



Assuring the integrity of offshore carbon dioxide storage

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ABSTRACT

Carbon capture and storage is a key mitigation strategy proposed for keeping the global temperature rise below 1.5 °C. Offshore storage can provide up to 13% of the global CO₂ reduction required to achieve the Intergovernmental Panel on Climate Change goals. The public must be assured that potential leakages from storage reservoirs can be detected and that therefore the CO₂ is safely contained. We conducted a controlled release of 675 kg CO₂ within sediments at 120 m water depth, to simulate a leak and test novel detection, quantification and attribution approaches. We show that even at a very low release rate (6 kg day⁻¹), CO₂ can be detected within sediments and in the water column. Alongside detection we show the fluxes of both dissolved and gaseous CO₂ can be quantified. The CO₂ source was verified using natural and added tracers. The experiment demonstrates that existing technologies and techniques can detect, attribute and quantify any escape of CO₂ from sub-seabed reservoirs as required for public assurance, regulatory oversight and emissions trading schemes.

1. Introduction

Capturing and storing CO₂ (CCS) is an accepted strategy for mitigating climate change [1] by removing the CO₂ from the atmosphere and reducing global warming. Storage of CO₂ has been demonstrated

both onshore and offshore in aquifers or depleted hydrocarbon reservoirs. Offshore storage provides the largest and probably most cost-effective means of developing >100 GT storage by 2050 [2]. To date, particularly in the USA, enhanced oil recovery is commonly used for onshore storage, although the storage is not long term as the CO₂ is recycled for further use. Recently the U.S. Department of Energy has

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List of abbreviations

CCS	Carbon Capture and Storage
MMV	Measurement, Monitoring and Verification
IPCC	Intergovernmental Panel for Climate Change
ROV	Remotely Operated Vehicle
AUV	Autonomous Underwater Vehicle
ISFET	Ion Sensitive Field Effect Transistor
DIC	Dissolved inorganic carbon
ORP	Oxidation-reduction potential
VPDB	Vienna Pee Dee Belemnite
STEMM-CCS	Strategies for the environmental monitoring of marine CCS

identified the Gulf of Mexico as a region for long term offshore CO₂ storage [3] and is investing in exploring this potential. Most other countries with CCS ambitions are using offshore storage reservoirs: Japan has an offshore demonstration CCS project at Tomakomi, Australia has recently passed a bill that allows large scale offshore carbon dioxide storage, and in Europe most operating, and planned, storage facilities are offshore (e.g., Snøhvit, Sleipner). The main barriers for the wider use of CCS are political, public acceptance and the perceived cost of initial and ongoing operations. To promote investment in CCS, Europe has an incentivising regime, the European Union (EU) Emissions Trading Scheme (ETS), that rewards companies for permanently storing CO₂. The United States of America have recently introduced carbon capture tax credits (45Q) of up to \$50 per ton of CO₂ stored permanently [4]. A secondary issue is the long-term liability for secure CO₂ storage over the whole project lifecycle, including after injection operations have ceased.

Safe, long-term containment of geologically stored CO₂ both onshore or offshore is ensured with risk-based Measurement, Monitoring and Verification (MMV) programmes public reassurance and compliance with legislation [5]. Monitoring of offshore CO₂ injection wells and changes in the subsurface reservoir follow well developed standard industry approaches. However, monitoring of offshore storage reservoirs requires novel methodologies to detect, attribute and quantify leakage defined as CO₂ seeping into the water column [4]. Robust monitoring is required for public assurance and for qualification for tax credits under the EU ETS [6]. The consensus is that the risk of storage failure is considered very small [1] but these risks must be considered in a regulatory sense. Large scale breaches of containment will potentially have more impact but would be relatively easy to detect due to loss of pressure at the injection point. However, detecting a small leak within a large area of the seabed, with often poorly understood ‘normal’ conditions, makes monitoring a challenge, and quantification of fugitive emissions remains difficult [7].

Attribution of CO₂ must be done to avoid ‘false positives’. Natural sources of CO₂ in marine systems (e.g., biological respiration of organic material) cause variations in seawater inorganic carbon concentrations, increasing CO₂ and decreasing pH in the water column. A variance above a calculated threshold around a CCS demonstration project in Japan halted operations because it was assumed the reservoir integrity was breached. A subsequent investigation showed the CO₂ came from the microbial degradation of organic matter from a surface water phytoplankton bloom (Jun Kita, METI pers comm.). The identification of low error, high sensitivity anomaly criteria is therefore paramount.

A range of computational approaches are able to quantify impact from leakage and suggest cost-effective strategies for monitoring. These models combine benthic, hydrodynamic, and biogeochemical processes to describe the evolution of multiphase CO₂ plumes in the environment [8,9]. From these models one can derive highly sensitive low error criteria that distinguish anomalous CO₂ from natural variability, based

