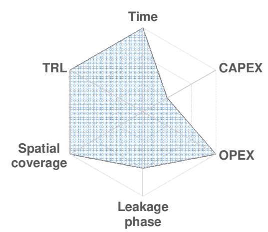
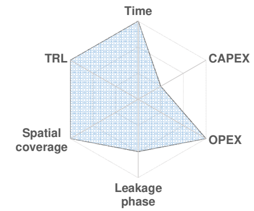
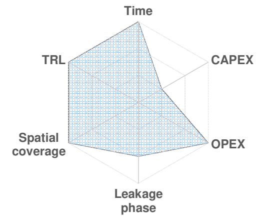
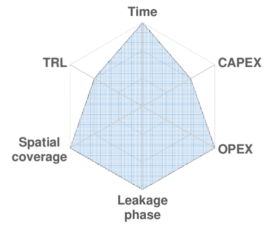
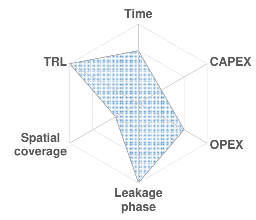
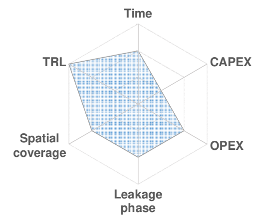
SUPPLEMENT

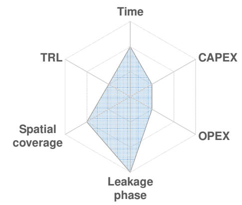
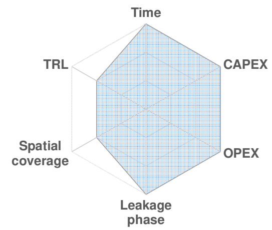
“Suitability analysis and revised strategies for marine environmental carbon capture and storage (CCS) monitoring”

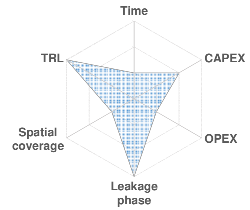
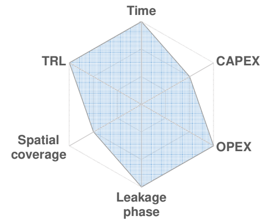
Supplement Table 1: Monitoring approaches tested during the STEMM-CCS release experiment for CO_2 leakage detection (D), attribution (A), and quantification (Q) in alphabetical order. The methods are split in techniques and technologies for data collection and approaches that can be used for data evaluation (with data acquired from the different techniques and technologies). The monitoring task for which each method was evaluated is highlighted in grey. If the technique/technology can fulfil more than one monitoring task, this is also indicated; if the indication is given in brackets, the method is possibly suitable or under development. In the graphical display the larger the surface area of the blue polygon, the better the method is in measuring the parameters that we included in the suitability analysis. For a more detailed description of the different approaches see Flohr et al., (2021a) and http://www.stemm-ccs.eu/monitoring-tool. na = not applicable.

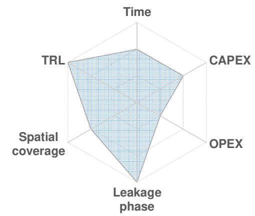
Tool/Technique and reference to publication related to testing for CCS monitoring	**Monitoring task**			**Capability and parameter(s) measured**	**Strength**	**Limitation**	**Confidence of measurement**	**Overall recommendation**	**Survey platform**			**Graphical display of suitability analysis**
	D	**A**	**Q**						**Vessel**	**AUV**	**ROV**	
Approaches for leakage detection tested during the STEMM-CCS experiment												
Active acoustics from ship: single beam echosounder (e.g. EK60/80)	+			Detection of gas bubbles in the water column	Well-developed imaging technique, suited to commercial applications. Gas bubble detection in the water column is straight forward	Because of the limited field-of-view, and specific acoustic frequencies used, the rise heights of the CO_2 bubbles can be underestimated	Very sensitive to gas in the water column and the probability of detecting gas is very high (95%)	It is recommended that the data is collected at all possible frequencies (typically frequencies are 18, 38, 70, 120 and 200 kHz)	✓			
Active acoustics from ship: multibeam echosounders and sonars				Detection of bubbles straightforward in the water column at large range	Well-suited to wide-area coverage in all water depths	Because of the limited field-of-view, and specific acoustic frequencies used, the rise heights	Very sensitive to gas in the water column and the probability of detecting gas is very high (95%)	Strongly recommended	✓			

