What have we learnt from CO_2 release field experiments and what are the gaps for the future?

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Abstract

Legislation and guidelines developed for Carbon Capture and Storage (CCS) have set performance requirements to minimize leakage risk, and to quantify and remediate any leaks that arise. For compliance it is necessary to have a comprehensive understanding of the possible spread, fate and impacts of any leaked CO_2, and the ability to detect and quantify any CO_2 seepage into marine or terrestrial environments. Over the past decade, a number of field scale CO_2 release experiments have been conducted around the world to address many of the uncertainties regarding the characteristics of near-surface expression of CO_2 in terms of the impact and quantitation of CO_2 leaks. In these experiments, either free phase or dissolved CO_2 was injected and released into the shallow subsurface so as to artificially simulate a CO_2 leak into the near-surface environment. The experiments differ in a number of ways, from the geological conditions, surface environments, injection rates and experimental set-up - including the injection and monitoring strategy. These experiments have provided abundant information to aid in the development of our scientific understanding of environmental impacts of CO_2 while assessing state of the art monitoring techniques.

We collated a global dataset of field-scale shallow (depths < ~25 m) controlled CO_2 release experiments. The dataset includes 14 different field experiment locations, of which nine intended to release CO_2 to the surface, and the remaining sites intended for CO_2 to remain in the shallow subsurface. Several release experiments have been conducted at half of these sites, and so in total, 42 different CO_2 release tests have taken place at the 14 sites in our dataset. We scrutinized our dataset to establish: (i) the range of experimental approaches and settings explored to date (such as the environment, subsurface conditions, injection strategy and whether gaseous or dissolved CO_2 were injected and in what quantities); (ii) the range of CO_2 injection and surface release rates at these experiments; (iii) the collective learnings about the surface and subsurface manifestation of the CO_2 release, the spread and fate of the CO_2, rates of CO_2 flux to surface, and methods of measuring these; (iv) the strengths and limitations of current approaches for detecting and quantifying CO_2. This allowed us to highlight where uncertainties remain and identify knowledge gaps that future experiments should seek to address. Further, drawing on the collective experiences, we have identified common issues or complications which future CO_2 release experiments can learn from.

Keywords: *Carbon Capture and Storage, CO_2 leakage, monitoring, detection, quantification, flux*

1. Introduction

Carbon Capture and Storage (CCS) is a promising climate mitigation technology, whereby CO_2 emissions are captured at source, compressed and transported and then injected into deep geological formations where they are intended to remain for geological timescales. Geological CO_2 storage sites are selected and engineered to minimize risk of leakage and maximise long-term storage potential. Small amounts of CO_2 leakage could be tolerated without negating the cost-effectiveness of CCS from both climate change mitigation and financial perspectives (Hepple and Benson, 2005, Zwaan and Gerlagh, 2009), and the

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migration of CO_2 or brines from the CO_2 store may beneficially relieve reservoir fluid pressure (Cihan et al., 2013). However unintended leakage of CO_2 or formation fluids would effect a number of stakeholders, incurring economic and financial costs (Bielicki et al., 2014), environmental impact (Jones et al., 2015) and also challenge the social and political acceptability of the technology (Ha-Duong and Loisel, 2009). As such any incidence of leakage from engineered stores could have ramifications for the CCS industry on a global scale, and so the viability of CCS depends on the reliable containment of injected CO_2 in the subsurface.

Legislation and guidelines developed for CCS set performance requirements that seek to minimize the risk of leakage from the storage complex. The IPCC (2005) recommend that CO_2 stores should operate with less than 1% CO_2 loss to the surface over 1,000 years. The US Department of Energy (US DOE) aims for 99% containment of CO_2 injected for the purpose of geological storage (Bielicki et al., 2015), whereas the EU CCS Directive (EU, 2009) requires CO_2 to remain 'permanently' in the storage formation. Any CO_2 that leaks from the storage formation must therefore be quantified for reasons of performance assurance, as well as carbon accounting (Dixon et al., 2015). Furthermore, legislation permitting subterranean CO_2 storage in the US, EU and Japan or subseabed in the North Atlantic require appropriate assessment of the risk of CO_2 leakage from the intended storage reservoir, the potential impacts of CO_2 leakage on the environment, and means of monitoring for leakage (Jones et al., 2015). In this context, 'environment' includes the near-subsurface (such as underground sources of drinking water) or surface (terrestrial or marine) ecosystems, including human health. Environmental impacts might source from the CO_2 itself (free phase or dissolved) and any co-injected impurities, or brines displaced as a result of pressure perturbation from CO_2 injection and migration or degraded by geochemical interaction of CO_2 and the surrounding rock, or mobilization of other fluids (e.g. methane). In the event of leakage of CO_2 into the near surface environment, the leak must be mitigated and the site eventually returned to baseline conditions.

To comply with site performance and monitoring requirements it is necessary to have a comprehensive understanding of the possible spread and fate of CO_2 in the deep and shallow subsurface, and the potential impacts of such leakage. Since approximately 40% of global storage capacity is located offshore (IEAGHG, 2008), it is important that leakage into marine and terrestrial environments is explored.

However, studies of sealing and non-sealing naturally occurring CO_2 reservoirs find that leakage to surface is globally rare, even at sites that would not be considered suitably secure for CO_2 storage (Miocic et al., 2016, Roberts et al., 2017b, Miocic et al., 2019). Should CO_2 migrate from the storage reservoir, multiple processes will attenuate the CO_2, such that the likelihood of CO_2 reaching the surface is low (Alcalde et al., 2018, Roberts et al., 2018). Improperly sealed wellbores present the most likely pathways of leakage (IPCC, 2005). There has been no leakage to surface at pilot and commercial scale CO_2 storage operations to date. In the absence of cases of CO_2 leakage, the CCS community have looked to natural analogues and field experiments to further scientific understanding of CO_2 leakage and its impacts, and to develop monitoring approaches that are capable of enabling any CO_2 leaks to be identified, attributed, and quantified (referred to as monitoring, measurement and verification, MMV, techniques). Indeed, since 2006 a number of field-scale controlled release experiments have been conducted around the world. The experiments release free phase or dissolved CO_2 into the shallow subsurface to artificially simulate a CO_2 leak into the near-surface environment. The experiments differ in regard to the geological and surface environments and experimental set-up, including the injection rate and monitoring strategy. Since CO_2 release is controlled, and so the injection rate and quantities are known, these experiments provide excellent opportunities to test methods of measuring and quantifying CO_2 fate, and compare changes to environmental conditions and ecosystem health. MMV methods for commercial-scale applications can be tested and calibrated while capability and expertise is developed through learning-by-doing at the field site. Further, field experience of acquiring baseline and post-release information is valuable for developing site monitoring protocols that fulfil the decrees of current environmental legislation.

A number of recent reviews have excellently summarised the significant contribution that these experiments have made to current scientific understanding of environmental impacts and state of the art monitoring techniques (Feitz et al., 2014b, Jenkins et al., 2015, Jones et al., 2015, Lee et al., 2016). However to date there has been no comprehensive examination of the collective learning at these sites with regards to the fate and spread of the CO_2 and the surface manifestation of the leakage. Similarly, there have been no syntheses of the injection rates and the leakage pathways that these sites mimic, nor a consolidation of lessons learned

for the design of an advanced experimental approach. To this end, we have collated a global dataset of field-scale controlled release experiments, detailing the experimental approach and findings about the surface and subsurface manifestation of the CO_2 release, the fate of the CO_2 and leakage quantification. The results were compared to observations from natural analogue and modelling studies and scrutinised to elucidate collective learnings and highlight where uncertainties remain. Future release experimental design and reporting will benefit from this work as the scientific community continue to seek methods to best characterise and monitor storage sites most effectively.

2. Method and approach: collating global CO_2 release experiments

We compiled a dataset of field-scale shallow controlled CO_2 release experiments for which the research results are publicly available (prior to May 2017). We focussed on field experiments that injected/released CO_2 into the subsurface with the aim that it would migrate and reach the surface or shallow subsurface rather than remain trapped in the injection formation.

Dataset variables, listed in Table 1, were populated through detailed review of published literature complemented by personal communication/interview with some of the key research scientists involved in projects or site custodians.

There is no standard unit for reporting CO_2 release rates into the subsurface and CO_2 fluxes from land surface or seabed to atmosphere or water column. As such, in the experiments we reviewed, rate of CO_2 leakage could be expressed 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). CO_2 flux, by definition, should be expressed 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. To enable direct data comparison, where possible, we harmonised the CO_2 release rates and CO_2 fluxes so that dataset parameters were presented in standardised units (see Table 1). 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. If specific information or data were not reported or available, where possible, these values were inferred, calculated or estimated from the published information; for example, seep width could be inferred from the spatial distribution of CO_2 flux, or vertical leak velocity could be calculated from the information about CO_2 injection depth and surface arrival time. When converting, for example, from CO_2 volume to CO_2 mass, in the absence of specific temperature and pressure conditions at the site we assume CO_2 properties at STP.