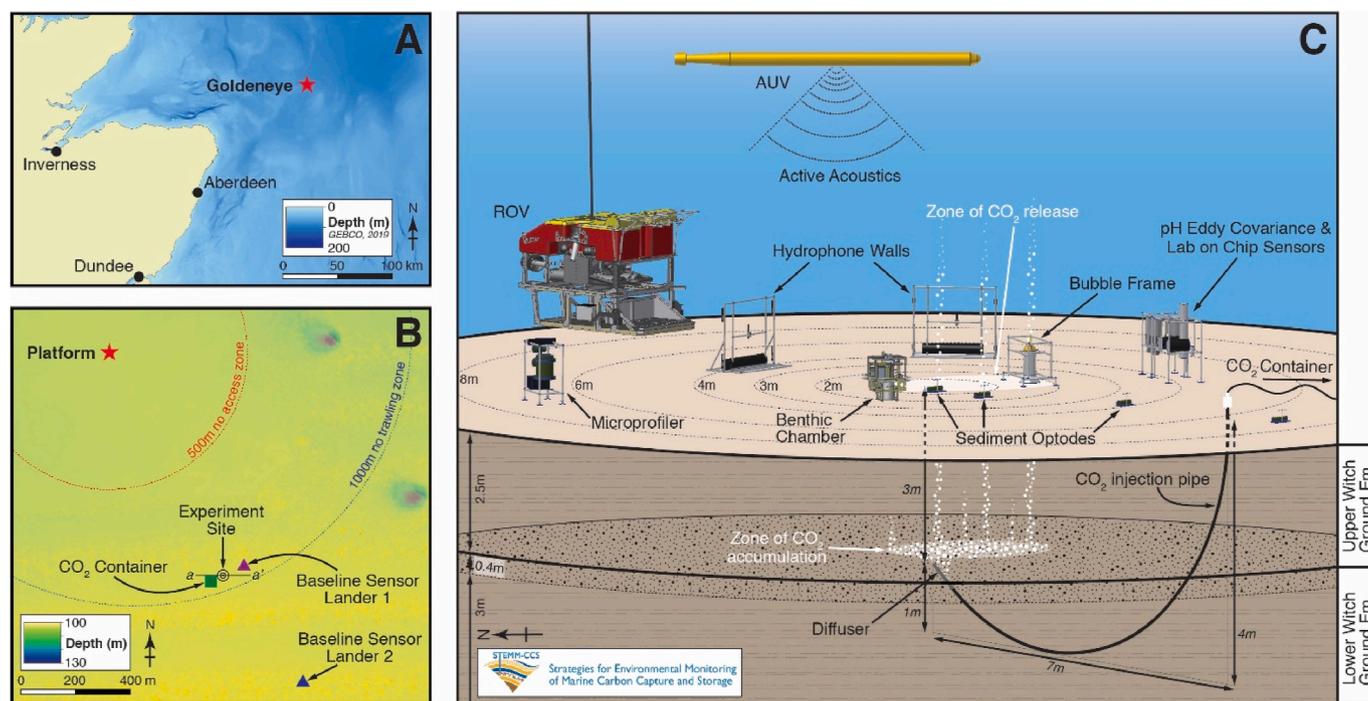


Fig. 1. Location and experimental geometry of the controlled CO₂ release experiment in the North Sea at 120 m water depth. **A**, Regional map showing the location of the Goldeneye Platform (red star), ~130 km NE of Aberdeen. **B**, Location of the controlled release experiment site SE of the Goldeneye Platform, seabed CO₂ container (~80 m SW of the experiment site), Baseline Sensor Landers. Chirp sub-bottom profile transect (a-a'; Fig. 3). **C**, Detailed experimental geometry around the locus of the release showing seabed instrumentation deployed by a Remotely Operated Vehicle (ROV). The CO₂ release was 3 m below the sediment surface immediately below a 30–50 cm thick sandy layer (stippling) at the top of the Lower Witch Ground formation. The rest of the Lower Witch Ground formation (~3 m) and the overlying Upper Witch Ground formation (~2.5 m) comprise moderately sorted sandy and silty muds.

on monitoring rates of change [10] and by defining stoichiometrically constrained multivariate bounds on CO₂ concentrations [11]. Simulated CO₂ release scenarios can then be used to guide optimal placement of sensors [12] and routing of autonomous vehicles [13] to deliver low cost and high assurance monitoring strategies.

To test the model predictions, as well as current and evolving technologies and techniques for detecting, attributing and quantifying leakage, a sub-seafloor CO₂ leak was simulated at a proposed CCS site.

2. Methods and logistics

2.1. Site selection

The chosen experimental site was above the Goldeneye hydrocarbon complex in the North Sea, located approximately 100 km north-east of Aberdeen, Scotland (Fig. 1a). The Goldeneye storage complex is a proposed CCS reservoir. The water depth at the experimental release site was 120 m. The site was situated 800 m from the platform (Fig. 1b), where near-surface sediments of the Witch Ground Formation are relatively soft, comprising 2.5 m of silty sediment overlying a 0.4 m sand layer, that in turn overlies a layer of silty mud between 8 and 17 m thick [14] (Fig. 1c).

2.2. Gas supply and control

Creating a simulated CO₂ leak at the Goldeneye site was technically challenging, the sub-seabed gas outlet was achieved by inserting a rigid, pre-curved steel pipe downwards into the sediment such that it followed its own curvature to describe a U-shaped path with its leading end stopping 3 m below the sediment/water interface and 1 m above its lowest point. The outlet end being significantly higher than the lowest point was designed to prevent the gas from tracking back up the outside of the pipe/sediment interface. Horizontally, the outlet end was approximately 7 m distant from the insertion point which, allowing for the landing footprint of the insertion rig, guaranteed the seabed surface remained undisturbed for at least 5 m from the outlet. The inlet end of the pipe remained protruding approximately 0.5 m above the seabed and was equipped with a quick-connect coupling for later connection to the gas supply.

The pipe insertion rig was a bespoke machine designed and built by Cellula Robotics (Burnaby, Canada). It comprised a 2.3 m cubic steel frame housing a subsea hydraulic power pack and a set of drive rollers that clamped the outside of the pipe and drove it axially into the sediment. The 6-tonne rig was complemented with lights and live video that enabled confirmation of a suitable site prior to landing (e.g., free from rocks or debris) and monitoring progress of the insertion process. Other features included a USBL beacon for recording of precise insertion location and a compass to indicate direction of the inserted pipe.

The rig was powered electrically and hydraulically from the ship via an umbilical cable that also carried engineering data and live video. The rig remained attached to the ship's winch wire throughout the insertion process and was recovered immediately on completion.

