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## The Impact of Water on CO<sub>2</sub> Leak Rate Measurements for CCS projects

Matt Myers<sup>a</sup>, Jennifer J Roberts<sup>b\*</sup>, Cameron White<sup>a</sup>, Linda Stalker<sup>a</sup>

<sup>a</sup>National Geosequestration Laboratory/CSIRO Energy, Perth, Australia, 6152.

<sup>b</sup>Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow, UK, G1 1XJ

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### Abstract

Chemical tracers are a promising technique to detect, attribute and quantify CO<sub>2</sub> leakage from geological CO<sub>2</sub> stores. Indeed, CO<sub>2</sub> release experiments have found it difficult to ascertain the fate, or quantify the volume of CO<sub>2</sub> without the application of tracers. However, a significant proportion of global CO<sub>2</sub> storage capacity is located offshore, and the marine environment poses constraints that could limit the success of using tracers. These constraints include uncertainties in the behaviour of tracers in marine sediments and the water column and sampling challenges. To model some of these challenges, we used a benchtop experimental setup to explore how well methane, a common constituent of captured CO<sub>2</sub> and of reservoir fluids, could aid the quantitation of CO<sub>2</sub> leakage in aqueous environments. The experiment simulated gas leakage into sediments that mimic the seabed, and we measured the partitioning of co-released gases under different environmental conditions and injection rates. We find that the style of seepage and the fate of the CO<sub>2</sub> are affected by the presence of a sand layer and the injection rate. This has implications for leak monitoring approaches, including how tracers may be used to quantify the leak rates and fate of CO<sub>2</sub> in aqueous environments.

*Keywords:* tracer; leakage; marine; experiment quantification; methane

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### 1. Introduction

Legislation and guidelines developed for Carbon Capture and Storage (CCS) have set a range of performance requirements to minimize leakage risk [1] and to quantify and remediate any leaks that arise [1-3]. Methods of measurement, monitoring and verification are therefore necessary to demonstrate CO<sub>2</sub> containment.

Detecting and quantifying CO<sub>2</sub> leakage is challenging because CO<sub>2</sub> can be naturally present or generated in the subsurface, biosphere and atmosphere. Chemical tracers that 'fingerprint' CO<sub>2</sub> injected for CCS could allow it to be differentiated from these other natural or background sources [4]. The effective application of chemical tracers could provide valuable information about the migration and fate of CO<sub>2</sub>.

However as yet tracers have not been tested for offshore storage, and there is significant uncertainty about their behavior in marine environments [5]. The QICS project (Quantifying and Monitoring Potential Ecosystem Impacts of Geological Storage; [www.qics.co.uk](http://www.qics.co.uk)) is, to date, the only sub-seabed CO<sub>2</sub> release experiment that has been conducted. The project highlighted the difficulties attributing and understanding the fate of injected CO<sub>2</sub> without chemical fingerprinting approaches, even with a very high intensity monitoring program [7-9]. The project illustrates the need to develop and test techniques to measure and quantify the fate of CO<sub>2</sub> leakage to seabed.

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\* Corresponding author. Tel.: (+44)141 5483177

E-mail address: [jen.roberts@strath.ac.uk](mailto:jen.roberts@strath.ac.uk)

To this end, we used a benchtop experimental setup to simulate gas leakage across the sediment-water interface and into the atmosphere. We used methane ( $\text{CH}_4$ ) as a tracer.  $\text{CH}_4$  is a common constituent of captured  $\text{CO}_2$  and of reservoir fluids [10] but is present at trace levels in the atmosphere, and could therefore act as a low-cost tracer that could aid identification, attribution and quantitation of leaked  $\text{CO}_2$  see e.g. [5, 11].

We used an in-line infrared based cavity ring down spectrometer to continuously measure the gas concentrations in the headspace. From this, we deduced the gas dissolution, leak distribution and partitioning of co-released gases, and explored how leak rates can be usefully constrained, and the best approaches of doing so.

The research questions addressed in the study are summarized in Figure 1.