We also noted the key monitoring tools that were used at each experiment - particularly for leakage quantification, CO_2 attribution and fate, including the presence of any added chemical tracers. The Table 1 dataset is incomplete for many of the CO_2 release experiments studied; either those data were not collected or they are not yet publicly available.

Variable	Sub variable	Description	Units/note	SI
Basic descriptive information	Acronym	Acronym of the site name		Y
	Location	Longitude, latitude, country	degrees	Y
	Project aims	Principal research aims	broad aims	Y
		Release to surface intended or not		Y
	Funding body	Source of funding		N
		Funding total	€ Euros	Y
	Project partners			N
	Key contact	Name and contact email of Principle Investigator		N
	Project status	Project completed / more CO_2 releases intended		N
Experiment set-up and site information	Well information	Depth below ground surface of CO_2 injector	metres	Y
		Borehole type (deviated, vertical or inclined)		Y
		Properties of CO_2 injector (single or multiple source)	Number of release points	Y
		Properties of the intended injection formation	Rock type; thickness	Y

	Geological information	Properties of the overlying formation	If different from injection formation	Y
		Soil properties	Type; thickness	Y
	Ecosystem type	Terrestrial/marine		Y
		The surface ecosystem at the site	Incl. vegetation type.	Y
	Hydrological characteristics	Water table depth and flow direction	metres	Y
CO_2 injection (for each experiment)	CO_2 properties	CO_2 source; gas composition	(% CO_2)	Y
		$\delta^{13}C$ composition	‰	Y
		Injected phase	Gas or water containing dissolved CO_2	Y
	Injection rate	Steady, variable, or incremental		Y
		Maximum and minimum	$g(CO_2)/s$; gs^{-1}	Y
	Injection periods	Date injection started & ceased	Day/month/year (time)	Y
		Total injection period	days	Y
	Quantity of CO_2 injected	For each experiment	kg	Y
	Overall	Number of experiments at the site		Y
		Total quantity of CO_2 injected	kg	Y
CO_2 fate	Surface leakage	Surface leakage?	Y/N	
		Lag time (between start of injection and surface arrival)	hours	Y
		Flux rate*	$g(CO_2)/s/m^2$; $gs^{-1}m^{-2}$	Y
		Vertical leak velocity**	m/s	Y
		Proportion of injected CO_2 released to surface	%	Y
		Distribution	Patchy, uniform	Y
		Hotspot radius***	metres	Y
		Leak location (with respect to the injector)	above injector / deviated	Y
		Temporal changes		Y
	Subsurface spread (soil gas)	Detected in soil gas?	Y/N	
		Maximum soil gas concentration	%	Y
		Lag time (between start of injection and arrival in soil gas)	hours	Y
		Distribution		Y
	Subsurface spread (groundwater)	Detected in groundwater?	Y/N	
		Method / parameter (e.g. pH, conductivity, etc.)		
		Lag time (between start of injection and detection in groundwater)	days	
Additional monitoring	Monitoring area	Area of surveillance	m^2	Y
	Baseline	Baseline monitoring period	days	Y
		What was monitored (e.g. CO_2 flux, soil gas, plant/ecosystem diversity)		Y
	Recovery	Post-injection monitoring period	days	Y
		Time to return to baseline conditions	Days	Y

***Table 1**. Simplified list of variables collected for each CO_2 release experiment and the data included in the Supplementary Information (SI). Data were collected from the published literature and from correspondence with project researchers. Table 2 summarises key variables. *Where possible, if CO_2 flux (rate of CO_2 leakage per unit area) was not reported it was calculated from information about the leakage area and the reported total leakage rate; **Vertical leak velocity was calculated from the injection depth and the lag time between CO_2 injection and arrival at the surface (or near-surface); ***Where information about the hotspot width was not reported, if possible, it was estimated from published flux maps.*

3. Results and discussion

The detailed dataset includes 14 different field experiment locations around the world. We refer to each by their project acronym or their location. These are shown in Figure 1, and a summary table of experimental parameters and results is provided in Table 2. Full data are available in the Supplementary Information.

We applied an injection depth cut off to the reviewed sites in order to focus on experiments which intended for the injected CO_2 to leak towards the surface. Only two experiments injected CO_2 deeper than 25 m; Plant Daniel (Trautz et al., 2012) and Cranfield (Yang et al., 2013) (which inject at 54 and 73 m, respectively) both of which were push-pull experiments investigating the effect of CO_2-bearing brines on groundwater quality. These were excluded from our dataset. The K-KOSEM EIT site in Korea is not included because at the time of writing there was little publicly available information about the experimental approach and results.

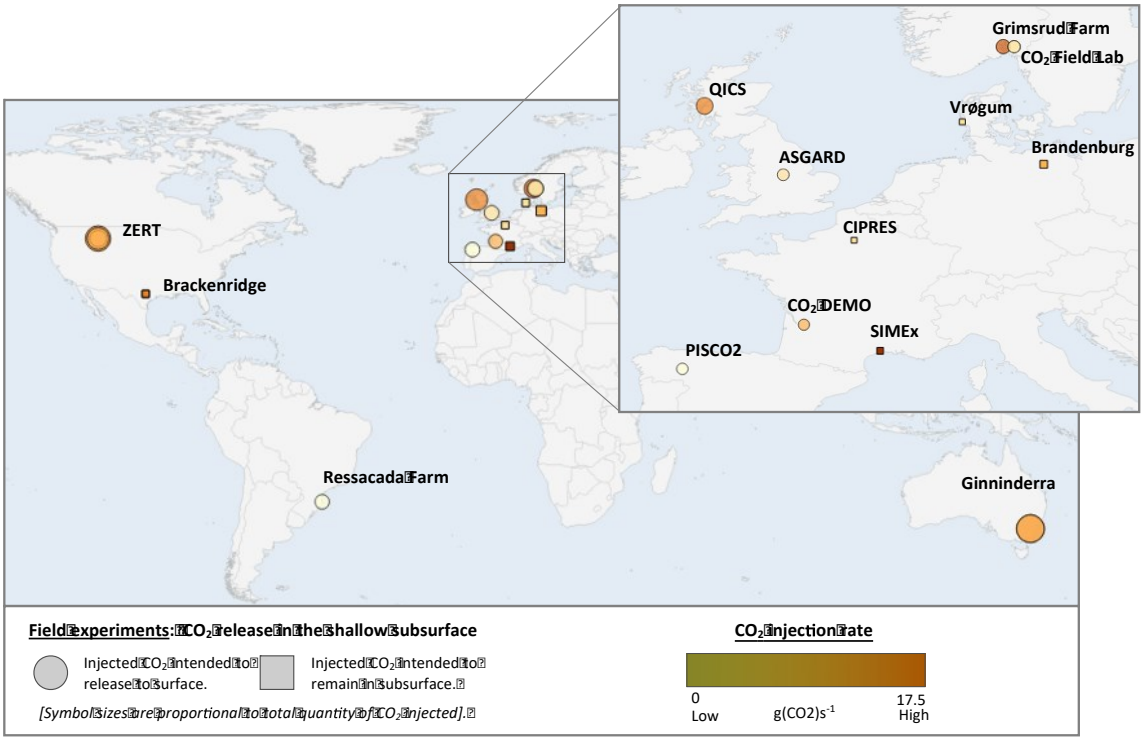

Fig. 1: Map of CO_2 release experiments around the world considered in our study. Symbols are coloured according to the CO_2 injection rates at the site, and sized proportional to the total amount of CO_2 injected over the lifetime of the sites (i.e. for some sites the total amount will be the sum of multiple injections).

Table 2. Global compilation of controlled CO_2 release experiments at depths shallower than 25 m (with results published prior to May 2017). Half of the sites have conducted more than one release experiment ('No. of exp'), some of them preliminary tests, and the experiment phases often differed in the length ('inj. length (days)') and rate of CO_2 injection ('Max inj. rate t(CO_2)pa'). The style of the injection also varies between sites, injecting CO_2 as a gas (g) or dissolved in water (diss), and via an inclined, vertical (v) or horizontal (h) well, and at a steady, incremental (incr.) or variable (var.) injection rate. For the CO_2 flux, modelled and measured are differentiated to make clear where values are informed by field measurements and where values are informed by modelling of the process based on other measured parameters.