The CO₂ gas supply was stored in liquid state in a pair of 2.8 m³ capacity bespoke storage tanks, connected to act as one storage volume. This tank was sufficient to accommodate 3 tonnes of liquid CO₂ with a 1.7 m³ vapour headspace at 20 °C. Cryogenic storage was not viable offshore so the tanks were uninsulated and the CO₂ was stored at ambient temperature; water temperature at the 120 m deployment depth was around 8 °C which resulted in a gas pressure of 42 bar. The two tanks were mounted in a steel deployment frame of similar size to a 20-foot ISO shipping container. The frame also housed the additional tracer gases, gas mixing and control equipment, batteries, and flexible hoses for connection to the sub-seabed release pipe. CO₂ was supplemented with precise ratios of tracer gases (58.98 ppm Kr, 1.77 ppm SF₆, 0.11 ppm C₃F₈).

The gas tank frame was deployed over the aft of the ship and lowered

to the seabed 80 m distant from the release pipe (Fig. 1B) to minimise any water flow disturbance at the release site during the experiment. A flexible, non-buoyant hose was extended from the gas tank frame by the Remotely Operated Vehicle (ROV) and connected to the quick-connect coupling on the exposed release pipe inlet. The gas flow was controlled by adjusting flow controllers on the gas frame using the ROV. The release rate was increased over the course of the experiment from zero to 286 kg/d.

Sensors of various types, described below, were placed on the seabed around the expected point of gas release using the ROV. Once gas was seen bubbling out of the sediment the locations of the equipment was further refined to ensure the optimal positioning for the various approaches used for gas detection, attribution and quantification. The ROV was also used to sample water and gas above the release site and replace/relocate the sensing systems when needed (Fig. 1C). Close to the release site the ROV was used to map the distribution of the dissolved CO₂, using high sensitivity optode based pH sensors alongside off the shelf ISFET based sensors. The mapping involved precisely driving the ROV on several vertical and horizontal transects across the experimental release site.

2.3. pH eddy covariance

Eddy covariance is a technique that has been used to calculate fluxes from sediments into an overlying water column. The eddy covariance flux [15] of hydrogen ions was calculated as the product of high frequency (5 Hz) turbulent fluctuations in vertical velocity and hydrogen ion concentration. The measurement location was 16 cm above the seafloor and 2.6 m from the approximate centre of the bubble streams. Vertical velocity was determined with an acoustic Doppler velocimeter. Hydrogen ion concentration was determined with an Ion Sensitive Field Effect Transistor (ISFET) mounted in a flow-through housing [16]. A gear pump pulled water from the measuring volume of the velocimeter to the ISFET at a flow rate of 0.15 L min⁻¹. The gear pump periodically reversed flow direction to expel accumulated debris. The ISFET signal was amplified ten-fold by a custom-built, auto-zeroing amplifier with temperature compensation. An AgCl reference electrode, with ceramic membrane to reduce velocity-sensitivity, was used in conjunction with the ISFET. The 90% response time of the ISFET signal was 1.2 s. The flux of hydrogen ions was calculated in half-hour intervals according to standard eddy covariance procedures [17]. The dissolved inorganic carbon flux was calculated from hydrogen ion flux using the known equilibrium change in seawater pH caused by a known addition of CO₂ [18]. For those calculations, the carbonate system was characterized by lab-on-chip measurements of pH [19,20] and alkalinity made immediately beside the eddy covariance sensors during the experiment.

2.4. Chemical gradient measurements for CO₂ flux measurements

Lab-on-chip sensors were mounted on landers and measured the pH and alkalinity at approximately 2.6 m south of the plume [20]. Each sensor had two intakes, at two heights above the seafloor (17 cm, 87 cm), and alternated measurements between these to characterize the time-dependent vertical gradient of each parameter. The current magnitude and direction were each measured at two heights: at 16 cm, with the current meter on the eddy covariance system on the same lander, and at 1.2 m with a current meter on the on another lander, 375 m away.

The total excess dissolved organic carbon (δDIC) contained within the plume was estimated from this data by taking advantage of the fact that the ellipsoidal currents caused the entire plume to sweep over the sensors once per tidal cycle. By summing the δDIC(t) over a tidal cycle we estimated the total δDIC of the plume during that cycle. To achieve this, pH and alkalinity data from the sensors were converted to DIC using the CO2SYS software [21,22] (using the time-averaged alkalinity value of TA = 2311 μmol/kg and with nutrient concentrations, temperature T

Table 1

Summary of CO₂ injection flow rates at 120 m water depth and associated volumes and masses.

Start (date time UTC)	End (date time UTC)	CO ₂ injection		
		Normal L/min	g/min	kg/d
May 11, 2019 15:19	May 14, 2019 15:27	2	4	6
May 14, 2019 15:27	May 15, 2019 06:48	5	10	14
May 15, 2019 06:48	May 17, 2019 16:54	10	20	29
May 17, 2019 16:54	May 19, 2019 15:50	30	59	86
May 19, 2019 15:50	May 22, 2019 11:17	50	99	143

= 7.74 °C, and salinity $S = 35.25$ as measured in the area). The two points of $\delta DIC(t)$ at the lander were used to parameterize a full vertical $\delta DIC(z,t)$ distribution based on a model of the bubble dissolution at the source. The vertical current profile $u(z,t)$ was estimated with the current measurements and a log-law velocity profile.

The total mass flow rate Q of the CO₂ into the water column at each point in time was estimated by

$$Q(t) = \int_{seafloor}^{openwater} \delta DIC(z,t) * u(z,t) * w(t) dz$$

where $w(t)$ the physical east-west width of the plume that each measurement represents, z water depth. $w(t)$ was estimated by combining the duration of the measurements with the setup geometry and time-varying current direction. To estimate the total content of the plume, the values of $Q(t)$ for each complete current cycle were summed.

