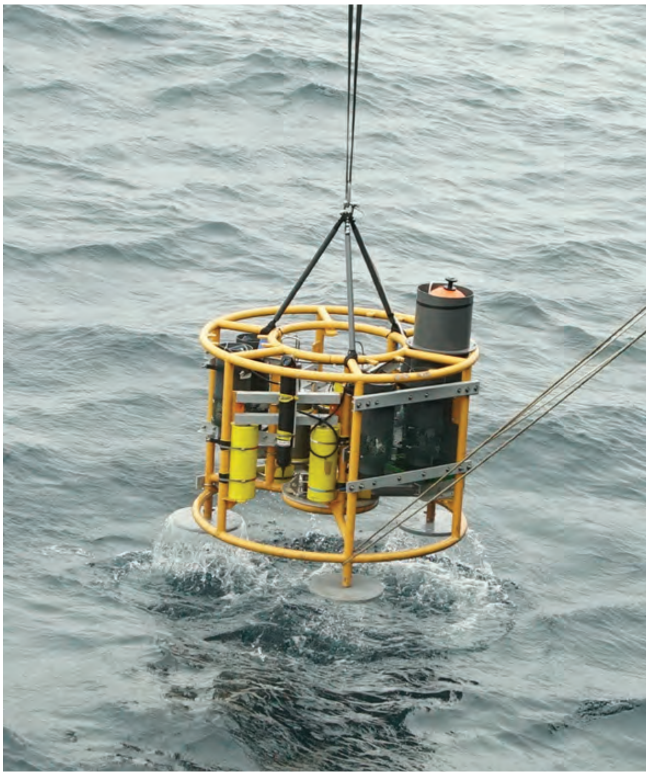


Figure 23: Deployment of sensors and lander at Goldeneye, May 2019. Image courtesy NOC.

Summary

STEMM-CCS has developed novel sensor technology that allows - for the first time - *in situ* characterisation of the marine carbonate system, thus enabling detection of CO_2 leaks from sub-seabed CO_2 storage sites. These technological advances include the design, development and demonstration of technologies for:

- CO_2 flux and leak measurement across the sediment-water interface, including benthic boundary layer landers for gradient flux, relaxed eddy accumulation measurements and sediment microprofilers.
- Collecting baseline environmental data, including landers equipped with novel chemical sensors for characterising natural biogeochemical variability at high resolution.

In addition, novel and commercial off-the-shelf sensors were integrated with a number of platforms including landers, AUVs and ROVs, for autonomous spatial and temporal high-resolution surveys of the CO_2 release site and profiling the CO_2 plume. STEMM-CCS has demonstrated that chemical sensor-based technologies can effectively detect and quantify CO_2 leakage from the seabed even in the absence of visual evidence (i.e. bubbles).

To help CCS operators assess and select an offshore, sub-seabed CO_2 storage site, STEMM-CCS developed and constructed an online tool, which can also assist with the identification and prioritisation of appropriate techniques that could form part of an operational site monitoring programme.

Computational techniques to aid monitoring and detection

Developing a monitoring system to facilitate the efficient assurance of storage integrity or the prompt and error-free detection of unintended emissions into the marine environment requires that we comprehend the signals of leakage, and how these differ from natural, often highly dynamic variability. This entails predicting the pathways of CO_2 transfer through sediments and across the sediment-water interface, the dynamics of gas bubbles, the movement and dispersion of dissolved CO_2 plumes and their impact on the marine chemistry, under a variety of environmental conditions. In addition, we need to characterise how these chemical attributes evolve due to natural biological and physical processes, which will always be site- and season-specific.

Marine observations and release experiments are expensive to undertake, and existing baseline data is biased towards the surface ocean and calm periods. However, the oceans are routinely described by models – typically time evolving, 3D coupled hydrodynamic-biogeochemical predictive systems which describe physical flows and biogeochemical fluxes, often explicitly modelling CO_2 chemistry. Systems using very high-resolution grids can predict the dynamics of individual CO_2 plumes as affected by sediment morphology, wind-, tidal- and circulation-driven mixing. These models, when properly quality controlled, provide a virtual marine environment or testbed within which we can quantify baselines, simulate unplanned release and assess monitoring strategies[9].

