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What have we learnt about CO_2 leakage in the context of commercial-scale CCS?

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Abstract

The viability of Carbon Capture and Storage (CCS) depends on the reliable containment of injected CO_2 in the subsurface. Robust and cost-effective approaches to measure monitor and verify CO_2 containment are required to demonstrate that CO_2 has not breached the reservoir, and to comply with CCS regulations. This includes capability to detect and quantify any potential leakage to surface. It is useful to consider the range of possible leak rates for potential CO_2 leak pathways from an intended storage reservoir to surface to inform the design of effective monitoring approaches. However, in the absence of a portfolio of leakage from engineered CO_2 stores we must instead learn from industrial and natural analogues, numerical models, and laboratory and field experiments that have intentionally released CO_2 into the shallow subsurface to simulate a CO_2 leak to surface. We collated a global dataset of measured or estimated CO_2 flux (CO_2 emission per unit area) and CO_2 leak rate from industrial and natural analogues and field experiments. We then examined the dataset to compare emission and flux rates and seep style, and consider the measured emission rates in the context of commercial scale CCS operations. We find that natural and industrial analogues show very wide variation in the scale of CO_2 emissions, and tend to be larger than leaks simulated by CO_2 release experiments. For all analogue types (natural, industrial, or experiment) the emission rates show greater variation between sites than CO_2 flux rates. Quantitation approaches are non-standardized, and that measuring and reporting both the CO_2 flux and seep rate is rare as it remains challenging, particularly in marine environments. Finally, we observe that CO_2 fluxes tend to be associated with particular emission characteristics (vent, diffuse, or water-associated). We propose that characteristics could inform the design and performance requirements for CO_2 leak monitoring approaches tailored to detect specific emission styles.

Keywords: leakage; CCS; seep rate; CO_2 flux; monitoring; risk assessment

1. Introduction

Large-scale deployment of carbon capture and storage (CCS) technology is anticipated in order to limit global temperature rise to 1.5°C, in line with the Paris Agreement, in the most cost-effective way [1-3]. The technology can be deployed to abate emissions from fossil fuel consumption (for energy, heat or hydrogen) and industrial processes (e.g. cement, steel), or for bioenergy and CCS (BECCS) which offers sustained net negative emissions. Concerns about leakage of CO_2, either as a free phase or as a dissolved constituent of formation waters, threaten the viability of CCS as an effective climate mitigation technology, despite significant leakage being very unlikely [4]. However, given

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the scale of geological uncertainty in the nature of and location of potential leakage pathways and the required performance lifetime of a CO_2 store (thousands of years), it is not possible to eradicate the risk of leakage altogether [5, 6]. The challenge therefore is to (a) demonstrate that containment risks can be minimised, i.e. to demonstrate effective risk management, and (b) demonstrate that leakage can reliably detected, i.e. to demonstrate robust and low-cost monitoring capabilities. However, there may differences between what level of risk (of leakage and/or impact) is acceptable to operators, regulators, investors, and publics.

1.1. What is acceptable leakage?

Acceptable rates of CO_2 leakage to surface posed from a climate change perspective are usually expressed as a percentage of the total volume injected, and are below 1% over 1000 years [5, 7, 8]. For example, Hepple and Benson [9] calculated that 0.01% leakage per year (i.e. 90% storage over 1000 years) is acceptable for a range of scenarios for climate mitigation and the IPCC recommend that to benefit medium-term mitigation efforts CO_2 stores should operate with less than 1% CO_2 loss to the surface in 1,000 years (IPCC, 2005). However, expressed in this way, the scale of the project (the rate of injection and the total injection period) determines the quantity of CO_2 that could permissibly be leaked, and therefore the potential environmental impact of CO_2 leakage to surface, which includes social risks (health hazards, water quality) other environmental risks (e.g. risks to groundwater quality or plant health). Further, as well as greenhouse gas emission accounting, risk of leakage to surface also affects market risks [10] and public perception risks [11]. Leakage therefore has implications for policy design, public perception, impact mitigation and regulatory compliance [12, 13]. It may therefore be more appropriate to instead consider what leakage is reasonably *monitorable*, i.e. what leakage can be reliably detected, and whether the risk posed by such leakage is acceptable in terms of the potential impact on different receptors (e.g. water resources, the shallow subsurface or animals and plants surface in rural or urban locations). Monitorability will be governed by a range of factors, including the geological characteristics of the CO_2 migration pathway and overburden, and so the leakage rate (from the storage formation and to surface), the environmental setting (offshore or onshore, natural background variation), accessibility (i.e. ease of conducting surveys), monitoring costs, public acceptability and so on. Generally, should CO_2 leak to surface, large seeps are more likely to be detected in a timely and cost-effective fashion than small seeps, and onshore seepage may be more readily detected by low cost remote sensing methods [14, 15].

1.2. Leakage pathways from the reservoir to surface

Uncertainties inherent in subsurface characterisation due to geological heterogeneity means that risk of leakage can be minimized, but not eliminated [6]. Understanding potential flow pathways and predicting the impact of geological features on CO_2 spread and fate is the first step of leakage risk assessment which will affect site selection, reservoir management, and the measurement monitoring and verification (MMV) approach(es). There are a range of potential CO_2 leakage pathways to surface from a breached storage formation, including artificial (drilling-induced permeability around the well-bore, or injection induced fracture opening) or naturally occurring features (geological discontinuities such as faults, fractures, or stratigraphic heterogeneities) [16].

It is important to note that rate of surface seepage of leaked CO_2 will not represent the rate at which CO_2 leaks from the primary storage formation. The migrating CO_2 will attenuate by a range of subsurface processes during ascent to surface, including solubility trapping, mineralization, residual gas trapping and accumulation into overlying units to form stacked reservoirs [17]. As such, 'performance requirements for surface seepage rates should not be construed as performance requirements for leakage from the primary storage reservoir' [9].

In the absence of experience of CO_2 leakage from commercial-scale storage operations, we must look to alternative means to understand potential characteristics of CO_2 leakage from breached stores, including estimates of possible CO_2 leak rates. These alternatives include: (a) industrial analogues, including accidental man-made seeps from subsurface activity, such as a leaky well bore; (b) natural CO_2 seeps, where geologically derived CO_2 leaks to surface via natural leak pathways; (c) artificially simulating leakage using fluid flow models, lab experiments, or field-scale release experiments where CO_2 is injected into the subsurface to artificially mimic a CO_2 seep.