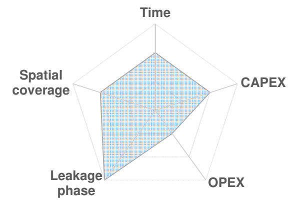
						of the CO_2 bubbles can be underestimated						
Active acoustics, sub-bottom profiler imaging on AUV	+			Detection of gas in sub-seabed sediments and gas bubbles in the water column	Capable of tracking CO_2 migration through seabed sediments and into the water column; Excellent for detecting gas migration through seabed sediments at flow rates > 86 kg d^{-1} in known risk locations	Cannot detect gas escape features < ~5 cm in diameter Limited swath width (1.9 m) results in long AUV missions or small survey area	Seismic reflection data using sub-bottom profiling is very sensitive to gas content within the top 5-10 m of sediments and probability of detecting gas is very high (90%)	Recommended for AUV flying at 2-7.5 m altitude with a swath of 1.4-1.9 m; resulting in penetration of 8 m into the sediment	✓	✓		
Multipurpose video-CTD, including mounted sensors	+	(+)	+	Can detect and monitor gas-rich fluid seepage from the seafloor using different sensors, e.g. for CO_2, CH_4, pH, O_2, T, S; Online video recording of seafloor; gas bubble imaging	Mobile system, that can cover larger areas (up to 2,000-4,000 m^2 of seafloor can be monitored and visualized during an 8 hour long campaign)	Operating, recording data, and data interpretation needs oceanographic background knowledge and offshore experience	The detection limits for seeping gas and related changes in water chemistry depend on the sensors used with the Vvideo-CTD and are usually TRL9 products	Towing of video-CTD in view of the seafloor, down- and upstream of the anticipated leakage site; Gas flux calculations possible if combined with current data from ADCP and plume modelling	✓			

Microprofiler (deBeer et al., 2021)	+			High resolution profiles of pH, O_2 and T measured at the sediment water interface and in the top 10 cm of the sediment; Determines the fate of dissolved CO_2 in the sub-seabed and the impact of the release on the environment	Very high (sub-mm) vertical resolution, and working at very low leakage rates; After a leak is detected the results are easy and fast to interpret	Very sensitive tracer for injected CO_2, but needs high level of specialized equipment and expert knowledge; Porewater profiles are chaotic close to the seep and cannot be used to quantify seabed CO_2 flux	Anomalies only detected within a few cm to a m of the seabed bubble seep	Instrument needs to be positioned near (<1 m) the release site.	✓		✓	
Passive acoustics or active (hydrophones) on seabed lander	+		+	Detection and quantification of gas bubble fluxes across seabed using the acoustic signal of the gas	Can detect gas and provides reliable estimates of gas flux across seabed from multiple seabed gas seeps; The technique is now well developed and suited to commercial applications	Specialist equipment; Equipment needs to be deployed within 10 m of the bubble stream to detect it and within 4 m to quantify flux; The exact distance to the bubble stream(s) must be known to accurately quantify the total flux	The sensitivity of the technique depends on the background noise conditions; In shallow water we have found that we can invert for gas flux using a single hydrophone at distances of 4 m; In deeper, quieter conditions, using multiple hydrophones, the maximum distance from the gas seep will be greater than this	An array of hydrophones allows beam-forming, which allows greater precision in flux estimation	✓		✓	