3.1 An overview of CO_2 release experiments

3.1.1 Global distribution

As can be seen in Figure 1, ten of the 14 field experiments included in this dataset are located in Europe (ASGARD, QICS, CO2 Field Lab, Grimsrud Farm, Vrøgum, CO2-Vadose/DEMO, CIPRES, SIMEx, Brandenburg,

and PISCO2), with the remaining four located in Australia (Ginninderra), South America (Ressacada Farm) and the USA (ZERT, Brackenridge). Of all these field experiments to date, there has been only one subseabed CO_2 release; QICS. The CO_2-DEMO and CO_2-Vadose projects occur at the same location; the CO_2-Vadose project intended for CO_2 to migrate to surface, but was prevented from doing so by a thin clay layer (Cohen et al., 2013, Rillard et al., 2015), and so the experiment was modified to inject above this clay later as the CO_2-DEMO project.

3.1.2 Timeline of experiments

The experiments in our dataset were conducted between 2006-2014, and, as shown in Figure 2, most CO_2 releases were conducted in the period 2011-13. Half of the projects performed more than one release experiment, and often the length and rate of CO_2 release differed between experiments (see Table 2). For example, release experiments have been conducted typically each summer at ZERT since 2007, where the injection rate has ranged from 0.62 to 3.47 gs^{-1} (or 19 to 110 t(CO_2)pa) (Spangler et al., 2010).

In total, there have been 42 different CO_2 release experiments completed at the 14 sites that we reviewed, releasing a total of 82.8 t(CO_2) into the subsurface over 994 days (i.e. 2.7 years). This is not a complete dataset, since some preliminary experiments may not have been published, and some experiments may not yet be reported.

While a couple of projects are awaiting funding for additional experiments, at least half of the sites have completed their intended activities and thus the infrastructure has been dismantled.

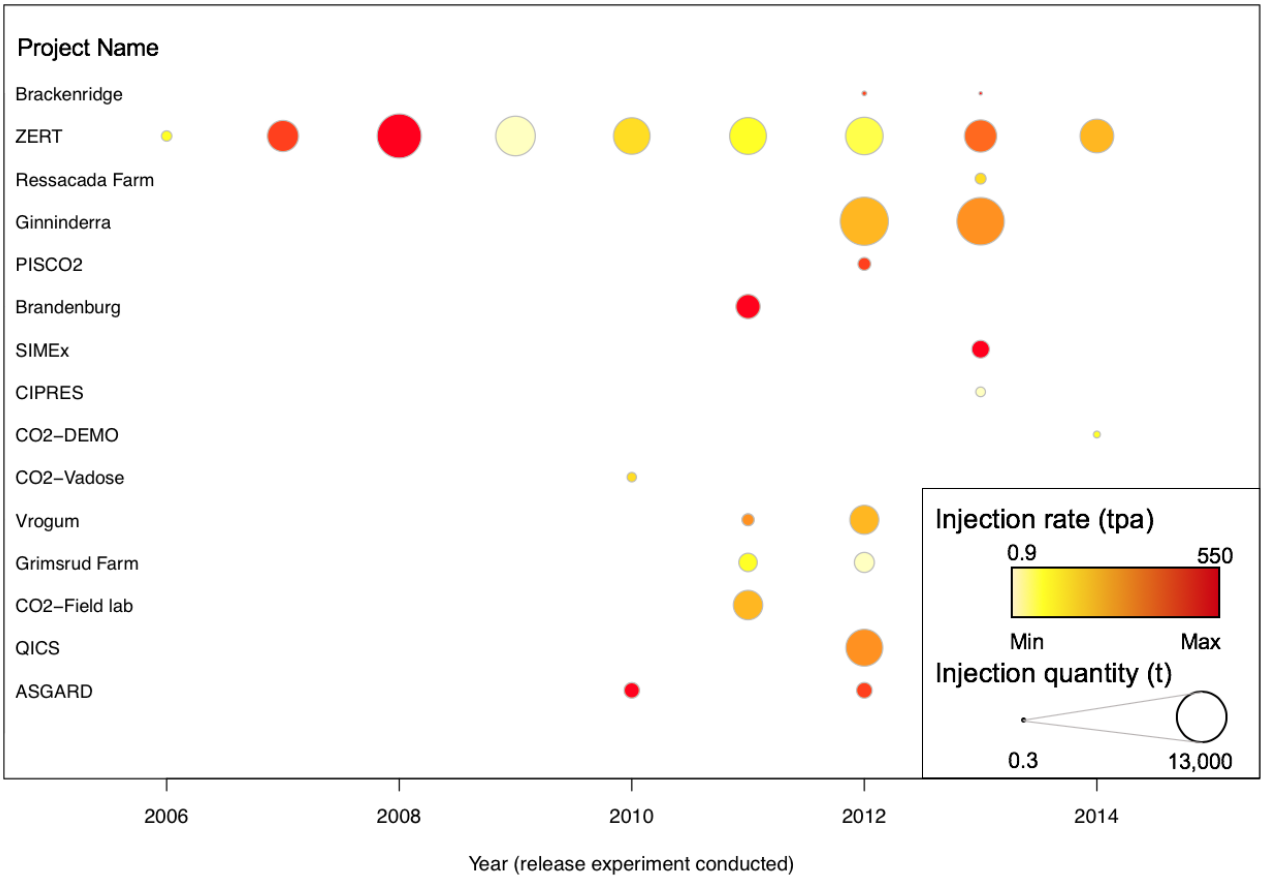

Fig. 2: The quantity of CO_2 injected (circle size) and injection rate (colour) for each of the experiments conducted at the shallow CO_2 release projects investigated, and the year that the experiments were conducted. The ZERT site has conducted the most experiments, and also the most varied injection rate (deeper colours indicate higher injection rate).

3.1.3 Objectives of CO_2 release experiments

The reviewed projects typically endeavoured to address one or more of the following principle aims:

1. Investigate **ecosystem** responses to the injected CO_2.
2. Establish the **fluxes**, transformations and fate of CO_2 as it migrates from the injection point.
3. Investigate **geochem**ical interactions between CO_2 and groundwater.
4. Test and calibrate **models** of CO_2 flow and fate.
5. Test a broad or specific suite of monitoring, measurement and verification (**MMV**) techniques.

The primary aims for each project are shown in Table 3. Most of the projects focussed on developing MMV approaches for detecting or quantifying CO_2 leaks, and these approaches have enabled additional questions to be explored, primarily about the environmental impact of leaked CO_2 (on groundwater and ecosystems). As such, the projects are typically made up of interdisciplinary teams composed of multiple partners (often at least one publicly funded partner), and total budgets tend towards €1 M or greater.

*Table 3: Common primary objectives of CO_2 release experiments, categorised according to the list above (Section 3.1.3). This table is not comprehensive; secondary objectives might have been addressed by certain experiments at the site or certain team members. *Consecutive experiments at ZERT focussed on different objectives.*

n	Acronym	Ecosystem	Fluxes	Geochem	Models	MMV
1	ASGARD	☒	☐	☐	☐	☒
2	QICS	☒	☒	☒	☒	☒
3	CO_2 Field Lab	☐	☐	☐	☒	☒
4	Grimsrud Farm	☒	☐	☐	☐	☐
5	Vrøgum	☐	☐	☒	☐	☒
6	CO2DEMO	☐	☐	☐	☐	☒
7	CIPRES	☐	☐	☒	☐	☒
8	SIMEx	☐	☐	☐	☐	☒
9	Brandenburg	☐	☐	☒	☐	☒
10	PISCO2	☒	☐	☐	☒	☒
11	Ginninderra	☒	☒	☐	☒	☒
12	Ressacada Farm	☐	☐	☐	☐	☒
13	ZERT*	☒	☒	☒	☐	☒
14	Brackenridge	☐	☐	☒	☐	☐
	Total	**6**	**3**	**6**	**3**	**12**

The majority of the CO_2 release experiments sought to mimic the effects of leakage of CO_2 gas, either from a point source or vertical feature (such as from poorly sealed well casing), or a linear feature (such as from a fault). Two sites, CIPRES and Brackenridge, performed push-pull experiments using CO_2 dissolved in water to explore the effect of CO_2 on groundwater quality. Groundwater was pumped from the aquifer and saturated with CO_2 before being re-injected into the same horizon (Gal et al., 2014, Mickler et al., 2013).

As Table 2 details, for eight of the CO_2 release facilities it was crucial that the injected CO_2 was released to surface. The remaining five experiments intended that the CO_2 remained in the shallow subsurface except Vrøgum which aimed to image the CO_2 but did not aim specifically for subsurface retention or surface release. In some cases the project was modified to ensure that CO_2 was released to surface as intended.

3.2 Experimental design

The site characteristics and experimental set-up varied between each of the projects that we reviewed, although some projects mimicked or built on the experimental design of other sites; for instance the Ginninderra experimental set-up is closely based on ZERT (Feitz et al., 2014a).