Understanding what leakage looks like (simulating leak dynamics)

In STEMM-CCS we developed a suite of model systems, (Fig. 24) which allow prediction of gaseous and dissolved CO_2 flow through sediment pore space, across the sediment-water interface, into the water column as a result of buoyant bubble plumes and further dispersal due to hydrodynamic flow in the water column[10].

As a result of this combined body of work we have a growing set of quantified release scenarios, ranging over at least seven orders of magnitude (see Fig. 28). Plume size (and therefore impact and detectability) primarily relates to

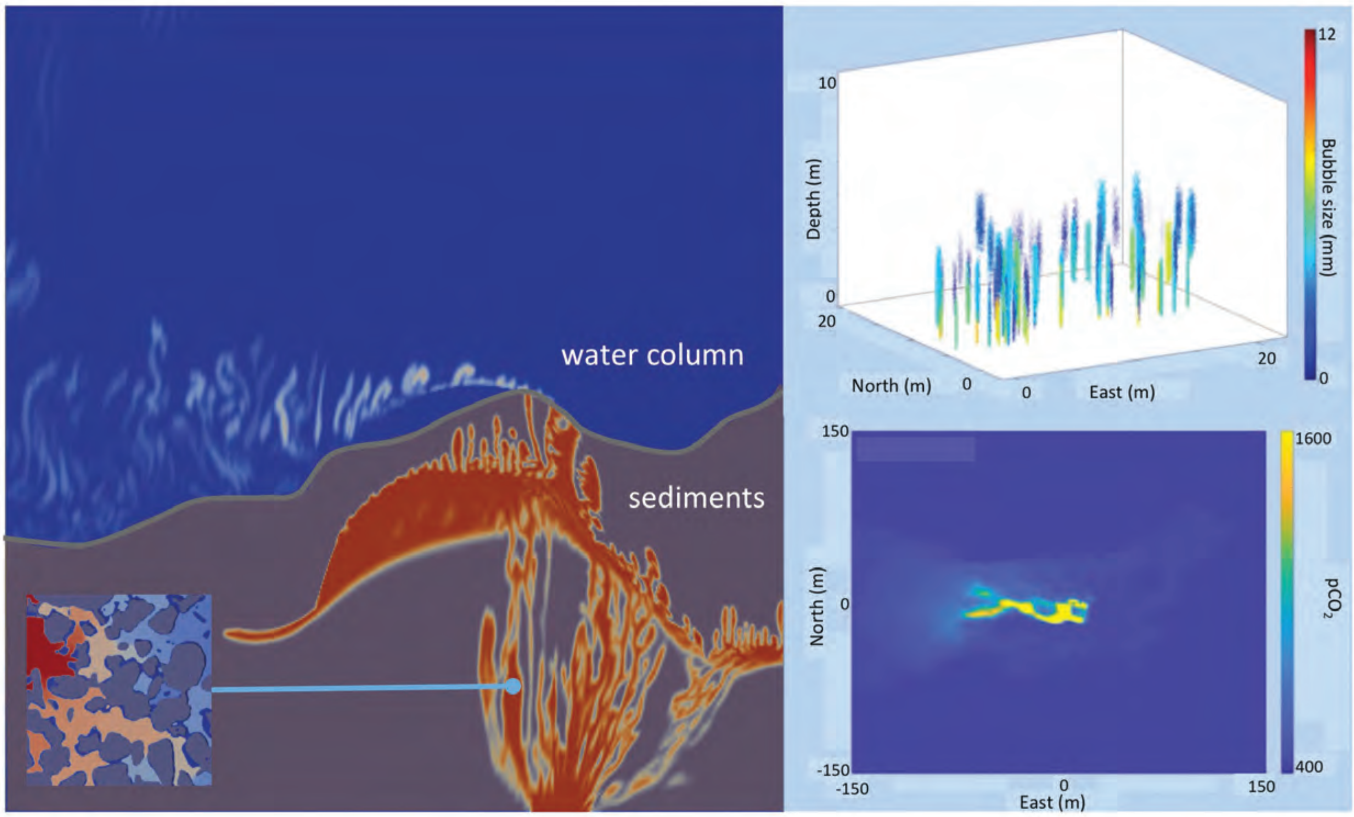


Figure 24: Main picture: Modelled flow through porous sediment (red) and into the water column (white) in the meter scale with inset flow through porous media at the pore scale. Top right: modelled CO_2 bubble plumes rising and dissolving in the water column. Bottom right: plan view flow of dissolved CO_2 concentration in the water column.