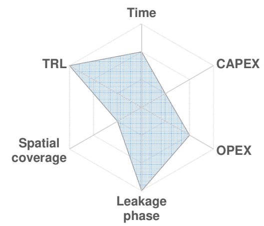
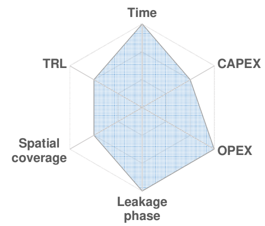
pH eddy covariance on seabed lander (Koopmans et al., 2021)	+	(+)	+	Detection and quantification of DIC flux from observations of turbulent fluctuations in pH and water velocity	Capable of detecting and quantifying the smallest of emission sources, including natural CO_2 production by sediments	Must be located downstream of the source, within approximately 10 m to detect the smallest of leaks (6 kg d^{-1})	At the lowest injection rate (6 kg d^{-1}) the pH flux due to CO_2 dissolution was 20-times the natural background flux	High potential for geochemical leak detection and quantification, including quantification of naturally occurring CO_2 emission in seafloor sediments; Instruments are not ready for commercial application (TRL 7)	✓		✓	
pH optodes (custom-made)	+		(+)	Measure changes in pH in the water column and the sediment, and can be attached to any stationary or mobile device	Compact and lightweight (length of 30 cm, diameter 6 cm and weight in water 0.85 kg); Can be deployed for serval months due to very low power consumption (~1 mW at the acquisition rate of 6 points per min)	Sensors currently still drift (with significantly slower drift at low temperatures and drift compensation algorithms significantly improve the results upon long term deployment); Currently not commercially available.	The resolution of the current system is 0.002 pH units, but it may probably improve in future	The devices should be deployed within several meters from the gas bubble streams; Compact design and low cost of the optodes enables application of multiple optodes at different positions from the expected leak; Whereas the temperature effects are compensated by the integrated temperature sensor, an external salinity sensor and correction of the data in post-processing are recommended if significant (> 5 PSU) salinity fluctuations occur	✓		✓	

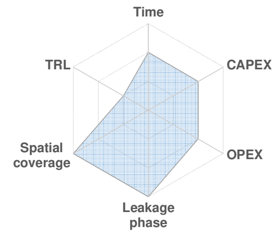
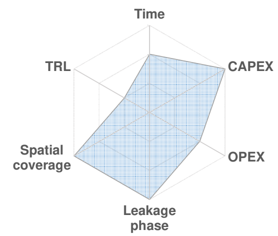
Porewater geochemistry in surface sediments (Lichtschlag et al., 2021)	+	(+)		Can detect leakage within sediments and attribute it to a reservoir if the background information is available; Based on the results, the CO_2 distribution in the sediment can be modelled	Can also detect precursor fluids; Many different dissolved geochemical species can be used as leakage indicators (e.g. TA, cations, anions, nutrients)	Needs sediment recovery, pore water extraction and analyses in the laboratory, hence is time consuming and needs expert knowledge; Anomalies can only be detected within a few cm to a m of the bubble seep	Confidence of measurements depends on analytical capability of the instrumentation used and the background geochemical composition	Best be compared to a near-by reference site that is not affected by CO_2 or to baseline measurements; Should be used at higher risk areas, such as abandoned wells and pockmarks	✓		✓	
ROV chemical sensing (Monk et al., 2021)	+	(+)	+	Can map the plume and quantify its leakage rate by putting commercial or novel pH sensors on an ROV	Can be a highly sensitive and low-cost implementation of monitoring if an ROV is already on-site; Running sensors on an ROV may not require extra equipment or deployment time	Requires an ROV and therefore a ship; pH sensors require calibration before use; Accuracy of results depend on accurate spatial data from the ROV and better results are obtained if the ROV can measure close to the seafloor; Requires some understanding of local hydrodynamics and current patterns	Confidence of measurements depends on analytical quality of pH sensors (see options in this table), but are generally quite high	Since plumes like the one created here have a strong vertical gradient, it is ideal to mount the sensor on the bottom half of the ROV and measure near the seafloor; If possible, it is very useful to integrate the sensor's data output to the ROV tether to get real-time data back on the ship for early warning and feedback on monitoring activity	✓		✓	