2.5. Impacts of CO₂ release on sediment porewater chemistry

The release of CO₂ into sediments can alter the chemistry of porewaters in sediments and these changes could potentially be used as indicators of leaking CO₂ from storage sites. To assess this we deployed an autonomous deep sea microprofiler, to look at chemical changes in the upper 10 cm of the sediments. Microprofiles were measured in the sediments along 4–20 m long transects from the outside of the area towards the vent area. The in situ deep-sea microsensor profiler [23] was equipped with microsensors [24] for O₂, H₂S, pH, ORP (oxidation-reduction potential) and temperature. In addition the ROV took core samples up to 30cm in length which were analysed for redox sensitive elements such as iron and manganese.

2.6. Acoustics

To determine if it was possible to image gas in the sediments above the release site we used a high resolution seismic reflection data collected using a chirp profiler (14–21 kHz) integrated on a GAVIA Autonomous Underwater Vehicle (AUV) system. The AUV-chirp data was collected at either 2 or 7.5 m elevations above the seabed, with a line separation of 2–5 m. The data has a vertical resolution of 2 cm and a horizontal resolution at a depth of 3 m (i.e. the release point) of 70 cm–100 cm.

To demonstrate the use of acoustic system for the flux of the gas from the sediments an array of 5 calibrated hydrophones was deployed 3.3 m (Fig. 1) away from the locus of injection to record the acoustic signature of gaseous CO₂ bubbles emitted from the seabed into the water column and calculate CO₂ fluxes using inversion methods [25].

Further details of the experimental design and logistics can be found in Flohr et al. 2020 [26].

3. Results and discussion

During the experiment 675 kg of CO₂, with added tracers, was injected at 3 m depth into the sediment over a period of 12 days [26]. The release of CO₂ was initiated at 6 kg day⁻¹ on May 11, 2019 and the flow rate was increased in a stepwise manner to a maximum flow rate of 143 kg day⁻¹ (Table 1) similar to measured gas flow rates observed at leaking abandoned wells [27].

3.1. Detection

Aside from designing cost-efficient search strategies, the key element for successful leakage detection are sensors that can be deployed remotely and detect potentially small anomalies from a distance with high fidelity. Active acoustics were highly effective at detecting CO₂ bubbles in the water column and CO₂ gas accumulation in sediments. Within minutes of the start of injection at the lowest rate, bubbles were observed in the backscatter of the hull mounted (EK60) shipboard acoustic system. In 120 m water depth the shipboard system had a seabed swath of 15 m and was able to detect bubble streams with a spatial footprint of only a few metres. The fast dissolution of the CO₂, along with tidally modulated reduction in bubble flow due to changing head pressure, may limit this form of detection [28]. This approach is unable to identify the gas species that are in the bubbles. Close to the

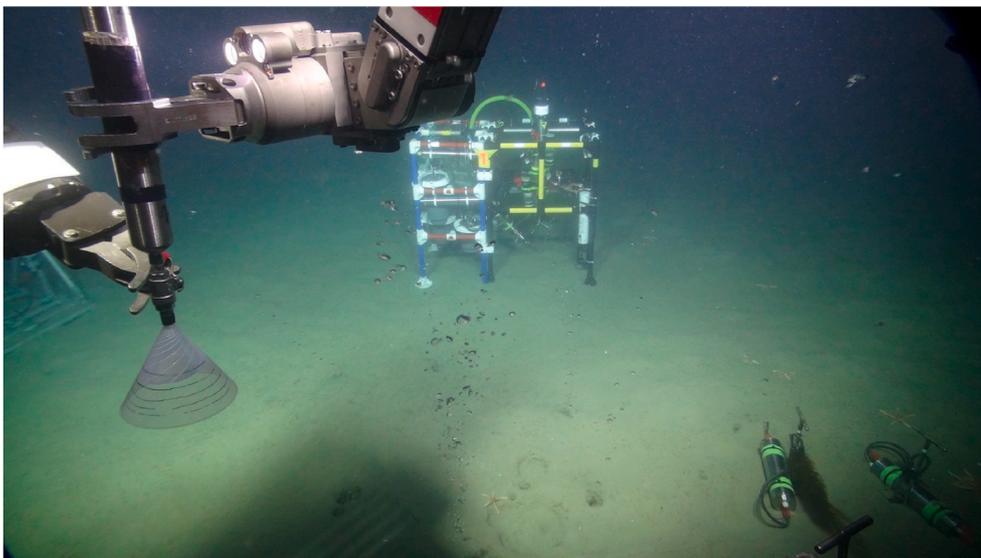


Fig. 2. Photograph of a vertical stream of gas bubbles emitted from seafloor. The left manipulator arm of the remotely operated vehicle closing the inlet valve of the gas bubble sampler in the left foreground, a lander with autonomous geochemical sensors in the centre back, and the right shows optode sensors in the sediment.