3.2.1 Site & well geometry

At all sites, CO_2 was delivered to the subsurface by a borehole that was either horizontal (favoured at the shallower sites), at a 45° angle (ASGARD, CO_2 Field Lab and Vrøgum) or vertical (favoured for deeper experiments; Table 2). For experiments injecting free-phase CO_2, the gas was usually released via several perforations along the pipeline rather than a single point of injection.

Several of the experiments have a number of physical blocks or plots for CO_2 release; the experimental area at ASGARD was divided into three blocks of eight replicate 2.5 × 2.5 m plots (Smith et al., 2013) and at PISCO2 the CO_2 was injected through a grid with 16 pinholes (Gasparini et al., 2015) via a horizontal grid arrangement of thin pipes. Similarly, ZERT's 70 m long horizontal well was divided into six zones by inflatable packers (Spangler et al., 2010). The set-up at Ginninderra is similar; the 100 m long pipe is partitioned into five 16-m long segments (Feitz et al., 2014a).

Sites were often designed to facilitate specific needs. For example, the ZERT pipeline was laid at 45° North to maximise data resolution, and a reference grid was laid over the ground surface (Spangler et al., 2010) which subsequent projects adopted (e.g. CO_2 Field Lab, Jones et al., (2014a)). A line of perforations in the inclined well at Vrøgum aimed to simulate gas bubbling from a short fissure into flowing groundwater (Cahill et al., 2014). Finally, QICS released CO_2 to seabed via a deviated well drilled from the mainland to fulfil access and logistics criteria (Blackford et al., 2014).

3.2.2 Depth characteristics of CO_2 release experiments investigated

The CO_2 injection depths ranged from 0.6 m (ASGARD) to 25 m (CIPRES). The deepest experiment to release CO_2 to surface was CO2 Field Lab, where the gas was injected at 20 m depth below ground level. Figure 3 shows the injector depth and the maximum depth of the water table by experimental site.

Most projects released CO_2 into sands or gravel. CO_2-DEMO was the only shallow release experiment that injected CO_2 into a (lithified) carbonate formation. Other exceptions include ASGARD which released CO_2 into soil (Smith et al., 2013), and PISCO2 used an artificially constructed sand unit (Gasparini et al., 2015). For most projects the overburden units were the same as, or similar to, the injection formation, although thicker overburden (deeper experiments) tended to be comprised of several sediment formations making observations and interpretations of gas movement more complex.

The water table was relatively shallow at most of the projects, though it usually varied seasonally. For example, the water table at ZERT was less than 1.5 m, and in springtime the water table could rise to surface level (Spangler et al., 2010). Generally, the vadose zone thickness was < 4 m for all onshore experiments besides the CO_2-DEMO site, where it was ~21 m thick (Loisy et al., 2013).

At four sites CO_2 was always injected above the water table (ASGARD, CO_2-DEMO, PISCO2, and Grimsrud Farm), whereas at ZERT, Ginninderra and Ressacada Farm the injector could have been in the vadose or saturated zone, depending on the season. At all other sites, CO_2 was injected consistently below the water table. Most experiments (particularly those that intended to release CO_2 to surface) were conducted in the dry season, with the exception of Ginninderra, which purposefully conducted experiments in both the dry and wet season to explore the effect of seasonality (Feitz et al., 2014a).

The only offshore release experiment, QICS, released CO_2 into sediments 10 m below seabed.

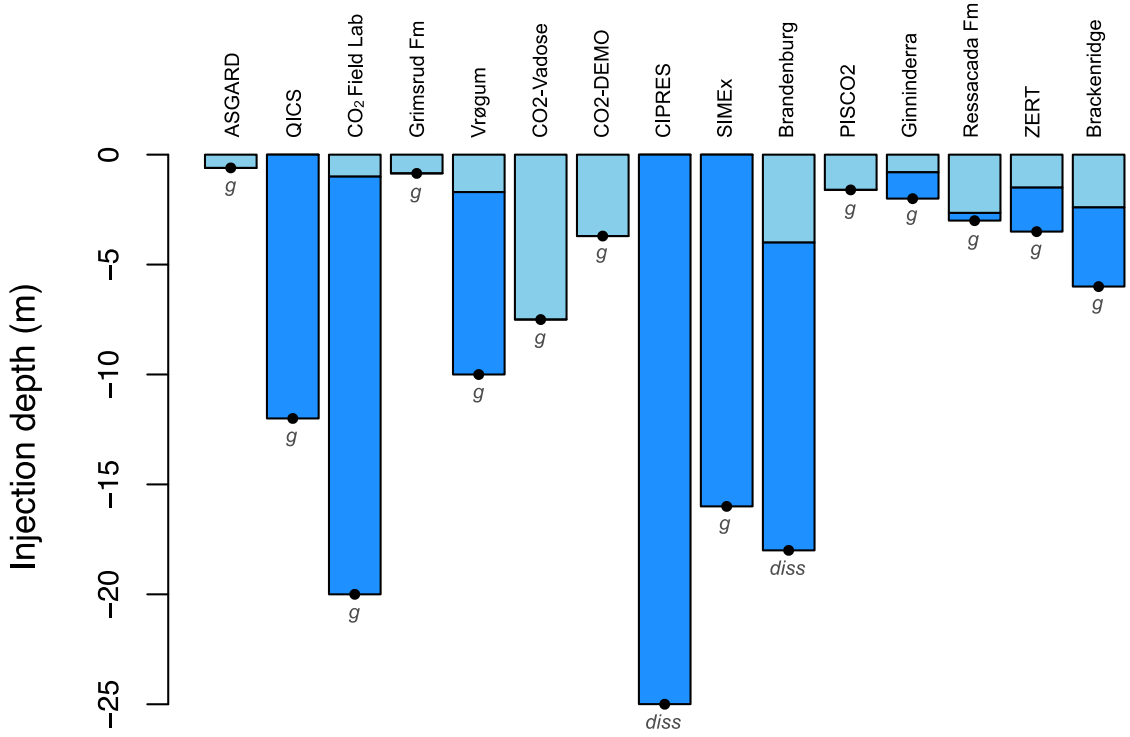

Fig. 3. The injector depth (black circle) and thickness of the vadose (pale blue) and the saturated zone (dark blue) for each CO_2 release project in our global dataset. The CO_2 injection phase is noted, where CO_2 gas (g); CO_2 dissolved in water (diss).

3.3 CO_2 injection parameters

3.3.1 Properties of injected CO_2

All experiments released free-phase CO_2 gas into the subsurface except SIMEx and Brackenridge which injected water containing dissolved CO_2.

All experiments used high purity (99.9%) food grade CO_2, though at CO_2-DEMO it was mixed with noble gases so that 90.57% CO_2, 5% Kr and 5% He was released (Rillard et al., 2015). Food grade CO_2 procured through chemical suppliers is often depleted in ^{13}C since it is commonly sourced from processes using hydrocarbons (e.g. natural gas to urea conversion (Stalker et al., 2013)). As such, the CO_2 used for most experiments had $\delta^{13}C$ values towards -30 ‰, though the exact values were site and CO_2 source specific. Carbon isotope signatures of CO_2 captured from industrial sources are typically very negative (Flude et al., 2016). Therefore the carbon isotope values for CO_2 released at field experiments can be considered representative of the CO_2 that might leak from large-scale industrial stores. Possible exceptions are CO_2 that is sourced from biomass combustion, or biologically derived CO_2 which are likely to be less negative ($\delta^{13}C(CO_2)$ <-6 - <-15 ‰) than CO_2 derived from hydrocarbon sources (Flude et al., 2016).

3.3.2 CO_2 injection strategy

As shown in Table 2 a steady or incrementally increasing injection strategy was favoured by most experiments, though the rate varied unintentionally at SIMEx due to some challenges experienced during operation (Pezard et al., 2015b). The maximum and minimum injection rates for the CO_2 release experiments conducted at each site are shown in Figure 4. We find that there was a wide range in the rate of CO_2 injection at these experiments; the highest rate was 4.9 gs^{-1} (153.3 $t(CO_2)pa$) at CO2 Field Lab, and the smallest injection rates were 0.03 to 0.04 gs^{-1} (0.95 and 1.3 $t(CO_2)pa$ at PISCO2 and Brackenridge respectively). The

majority of experiments however inject CO_2 between 0.05 - 2 gs^{-1}, which is equivalent to 1.6 - 63 t(CO_2)pa. The injection rates were largely selected based on possible permissible leak rates from engineered storage sites and modelled properties such as injectivity (e.g. Spangler et al., (2010)). A release rate of 2 gs^{-1} or 63 t(CO_2)pa is equivalent to less than 0.001% per year of a large scale CCS project injecting 1Mt(CO_2)pa for 40 years (as specified by the United States Department of Energy (US DOE) for a project aiming for over 1000 years of storage), and are in the range of natural CO_2 emissions. For example, in Italy there are hundreds of natural CO_2 seeps that most commonly emit between 10-100 t(CO_2)pa (Roberts et al., 2011).