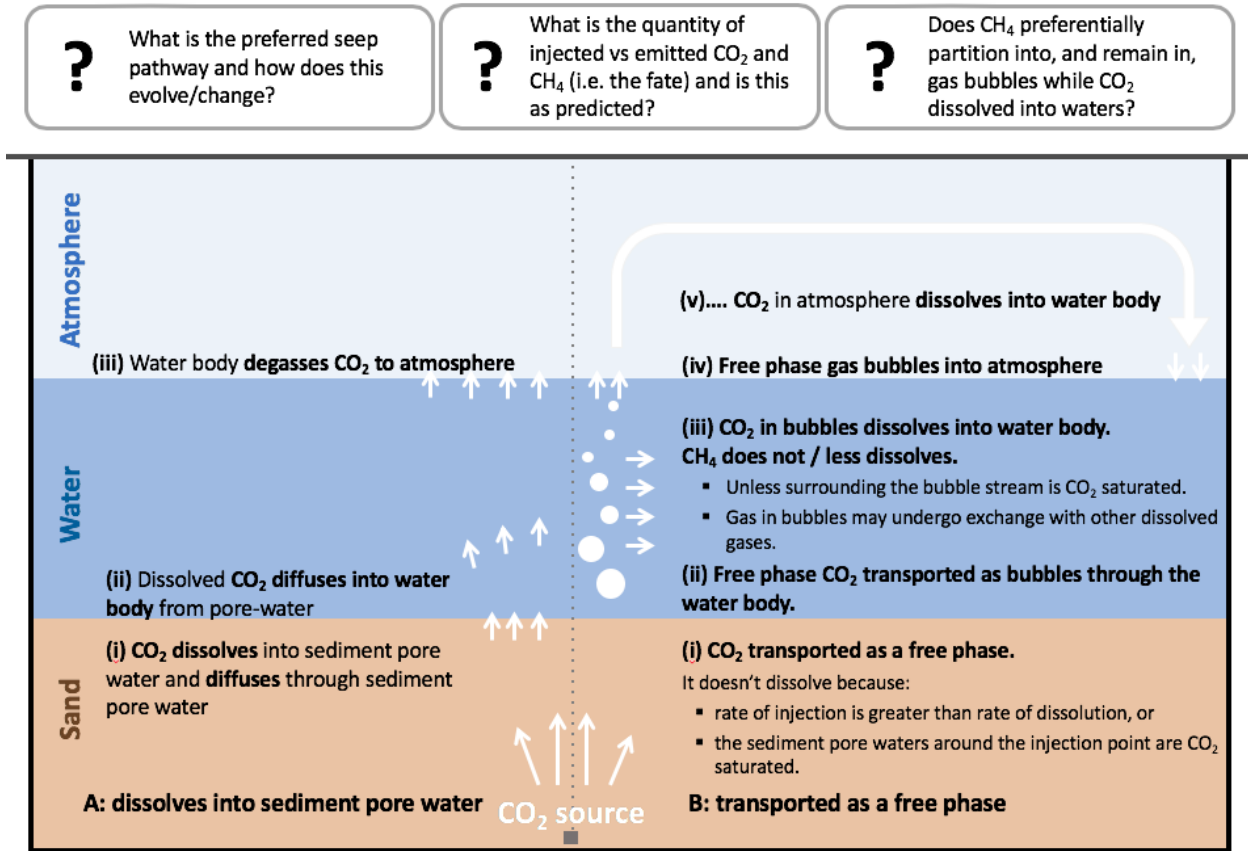


Figure 1: Schematic of potential pathways and fate of the injected  $\text{CO}_2$  and tracer, and the research questions being addressed in this study?

## 2. Methods

### 2.1. Experimental set up

We designed laboratory experiments that simulated leakage of a  $\text{CO}_2$ - $\text{CH}_4$  mixture into sediments that mimic aqueous environments such as lakes or the seabed. The experimental set up is shown in Table 1. Essentially, we filled a container with cleaned quartz silica sand (sand with 80 - 130  $\mu\text{m}$  particle size) and distilled water, and constructed a lid from an acrylic sheet to isolate the environment within the container from the atmosphere. Bulkheads in the lid powered a fan (to circulate the air inside the container), allowed a recirculating loop to a gas analyzer (a Picarro

G2201-i CRDS), and supplied a gas mixture (78.7(CO<sub>2</sub>):21.3(CH<sub>4</sub>) by volume) to the center of the container via a tube.