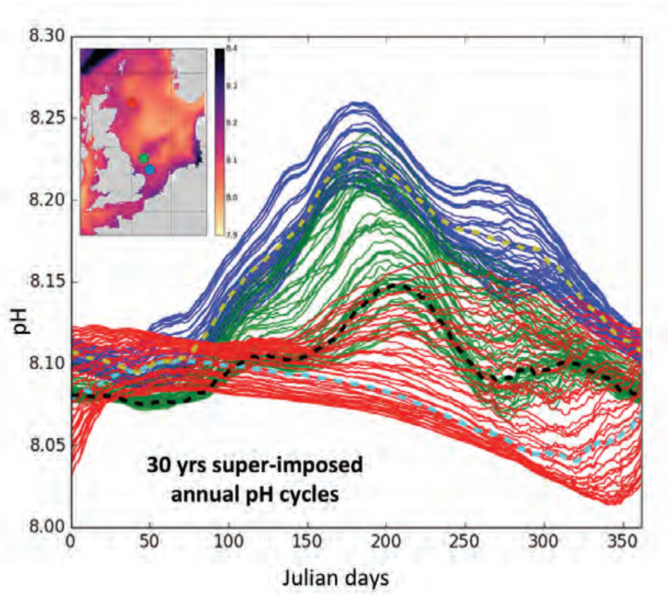


Figure 25: Modelled annual cycles of daily seafloor pH from three different sites over 30 years. Inset: Map of annual mean pH with sites identified by colour, (red – Goldeneye, blue – Endurance, green – Bunter formation.

release rate. Plumes are highly dynamic in space and time, often circulating around a release point on a tidal ellipse, with the strength of the perturbation decreasing with distance (Fig. 24). Because these models in their native forms tend to be computationally expensive, STEMM-CCS has also invested in the development of fast emulator models which allow multiple scenarios and statistical and machine learning approaches to monitoring optimisation (Fig. 28)[11, 12].

Understanding and quantifying natural variability

It is vital to understand the natural variability of marine CO_2 (Fig. 25) as this may mask the signal from an unplanned release and defines the unperturbed (baseline) state should an environmental impact assessment be necessary. Natural variability is driven by a complex range of factors, which include advection of water masses of different origin, influence of nearby riverine plumes, atmospheric CO_2, temperature, biological activity, in-situ mixing and geochemistry of the sediments. Conducting a comprehensive survey of the carbonate system to characterise the daily to seasonal to inter-annual and spatial variability of a particular storage site could be prohibitively expensive. However, evaluated coupled model systems enable us to predict and quantify natural variability and its heterogeneity. The example shown in Fig. 25 illustrates that within one regional sea, there are very distinct short-term, seasonal and inter-annual CO_2 dynamics near the sea floor, here using pH as a measure of concentration of CO_2[13].

Defining anomaly criteria for monitoring

Perturbations arising from a release may be small, and of a similar magnitude to natural changes in CO_2 concentration especially if monitored at some distance from a release point. The challenge therefore is to develop highly sensitive criteria that identify anomalous chemistry as distinct from natural dynamics, minimising the chance for false positives. By combining models of release scenarios and natural variability we can use this information to identify optimal detection criteria, identifying the most sensitive discriminators applicable to a given site or even season.

STEMM-CCS has developed two types of criteria, one based on departures from natural ratios of easily measured marine chemical components (C_{seep}; see p21)[14, 15], the other based on recognising unnatural rates of change in CO_2 concentrations[13]. The former is based on the fact that leakage only impacts CO_2 concentrations, whereas