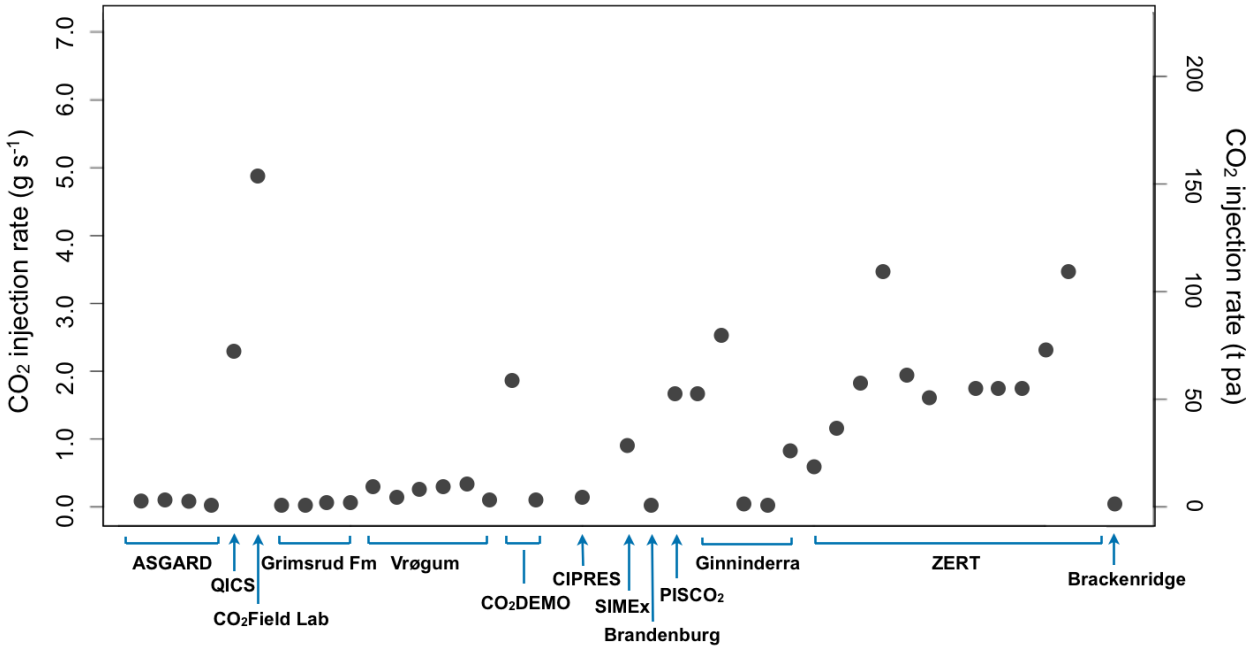

Fig. 4. The maximum injection rate at each experiment conducted at shallow CO_2 release projects worldwide. Projects show a range of CO_2 injection rates, and are typically selected to either represent a given leakage scenario from an engineered store, or to ensure the aims of the release experiment are achievable.

The length of CO_2 injection at the experiments we reviewed varied from a couple of hours to several months. Most experiments injected CO_2 for periods shorter than 1 month, and in fact the longest injection period was <5 days at five of the sites (CO2 Field Lab, CO_2-Demo, Brackenridge, CIPRES, and SIMEx). On the other hand, experiments at Grimsrud Farm and Ginninderra lasted up to ~3 months, and we note that the Plant Daniel field experiment (not included in our dataset), lasted 5 months and so was the longest field experiment conducted to date (Trautz et al., 2012). Generally, experiments investigating ecosystem responses to CO_2 (c.f. Table 1) injected for the longest periods.

Some of the projects' outputs suggest that longer release experiments would have been preferable; at CO2 Field Lab it was concluded that <5 days was not long enough for CO_2 leakage to reach steady state (Jones et al., 2014a). Similarly the QICS researchers felt that the CO_2 release period (37 days) was not long enough, since the effect of CO_2 on shallow pore water chemistry was only detected a couple of days before injection stopped (Lichtschlag et al., 2015, Taylor et al., 2015a).

Finally, the injection strategy for any project would be moderated by a number of other constraints beyond the design parameters, including CO_2 availability, injectivity, project budget, and so forth.

3.4 The fate of CO_2

3.4.1 The surface characteristics of CO_2 leakage

CO_2 flux tended to be measured by flux chambers, though other methods such as Eddy Covariance or laser techniques complemented these measurements. Stable carbon isotopic compositions were also found to be a sensitive indicator of the arrival of introduced/injected CO_2 (Moni and Rasse, 2014, Moreira et al., 2014a, Moreira et al., 2014b, Stalker et al., 2015).

Where CO_2 leaked to surface, CO_2 fluxes above baseline were usually detected within 24 hours of the start of injection. For example, CO_2 injected at ZERT arrived at the surface within ~5 hours (Lewicki et al., 2010), and CO_2 bubble streams were observed at QICS within 3 hours of injection commencing. The greatest lag time between injection and surface release was observed at Ressacada Farm and PISCO2 where surface fluxes of CO_2 were not detected for 3 and 4 days respectively (Feitz et al., 2014b, Gasparini et al., 2015). Unfortunately the sampling frequency was not high enough to capture the exact arrival time at a number of experiments.

The surface leakage was typically expressed as (several) patches or 'hotspots' showing CO_2 flux above background levels. The area of the surface hotspot was usually defined by CO_2 flux above baseline, where CO_2 flux and soil gas concentrations decreased radially from maximum levels at the centre of the hotspot. The hotspots that developed at CO_2 release experiments were typically between 2.5 – 5.5 m radius, though leakage at Ginninderra was less patchy and occurred over a larger area than at other field sites (Feitz et al., 2014a). These patches were often static once leakage had become established, for example, the leak patches at CO2 Field Lab coalesced as injection continued and then remained stable (Jones et al., 2014a). The CO_2 bubble streams at QICS were mobile, but concentrated in two (static) patches (Blackford et al., 2014) and the characteristics of the bubble stream (e.g. bubble density and bubble size) were affected by tidally-induced changes to hydrostatic pressure (Sellami et al., 2015). Patchy CO_2 leakage matches observations of leak distribution at natural CO_2 seeps (Beaubien et al., 2008, Smets et al., 2010, West et al., 2015).

Plants and soil microbiology were found to be affected by elevated CO_2 concentrations in the soil gas and land surface at the patches of CO_2 leakage. These effects were visible within a couple of days of CO_2 leakage, though some plant species were found to be more resistant than others (Jones et al., 2015, West et al., 2015). Observations at field and natural CO_2 release sites in a range of environments have found that soil gas concentrations of 10% CO_2 and surface flux rates of 0.8 kgm^2day^{-1} is the cut-off above which the CO_2 begins to impact the ecosystem (West et al., 2015). Since hyperspectral imaging can detect changes to vegetation, such as leaf chlorophyll levels, these are therefore a promising remote sensing monitoring tool (Bellante et al., 2013, Feitz et al., 2014b).

We note that there may be a correlation between the hotspot radius and the CO_2 injection rate, as shown in Figure 5a, where the hotspot radius is larger at experiments with higher CO_2 injection rates. The hotspot radius is not necessarily larger for greater quantities of total CO_2 injected. However we find no relationship between injection rate and maximum CO_2 flux rate (graph not shown here). The flux rate and seep patch radius, shown in Figure 5b, may also be correlated but there are too few data points to draw any reliable conclusions. The injection depth however seems to have no effect on the CO_2 flux rate, nor does the injection rate control the vertical velocity of CO_2, though we do note that the vertical flow velocity was fastest for the deepest experiments where the density difference between CO_2 and surrounding pore fluids would have been greatest (see Table 2).