This work aims to examine current knowledge regarding the quantities of CO_2 that leak to surface in a range of geological and environmental settings, and consider what this means for monitoring design at CCS sites.

First, we collate a global database of quantified CO_2 degassing at sites of natural and man-made CO_2 seeps. CO_2 seepage can be reported in a range of different units, and so we harmonise all measurements to report values in the same units to enable comparison. We then calculate what rates could be 'permissible' (from a climate change perspective) should leakage occur from a range of commercial scale CO_2 injection operations, and compare these values to the seep rates in the global database. We examine the global dataset of CO_2 seeps to constrain any relationship between seep rate, styles and setting, to assess what scale and style of seepage would be most comparable to that which might arise from CCS, and whether such leaks would be readily detectable or monitorable in different environments or settings.

Thus, our work enables the potential range of emissions from CO_2 stores to be characterised for different emission pathways and geological contexts. This is important not only for assessing potential seep scenarios and designing appropriate monitoring capabilities, particularly for very small seeps that are difficult to detect and quantify, but is also helpful resource for communicating and visualising leakage to relevant stakeholders, including regulators and the publics.

2. Method

2.1. Global database of CO_2 seep quantities

CO_2 leakage can be quantified in terms of CO_2 flux, i.e. the seep rate per unit area, or total CO_2 emission rate (in mass or volume of CO_2). We collated a global database of quantified CO_2 gas seeps where CO_2 emission rate or flux is reported or can be deduced from the site description. This database includes the following categories of seep:

- *CO_2 release field experiments*: where CO_2 gas is intentionally released into the shallow subsurface to artificially simulate CO_2 seepage.
- *Natural CO_2 seeps*: seepage of naturally occurring CO_2. These may be onshore (on land or through lakes and river beds) or offshore. We note whether seepage is related to volcanic processes, and observations such as area of degassing, style of seepage, and proposed origin and leak pathway.
- *Industrial CO_2 seeps:* degassing rates at occurrences of man-made CO_2 leakage, such as a leaking well bore. We do not consider gas emissions from events such as blowouts during drilling. While there are some cases of such events in CO_2-prone regions like Greece [34] and Italy [35], these do not present leak pathways for CO_2 that would need to be detected and monitored via MMV programs.

There is no standard unit for reporting CO_2 leak rates and fluxes. CO_2 leakage may be reported in terms of mass (g, kg, tonnes) or volume (mL, L) or concentration (mol, mmol) per unit of time (which might be expressed as per second, per min, per hour, per day, per year). Where seepage volume is reported, we assume CO_2 properties at standard temperature and pressure (STP) to calculate CO_2 mass (where gas composition is not reported, we assume that the emitted gas is 100% CO_2). CO_2 flux, by definition, should be given as the rate of CO_2 leaked per unit area (usually m^2). If no area unit was provided, the reported value is the CO_2 leakage rate (rate of CO_2 leaked), rather than flux specifically. Where the total seep rate is reported but seep flux is not, where possible, we estimate the average flux using descriptions or images of the seepage area. To enable direct data comparison, we harmonized the CO_2 release rates and CO_2 fluxes so that dataset parameters were presented in standardized units. We elected to express CO_2 flux as $g(CO_2)s^{-1}m^{-2}$ and total rate of CO_2 leakage as $g(CO_2)s^{-1}$, but we also consider CO_2 leakage rate as tonnes per annum, $t(CO_2)$pa, since this is the standard unit for carbon accounting.

2.2. Determining leakage from commercial scale CO_2 stores

To place seep rates and fluxes in the global database within the current legislative context and explore their ramifications for commercial CCS operations, we consider the range of scales for commercial CO_2 storage operations. We examine the portfolio of current and planned geological CO_2 storage projects to obtain minimum and maximum feasible injection rates:

- *Minimum:* There are currently few large-scale projects injecting CO_2 for the purpose of permanent geological storage [36]. For CO_2 storage to be commercial scale, it is generally accepted that injection rates must be at least 1 $Mt(CO_2)$pa [37], which is the capture rate at 3 of the 4 projects operating in 2017. The smallest 'large scale'

CCS project is Snøhvit (Norway), which has been injecting CO_2 since 2008. The reported capture rate at Snøhvit is 0.7 Mt(CO_2)pa. However the annual injection rate is much smaller than this value, since to date only 3 Mt has been stored at this site (giving an average CO_2 injection rate of 0.4 Mt(CO_2)pa). The GCCSI [38] defines large-scale CCS facilities to be those injecting above 0.4Mt(CO_2)pa, unless the project is capturing CO_2 from coal, in which case at least 0.8 Mt(CO_2)pa must be stored. For our work, we assume a minimum injection rate for a commercial scale CCS project of 0.4 Mt(CO_2)pa.

- *Maximum*: CCS roll-out will be coupled with CCS scale-up. The largest dedicated geological storage project in development to-date is the Gorgon Carbon Dioxide Injection Project, located off the coast of Western Australia. Once operational it will inject 3.4 - 4.0 Mt(CO_2)pa for 25-30 years [38]. Annual CO_2 injection rate at CO_2 Enhanced Oil Recovery (EOR) projects may be greater than the injection rates for dedicated geological storage. However, the overall quantities of CO_2 sequestered within the formation at the end of the EOR project lifetime are difficult to estimate because CO_2 is usually recycled. For this reason our study assumes a maximum injection rate of 5 Mt(CO_2)pa for a commercial scale dedicated geological storage CCS operation.

While many factors may influence the lifetime of a CO_2 injection project, at the crudest level, the injection period will depend on the storage site capacity and injection rate. The design life of powerplants tend to be on the order of ~40 years, while the typical life span of oil and gas reservoirs (from which CO_2 may be separated and injected for storage, such as a Sleipner) is ~30 years. The European Commission considers that the operation period could last between 5-50 years [39]. Thus, CCS projects are typically likely to be operational for several decades. However, the proposal to move towards CO_2 storage hubs mean CO_2 from multiple sources could, in theory, be injected into a storage formation until it reaches capacity [40], which could take longer. For simplicity, for this work we consider 40 years of CO_2 injection to be the project life span.