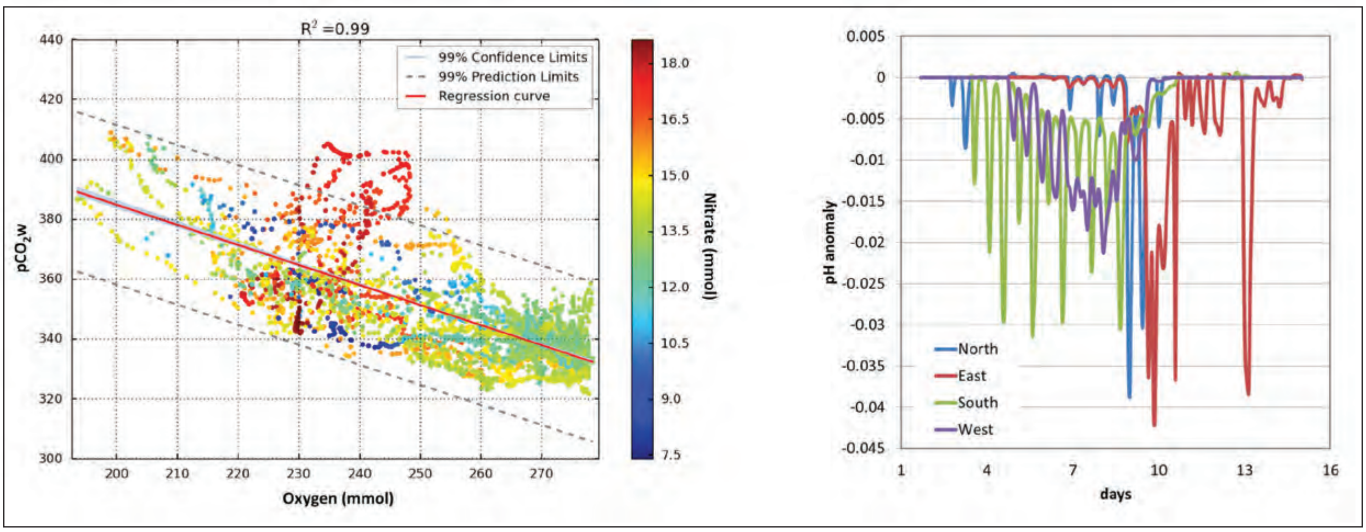


Figure 26: Left - illustration of covariance between pCO_2, oxygen and nitrate,. Right - anomaly signals as sensed at cardinal points around a leakage simulation, showing tidal signal.

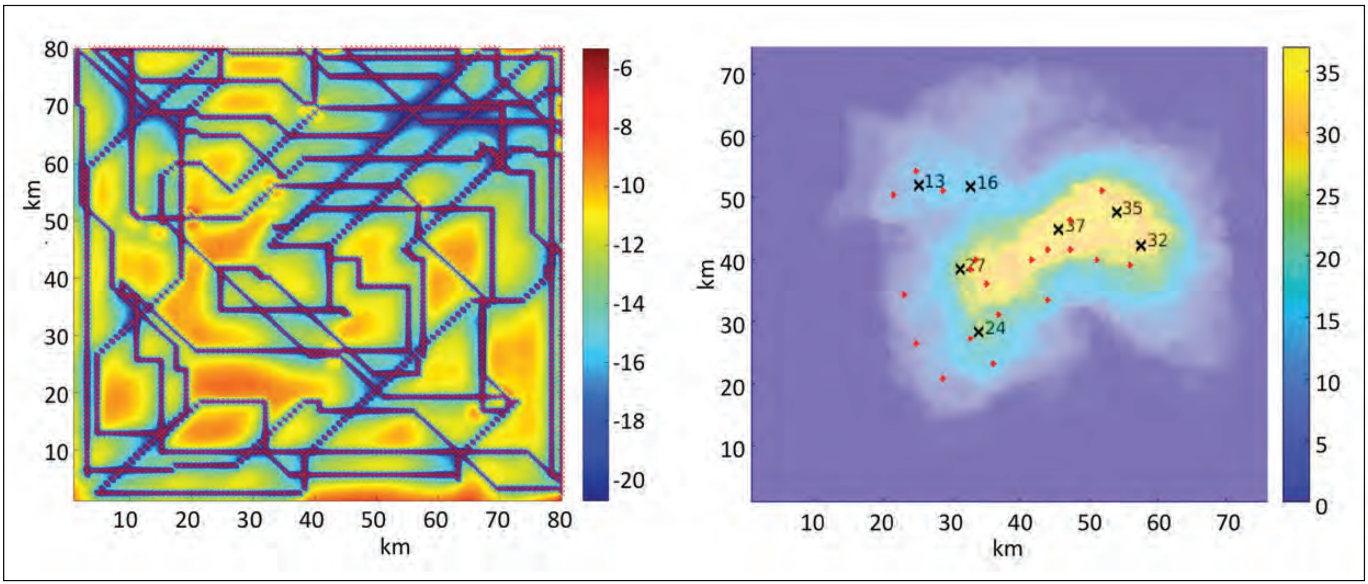


Figure 27: Left - Optimal path taken by an AUV[17]. Right - Optimal sensor placements using simulation of 36 leaks at different locations Sensors placed such that any of 36 leaks would be detected while keeping the number of sensors minimal[16].