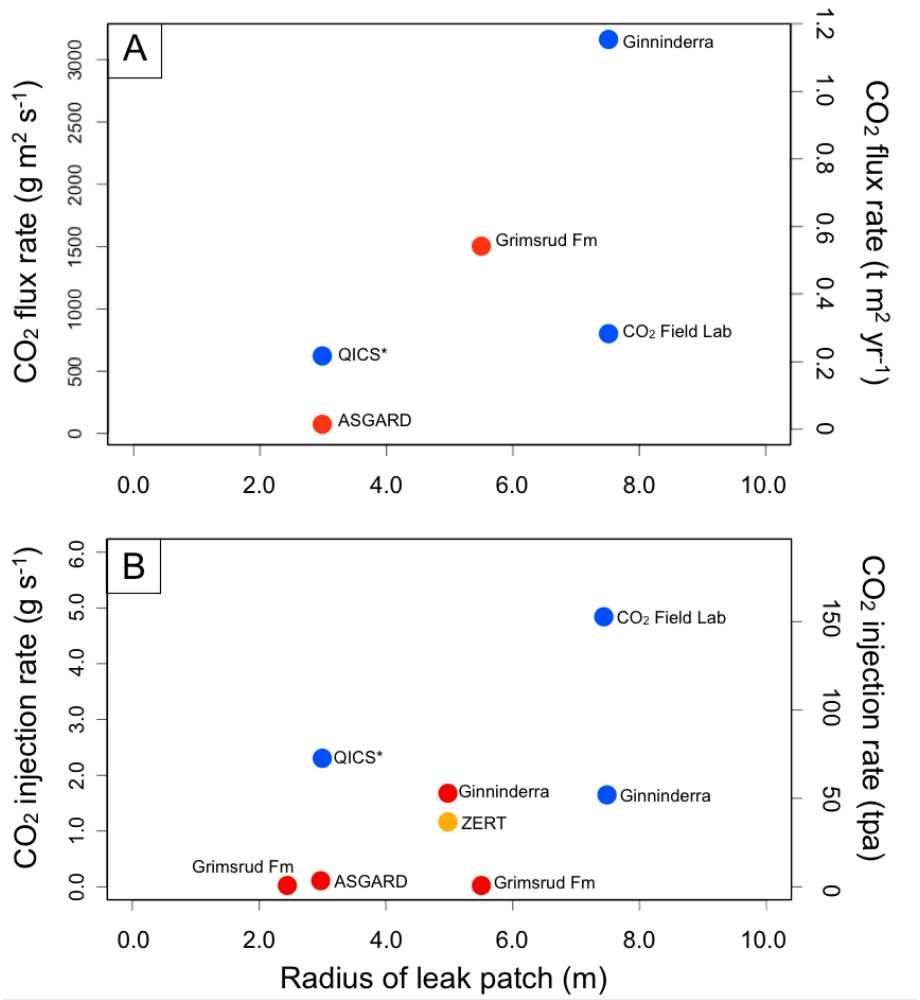

Fig. 5: Radius of the leakage patch and (A) maximum CO_2 flux rate and (B) maximum injection rate. The symbol colour indicates whether the CO_2 injection depth was into the saturated zone (blue) or the vadose zone (red) or if this was variable throughout the experiment (orange). The patch width appears proportional to the flux of leaked CO_2. Note some sites conducted more than one release experiment. QICS is starred as the leakage radius might be considered to be either <3 m or >5 m, since the bubbling could be interpreted to occur in two smaller patches or in one larger patch (Blackford et al., 2014).

CO_2 hotspots often didn't occur vertically above the point of CO_2 injection. In some cases, the lateral migration distance of CO_2 that emerged at hotspots was greater than the depth of the CO_2 injector - even when this was shallow. For example, at Ressacada Farm the hotspot developed in a surface depression next to a road located ~30 m away from the CO_2 release point (which was at 3 m depth) (Feitz et al., 2014b). At the subseabed QICS injection site, patches of CO_2 bubble streams established ~ 10 m west of the CO_2 diffuser (Blackford et al., 2014), along strike of the sediment structure (Cevatoglu et al., 2015).

Despite attempts to minimise subsurface disturbance during site construction, a number of projects found the soil structure was disturbed to an extent that the characteristics or location of the resulting CO_2 leak were affected. For example, at ZERT, despite the use of directional drilling to install the CO_2 pipeline (Spangler et al., 2010), the CO_2 leakage locations corresponded to small elevations in the horizontal well. It is thought that gas collected at these high points within the pipe before leaking to the surface (Strazisar et al., 2009). CO_2 released at Grimsrud Farm preferentially leaked along the border of the two artificial plots (i.e. where the soils in the experimental plot contacted with undisturbed surrounding soils) (Moni and Rasse, 2014), and preferential flow pathways developed at the artificial PISCO2 site where injection and pumping tests were performed prior to CO_2 injection (Gasparini et al., 2015).

3.4.2 The subsurface characteristics of CO_2 leakage

CO_2 was often detected in soil gas prior to surface flux, and so was usually detected within a matter of hours following the start of CO_2 injection. Towards the centre of the hotspots, soil gas could reach up to 100% CO_2, but the extent of lateral spread of CO_2 in the subsurface tended to be much greater than the footprint of surface degassing. Soil gas saturation was spatially and temporally variable, depending on weather (see next section), subsurface structure, and CO_2 flow rate. For example, at ASGARD CO_2 moved preferentially through the higher permeability sandy and gravely deposits lying beneath the injection point, rather than migrating through the overlying soils (West et al., 2009). Soil gas monitoring at CO2 Field Lab detected CO_2 in soil gas directly above the injector shortly after injection commenced. However, there was no CO_2 flux to surface in this region; leakage was established northeast (up dip) of the injector a day later, following an increase in the injection rate (Barrio et al., 2013, Jones et al., 2014a). It is believed that CO_2 initially leaked up the well casing but then, at higher injection rates, the CO_2 favoured an alternative pathway to establish leakage away from the wellbore. Observations at QICS and CO2 Field Lab also found that the subsurface CO_2 flow path was affected by CO_2 injection rate (Blackford et al., 2014, Cevatoglu et al., 2015). Sediment grain size controlled CO_2 flow initially at QICS until the gas pressure or gas volumes overrode the stratigraphic controls, spatially focussing the CO_2 flow via the formation of chimney structures (Cevatoglu et al., 2015).

In the saturated zone, maximum gas saturation in the sediments was ~7% at Vrøgum and CIPRES (Pezard et al., 2015a). CO_2 saturation at Vrøgum was found to be proportional to the grain size properties of the sediments, and so CO_2 spread was governed by the permeability and structure of the subsurface (Lassen et al., 2015). Gas concentrations were greater in higher permeability sediments, and the geochemical effects (pH, EC) of CO_2 faster and more uniform (Cahill et al., 2014, Schulz et al., 2012, Yang et al., 2015). As a result the plume spread towards regions with higher permeability, even overcoming groundwater flow to do so (Yang et al., 2015). CO_2 migration was successfully imaged by resistivity changes which are incurred as migrating CO_2 partially displaces the pore waters. For example, at Ressacada Farm resistivity changes were consistent with CO_2 leakage pathway to the hotspot location (Oliva et al., 2014).

Similar to the subsurface spread of CO_2 gas, the spatial extent of geochemical impacts was also much wider than the extent of surface release. For instance, bubble vents at QICS were located within 10 meters of the subseabed injector, whereas the spatial extent of the geochemical impact of the injected CO_2 in the sediments and pore waters was contained to 25m of the injection point (Lichtschlag et al., 2015). Monitoring techniques deployed at Vrøgum and Brandenburg observed a two-phase geochemical evolution of the CO_2 leak, where a pulse in ion concentrations is followed by persistent acidification (Cahill et al., 2014, Yang et al., 2015). In the early stages of injection there tended to be a delay before any chemical changes were detected, thought to result from initial CO_2 gas flow in discrete channels, limiting the contact with the water-phase and so restricting the quantity of CO_2 that dissolves into the groundwater (Lassen et al., 2015). The Vrøgum researchers also noted that the unconfined aquifers were susceptible to recharge which caused rapid and inconsistent changes to the groundwater properties quite distinct from the changes caused by the presence of CO_2 (Cahill et al., 2014).

3.4.3 Temporal effects on CO_2 fate

The location, width and intensity of the hotspots that developed at onshore CO_2 release experiments were dependent on climatic conditions, including diurnal temperature (which affected wind speed), rainfall and pressure. For instance, CO_2 flux was significantly impeded by rainfall at ASGARD and temporarily stopped when the soil froze (Smith et al., 2013, Jones et al., 2014a). Generally, CO_2 flux was consistently highest in periods of low rainfall, and CO_2 soil gas concentrations were lowest in periods of low atmospheric pressure. These effects are presumably due to a combination of factors, such as the swelling and saturation of soil in wet periods, rainwater preferentially percolating via the same high-permeability pathways favoured by leaking CO_2, and the elevated pressure gradient between surface and subsurface in periods of low pressure. At the offshore QICS experiment, rates of CO_2 bubbling were also observed to vary significantly with tidally induced changes in hydrostatic pressure (Blackford et al., 2014, Sellami et al., 2015).