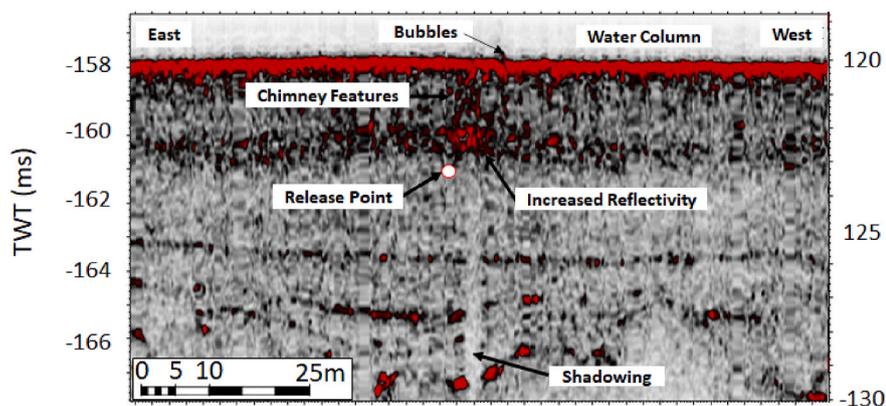
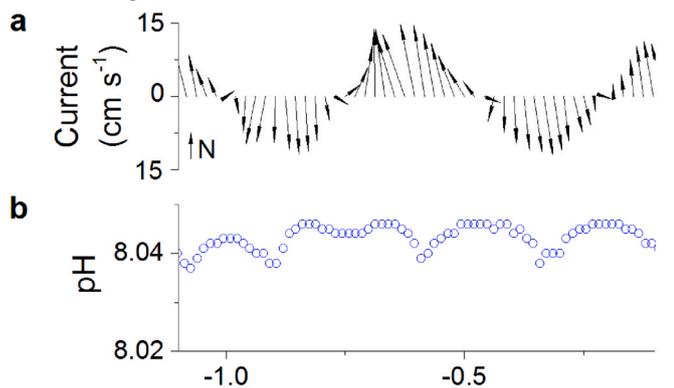


Fig. 3. Chirp sub-bottom profile over the controlled CO₂ release site (white dot) when the release rate was 143 kg day⁻¹ and 361 kg had been injected. The enhanced reflectivity from 3.0 to 2.5 m beneath the seabed shows the pooling of gas within a sandier unit. There is inflation of reflectors due to the presence of gas, and the generation of vertically aligned reflectivity which are interpreted as fluid flow conduits to the seabed (chimneys). The chirp profiler data was collected from an autonomous underwater vehicle at an elevation of 2 m. The profile position is shown in Fig. 1.

Natural pH oscillation



CO₂ release detection

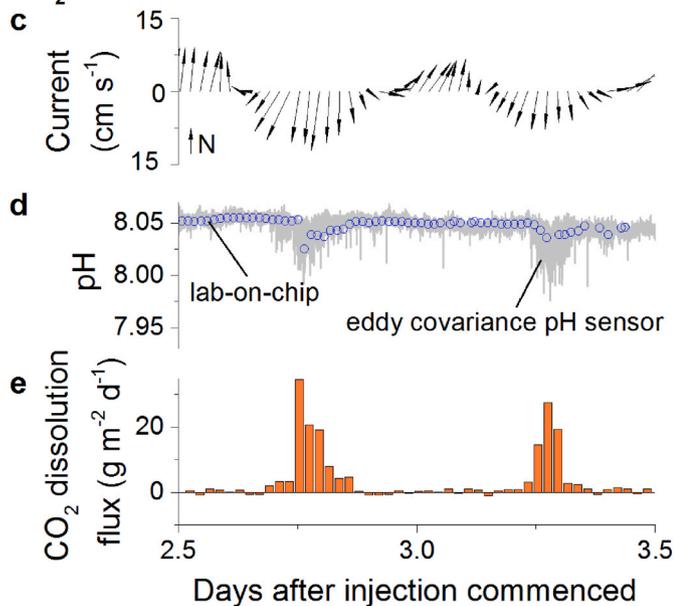


Fig. 4. Natural, leak-like pH variation before release commenced and detection of CO₂ emission using aquatic eddy covariance (injection rate 6 kg day⁻¹). a, b Natural baseline oscillations in pH due to the effect of tidal currents on thermal stratification (measured by lab-on-chip pH sensor). c, d After injection commenced, the low pH signal from CO₂ bubble dissolution was observed on south-bound flow (note change in pH scale). e, Detection of CO₂ emission by pH eddy covariance. A small, net positive flux was observed during north-bound flow (one-tailed *t*-test, *p* < 0.05) due to naturally occurring CO₂ production in sediments.

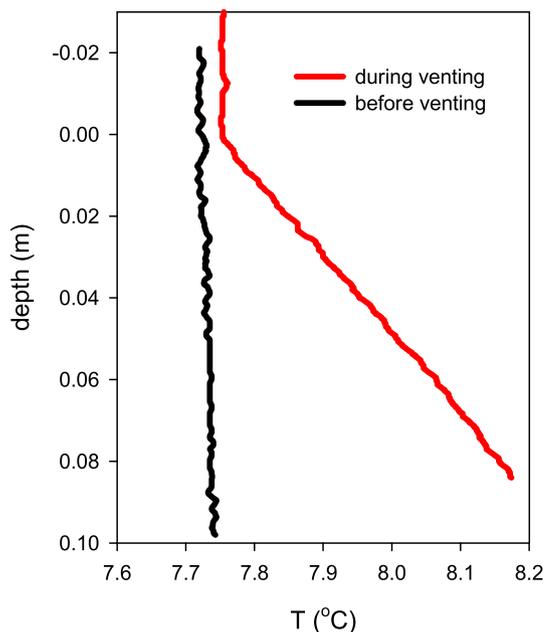


Fig. 5. Thermal changes in sediments due to carbonate and silicate mineral dissolution facilitated by released CO₂ in sediment pore waters.

leak, bubbles were seen as they emerged into the water column (Fig. 2). However, this technique relied on the use of an insitu imaging system mounted on an ROV or AUV, or a platform-based video/camera system (lander or ship deployed) and was therefore not suitable for long term autonomous monitoring.

The Chirp profiler data (Fig. 3) demonstrated increased reflectivity at 3 m depth in the seabed sediments, suggesting that gas pooled within the sandy layer, with fluid flow conduits (chimneys) visible when gas release was at a maximum. Initially gas migrated through the subsurface as individual bubbles rising upwards due to buoyancy forces (stable fracture propagation), however at higher injection rates these bubbles began to collide forming elongated fractures that rose rapidly to the surface (dynamic fracture propagation) forming open fluid flow conduits [29].