Based on 40 years of injection, in our model we consider the lower-bound CCS project (0.4 Mt(CO_2)pa injection rate) with total of 16 Mt CO_2 stored, and the upper-bound CCS project (5 Mt(CO_2)pa injection rate) with a total of 200 Mt. The climate permissible leak rates for these CCS project end members are shown in Table 1. In this work we assume that the permissible leakage refers to surface leakage (i.e. CO_2 loss to atmosphere) rather than CO_2 migration from the intended storage complex.

Table 1. Minimum and maximum storage scenarios and leakage rates permissible in terms of long-term climate change impacts, which we refer to as 'climate permissible' leak rates.

	Annual injection rate / Mt(CO_2)pa		Total CO_2 stored/ Mt(CO_2)	
	0.4	5	16	200
Climate permissible leak rate from IPCC (2005)*				
t(CO_2)pa	4	50	16	200
g(CO_2)s^{-1}	0.0128	0.159	0.51	6.34

*maximum permissible leak rate per annum to stay above 99% containment (IPCC, 2005) over 1000 years, determined to be appropriate performance from a climate change mitigation perspective.

3. Results

3.1. 3.1 Global database of CO_2 seepage

In total, data from 55 different CO_2 seeps were compiled and the data harmonized to express flux and leak rate in common units (g/m2/day and t/day, respectively). The global dataset is shown in Figure 1 and summarized in Table 2. The dataset includes 14 man-made (8 field experiments, 6 industrial analogues), and 41 natural seeps. 9 seeps are located offshore (8 natural, 1 field experiment). Many additional occurrences of natural and man-made CO_2 seepage were not included because no information about seep rate or flux could be found in the published literature.

CO2 flux is reported for 39 sites (70% of the dataset), seep rate at 49 sites (90% of the dataset), and both flux and seep rate measurements are reported for 30 sites (55% of the dataset). For the majority of locations, a single value (mean or maximum) seep flux or rate was determined. At other locations, a range of values are provided, either reporting values measured at different locations within a seep system or reporting maximum and minimum calculated values for the approach used to determine flux or seep rate. For 19 sites, the CO_2 clearly originates from volcanic sources, or geothermal processes related to volcanism – though very few seeps are fumarolic (i.e. high temperature) expressions. Over a third of the dataset comprises of CO_2 seepage located in Italy (17 terrestrial, 2 marine, and 1 industrial analogue), which is a region of anomalous earth degassing [41, 42].

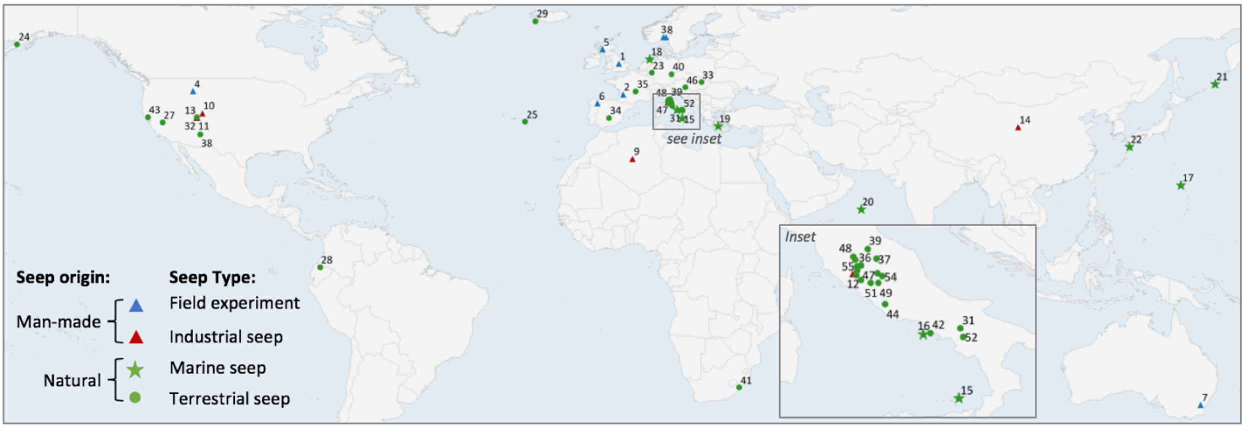


Figure 1: Location and type of CO_2 seeps around the world where CO_2 flux and/or CO_2 leak rate has been measured or estimated. The dataset includes 14 man-made (8 field experiments, 6 industrial seeps), and 41 natural seeps (8 marine and 33 terrestrial). Over a third of documented seeps are located in Italy (inset).

Table 2: Summary of CO_2 seeps considered in this global dataset. All CO_2 seeps included in the dataset have CO_2 flux or CO_2 leak rates reported in the published literature.

n	Name	Country	Type (v = volcanic origin)	Key reference
1	ASGARD	England	Artificial - Experiment	[28]
2	CO2-DEMO	France	Artificial - Experiment	[43]
3	CO2Field Lab	Norway	Artificial - Experiment	[31]
4	ZERT	USA	Artificial - Experiment	[32]
5	QICS	Scotland	Artificial - Experiment	[25]
6	PISCO2	Spain	Artificial - Experiment	[44]
7	Ginninderra	Australia	Artificial - Experiment	[26]
8	Grimsrud Farm	Norway	Artificial - Experiment	[45]
9	KB5 (In Salah)	Algeria	Artificial - Industrial	[46]
10	Rangely	Colorado (USA)	Artificial - Industrial	[22]
11	Crystal Geyser	Utah (USA)	Artificial - Industrial	[29]
12	Banditella	Italy	Artificial - Industrial	[47]
13	10 mile geyser	Utah (USA)	Artificial - Industrial	[29]
14	Qinghai	China	Artificial - Industrial	[20]
15	Panarea	Tyrrhenian Sea	Natural – Marine (V)	[48]
16	Ischia	Tyrrhenian Sea	Natural - Marine (V)	[49]
17	Champagne	Philippine Sea	Natural - Marine (V)	[50]
18	Salt Dome Juist	S. German North Sea	Natural - Marine	[51]
19	Milos	Mediterranean Sea	Natural - Marine (V)	[52]
20	Dominica	Caribbean Sea	Natural - Marine (V)	[53]