Before each experiment was conducted, the system was first purged so that the container reflected atmospheric levels (i.e. approx. 400 ppm CO<sub>2</sub>; 1.78 ppm CH<sub>4</sub>), and so that the tubing was emptied of any residual gas.

Gas was continuously injected at the specified flow rate until the concentration of gas in the headspace exceeded the reliable tolerance threshold of the Picarro CRDS system (1500 ppm for both CH<sub>4</sub> and 2000 ppm for CO<sub>2</sub>). The duration of the experiment was therefore dependent on gas injection rate. Gas measurements were acquired continuously with a measurement every 1 to 5 seconds **approximately**. During the experiments, the fan gently mixed the air in the headspace.

## 2.2. Experimental conditions.

Experiments were performed for three experimental conditions: (A) an empty container (i.e. the control experiment); (B) a container with water only; (C) a container with water and sand. The parameters for condition are shown in Figure 2. We investigated flow rates from 0.88 to 8.8 mL/min and repeated each experiment a minimum of 3 times.

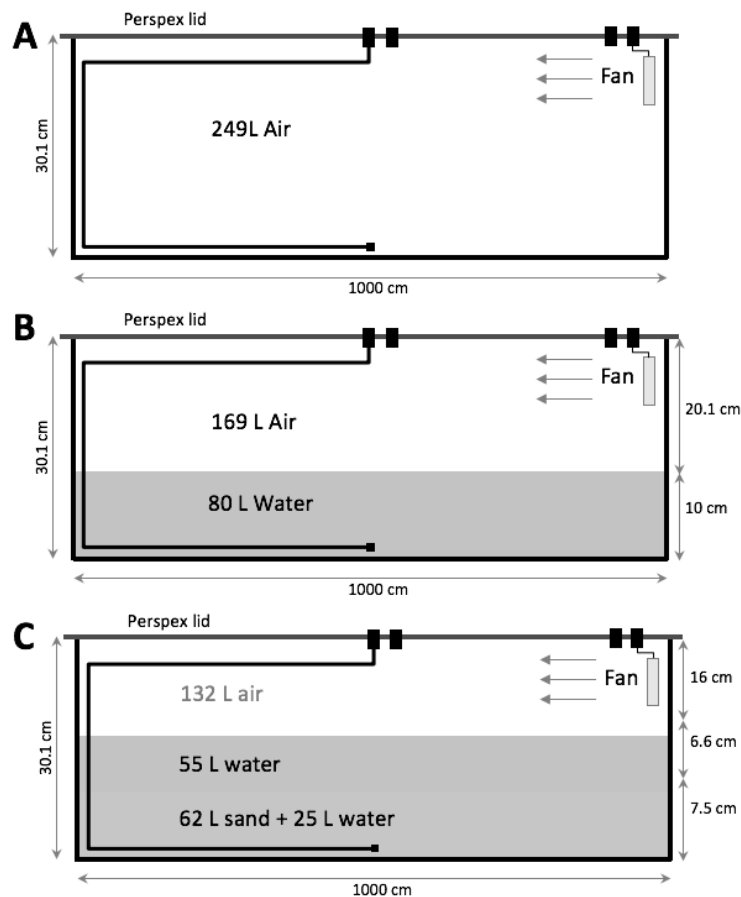


Figure 2: Summary of experimental environments. Experiment A is a control experiment which assessed whether the system was closed and that the gas concentrations raised as predicted. Flow rates were constant for experiments A & B (0.88 mL/min) but were varied for experiment C from (1) 0.88, (2) 1.76, (3) 4.40, (4) 8.80 mL/min.

### 3. Results

For experiments B and C, gas bubbling through the water column and into the headspace occurred immediately once injection had started. For experiment B, bubbles occurred constantly and regularly, whereas in experiment C bubbling was intermittent and irregular (i.e. periodic). This led to some complexity in the data processing, but is typical of field observations (reference what you and Andrew F have been doing, show a pic even?? – or you may have referred below in discussion?).