Geochemical techniques were also effective at detecting CO₂ at the lowest rates of release. Accurate and precise (better than 0.01 pH) spectrophotometric pH lab-on-chip sensors [30] detected the CO₂ leakage, 2.6 m horizontally away and 7–9 m above the leak point. This approach compensated for natural tidal mixing producing signals similar to leakage, supporting model predictions that anomalies of 0.01–0.02 ΔpH over sub-hourly timescales can be effective discriminators [10]. Further, at the lowest CO₂ injection rate, a pH eddy covariance

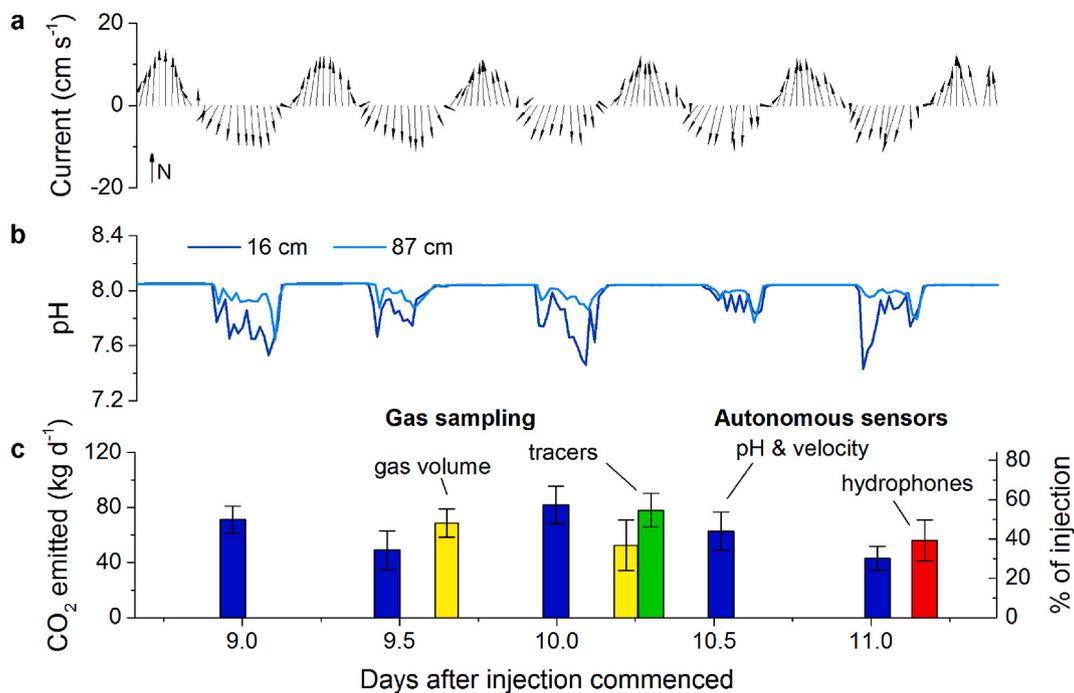


Fig. 6. Detection and quantification of total CO₂ emitted from the seafloor at the highest release rate. **a**, Direction and magnitude of tidal currents, which drive the CO₂-enriched water towards the chemical sensors during south-bound flow. **b**, pH of the water at 16 and 87 cm above the sea floor, 2.6 m south of the release point. **c**, estimates of the total flow rate of CO₂ emitted from the seafloor in kg day⁻¹ (left y-axis) and as a fraction of actual CO₂ injection (right y-axis). These estimates are determined from: physical measurement of bubble flow rate using funnels of the gas bubble samplers (“gas volume”); analysis of tracer concentration in gaseous samples collected ~15 cm above the sea floor (“tracers”); passive acoustics measuring sound of bubble ebullition (“hydrophones”); and lab-on-chip pH measurements coupled with velocity data and models of bubble dissolution and hydrodynamics (“pH & velocity”). The first three techniques estimate gaseous CO₂ emission from seafloor while the last one estimates the total CO₂ in the plume after complete dissolution.

system (co-located 2.6 m from the centre of the bubble streams) detected significantly increased vertical fluxes in hydrogen ions, produced by CO₂(g) dissolution near the seafloor (Fig. 4). The eddy covariance technique was highly sensitive and specific: even at the lowest release rate (6 kg day⁻¹), the peak signal was 20x that of natural background CO₂ production [31].

Sediment temperature sensors were also effective for leak detection. Dissolution of CO₂ gas in sediments reduces pore water pH, triggering the dissolution of carbonate and silicate minerals. The dissolution reactions of CO₂ and carbonate minerals in pore water are exothermic, resulting in conduction of heat to the sediment surface (with a thermal gradient in excess of 5 °C m⁻¹ (Fig. 5; [32]).

3.2. Attribution

To determine if a detected leak signal is naturally occurring or CCS-related, a thorough characterisation of natural geochemical conditions is needed [33]. A robust approach to attribution is to examine the stoichiometry of biologically active chemical species at the location of the signal, compared to that predicted from model or systematic observations [11,34]. For example, signals caused by natural organic matter mineralization, e.g., related to a phytoplankton bloom, will decrease pH and dissolved oxygen, whilst increasing nutrient concentrations. We confirmed this approach using novel spectrophotometric lab-on-chip pH, alkalinity, nitrate, and phosphate sensors [35,36]. Data revealed a change in pH with no equivalent change in nutrient concentrations, ruling out organic carbon remineralisation as a source of the increased CO₂ concentrations and concomitant pH drop.