21	Ushishir volcano	Sea of Okhotsk	Natural - Marine (V)	[14]
22	Kagoshima Bay	East China Sea	Natural - Marine (V)	[54]
23	Laacher See	Germany	Natural – Terrestrial (V)	[28]
24	Ukinrek Maars	Alaska (USA)	Natural – Terrestrial (V)	[55]
25	Furnas	Azores (Portugal)	Natural – Terrestrial (V)	[56]
26	Latera	Italy	Natural - Terrestrial (V)	[57]
27	Horseshoe Lake	California (USA)	Natural - Terrestrial (V)	[58]
28	Pululahua caldera	Ecuador	Natural - Terrestrial (V)	[59]
29	Rekjanes Ridge	Iceland	Natural - Terrestrial (V)	[60]
30	Rapolano Fault	Italy	Natural - Terrestrial	[61]
31	Mefite d'Ansanto	Italy	Natural - Terrestrial	[62]
32	Little Grand Wash fault	Utah (USA)	Natural - Terrestrial	[29]
33	Mátraderecske	Hungary	Natural - Terrestrial (V)	[58]
34	La Sima	Spain	Natural - Terrestrial	[63]
35	Sainte-Marguerite	France	Natural - Terrestrial	[64]
36	Pienza	Italy	Natural - Terrestrial	[65]
37	Umbertide	Italy	Natural - Terrestrial	[65]
38	Butte Travertines	Arizona (USA)	Natural - Terrestrial	[66]
39	Caprese Michelangelo	Italy	Natural - Terrestrial	[67]
40	Cheb Basin	Czech Republic	Natural - Terrestrial	[27]
41	Bongwana Fault	South Africa	Natural - Terrestrial	[19]
42	Solfatara	Italy	Natural - Terrestrial (V)	[58]
43	Clear Lake	California (USA)	Natural - Terrestrial (V)	[58]
44	Cava dei Selci	Italy	Natural - Terrestrial	[68]
45	Florina	Greece	Natural - Terrestrial	[28]
46	Stavešinci	Slovenia	Natural - Terrestrial	[69]
47	Salcheto	Italy	Natural - Terrestrial	[70]
48	Ambra	Italy	Natural - Terrestrial	[71]
49	Montecchie	Italy	Natural - Terrestrial (V)	[70]
50	Bagni San Filippo	Italy	Natural - Terrestrial (V)	[70]
51	Poggio dell'Ulivo	Italy	Natural - Terrestrial	[71]
52	Varchera	Italy	Natural - Terrestrial	[70]
53	Fosso Biscina	Italy	Natural - Terrestrial	[72]
54	San Faustino	Italy	Natural - Terrestrial	[72]
55	Selvena	Italy	Natural - Terrestrial	[65]

3.1.1. Artificial seeps

Of 16 CO_2 release experiments reported to date around the world [33] surface CO_2 seepage was detected at 9 sites, and 8 experiments present estimates of CO_2 leak rate and flux. One experiment (QICS) was located offshore.

There are 6 industrial analogues for CO_2 seepage. These include unintended leakage at two CO_2 injection operations: micro-seepage at CO_2-EOR operations in Rangely (USA) [22]; and wellhead leakage at KB5 well at the In Salah CO_2 injection project due to a missing flange [46]. Other analogues include geyser style seepage from two abandoned boreholes (Crystal Geyser and 10-mile Geyser, Utah) [29], diffuse gas emission from an abandoned coal mine at Banditella, Italy [47] and an abandoned water well in Qinghai [73]. None of the industrial analogues studied here report CO_2 flux, only total leak rate, but in most cases the seep area is typically small – limited to the wellbore or its vicinity – and therefore flux would be anomalously high. The quantity of CO_2 emitted from blowouts have been estimated for Sheep Mountain (USA), Torre Alfina (Italy) and Florina (Greece) but these are not included in the dataset, nor are production rates from wells commercially exploiting CO_2, as these do not represent potential CO_2 leak pathways for CCS that would require MMV.

3.1.2. Natural seeps

Seepage data were compiled for 41 natural CO_2 seep sites (where the exhaled gas comprises >95% CO_2), including 8 marine and 33 terrestrial CO_2 seeps. All but one of the marine systems are hydrothermal or volcanic origin; the origin of CO_2 for the remaining seep (Salt Dome Juist) is unknown [51]. Offshore seepage often occurs over a relatively large area and can be observed as a number of rising streams of CO_2 bubbles. Where water depth was particularly great, such as at Champagne Arc, the CO_2 was supercritical or liquid form. For example, at Hatoma Knoll, East China Sea (not included in the dataset because no seep rates or fluxes have been reported) bubbles of liquid CO_2 were observed to rise through the water column, eventually disappearing as they became hydrates [74].

Most terrestrial seepage is diffuse, over many square meters, sometimes visible due to slight discoloration of the ground where the emissions have inhibited or in some cases encouraged plant life. At 6 seep sites (Florina, Mefite D'Ansanto, Caprese, Butte Travertine, Little Grand Walsh Fault and Northern Salt Wash Graben) seeps with measured leak rates occur close to known subsurface accumulations of CO_2 and so can be inferred to represent natural leakage from a CO_2 reservoir.

There are some occurrences of CO_2 vents (mostly in Italy, e.g. Caprese Michaelangelo, Umbertide, Mefite, Pienza) where degassing is confined to a single focused gas vent, usually situated within a depression filled with muddy water. As venting is usually constrained to a small area, it is relatively easy to measure the total flux compared to diffuse degassing areas [65].

3.2. CO_2 flux and leakage rates

The measured and estimated seep flux and seep rates are shown in Figure 2 and 3. Non-volcanic emissions represent CO_2 release processes more analogous to leak pathways from engineered CO_2 stores. Natural marine and terrestrial non-volcanic CO_2 seeps show a range of seep rates and fluxes. Figure 2a shows that field experiments tend to simulate leak rates smaller than most other industrial or natural seep analogues, offshore or onshore. Field experiments tend to release CO_2 on the order of 1-100 t(CO_2)pa whereas natural seeps release 10 – 100,000 t(CO_2)pa.

Most CO_2 seeps, natural or artificial, emit 100 – 100,000 g/m^2/day. Seep flux data was not available for any industrial analogue for CO_2 seepage, and could not be calculated because the leakage area was not reported. Seepage at K5B or Rangely (n. 9, 10 in Table 2) were very focused, and so the corresponding CO_2 flux values would have been anomalously high. While field experiments tend to simulate leak rates lower than most natural or industrial seeps, the fluxes simulated by field experiments are similar to many marine and terrestrial natural seeps (Figure 2b).