Our results are shown in Figure 3. They show a significant depletion in the rate of increase in CO<sub>2</sub> relative to CH<sub>4</sub> compared to the composition of the gas mixture (i.e. as the experiment evolves the concentration of CH<sub>4</sub> in the gas bubbles increases relative to the CO<sub>2</sub>). Interestingly, this depletion becomes less significant as the flow rate is increased in experiment C.

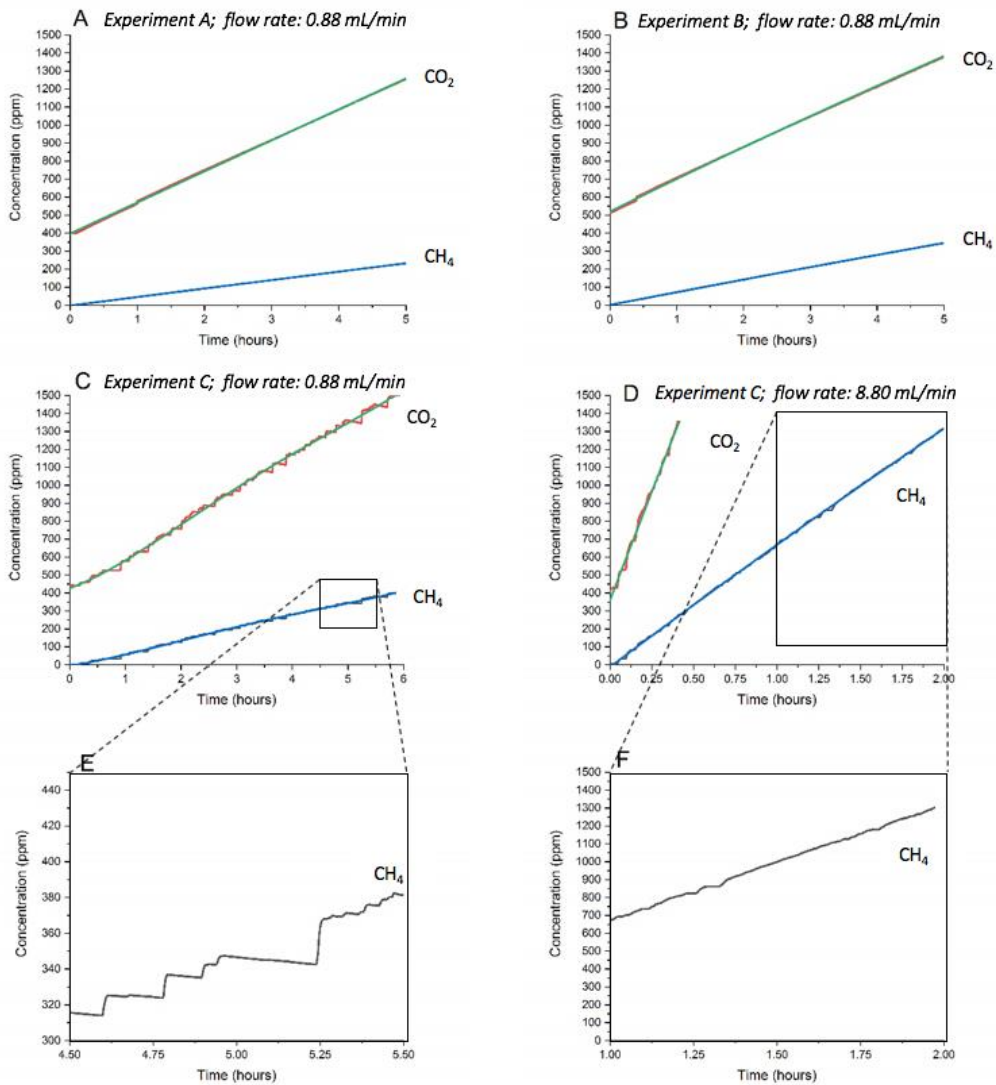


Figure 3: Results of CO<sub>2</sub> and CH<sub>4</sub> concentrations for experiment A (A), B (C), C (C-F), where C and D show different injection rates for experiment C and E and F show zoomed-in results from these experiments. Images A-D show 4th degree polynomial fit lines, necessary to adjust results for the quantitation problems arising from the bubbling intermittency.