The geochemical changes in the water column from the leakage in the marine system were determined by using water column sensors for pH, nitrate, alkalinity, phosphate, oxygen, H₂S and temperature. This was done by using both fine scale surveys using the ROV and wider scale surveys using an AUV equipped with pH sensors and a towed video

guided CTD with pH, pCO₂ and methane sensors. The sensors indicated that changes in pH were vertically and horizontally limited to within a few metres of the bubble seep, confirming a rapid dissolution of the CO₂ bubbles that escaped across the seabed [37].

Another option for preventing false positives is to ‘label’ the CO₂ in the storage reservoir with tracers: these are chemical constituents that are either inherent to the injected CO₂, arising from natural processes within the reservoir, or have been purposely added to the injected CO₂. In the release experiment natural tracers ($\delta^{13}\text{C}_{\text{CO}_2}$, $\delta^{18}\text{O}_{\text{CO}_2}$, CH₄) and a set of added tracer gases (octafluoropropane (C₃F₈), sulfur hexafluoride (SF₆) and krypton (Kr)) were tested for the first time in combination in a marine setting. Dissolution of injected CO₂ ($\delta^{13}\text{C}_{\text{CO}_2} = +19.4 \pm 0.92\%$ VPDB) into sediment pore waters and the water column was detected by enriched stable isotopic signatures of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) in pore waters (5–25% VPDB compared to background values of -1.9 to -4.0% VPDB) and in the water column ($+5.22\%$ VPDB compared to background values of $0.61 \pm 0.03\%$ VPDB) as well as by the added tracers. The gas bubbles emerging from the seafloor were analysed on board the ship for CO₂, CH₄, SF₆ and C₃F₈. This confirmed that the CO₂ collected was that which had been injected into the sediments and provided a tool for quantifying the extent of CO₂ dissolution within the sediment pore waters.

We investigated the impact that the CO₂ release had in the surface sediments above the release site, by direct in situ microsensor measurements of pH, redox potential, O₂ and temperature [38]. The venting induced highly variable and dynamic effects on the pore water profiles of O₂, pH, and redox potential, confined within the venting channel. Irregular gas bubble migration in the surface sediments induced mixing of the porewater in close proximity to the bubble release sites and hindered our ability to model porewater profiles satisfactorily [39]. The pH values occasionally dropped to below 6, because CO₂ dissolution induces carbonate and silicate mineral dissolution. The loss of CO₂ in the sediment is primarily controlled by the lateral diffusion of dissolved CO₂

Table 2
Summary of leakage rates determined by independent methods at an injection flow rate of 143 kg day⁻¹ (* statistically significant outlier, weighted mean (Maximum likelihood) flux is calculated without the outlier data point). The p-value analysis tests whether data points share a common mean, by comparing each data point with the weighted mean of all the other points.

Day	Leakage into water column (kg/d)	p-value	Method
9	71 ± 10	0.3097	Gradient flux
9.5	49 ± 14	0.3312	Gradient flux
10	82 ± 14	0.1265	Gradient flux
10.5	63 ± 14	0.9626	Gradient flux
11	43 ± 9	0.0129*	Gradient flux
9.65	69 ± 10	0.4838	Funnel
10.26	52 ± 19	0.5955	Funnel
10.26	78 ± 12	0.1613	Tracer
11.17	56 ± 15	0.6785	Acoustic
Weighted Mean flux	67 ± 4.5		

away from the vent channel, explaining the observed CO₂ loss by the added tracers. Whereas natural vents are often detected using redox potential anomalies [40], artificial CO₂ leakage does not induce redox effects.

3.3. Quantification

At the peak release rate (143 kg day⁻¹), CO₂ emission into the water column were quantified by gas sampling and in situ measurements using autonomous sensors as well as acoustic techniques (Fig. 6; Table 2). With gas sampling, we quantified emission using the volume collected in an inverted funnel over time. The gas samples were also analysed for tracer content; as the added tracers are much less soluble than CO₂, the change in tracer:CO₂ ratio was used to determine the proportion of the injected CO₂ that dissolved in the sediment pore waters.

The pH reduction was greatest near the seafloor where CO₂ concentration in the water column was at a maximum (gradient flux method): 2.6 m downstream of the bubble streams, the sensors recorded negative pH anomalies (0.3–0.5 pH) 16 cm above the seafloor, and 0.1–0.2 pH units at 88 cm altitude (Fig. 6b). The total mass of CO₂ emitted into the water column calculated from pH measurements in combination with water velocities and direction to determine the spatial coverage of the plume and its rate of transport was between 43 and 82 kg day⁻¹ (Fig. 6c; Table 2). In addition, autonomous hydrophones were also used to quantify gaseous CO₂ emergence from the sediment from the “plop” sound made as surface tension encloses a bubble [41] (56 ± 15 kg day⁻¹; Fig. 6c). Based on these autonomous sensors, 30%–57% of the injected CO₂ gas was emitted into the water column, a greater proportion than that observed during a previous experiment in shallow waters off the west coast of Scotland [28]. All of these rates of emission agree with rates determined directly by gas sampling. Therefore, autonomous techniques are capable of quantifying CO₂(g) emission even at relatively low rates consistent with gas leakage along the outside of abandoned wells [42].

Analysis of the CO₂ in the water column (Table 2), indicates that 53% ± 3% of the injected CO₂ remained within the sediments in gaseous and dissolved form, equivalent to 360 ± 20 kg of CO₂ over the duration of the experiment (11 days). Approximately 91 ± 32 kg of gas was detected in sediments by the Chirp sub-bottom profiler after 361 kg had been injected, meaning 25% ± 9% of the injected gas remained in the sediment in gaseous form [29]. The remainder (22% ± 12%) was presumed to be dissolved in the sediment pore water by this point in the experiment; eventually all gaseous CO₂ will go into solution and be neutralized

by reaction with carbonate and silicate minerals. As discussed above, elevated temperature and reduced pH in sediment porewaters measured using microprofilers evidence CO₂ dissolution. Fracture-generated, stable open conduits between the release point and the seabed [29] nevertheless limit the extent of CO₂ dissolution in sediments, permitting near-instantaneous flow of gaseous CO₂.