Indeed, CO_2 fluxes for all seeps (Figure 2b) are more similar than the seep rates (Figure 2a), which show many orders of magnitude variation between sites. This implies that seeps emitting very large quantities of CO_2, do so via seepage over larger areas. Figure 4 shows the (log-log) relationship between seep area and seep rate (a) and flux (b), and there is no clear relationship with either. Seep area can only be deduced for 19 seeps, and so the data in Figure 3 is not comprehensive.

In Figures 2a and 3, horizontal orange lines depict the maximum 'climate permissible' leak rates for small (16 Mt) to large (200 Mt) scale commercial scale CO_2 stores (see Table 1). Seep rates simulated by field experiments are towards the climate permissible leak rates for small scale commercial CO_2 injection operations (see Table 1), whereas the majority of other seeps in the dataset have much higher seep rates.

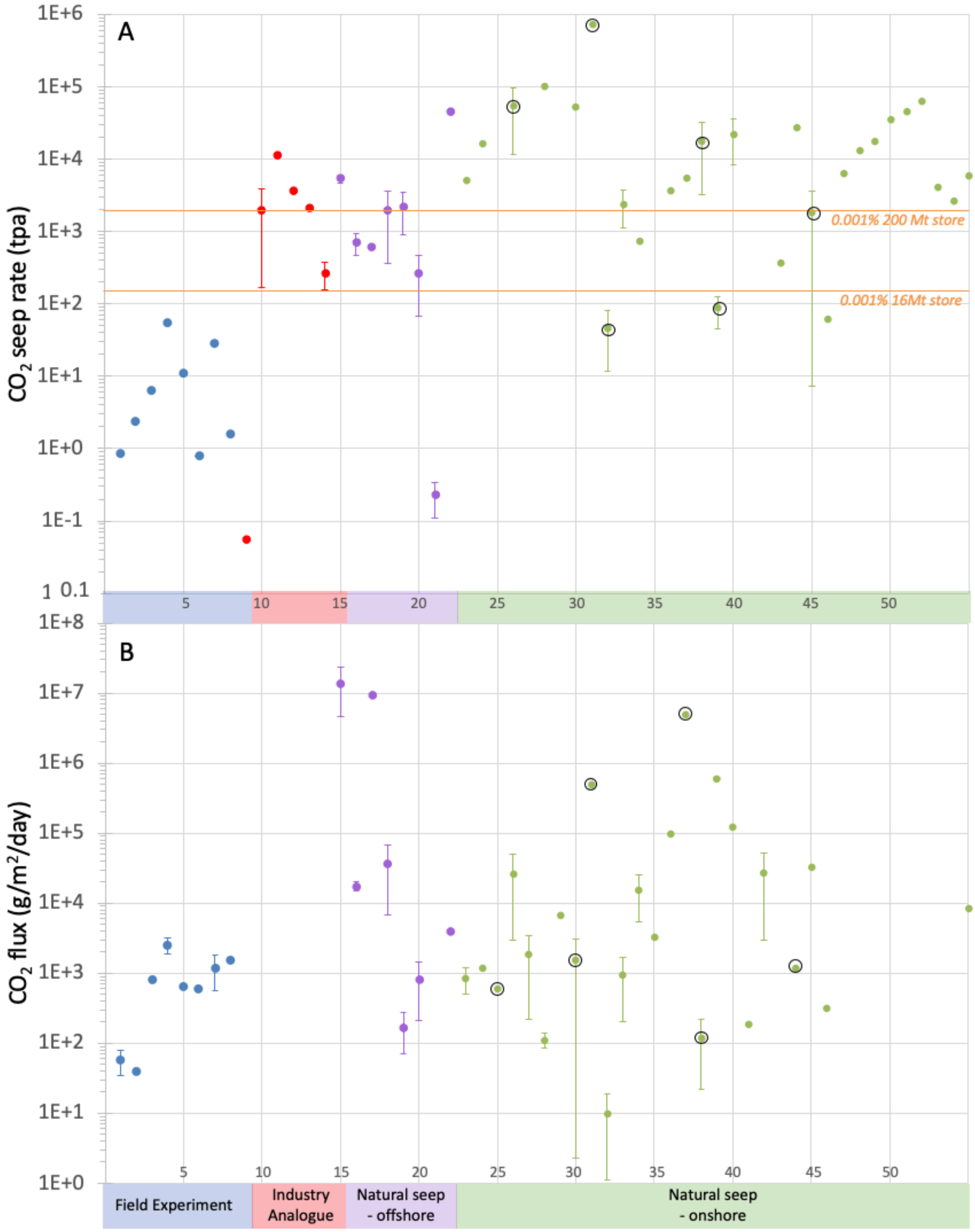


Figure 2: (A) Seep rate (tonnes of CO_2 per annum) and (B) CO_2 flux for each seep in the global seep database; see Table 2 for seep number. For data points with error bars, the mean value is plotted, otherwise the point shows either the maximum or the mean value. Horizontal orange lines depict the maximum climate permissible leak rates for small (16 Mt) to large (200 Mt) scale commercial scale CO_2 stores, see Table 1. A ring around the symbol indicates where seeps are associated with a subsurface CO_2 accumulation.