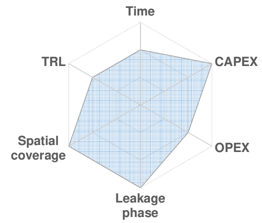
Traditional CTD and water sampling from ship	+	(+)	+	Stainless steel Conductivity Temperature Depth (CTD) frames with a variable set of Niskin bottles are commercially available and routinely used to collect discrete water samples along the water column at specific predetermined depths; Variety of parameters can be recorded (hydrography and carbonate chemistry depending on sensors attached) and several water samples can be collected for the analysis of e.g. dissolved gases (such as O_2, DIC, CH_4...) inorganic nutrients (such as nitrates, phosphate and silicate) and dissolved and particular organics	Water column sampling is a powerful tool to determine the distribution and variation of the parameters of interest, however, sampling is limited in space and time	High resolution data from sensors can be obtained, however, multiple casts or slow towing are required to acquire a broad picture of the marine environment and to detect variations in case of leakage; Must be close to the seafloor to detect smaller leaks	The accuracy and precision of the measurements are determined by the specific analytical method used	The ship would need to be positioned above the area of leakage and the CTD frame should be deployed within meters from the bubble streams in order to detect changes in the water column; A real-time video image is beneficial to determine the location of the leakage and proceed with sampling	✓			

Approaches for leakage attribution tested during the STEMM-CCS experiment												
Tracers (added and inherent) (Flohr et al., 2021a)	+	+	(+)	Attribution, detection and quantification of leakage in gaseous and dissolved phase	Very sensitive for tracing injected CO_2 in porewaters and water column at low injections rates (6 kg d^{-1}); Can be used to quantify CO_2 flux across seabed from changes in gas composition; Tracer concentrations can be determined onboard ship	Tracers cannot currently be measured in real time / in situ and analyses require specialist equipment and expertise; Gas sampling must be done using an ROV; Use of tracers in CCS monitoring requires knowledge of tracer properties (e.g. solubility, fractionation factors) at relevant pressure, temperature and salinity conditions and in the presence of different phases (gas, water, oil)	Analytical methods for tracer analysis are very sensitive; Certainty of trace gas measurements depends on gas species; Detection limits for the method (FT-IR) used is in the ppb (parts per billion) range in gas samples Sensitivity for isotopes depends on the gradient between both end members (CO_2 gas and water)	In general, temperature, salinity, pressure data need to be available to process and interpret gas and dissolved tracer results	✓		✓	

Approaches for leakage quantification tested during the STEMM-CCS experiment

Benthic chamber	(+)	(+)	+	Measuring fluxes of solute concentrations across the sediment-water interface; Measured parameters are DIC, but also oxygen, nutrients, temperature	Commercially available, well tested and can detect low fluxes Allows for the attribution of the source of CO_2 (i.e., abiogenic vs biogenic)	Must be deployed very close to the suspected emission source (where sediments are affected), but cannot be positioned directly over a bubble stream	Benthic flux chamber is a well-established and accepted technique for determining solute fluxes across the sediment-water interface; Detection limit depend on the use of high-accuracy laboratory methods for the analysis of the various biogeochemical parameters; The deployment duration affects the certainty of the flux measurements	Equipment should be deployed in the immediate vicinity of a suspected CO_2 source (but not immediately above bubble gas sources)	✓		✓	
Lab on Chip gradient (Schaap et al., 2021)	+		+	A Lab on Chip sensor measures dissolved inorganic carbon (DIC), or a combination of pH and total alkalinity to quantify the excess DIC in the water which is a result of dissolved CO_2 bubbles; The total mass flow is established by measuring at two heights above the seafloor and combining the data with current measurements	Very accurate way for quantification leakage of dissolved CO_2; Deployments at the seafloor of up to one year have been demonstrated	Needs a medium level of expertise	The sensors are quite sensitive and pick up pH changes of > 0.01 pH units; Estimates of quantification in this experiment have uncertainty around 20%	For only detection of a leak, no further equipment would be required; For quantification, one would need salinity and temperature (to correct for these in the sensors) and current data; One would also need an estimate of the distance from the leak from another method, or to estimate the leak position by having two systems deployed in different positions	✓		✓	