From Table 2 it can be noted that with the exception of one result obtained from the Gradient flux method, 8 of the 9 measurements are not statistically different from each other ($p > 0.05$) and yield a flow rate of 67 ± 4.5 kg day⁻¹, which is remarkably consistent considering the complexity of the marine environment and the different approaches taken.

At Goldeneye, the naturally occurring annual pH range in bottom waters is 0.15 pH units [43]. CO₂ driven impacts on biogeochemical processes are generally not seen with perturbations less than 0.1 pH units below the natural range [44]. The volume of water in which the reduction of pH was greater than 0.15 units was estimated from experimental data to be 17 m³ downstream of the site, based on the ROV's pH spatial surveys. This was very consistent with pre-experiment models which estimated that this volume would be 21 m³, similarly the volume acidified by ≥0.01 pH unit is calculated as 1000 m³, which validate model-derived estimates which predict 815 m³ for the same release rate [45]. This demonstrates that the volume of water affected by a readily detected leak is quite small [46] and validates the use of models in predicting this volume, but also illustrates the challenge in monitoring an affected volume of such small size. In the sediments, pH reduction of >0.15 units in the very surface sediments (uppermost 10 cm) was limited to a radius of a few centimeters, indicating that the CO₂ rose vertically and entered the water column. The experimental release had a short duration, but our results approximate steady state conditions due to the effectiveness of seawater buffering of pH and rapid mixing.

4. Conclusions

To make CO₂ storage in terrestrial geological reservoirs an effective and safe long-term CO₂ removal strategy, acceptable surface leakage rates (i.e. CO₂ escaping back into the atmosphere) of 0.01% reservoir loss per year have been proposed [47]. No such acceptable leakage rates have been proposed for the marine environment. Applying the above terrestrial leakage rates to the injection of 1 Mt/yr over 20 years that was projected for the Goldeneye reservoir [48], corresponds to acceptable leakage rates of 274 kg/d after the first year of injection and 5480 kg/d after 20 years of injection when full storage capacity is reached. During the STEMM-CCS release experiment CO₂ gas was injected at flow rates of up to 143 kg/d and leakage into the water column ranged between 43 and 82 kg/d. The injected CO₂ was detected in all its forms (gaseous and dissolved in the sediments, and gaseous and dissolved in the water column) during the experiment. As CO₂ leakage is unlikely to be continuous over the whole reservoir area but is more expected to be preferentially transported through small, focused fractures and faults or through poorly-sealed abandoned wells [6], both the flow rates and the type (point-release) of our simulated leakage suggest that for practical purposes a 0.01% loss threshold could be adopted for offshore storage.

Previous work has demonstrated that the environmental recovery from small leaks – on the order of under 1000 kg/d, is measurable in days to weeks [28]. The impacted area, but more crucially detection length scale, correlate with release rate [45], thus with the techniques demonstrated here we are confident that non-catastrophic leaks can be detected, attributed, and quantified at a lower release rate than that which causes significant environmental harm. While this paper focusses on “leakage” across the seabed, it should be noted that any approved Carbon Capture Storage Complex will have multiple barriers which make leakage extremely unlikely, with full monitoring and mitigation controls in place [49,50].

The work described herein allows us for the first time to demonstrate that we are able to detect, attribute and quantify CO₂ leakage from an

Table 3

Summary of techniques used during the experimental gas release. D, Detection; A, Attribution; Q, Quantification. Shaded cells represent methods/analyses performed in-situ, and unshaded cells represent methods that relied on sample collection and subsequent analysis on board the ship or on shore.

Measurement target	Technique/method	D	A	Q
Seafloor and sub-seafloor	Benthic biological imaging	x		
	Sediment coring	x	x	
	Sediment microprofiler	x		
	Sediment optodes	x		
	AUV Chirp Profiler	x		x
Gaseous CO ₂ in the water column	Bubble imaging			x
	Funnel capture of gas bubbles			x
	Gas sampling	x	x	x
	Passive acoustics	x		x
	Multibeam and sidescan acoustics	x		
Dissolved CO ₂ in the water column	Video-CTD imaging	x		
	Niskin bottle sampling	x	x	
	In situ/pumped CTD sampling	x	x	x
	Benthic chambers	x	x	x
	Eddy covariance	x	x	x
	Chemical gradient measurements	x	x	x
	Chemical mapping with ROV pH sensing on an AUV	x	x	

offshore carbon dioxide storage reservoir. With the techniques demonstrated here (Table 3) we are confident that non-catastrophic leaks can be detected, attributed, and quantified at a far lower release rate (6 kg day⁻¹) than that which causes significant environmental harm. The work demonstrates the importance of using model-derived approaches in combination with observed data to determine what is possible using current and emerging technologies and approaches. It informs the application of legislation and allows the design of cost efficient monitoring programmes to be used by operators.

Author contributions

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Data and materials availability

All data from the shipboard operations are available in Pangaea or the BODC data repositories.

Methane and CO₂ data, POS527: <https://doi.org/10.1594/PANGAEA.910413>.

ADCP data, POS534: <https://doi.org/10.1594/PANGAEA.908919>.

Lander ADCP data and biogeochemical data POS518 and JC180: <https://doi.org/10.1594/PANGAEA.908935>, <https://doi.org/10.1594/PANGAEA.909624>.

Physical oceanography data POS534: https://doi.org/10.1594/PA_NGAEA.910583.

Cruise report and cruise track.

JC180: https://www.bodc.ac.uk/resources/inventories/cruise_inventory/report/17236/

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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