There is evidence also that longer-term seasonal variations influence the location, size and style of subsurface migration and leakage of CO_2 at artificial release experiments. This matches the seasonal changes that have been observed at natural CO_2 seeps (Heinicke et al. (2006) and references therein). For example, release

experiments at Ginninderra were performed in both the wet and dry seasons to explore the influence of seasons on the quantity and style of CO_2 release to surface. The injector depth at the site was such that in the wet season CO_2 was released into the saturated zone, and in the dry season, it was released into the vadose zone. In the wet season, CO_2 leaked to surface via one large patch (16 m x 30 m). This was located in a sandier region of the site, where soil gas saturation reached 80%. In contrast, leakage was more distributed in the dry season, occurring in three smaller patches which had lower and more steady-state fluxes than the single large patch that established in the wet season experiments (Feitz et al., 2014a). These hotspots established in the more clay-rich regions, and soil gas saturation in the hotspots were lower, reaching a maximum of 60%. In addition, soil surveys aided by krypton tracer found that CO_2 spread much further from the horizontal well in the wet season (Schroder et al., 2017). It is hypothesised that the greater extent of the vadose zone in the dry season allows greater quantities of CO_2 to accumulate in the subsurface, and so limits the intensity of CO_2 release to surface (Feitz et al., 2014a, Schroder et al., 2017).

3.4.4 Quantifying CO_2 leaked to surface

Quantifying the proportion of injected CO_2 that is released to surface (atmosphere or seabed) has proven very challenging at release experiments (Feitz et al., 2014b). Out of the 30 release experiments in our dataset (at nine projects) which released CO_2 to surface, estimates of quantities leaked to surface are provided for only ten experiments (at seven projects). These estimates were usually derived from measurements of CO_2 flux (see Table 2) and not all reported estimates account for baseline CO_2 flux.

Estimates of total leakage range from 5% of the injected CO_2 at CO2 Field Lab (reported to be a likely underestimate (Barrio et al., 2013)), up to 82-83% (at Grimsrud Farm (Moni and Rasse, 2013) and PISCO2 (Gasparini et al., 2015)) and 90.3% (for the preliminary vertical experiment at ZERT). The project researchers report that these calculations proved difficult for several reasons, including:

- Given the spatial and temporal distribution of CO_2 degassing, it is difficult to take continuous or detailed measurements of the seep site (Jones et al., 2014a).
- At ASGARD, ZERT and Grimsrud Farm the CO_2 migrated beyond the initial monitoring boundaries making it difficult to estimate the relative proportions of CO_2 that leaked to surface, remained in soil gas or dissolved (West et al., 2009, Lewicki et al., 2010, Moni and Rasse, 2014).
- The background soil respiration rate can be very variable.

These issues have led to the calculation of negative fluxes (Lewicki et al., 2010).

The proportion of CO_2 that leaked to surface varied in response to various environmental factors (see Section 3.3.1). However it was not possible to quantitate these effects, except at QICS, where the quantity of CO_2 that reached seabed as a free phase ranged from 8-15%, depending on the tide (Blackford et al., 2014, Mori et al., 2015). As such, none of the experiments that we reviewed reported how the total proportion of CO_2 that leaked to surface varied as the experiment progressed. However, several experiments reported how the flux evolved as CO_2 injection continued. Usually leaked CO_2 was detected within hours after CO_2 injection started (see section 3.3.1), and CO_2 fluxes showed a steady increase until it plateaued (i.e. reached steady-state).

Figure 6a shows the estimated proportion of CO_2 that leaked to surface and the depth of the CO_2 injector. The two deepest experiments in the dataset (CO_2 Field Lab and QICS) leaked the smallest proportion of CO_2 to surface/seabed, though as previously mentioned the value for CO_2 Field Lab is likely an underestimate (Barrio et al., 2013).

There is a more obvious trend between the proportion of CO_2 that is released to surface and the maximum injection rate (Figure 6b), but again, there are too few data points for this trend to be statistically significant.

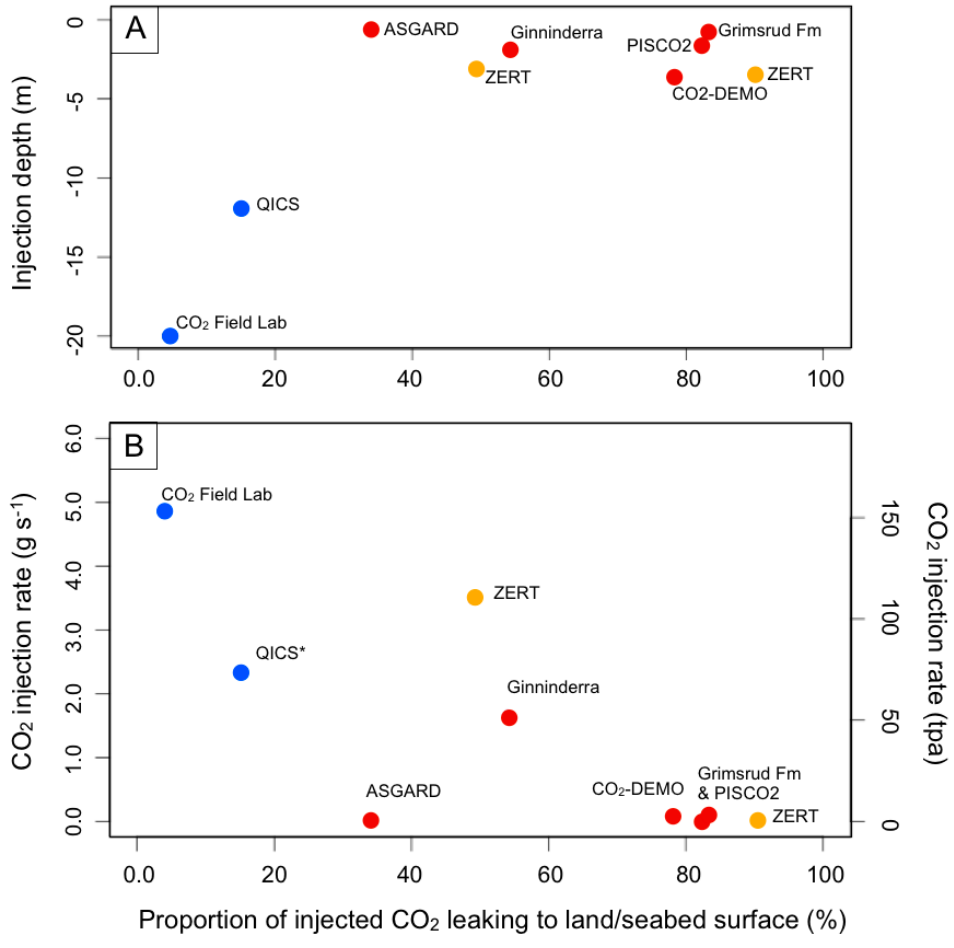

*Fig. 6: The estimated proportion of injected CO_2 that leaked to land surface or seabed as a gas at the field experiments plotted against (A) injection depth and (B) injection rate. The symbol colour indicates whether the CO_2 injection depth was into the saturated zone (blue) or the vadose zone (red) or if this was variable throughout the experiment (orange). *offshore.*

Several experiments have tested added tracers as a method of detecting CO_2 leakage, including perfluorocarbon (PFC) (ZERT), SF_6 (Brandenburg), noble gases (krypton, Ginninderra; helium and argon, CO_2-DEMO). For tracers to quantify CO_2 leakage they must behave predictably and preferably conservatively (i.e. mimic the CO_2 behaviour). Co-released noble gases at CO_2-DEMO included helium and argon, which both arrived ahead of the CO_2, and so behaved as precursor tracers for the leakage of CO_2 in the vadose zone (Rillard et al., 2015). Krypton co-injected at the Ginninderra tests, and PFC tracers used at the 2007 ZERT experiments were found to correlate with soil–gas results and so track the injected CO_2 (Strazisar et al., 2009). However, observations at ZERT also indicated that the distribution of PFC was also affected by small changes in topography and possibly also gas density and/or soil properties (Strazisar et al., 2009, Spangler et al., 2010), apparently differently to the CO_2. No CO_2 release experiment has yet attempted to quantify CO_2 fate or surface flux using chemical tracers.

3.4.5 Quantifying the fate of injected CO_2

Only one experiment, QICS, reported comprehensive estimates of CO_2 fate in each of the different phases of the studied environment, each quantified using different approaches. A maximum of 15% of injected CO_2 was estimated to reach seabed as bubble streams, and geochemical modelling based on pore-water observations estimated that 14-63% remained dissolved within the sediment pore water (Taylor et al., 2015a). The proportion that remained trapped in the sediment (Cevatoglu et al., 2015) was imaged by repeat seismic surveys. A different remote method imaged the proportion of CO_2 trapped as free phase gas at Vrøgum. Cross-borehole ground penetrating radar used in the July 2012 experiment found 30–40% of the injected CO_2

volume was trapped in this way, and it was inferred that the remaining CO_2 must have dissolved or migrated (Lassen et al., 2015).

Although there have been detailed geochemical surveys at ZERT since the 2008 field campaign, it has been difficult to estimate the quantity of CO_2 that dissolved into the groundwater. Fluctuations in the water table mean that CO_2 interacts with a changing column height of groundwater, and the groundwater speed at the site was unknown. Further, the very action of bubbling CO_2 through the groundwater is thought to perturb the groundwater flow at the site (J. Thordsen, Pers. Comm).