Supporting technology for leakage detection, attribution and quantification tested during the STEMM-CCS experiment												
Cseep: Stoichiometric analysis in water column using data for carbonate system parameters, T, S, and nutrients from cruises (historical in GLODAB v2; STEMM-CCS Poseidon and JC cruises) and from sensors deployed on STEMM-CCS landers (Omar et al., 2021)	+	(+)	+	Detects leakage through the quantification of the natural variability in the concentration of Dissolved Inorganic Carbon (DIC); Requires data for any two of the four measurable parameters of the CO_2-system (DIC, TA, pH, and pCO_2), salinity, temperature, and nutrients or dissolved O_2	Very sensitive tracer of CO_2 anomalies in the water column; Can be used to verify if source of CO_2 is abiogenic; might in future be used for quantification as well as attribtution	Limit of detection is several times the measurement error in DIC due to accumulation of errors throughout the computations; High level of expertise required to establish the method for a new site; Anthropogenic CO_2 also enters from the atmosphere. The effect of this uptake (≈1.2 ±0.3 μmol kg^{-1}, can produce significant DIC change in the long term and, thus, is actually a required input into Cseep computation	During STEMM-CCS the total uncertainty associated with the baseline DIC was around 10% of the natural DIC variability	Effective low-cost method for emission detection, and needs to be a few meters above the seabed sources; Additionally, a site-specific model for the drivers of the natural DIC variability is required	na	na	na	
CO_2 leak model (based on field measurements) (Gros et al., 2021)	+		+	Simulation of the behaviour of gaseous or liquid carbon dioxide released in the sea based on observed bubble stream positions, initial bubble size distribution, gas composition, pH and/or pCO_2 in the water, and measured ambient water currents; For leak quantification, the CO_2 flow rate in the	Fast result; Can assess the footprint of impact for different leak scenarios	Depends on the quality and quantity of field data, especially requires measured water currents, precise knowledge of positions of the bubble streams and positions of the field measurements, as well as initial	Simulations can provide an estimate of the range of leak flow rate leading to the smallest overall deviation between the field measurements and simulations; The method was successfully applied to a leakage rate of 143 kg d^{-1} during the release experiment,	Leakage quantification is dependent on the availability of high-quality field data; Important parameters include precise position determination, knowledge of the initial bubble size distribution and	na	na	na	

				model is fitted such as to minimize the discrepancy between simulated pH or pCO_2 and corresponding field measurements		bubble size distribution; The spatial distribution of pH and/or pCO_2 in the water column must be measured to constrain the leakage rate	with a quantified flow rate within a factor of <2 of the actual leak flow rate (Gros et al., 2021) and for a leakage rate of 85 kg d^{-1} during the ECO2 experiment (Vielstädte et al., 2019)	measured pH and/or pCO_2 distribution				
Rates of changes (ROC) model (Blackford et al., 2017)	+		+	This model identifies anomalies of chemistry as distinct from natural dynamics, minimizing the chance for false positives	Very quick without direct measurements; Can cover large areas and can be easily adapted to different sites	The model is only as good as the input parameters, hence enough background information is needed	Given that the input data can be supplemented by model derived data, there is an element of estimation, however, these can and should be minimized by evaluation against observation data, specific to the site of interest	A model specific to the proposed storage region is required; Most, if not all coastal and shelf seas in the vicinity of developed nations will have suitable marine hydrodynamic-biogeochemical models in the R&D sector	na	na	na	

References

Blackford, J., Artioli, Y., Clark, J. and de Mora, L. (2017) Monitoring of offshore geological carbon storage integrity: Implications of natural variability in the marine system and the assessment of anomaly detection criteria. International Journal of Greenhouse Gas Control 64, 99-112.

de Beer, D., Lichtschlag, A., Flohr, A., Erk, M.v., Holtappel, M. and Haeckel, M. (2021) Sediment acidification and temperature increase in an artificial CO_2 vent. International Journal of Greenhouse Gas Control, 105, 103244.