natural processes that affect CO_2 concentration also have a proportionate signal in either physical (e.g. temperature) or biological (e.g. oxygen) variables. The latter utilizes the tidally induced mobility of CO_2 plumes, creating fluctuations over space and timescales that are different from the spatiotemporal gradients that result from natural processes. Both approaches allow us to define very sensitive discriminators of leakage (Fig. 26).

Monitoring strategies: optimising sensor deployment and locating leaks

Designing efficient, low-cost monitoring programs to detect discharges which could theoretically occur anywhere within an area of several hundred square kilometres is challenging. Building on knowledge of leak morphology, natural variability and anomaly criteria, models allow us to devise cost-efficient deployment of sensors to maximise detection. By quantifying how water movement impacts dispersion of CO_2 plumes, models can determine the minimum number of sensors and their optimal locations[16], or the optimal deployment pathway of Autonomous Underwater Vehicles (AUVs)[17] to maximise the likelihood of detection using Bayesian techniques[18] (Fig. 27).

Model simulations suggest that a release event of 1 T day^{-1} may be detectable at 50 m distance, scaling to 5 km distance for a 100 T day^{-1} release, although local hydrodynamics would cause significant variability in the detection length-scale.

Risk assessments and communication

Environmental risk assessments are generally required by permitting authorities. In STEMM-CCS we developed a meta-analysis of a large range of leak simulations, which shows a coherent relationship between a hypothetical leak rate and the potential area impacted[19] (Fig. 28). This analysis is also a useful tool for informing stakeholders (including the public) of risks. It shows that the potential

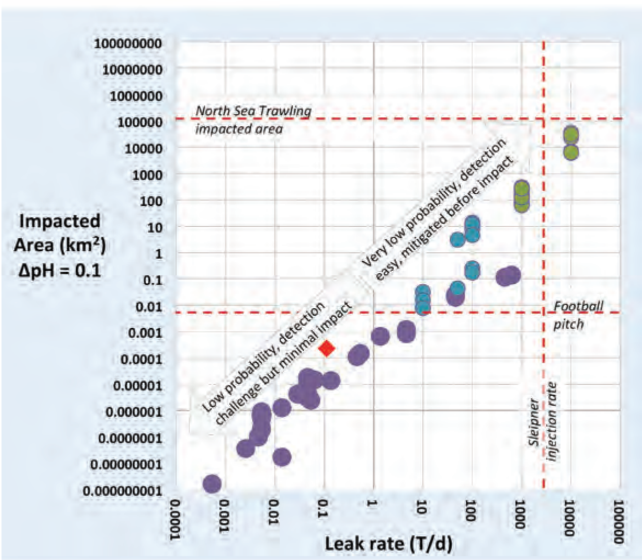


Figure 28: Model ensemble relationship between CO_2 release rate and impacted area. Different colours refer to different source models. The size of a typical football pitch is indicated as a reference point. A decrease of 0.1 pH unit is a conservative indicator of impact potential.

impact from a small CCS leak will be very local, and that only releases approaching the rate of storage are likely to have some degree of regional scale impact - which would be easy to detect and begin to mitigate. Importantly, potential risks from CCS must be contrasted with impacts of not performing climate mitigation, which are certain, global and severe.

Summary

A challenge for offshore CCS storage operations is that marine environments are so diverse that a generic definition of baselines, anomaly criteria and monitoring strategies will have little value, although the fundamental principles will be transferable from location to location. The positive outcome is that we can use models, ideally coupled with some observational data to ensure accuracy, to work out optimal criteria and strategies for individual storage sites, which will both minimise the cost of such monitoring whilst maximising rigour and thereby public acceptance.