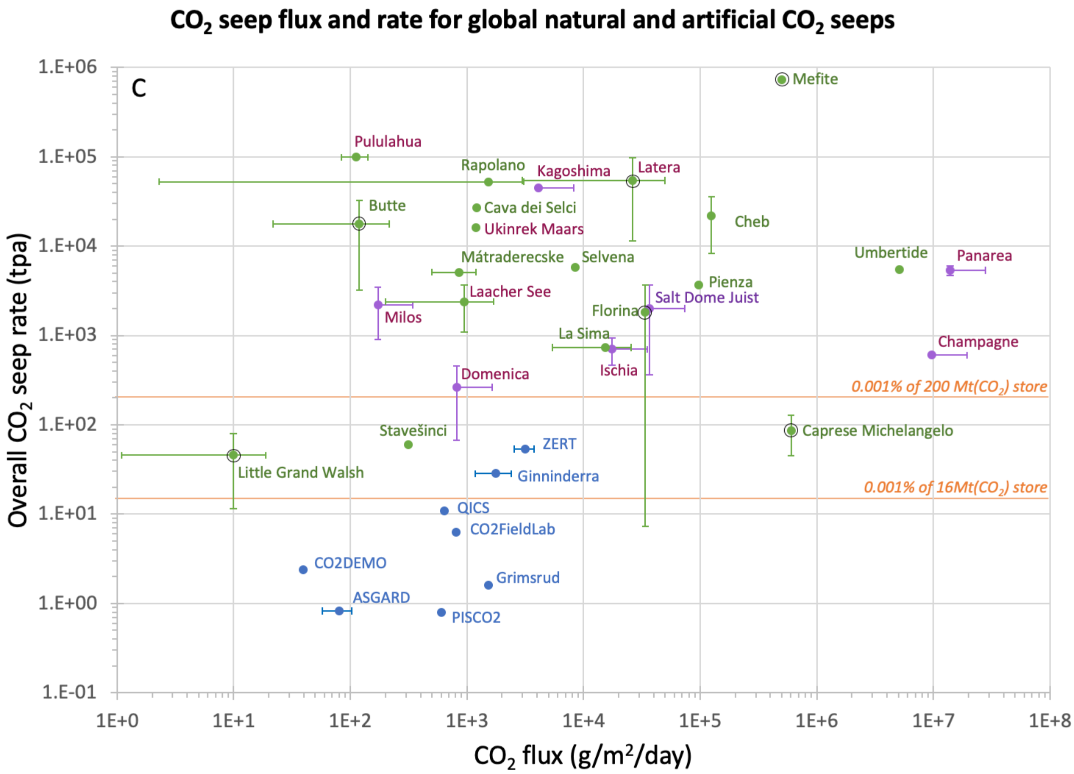


Figure 3: Log-log graph of CO_2 seep flux and total leak rate where both values have been measured or can be estimated (55% the global dataset). CO_2 release experiments are shown in blue, natural offshore seeps in purple, and natural onshore seeps in green. A ring around the symbol indicates where seeps are associated with a subsurface CO_2 accumulation. The seep's identifying name is adjacent to the data point, and mauve text identifies seeps of volcanic CO_2 origin, and therefore less comparable to CCS settings. Error bars show the potential range of estimated values and are not available for all data points. Horizontal orange lines depict the maximum climate permissible leak rates for small (16 Mt) to large (200 Mt) commercial scale CO_2 stores, see Table 1.

4. Discussion

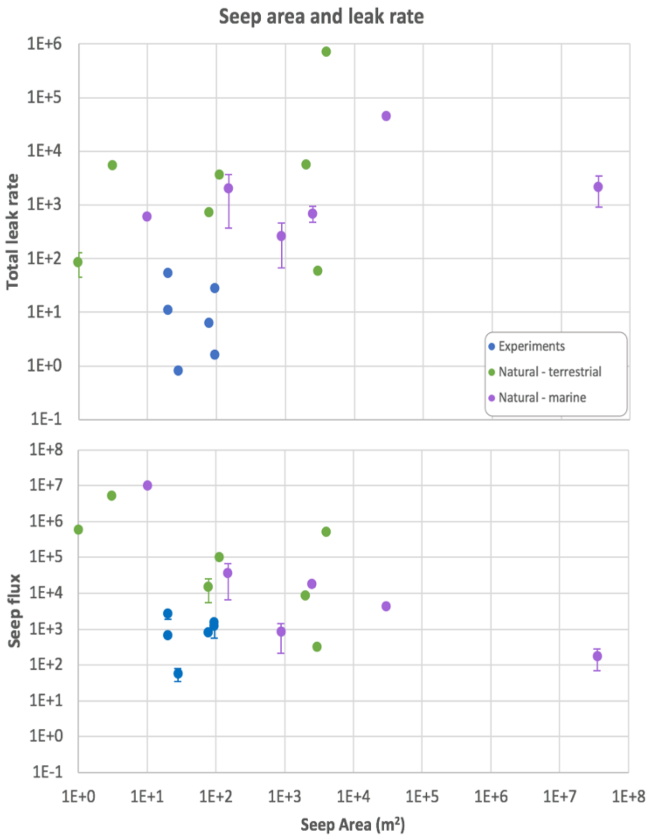
Natural and man-made CO_2 seeps have been widely studied as analogues for leakage that might arise from breached CO_2 stores. Their study has informed understanding of the potential surface expression of CO_2 leakage and the development of methods for detection and leak quantitation.

Our global seep dataset of harmonized seep flux and seep rates shows that CO_2 seepage occurs on a range of scales and settings, but that between sites the seep rate varies more than the seep flux. It also indicates that our capabilities for leak quantitation or our appetite to quantify leakage remain limited; of the known natural CO_2 seeps documented around the world, relatively few have CO_2 emission estimates reported. Studies at 33 natural seeps report emission measurements but estimates of both flux and total seep rate are available for only 18 sites (55% of the dataset). Studies at CO_2 release experiments and at natural analogues (see Roberts et al. [75], this conference) have highlighted the challenges in estimating total CO_2 release rates from the measured fluxes. This knowledge gap needs addressing for CCS MMV to be able to confidently and robustly quantitate any potential CO_2 leaks to surface. This is particularly the case for offshore or aqueous seeps. Few marine seep systems have quantified fluxes, whether the emitted gasses are CO_2 as shown in this work, or methane [17].

Further, estimating the area of seepage can be difficult. In the case of diffuse seepage, the seep area is defined by the area where CO_2 flux is above background. However, where there are several patches of diffuse seepage, or seepage is highly localized at several vents across an area (such as at Caprese Michaelangelo (n. 39) or marine seeps Panarea or Milos (n. 15, 19)), the area of leakage becomes much trickier to define. For example, should there be five 1 m^2 vents across a 100 m^2 area, it could be determined that the area of seepage is the area where vents are found (i.e. 100

m^2; larger area; lower reported flux), or that the area of seepage is best represented by area of the vent mouths or bubble stream emergence points only (i.e. 5 m^2; small area; higher reported flux).

Figure 4: Seep area and (a) CO_2 leak rate and (b) CO_2 flux. Seep area can only be deduced for 19 (of 55) seeps, and so the data is not comprehensive.



