Chemical tracers for sub-seabed CCS leak detection

Storing industrially-generated carbon dioxide (CO_2) in depleted sub-seabed hydrocarbon reservoirs is seen by many as an important strategy to combat climate change. Providing reassurance of the integrity of these reservoirs is key in gaining public confidence in CCS. Using chemical tracers to 'label' stored CO_2 can provide the necessary tool to detect, trace and quantify any escaped CO_2 in the unlikely event of a reservoir breach.

Collecting carbon dioxide (CO_2) generated from industrial processes, transporting it and storing it deep underground, carbon dioxide capture and storage (CCS), is seen by many as a practical mitigation strategy to slow the progress of global warming and climate change. Among potential sites for CCS below the seabed are depleted or near-depleted oil and gas reservoirs; injecting anthropogenic CO_2 into these would be effectively putting it back from whence it came. Due to the nature of these sites and provided that amounts and speeds of injections of CO_2 are carefully calculated, the opportunity for any leakage back into the overlying sea or atmosphere is highly unlikely. Yet to provide further confidence among the wider public and regulators that the process is safe, and to meet legal requirements, it remains necessary to show that any leakage, should it occur, can be detected, attributed and monitored.

Industrial scale CO_2 storage projects are subject to stringent regulation to ensure that any leakage out of the storage reservoir, seepage to the seabed and release through sediments into the water column, can be monitored and assessed to ensure it is within acceptable limits. Ensuring leaks can be reliably detected and measured is thus essential for building confidence in regulators, other interest groups and the wider public. Seepage rates of 0.001%-0.1% per year, equivalent to a loss of 1% of CO_2 to the surface over 1000 years, are considered acceptable levels. However, detecting such seepage rates is difficult under the best circumstances and is further complicated by natural CO_2 emissions and fluctuations. These may originate from outgassing magmas, other geological processes, naturally occurring hydrocarbons close to the seabed surface and from biological activity. One strategy is to use chemical tracers which are detectable at very low concentrations within the injected CO_2, and distinguishable from any background or natural levels, so 'fingerprinting' the injected CO_2 for identification.

Three categories

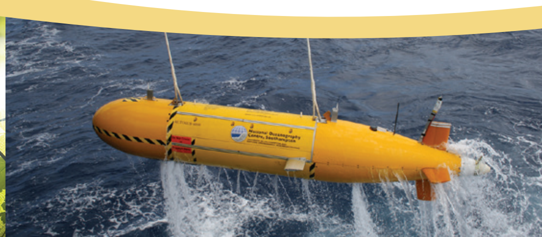
Tracers fall into three broad categories characterised by how they relate to the CO_2 stream being injected. **INHERENT** tracers are those which are part of the natural composition of the CO_2 stream. They may include different CO_2 or O_2 isotopes which give a unique isotopic signature, or other identifiable components acquired as part of the capture process. Tracers may be **INDIRECT** having resulted from contributions from natural components of the store, or changes to the CO_2 resulting from reactions with the natural environment of the storage reservoir, mineral dissolution for example. It will be necessary to obtain a baseline analysis of the storage site for later comparison in the event of a suspected leak. The third category is when tracers are **ADDED**, which as the name implies are introduced into the CO_2 stream at identifiable levels and compositions prior to storage. These might include another CO_2 source with its own cocktail of chemicals or isotopic identity, or artificially added chemicals providing a unique 'fingerprint'.

Whether a tracer is inherent, indirect or added affects the costs of monitoring, and potentially the reliability of tracer monitoring. Inherent tracers may vary over time, and if CO_2 during the injection lifetime comes from different sources, there is room for amalgamation of tracer properties and variation in relative quantities rendering them less easy to differentiate, thus not being suitable. The more expensive option is to add tracers of a known composition at a known concentration or, for added confidence, a suite of known tracers is always going to be more effective than a single tracer. If the 'cocktail' is chosen correctly it should allow for the vagaries of the storage site and through time, so providing more reliability and certainty.

Things to consider

When using tracers to identify the source of any CO_2 seepage, there are aspects of the context that should be considered. Each site or reservoir will have its own characteristics both within the store or above in the sediment and overlying water column. So a one-size-fits-all may not apply and careful reservoir baseline studies, and characterization of the physical, often changing, nature of the seabed and the water column above are required before a suite of tracers is employed and injection commences.