Flohr, A., Schaap, A., Achterberg, E.P., Alendal, G., Arundell, M., Berndt, C., Blackford, J., Böttner, C., Borisov, S.M., Brown, R., Bull, J.M., Carter, L., Chen, B., Dale, A.W., Beer, D.d., Dean, M., Deusner, C., Dewar, M., Durden, J.M., Elsen, S., Esposito, M., Faggetter, M., Fischer, J., Gana, A., Gros, J., Haeckel, M., Hanz, R., Holtappels, M., Hosking, B., Huvenne, V.A.I., James, R.H., Koopmans, D., Kossel, E., Leighton, T.G., Li, J., Lichtschlag, A., Linke, P., Loucaides, S., Martínez-Cabanas, M., Matter, J.M., Mesher, T., Monk, S., Mowlem, M., Oleynik, A., Papadimitriou, S., Paxton, D., Pearce, C.R., Peel, K., Roche, B., Ruhl, H.A., Saleem, U., Sands, C., Saw, K., Schmidt, M., Sommer, S., Strong, J.A., Triest, J., Ungerböck, B., Walk, J., White, P., Widdicombe, S., Wilson, R.E., Wright, H., Wyatt, J. and Connelly, D. (2021a) Towards improved monitoring of offshore carbon storage: A real-world field experiment detecting a controlled sub-seafloor CO_2 release. International Journal of Greenhouse Gas Control, 106, 103237.

Flohr, A., Matter, J.M. , James, R.H., Saw, K., Brown, R., Gros, J., Flude, S., Day, C., Peel, K., Connelly, D., Pearce, C., Strong, J.A., Lichtschlag, A., Hillegonds D.J., Ballentine, C.J. and Tyne R.L. (2021b) Utility of natural and artificial geochemical tracers for leakage monitoring and quantification during an offshore controlled CO_2 release experiment International Journal of Greenhouse Gas Control, 111, 103421.

Gros, J., Schmidt, M., Linke, P., Dötsch, S., Triest, J., Martínez-Cabanas, M., Esposito, M., Dale, A.W., Sommer, S., Flohr, A., Fone, J., Bull, J.M., Roche, B., Strong, J.A., Saw, K., Brown, R., Koopmans, D. and Wallmann, K. (2021) Quantification of dissolved CO_2 plumes at the Goldeneye CO_2-release experiment. International Journal of Greenhouse Gas Control 109, 103387.

Koopmans, D., Meyer, V., Schaap, A., Dewar, M., Färber, P., Long, M.H., Gros, J., Connelly, D. and Holtappels, M., (2021). Detection and quantification of a release of carbon dioxide gas from the seafloor using pH eddy covariance and measurements of plume advection. International Journal of Greenhouse Gas Control.

Lichtschlag, A., Cevatoglu, M., Connelly, D., James, R. and Bull, J. (2018) Increased fluid flow activity in shallow sediments at the 3 km Long Hugin Fracture in the central North Sea. Geochemistry, Geophysics, Geosystems 19, 2-20.

Monk, S., Schaaep, A., Hanz, R., Borisov, S., Loucaides, S., Arundell, M., Papadimitriou, S., Walk, J., Tong, D., Wyatt, J. and Mowlem, M. (2021) Detecting and mapping a CO_2 plume with novel autonomous sensors on an underwater remote-operated vehicle. International Journal of Greenhouse Gas Control.

Omar, A.M., García-Ibáñez, M.I., Schaap, A., Oleynik, A., Esposito, M., Jeansson, E., Loucaides, S., Thomas, H. and Alendal, G. (2021) Detectionand quantification of CO_2 seepage in seawate rusing the stoichiometric Cseep method: results from a recent subsea CO_2 release experiment in the North Sea. International Journal of Greenhouse Gas Control, 108, 103310.

Schaap, A., Koopmans, D., Holtappels, M., Dewar, M., Arundell, M., Papadimitriou, S., Hanz, R., Monk, S., Mowlem, M. and Loucaides, S. 2021) Quantification of a subsea CO_2 release with lab-on-chip sensors measuring benthic gradients. International Journal of Greenhouse Gas Control, 110, 103427.

Vielstädte, L., Linke, P., Schmidt, M., Sommer, S., Haeckel, M., Braack, M. and Wallmann, K. (2019) Footprint and detectability of a well leaking CO_2 in the Central North Sea: Implications from a field experiment and numerical modelling. International Journal of Greenhouse Gas Control 84, 190-203.