The presence of and thickness of sand has an effect on the fate of the release gases and the concentration measurements in the headspace. In experiment B, ~25% of the CO<sub>2</sub> dissolves into the water body, and negligible CH<sub>4</sub>. At the same flow rate, a similar amount of CO<sub>2</sub> dissolves in experiment C.

The gas injection rate also affects the fate of the released gases. Increasing the flow rate decreases the effects of CO<sub>2</sub> dissolution into water and reduces the irregularity of the bubbling. While ~25% of CO<sub>2</sub> and negligible methane dissolves in experiment C for lower flow rates (0.88 and 1.76 mL/min), at higher rates (4.4 and 8.8 mL/min) this reduces to ~5%. At high flow rates, less CO<sub>2</sub> is dissolving.

#### 4. Discussion

Our results shed light on the conditions and processes that affect the fate of CO<sub>2</sub> and have implications for how tracers may be used to quantify CO<sub>2</sub> leak rates in aqueous environments.

Firstly, our experiments show that the CH<sub>4</sub> concentration and/or flux is not strongly interacting with the water column. This implies it is therefore possible to use CH<sub>4</sub> as a chemical tracer to determine the fate or loss of CO<sub>2</sub>, and by knowing the inherent ratio between CO<sub>2</sub> and CH<sub>4</sub> a calculation of the total amount of CO<sub>2</sub> leaking can be assessed accurately. This is provided that the CH<sub>4</sub> is not consumed by methanophiles in the marine environment prior to being detected [5].

Secondly, low release rates affect the style of emission. For experiment C, low flow rates led to much more intermittent bubbling, which made our calculations of the evolution of gas seepage complicated. The methodologies developed for CCS that detect and quantify gas emission at aqueous seeps must be capable of doing both, even when gas release is intermittent and occurs at a point location (see [12]).

Thirdly, our observation that the release rate affects how much CO<sub>2</sub> dissolves is important. This implies that quantitation of leakage for more rapid leaks could be approximated by simply measuring the rate of CO<sub>2</sub> leakage from gas bubbling. However, for lower rates, quantitation must account for dissolution of CO<sub>2</sub>. Future experiments will further investigate the effect of environmental conditions (e.g. sand properties, thickness) and injection rate on CO<sub>2</sub> fate.

While it is probable that other inert tracers might be selected for use at commercial CCS stores, CH<sub>4</sub> is a common constituent of CO<sub>2</sub> from pre-combustion capture [10] and is present at trace levels in the atmosphere and so could act as a low-cost tracer for CCS. Future work will explore other preferred tracers including inherent CO<sub>2</sub> isotopes and noble gases [5, 13].

#### 5. Conclusions

We have explored how well chemical tracers for CCS can aid the quantitation of CO<sub>2</sub> leakage and CO<sub>2</sub> fate in aquatic environments by using an experimental set up to simulate gas leakage into sediments. We measured the partitioning of co-released gases at different flow rates and used the data to determine the apparent emission rate and fate of CO<sub>2</sub>. We used CH<sub>4</sub> as a tracer as it is low cost and easy to measure in situ and it is a candidate tracer for CCS, however other inert compounds may be more desirable for commercial use.

We found that the fate of the CO<sub>2</sub> (i.e. the degree of CO<sub>2</sub> dissolution) is affected by the leakage rate more than the physical conditions of the aqueous leakage pathway (i.e. the presence of sand). While further work needs to be done to accurately quantify the impact with varying depths of water, water chemistry and sediment thickness, our results suggest that tracers could be used to successfully deduce the fate and quantity of CO<sub>2</sub> leakage in marine or aquatic environments if the tracer does not interact with water.

This work contributes to ongoing efforts to improve environmental monitoring techniques and provides a basis for understanding how bodies of water and/or sediment influence CO<sub>2</sub> leak style and monitoring outcomes.

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