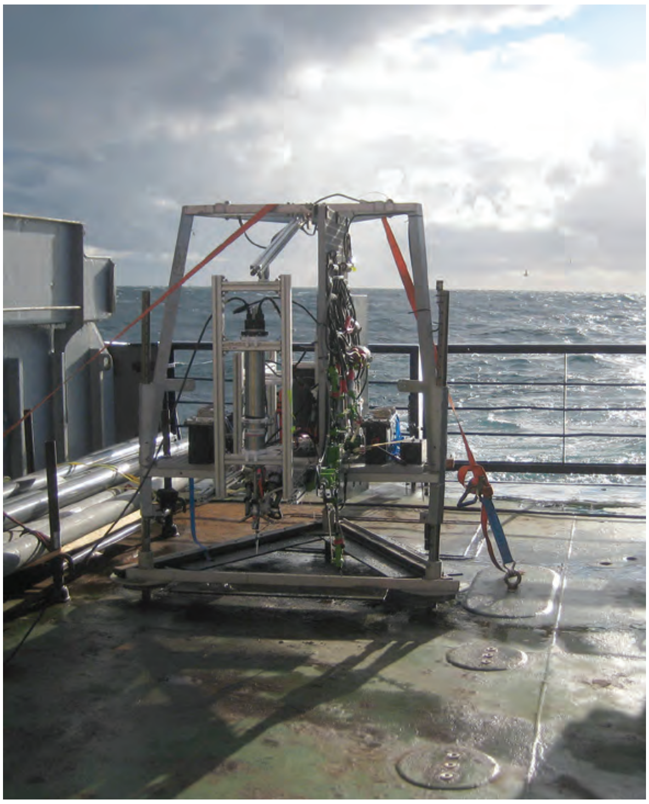


Figure 29 (right and below): Deployment of seafloor landers to measure environmental parameters at Goldeneye. Images courtesy D. Koopmans (right) and P. Linke (below).

Impact and conclusions

STEMM-CCS has been one of the most ambitious projects to be launched around the study of offshore carbon capture and storage. The principal aims included understanding and predicting risks from geological features that might act as conduits for leakage in future storage operations in marine basins, and to develop a suite of novel technology and approaches for marine monitoring of CCS operations. These technology developments are relevant not only to CCS but also to other offshore activities such as platform decommissioning and environmental impact assessments for offshore operations such as wind farm placement.

The STEMM-CCS project completed the first ever drilling of a pockmark at the Scanner site in the North Sea, providing new insights into how and when these features formed and delivering a reassuring assessment of their potential to act as points of connectivity to storage reservoirs. The impact of this is improved knowledge of CCS containment in different geological settings, which will help operators plan CO_2 reservoir site selection and design appropriate monitoring strategies.

The showpiece of our work was the first ever sub-seabed release of CO_2 in a "real-world" marine environment. Working with the subsea robotic systems specialists Cellula Robotics, we developed a novel engineering approach and hardware to place a pipe below the seabed sediments in order to release gas and simulate a breach in CCS reservoir caprock integrity. We also overcame significant technical challenges to achieve a means of placing the gas on the seabed in 120m water depth, with the capability to precisely release the CO_2 and mix it with a tracer prior to injection into the sediment. This experiment was designed to mimic and enable measurement of the various physical and chemical processes that CO_2 might undergo in a real-world CO_2 escape scenario, as well as providing a means to quantify the dissolution of the CO_2. The designs produced have a legacy in similar experiments around the world, with the Australian CCS community actively considering the reproduction and use of these designs in their field assessments of monitoring approaches in different marine environmental settings.

One of the challenges for operators of CCS reservoirs is to assure regulators that they can detect any accidental release of CO_2. Thus a large part of our efforts in STEMM-CCS centred on the detection of any release - either as bubbles, or in the more challenging dissolved phase. Since most offshore reservoirs have an extremely large footprint - for instance, the Goldeneye reservoir extends over more than 120km^2 - cost-effective methods for undertaking large environmental surveys must be developed. In the project we used an off-the-shelf Autonomous Underwater Vehicle (AUV) equipped with a set of observing technologies, including seabed imaging, sub-seabed imaging and sensors for chemical and physical measurements in the water column. We deployed state-of-the-art acoustic methods to determine if the escaping bubbles could be detected by sound, a relatively cheap and well understood methodology normally used to detect bubbles from surface vessels. A whole new family of in situ sensors were developed and deployed to measure pH, Total Alkalinity, CO_2 and nutrients. These build on many years of scientific and engineering effort and successfully detected and quantified the escaping CO_2, as well as its fate and impact on the local seawater and sediment chemistry. This demonstrated that CO_2 leak detection and quantification can be achieved using sensors and small vehicles, bringing significant implications for the cost of site monitoring and therefore long-term economic feasibility of CCS.