4.1. Seep flux

CO_2 fluxes for all seeps are more similar than the seep rates, which show many orders of magnitude variation between sites. Continuous monitoring studies at seeps find that CO_2 flux varies with near-surface environmental changes, water table depth, climatic parameters (temperature, air pressure, rainfall). As such the values reported in our global dataset may not be representative of long term emission, however the extent of the variation in flux at one site is not significant compared to the extent of the vairaiton in flux between different seeps.

Seep flux and seep environment (onshore/offshore) affects the seep style – i.e. the characteristics of the seepage. We find that terrestrial seeps fall into categories of characteristics associated with the gas flux rates (Figure 5a). CO_2 venting occurs where degassing is focussed over a small area (e.g. a few m^2) and so tends lead to very high fluxes. In contrast, the lowest seep rates tend to be associated with travertine mounds, perhaps indicating that seepage associated with groundwaters or mineral reactions is quite slow fluxes or distributed emissions. Between venting and travertine end-members is the diffuse seep style. Diffuse seepage is exhibited by most natural terrestrial seeps, all field experiments that released CO_2 to surface, and typically, diffuse seepage is associated with travertine or vent seeps too. Diffuse emission tends to occur in patches, which can reach tens of meters in diameter. Offshore seeps are harder to classify. The two highest flux seeps are very different in their degassing style; at Panarea, seepage occurs over a large area in relatively shallow seawater depths, whereas Champagne is a very deep vent where CO_2 is emitted as a liquid. In marine or aqueous environments, CO_2 seepage tends to occur as highly localized, often numerous, bubble streams that can be spatially and temporally variable (c.f. [76] this conference). This can make it challenging to estimate CO_2

fluxes, and also harder to define whether the style of seepage is diffuse or focused. Further, not included in our marine dataset is pockmark type emissions from CO_2 degassing. Pockmarks have been observed on seafloors, fed by gas chimneys that arose from very overpressured fluids in sediments. It is not clear if such edifices could arise from breached CO_2 stores, but subsurface images tracking the evolution of injected gas and the sediment structure at the QICS experiment found that small pockmark features developed, fed by gas chimneys in the sediment, like a small scale pockmark formation [77].

For onshore seeps, the seep characteristics identified could be used to design appropriate detection ranges for CCS MMV technologies, where different technologies aim to detect specific emission styles, and where the likely emission style is predicted by geological knowledge of the overburden. For example, different MMV methods with different capabilities may be required for detecting self-contained vent-style seepage compared to detecting diffuse, dispersed CO_2 emissions. Figure 5b shows the emission styles, arranged according to CO_2 flux and CO_2 emission rate, and colour coded according to how easily emissions can be detected, ranging from readily detectable either because there will be a large area of CO_2 anomaly, a large point CO_2 anomaly, or highly visible effects, and so the seep could be detected by low-cost, low-resolution MMV techniques. Other seeps, such as seeps with typically low emission rates or fluxes, or small spatial extent and minimal visible impacts will be need more targeted, higher resolution or more sensitive MMV techniques to detect and identify the seepage.

4.2. Seep rates in the context of CCS

In this work we assume that a) seepage occurs once CO_2 injection has ceased (i.e. once the full 40-200 Mt(CO_2) has been injected b) seepage occurs at a single location rather than via multiple leak pathways to multiple seep sites and that c) the climate permissible leakage refers to surface leakage (i.e. CO_2 loss to atmosphere) rather than CO_2 migration from the intended storage complex. That is, we assume that 100% of the leaked CO_2 seeps to surface. However CO_2 will be attenuated during ascent to surface, through processes such as residual trapping, mineralization and dissolution, and the degree of attenuation will depend on a number of factors including the CO_2 leak pathway, the medium the CO_2 encounters, presence of secondary reservoirs, the flow rate and flow baffles [4]. Even in the near surface, significant CO_2 dispersion and loss can occur, as CO_2 release experiments have demonstrated [33].

So, the question is whether it is the quantity of CO_2 that leaks to surface, or the quantity of CO_2 that leaves the storage formation, that is the important parameter. Current CCS performance legislation [78] refers to the latter, which would require the deployment of sophisticated monitoring of the subsurface and e.g. the application of tracers. From a climate change perspective, the former is of most relevance, and can be measured at seep sites. However, near surface CO_2 that is not immediately emitted as a gas (e.g. trapped in soil pore throats, or dissolved in pore waters) may eventually be emitted to atmosphere, but at a different time to the flux measurements that are made, and so the ‘climate permissible’ flux rate will need to be less than the values presented in Table 1.

With all these caveats, our work finds that CO_2 emission rates at natural seeps tend to be greater than would be climate permissible for engineered CO_2 stores. That is, should leakage to surface occur from an engineered store at rates similar to those of the natural seeps in our dataset, the leak would negate the ability of the CCS project to contribute to carbon emissions reductions. This may reflect sampling bias, where high flux or high emission rate seeps have been preferentially detected and studied. However, there are 8 seeps which reflect the maximum leak rates that need to be detectable at commercial CO_2 stores. These sites could be preferentially studied in order to advise the optimal MMV capability range.

To-date, 9 CO_2 release experiments have successfully simulated CO_2 seepage to atmosphere, and CO_2 emission rates can be estimated for 8 of these. The seep rate at these experiments are several orders of magnitude lower than the rates at most industrial or natural seep analogues. The simulated leaks are towards the ‘climate permissible’ leak rates from small scale commercial CO_2 injection operations (0.4 Mtpa), but much less than rate for larger scale operations. Thus, detecting problematic leakage from a commercial scale store may require less sensitive MMV approaches than those developed for the experiments.