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The chemical make-up of the strata into which the injected CO_2 and its tracers are injected will vary from site to site and potentially through time at any one location: good baseline data will need to be gathered. How the tracer partitions with brine, other fluids or the differing rock types within the formation or en route during injection, can affect the resulting concentrations being measured. Tracer chemicals might already exist in prospective reservoirs, especially where the reservoir has previously contained oil or gas and chemicals have been used during the extraction process or, when using tracers which occur naturally such as the noble gases.

Ideal tracers

Ideally tracers should be selected on a number of criteria:

1. Their behaviour within streams and reservoirs must be predictable at all potential conditions of temperature, pressure and salinity.
2. They must be equally dispersible within the CO_2 stream.
3. They must be easily sampled and detectable at very low concentrations.
4. They should be conservative and so not be altered at any of the injection stages, or through the lifetime of the storage.
5. Tracers should be of low risk in terms of human health and the environment and be cost effective and easy to obtain.

References

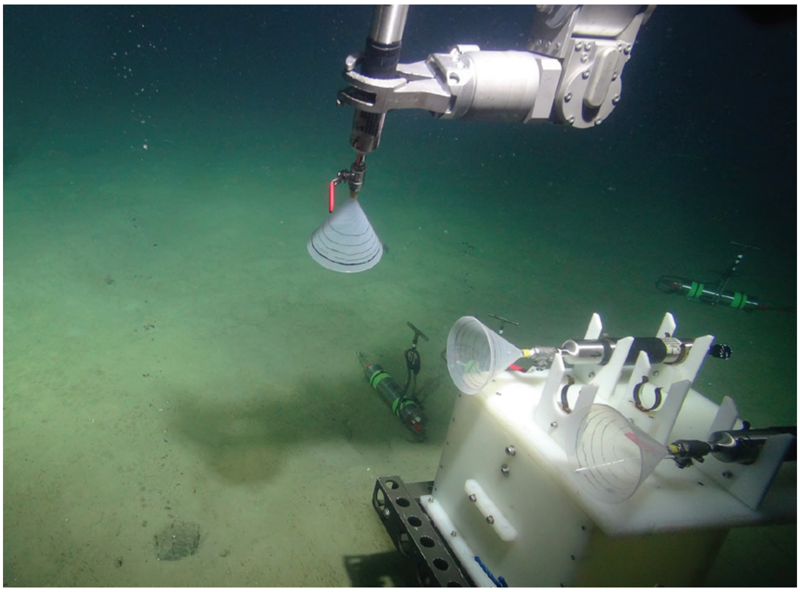
Flude, S. et al. Environ. Sci. Technol., 2016, Inherent tracers for Carbon Capture and Storage in Sedimentary Formations: Composition and Applications.

Roberts, Jennifer J, et al. International Journal of Greenhouse Gas Control, 2017, Geochemical tracers for monitoring offshore CO2 stores. https://doi.org/10.1016/j.ijggc.2017.07.021.

Tracers in the STEMM-CCS project

Part of the STEMM-CCS controlled release experiment at the Goldeneye site in the North Sea, 120 km off the Scottish coast, was to test the applicability of natural and artificial tracers for CO_2 leak detection and quantification in the natural environment. Over a period of 11 days, 675 kg of CO_2 was carefully released through a pipe buried 3 m below the seafloor. Tracer gases (both inherent and added) were added at very low concentrations to the injected CO_2 during the experiment to determine whether gas escapes can be reliably detected in a real-world situation. Samples were collected at the site to determine how much of the tracers dissolved into sediment pore water and seawater, and how much remained with the CO_2 that emerged at the seabed as bubbles.

Different analytical instruments were used for different tracers and for those in gas phase or dissolved in seawater; the concentration of CO_2, sulphur hexafluoride and octofluropropane in the gas bubbles was measured by infrared spectroscopy, for example. Results showed that the CO_2:tracer ratio changes as CO_2 dissolves in the sediment pore water and the remaining gas becomes enriched with tracers; the ratio tells us how much CO_2 has dissolved in seawater. The experiment was a success demonstrating that tracers and their ratios to CO_2 were detected. This is the first time that trace gases have been used to monitor the behaviour of CO_2 in marine systems.



Right: Using the ROV to collect CO_2 gas during the controlled release experiment. Image NOC/JC180.

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The STEMM-CCS consortium comprises 13 partners across Europe, coordinated by the National Oceanography Centre, UK. For more information please visit www.stemm-ccs.eu