The project clearly and unequivocally showed that we have tools that are available to carry out precise and effective monitoring of offshore CCS reservoirs. We have a high level of confidence that we are able to detect small releases of CO_2 at levels that are applicable for the regulations being developed for the control of offshore CCS operations.

The tools and techniques that have been developed through the STEMM-CCS project are applicable to a number of offshore applications, thus our findings are expected to be of global interest for those involved in CCS as far away as Australia, Japan and the USA. To make the STEMM-CCS results better accessible to stakeholders, the suitability of the methods tested during the project for conducting essential offshore CCS monitoring tasks have been summarised through an online monitoring and decision support tool. This tool, available at www.stemm-ccs.eu/monitoring-tool, rates the relative effectiveness of each tested technique for conducting future offshore CCS monitoring, including site selection, leakage detection, source attribution, quantification and environmental impact assessment. In addition to summarising the relative cost, sensitivity of the method, spatial coverage, processing time and commercial readiness level of the different methodologies, this tool also provides stakeholders with recommendations for deployment strategies for each approach and the ability to cross-compare multiple techniques in order to select the most appropriate method for monitoring other offshore CO_2 storage complexes.

The technologies developed and advanced within STEMM-CCS have significant commercial potential. For example, the chemical sensors for nutrients, pH, and Total Alkalinity are part of the intellectual property that has led the creation of a new start up company, Solent Sensors, to commercialise environmental sensor technology. This company is working with the National Oceanography Centre to develop a license for this IP and plans to employ 40 people in the Solent area by 2023/24. This will directly benefit local and UK economies and provide a new commercial-scale tool for service industries (e.g. environmental and monitoring consultancies), as well as applications in terrestrial water supply, aquaculture and agriculture across Europe and beyond. This will deliver efficiencies alongside better environmental protection and management in these sectors.

In its four years of work, STEMM-CCS has invested in the development and training of young scientists across the spectrum of offshore CCS-relevant disciplines. More than 20 postgraduate (PhD) and postdoctoral researchers were directly involved in STEMM-CCS effort, and indeed they represent a critical component of the project's work force without whom it would have been impossible to achieve such significant scientific advances. STEMM-CCS has encouraged development (at all career stages) beyond the boundaries of everyday research by providing opportunities and financial support to undertake placements in industry and elsewhere in the CCS research community. A series of training events has enabled project researchers to broaden their perspectives, learn from CCS experts outside the consortium, and strengthen their use of cross-platform tools and techniques to increase the impact of their research. The project has also undertaken outreach and dissemination activities with local communities who may be affected by CCS operations in the North Sea, and provided a range of resources to those wanting to learn more about the environmental aspects of offshore CCS.

In summary, STEMM-CCS has successfully developed and tested a robust methodology for establishing environmental and ecological baselines under 'real life' conditions. It has developed a suite of cost-effective tools to identify, detect and quantify CO_2 leakage from a sub-seafloor CCS reservoir, including an assessment of the utility of chemical tracers in the marine environment. Results have enabled the modelling and assessments of the local, regional and wider impacts of different reservoir CO_2 leak scenarios, including the potential role that fluid pathways in the shallow subsurface may play in reservoir integrity, and a decision support tool has been developed to assist operators in monitoring, mitigation and remediation actions. STEMM-CCS has delivered best practice for selection and operation of offshore CCS sites, and results have been shared with industrial and regulatory stakeholders in order to help increase confidence in the physical security of CCS, and to support the European Union on its journey towards a carbon neutral society.

RRS James Cook and the Goldeneye platform, as viewed from RV Poseidon in May 2019. Image coutesy P. Linke.

A word from the STEMM-CCS Scientific Advisory Board

STEMM-CCS has been an exciting and unique project that has advanced offshore environmental monitoring, specifically CO_2 leakage detection, attribution and quantification, and CO_2 storage site characterisation. It has been a complex undertaking, with work ranging from deployment of small state-of-the-art sensors, and long-term monitoring systems on the seabed, to engineering a CO_2 release system under the seabed, - with everything operating at 120m water depth. The partnership represented the leading marine research organisations in the EU and Norway.