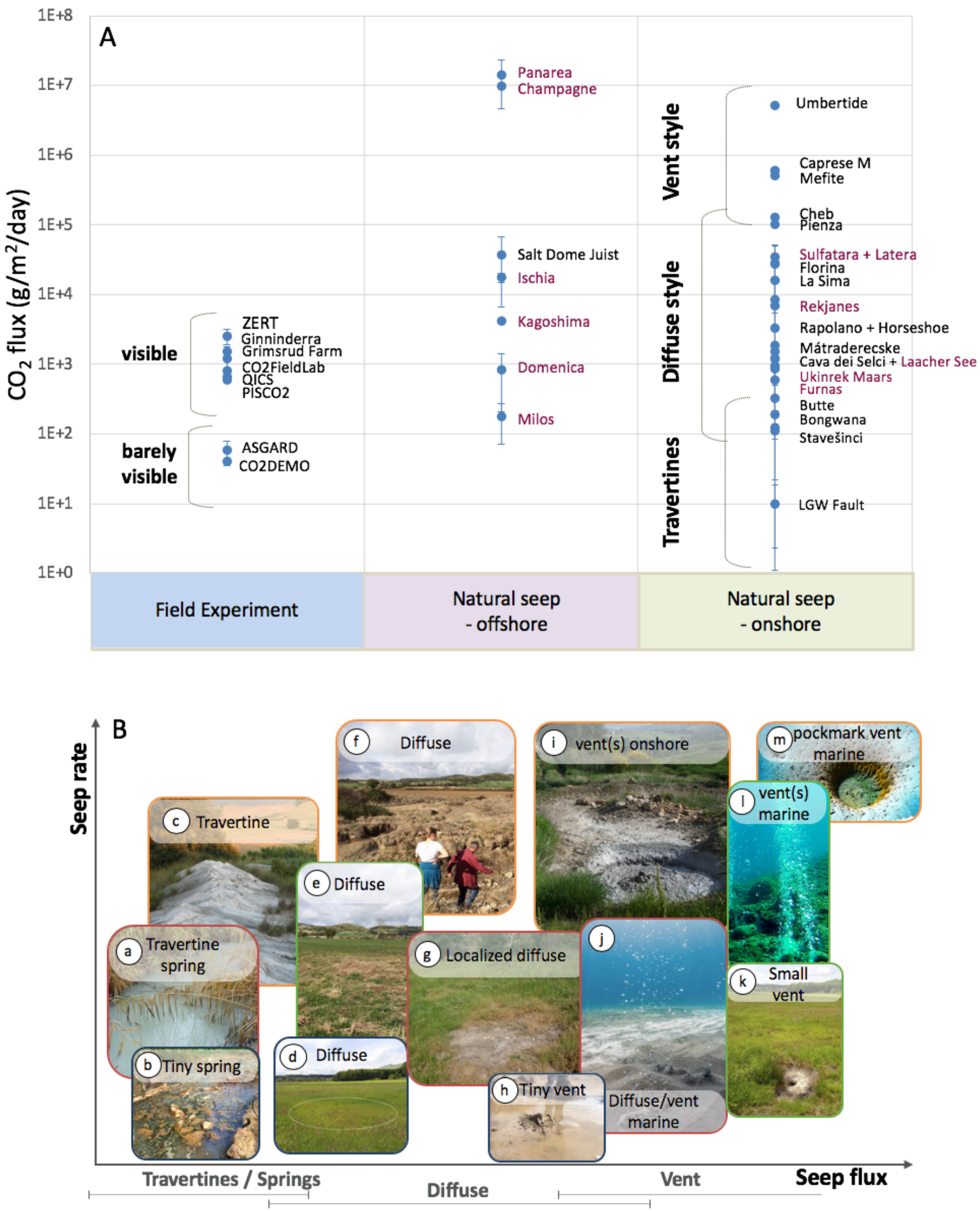


Figure 5: (A) Seep flux affects the seep style. Field experiments simulate diffuse seepage, which is exhibited by most natural terrestrial seeps. CO_2 venting is exhibited at high flux rates; where degassing is focused over a limited area (<1 m^2). For marine seepage, CO_2 emerges are highly localized bubble streams, where there may be several bubble streams per unit area. Low seep rates tend to be associated with travertine mounds, indicating a different pathway for CO_2 transport. Mauve text indicates volcanic setting and therefore less comparable to CCS relevant settings. (B) Schematic of seep styles and ease of MMV detection. The classes of seep characteristics could inform appropriate detection ranges for CCS MMV technologies. Emission styles are colour coded according to how easily emissions can be detected, where green is readily detectable by low-cost, low-resolution MMV techniques, orange is detectable using more sensitive or targeted MMV techniques, and dark blue is detectable using specific MMV approaches over targeted areas. Photos: Authors own (1, 5-9, various, Italy; 2. Daylesford, Australia); Dr Irena Maček (3. Italy; 4. & 11. Stavešinci, Slovenia); Dr Yiannis Issaris (10. Milos); RISCS (12. Panarea); Mazzini et al., 2017 EPSL. DOI: 10.1016/j.epsl.2017.02.014 (13. Troll pockmark).

Seeps that have climate permissible leak magnitudes could provide good examples to test or develop MMV that can confidently quantify seep rates at lower magnitudes. These include the Qinghai (n. 14, Table 2) industrial analogue in China, where seepage is occurring around an abandoned water borehole, the Domenica marine seeps (n. 20 in Table 2) and terrestrial seeps Little Grand Walsh (USA), Caprese Michelangelo (Italy), Clear Lake (USA) and Stavensci (Czech Republic) (n. 32, 39, 43, and 46 respectively in Table 2).

5. Conclusions

Although there are many seeps globally that emit CO_2 and that have been studied for CCS, there are relatively few seeps where CO_2 flux and emission rates have been estimated. Studies at natural and artificial seeps finds that there are numerous methods of estimating CO_2 seep rate from measured seep fluxes, ranging from the sophisticated technical to the simplistic. Measuring CO_2 flux and seep rate therefore remains challenging, and non-standardized. Measuring CO_2 flux and leak rate is particularly challenging in aqueous environments, such as offshore.

The global dataset we compile indicates that there is a great range of CO_2 seep fluxes and seep rates. Seep rate is more varied than seep flux, suggesting that high seep rates occur over large areas. CO_2 injection field experiments performed to date have simulated seep rates lower than most other natural or artificial seeps, though sampling bias and challenges in leak quantitation may mean that smaller natural seeps are underrepresented in this dataset.

Seep flux and seep environment (onshore/offshore) affects the seep style – i.e. the characteristics of the seepage. We find that terrestrial seeps fall into categories of characteristics associated with the gas flux rates. The seep characteristics identified could be used to design appropriate detection ranges for CCS MMV technologies, where different technologies or monitoring programs aim to detect specific emission styles (low-cost, low-intensity, broad approach vs higher intensity more targeted approach). The likely emission style is predicted by geological knowledge of the overburden.

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