In particular, the results of the STEMM-CCS project are being influential in Europe and beyond, notably in Japan and in the USA. The sensors and methodologies are being seen as valuable for all projects based on CO_2 geological storage offshore. I look forward to seeing the results of STEMM-CCS being applied around the world.

The highlight for me, after the successful field experiment of course, was getting the results presented in the annual London Convention meeting in October 2019. This coincided with a key development in the London Protocol: to consider allowing export of CO_2 for geological storage offshore - the last big international legal barrier for CCS. I will spare the detail, but this wasn't a given, and the London Protocol Parties rely heavily and appropriately on scientific evidence in its decision-making. STEMM-CCS helped provided this, along with IEAGHG and the IPCC Oceans and Cryosphere report, with an excellent summary of the project presented by Professor Doug Connelly.

Feedback on the STEMM-CCS presentation, received from the former chair of the London Convention's Scientific Group, Craig Vogt (ex US EPA), was notable: "We wrote the words in the guidance document in 2006 with good intentions, and now we have just seen the STEMM-CCS project prove we can do what we wrote". The guidance document referred to is the CCS-specific guidelines for regulators and operators to issue permits, including requirements for environmental monitoring.

I am very pleased to say that on 11 October 2019 the London Protocol Parties approved the Provisional Application of the 2009 CCS Export Amendment. This allows countries to agree to export and receive CO_2 for offshore geological storage. This now removes the last significant international legal barrier to CCS, and means that CO_2 can be transported across international borders to offshore storage. Thanks to STEMM-CCS for helping provide the scientific assurance to give countries confidence for environmentally sound CCS offshore.

Tim Dixon
General Manager
IEA Greenhouse Gas R&D Programme

It has been a pleasure to closely follow the cutting-edge research of the STEMM-CCS project over the past four years via the Scientific Advisory Board. As a geochemist who has implemented an array of environmental monitoring programs at several large-volume terrestrial CO_2 projects, I was interested to see the science of developing marine CCS environmental monitoring protocols. One of the things I learned is that anything done in the marine environment is orders of magnitude more difficult than its counterpart on land.

From the very beginning, I saw the project as being extremely ambitious in its goals, tackling some of the most challenging and important aspects of monitoring in the marine environment. I was eager to see how a large multi-disciplinary international team could manage, implement and integrate all the facets of such an innovative project in such a short time frame. Throughout all phases of the project, I saw a seasoned scientific team collaborating to make the work look effortless, but I know that was not the case. Hard work, dedication, and sleepless nights were undoubtedly a very big part of the equation that lead to the success of the project. A project that has achieved scientific advancement in wide-reaching areas such as engineering a first-of-its-kind sub-

seabed controlled release; developing state-of-the-art sensor and data transmission technology; overcoming the overwhelming difficulty of environmental baseline variability, and gathering elusive data on fluid escape structures.

All these advancements are necessary for CCS to reach the level of deployment required for reducing CO_2 emissions in accordance with the goals of the Paris Agreement, and for ensuring the safety and effectiveness of the technology. STEMM-CCS has now developed and tested a wide range of monitoring technologies and approaches. The 'learning-by-doing' and experience gained is irreplaceable. The next step is to take the learnings from STEMM-CCS and apply them to larger-scale CO_2 injection projects. In this way, the most reliable and effective monitoring tools are integrated into the economic and regulatory aspects of larger-scale projects to pave the way for technology implementation at scale. With the excellent work and outcomes of the STEMM-CCS project, the science is ready and waiting for the projects to come.

Katharine Romanak
Research Scientist
University of Texas at Austin

ROV ISIS being recovered to RRS James Cook during the controlled release experiment in May 2019, with the Goldeneye platform in the background. Image courtesy C. Pearce.

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The STEMM-CCS partnership

For more information about STEMM-CCS:

Prof. Douglas Connelly, Project Coordinator
National Oceanography Centre
European Way
Southampton
SO14 3ZH
United Kingdom
douglas.connelly@noc.ac.uk

www.stemm-ccs.eu @STEMM_CCS_EU STEMM-CCS@noc.ac.uk

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