3.5 Additional monitoring activities

The design of the monitoring array tended to be site specific, but there were usually a number of monitoring boreholes of various depths to obtain regular soil gas and water samples, as well as devices for measuring CO_2 flux. Atmospheric monitoring methods such as Eddy Covariance towers, or geophysical tools such as Ground Penetrating Radar (GPR) were used at some field release sites and for natural analogues. At the offshore QICS experiment a whole suite of monitoring approaches were deployed at and below seabed, at the sea surface and in the water column, using equipment installed by SCUBA divers and deployed on towed platforms (Blackford et al., 2014).

3.5.1 Pre-release monitoring

Pre-release monitoring must be conducted to characterise the environmental baseline at the experimental field site to be able to establish which changes result from CO_2 release, and which are simply due to environmental variability unrelated to the release experiment. The experiences at field experiments have highlighted not only the importance of rigorous baseline monitoring, but also the type of baseline data collected and the appropriate time period over which baseline data should be collected. At some experiments, baseline data was collected for only a couple of days prior to injection. In such cases the researchers concluded that this was not long enough (Lewicki et al., 2010, Jones et al., 2014a). Subsequent projects have collected more frequent or continuous baseline data for longer; for example, 2 weeks of continuous/daily monitoring was conducted at QICS and Ressacada Farm. Even so, at QICS this was not deemed long enough since the porewaters had not returned to baseline by the end of this period. Projects such as CO_2-DEMO and Vrøgum collected baseline data at intervals over a period of ~18 months prior to CO_2 release to allow a longitudinal baseline to be established. The spatial extent of baseline data should also be considered; for example, as Jones et al., (2014a) concludes, the location of the hotspots away from the point of CO_2 release shows how the areal coverage of baseline data must be spatially adequate, so that the hotspots do not establish where no baseline was collected.

Without adequate baseline, it becomes very difficult to, for example, report the flux of leaked CO_2. Further, there is no typical or standard baseline; background CO_2 flux and its variability are unique to each field experiment site. The variability of background is important to account for when interpreting CO_2 flux measurements. For example, at ASGARD, background CO_2 flux could vary by 3 to 4 fold, mostly in response to rainfall and air pressure (Jones et al., 2014b).

3.5.2 Post-release monitoring

Previous publications have seldom mentioned the value of continued monitoring of the field site once CO_2 injection has ceased. Post-release monitoring at field experiments provide important information about how CO_2 evolves in the absence of injection pressure, which is important for understanding CO_2 dispersion and fate. Further, post-release monitoring is relevant to environmental permitting at CCS projects. It is also relevant to the post-closure monitoring (both pre- and post- transfer of site responsibility) (EC, 2011), that is necessary to (a) verify that there is no leakage from the engineered store, or (b) to detect and quantify any leak arising and to establish when the leak has stopped following remediation.

We find that, while most CO_2 release experiments performed some post-injection monitoring, the length of monitoring period is widely variable, for example measuring for just one day only, or for only a couple of days over some period after injection ended. In many cases, the post-release monitoring was not sufficiently long enough to observe the decline in CO_2 concentrations to return to baseline conditions before sampling ceased. In fact, the ZERT 2008 experiments, QICS, and ASGARD are the only experiments to observe (via post release

monitoring) the return to baseline conditions. CO_2 flux at ASGARD returned to baseline within 2-3 days (Jones et al., 2014b), whereas at ZERT it took 15 days to return to baseline at the hotspots (above the well) but only 5 days to recover further (5 m) from the well (Lewicki et al., 2010). At QICS, while CO_2 bubble streams stopped shortly after the CO_2 injection stopped, concentrations of all pore water constituents returned to background values within 18 days (Lichtschlag et al., 2015), and microbial species took 90 days to fully recover. Vegetation recovery may take longer, and be species dependent. At Vrøgum the injection lasted 72 days but groundwater was monitored for 252 days (Cahill et al., 2014), and found that most of the free phase gas dissolved into the groundwater within 20 hours following the end of CO_2 injection (Lassen et al., 2015).

4. Discussion

4.1 Factors affecting CO_2 migration and fate

The information presented in the previous section illustrates the vast contribution that shallow CO_2 release experiments have made to current scientific understanding of near surface CO_2 flow pathways and CO_2 expression. We also present how observations of CO_2 leakage at field experiments (including patchy emissions, flux rates, seasonality etc.) also largely match studies of natural CO_2 seeps.

Preferential flow pathways channelling CO_2 leakage were found to be governed by hydrological factors (including water table depth, ground water flow, recharge, and soil properties), geomorphological factors, or recent, often anthropogenic, disturbance. Further, the migration of CO_2 and the characteristics of leakage seems to be affected by the injection rate. Since higher injection rates correlate with larger areas of leakage (i.e. greater hotspot width), higher CO_2 flux, and the proportion of CO_2 that leaks to surface, higher CO_2 injection rates may encourage lateral spread of CO_2 in the subsurface, particularly where vertical migration is restricted by the soil properties.

Field experiments have also highlighted that CO_2 flux will vary temporally in response to environmental parameters. This has important implications for CO_2 leak monitoring, since the period of surveying of a possible CO_2 leak above a CCS site (season, before or after rainfall, in the cool morning or hot afternoon, tidal levels) may greatly influence the measured value and its eventual interpretation.

4.2 Common issues at CO_2 release experiments

We identified several common issues that CO_2 release projects have encountered. Some of these issues challenged the research and impacted the levels of certainty of the conclusions that could be drawn from the experimental results. Other factors simply complicated the experimental set up, and in some cases they were addressed by the project team. Importantly, none of the issues prevented useful results from being obtained from each test, and in fact often they highlighted challenges relevant to applied CO_2 leak monitoring at commercial-scale storage sites. For example, site construction and pre-release tests affected the subsurface structure of several sites, which in turn influenced the CO_2 flow pathways. While this was unintentional, this exhibits the sensitivity of CO_2 flow to the near surface soil structure. Soils become altered or compromised through various widespread practices such as farming, roads, laying of sewerage and other anthropogenic activities and also non-anthropogenic causes. Similarly, the seabed sediment structure offshore might be compositionally variable due to trawling, or due to storm disturbance or currents, or activities during site characterisation, site construction and monitoring design. As such, disturbed soil structure is not unrepresentative of the environment in which CO_2 leaks might establish.

Unintentional leakage along the well bore occurred at many sites (including Ginninderra, CO2 Field Lab, ZERT, SIMEx and Brandenburg, and possibly also at ASGARD) and in many cases, corrective engineering was necessary (Barrio et al., 2013, Mickler et al., 2013, Pezard et al., 2015a, West et al., 2015). These challenges confirm previous work which identified that the well bore offers one of the most likely leak pathways at CCS projects (IPCC, 2005).

Knowledge exchange is extremely valuable for shaping future research, including reducing project risks. The amount of knowledge exchange between shallow CO_2 release projects is laudable. As an example, a number of researchers from the ZERT project (one of the first and longest-lived CO_2 release projects) have been heavily involved with the design and set-up of Ressacada Farm and Ginninderra. Collaborative work facilitates

589 developing solutions to problems encountered at previous experiments, and so maximises the project
590 success.

591 Table 4 summarises some of the common issues that CO_2 release experiments have encountered, and where
592 possible, recommends how future experiments might mitigate or minimise these issues.

	Common issues experience at CO_2 release experiments
Basic information	To make the project more accessible for the research community, regulator and wider public, and to facilitate the comparison of research effort on this topic, it can be helpful if each project: • Is referred to by a SINGLE designated project name or acronym. • Has a webpage or similar which hosts information about the project, such as the collective overarching aims of the research project. • Has a nominated contact for anyone wishing to enquire about the project. Ideally there would be a standard unit for reporting parameters such as CO_2 flux or arrival time and so on. Currently CO_2 might be reported in a range of units, including concentration. Similarly, there is no formal definition of how the spatial extent of a CO_2 hotspot is determined; the outer limit of the hotspot is usually defined by CO_2 flux above background by an arbitrary value which may not reflect the baseline.
Experiment set-up	At several projects, the initial planned injection depth needed to be modified to ensure that CO_2 reached the surface. For example, injection at Ressacada Farm was planned to be deeper, but a shallower depth was chosen after a preliminary survey found that clay lenses would cause significant subsurface spread of CO_2 and may restrict CO_2 release to surface (Moreira et al., 2014a). CO2-DEMO was a redesign of an earlier, deeper CO_2 release project where CO_2 did not reach surface. Layers of low permeability units above the injector at Vrøgum prevented CO_2 from reaching surface, and illustrated how subtle differences in lithology can significantly affect gas migration and dissolution (Cahill et al., 2014). These difficulties show the value of preliminary site investigations and tailoring the experiment to suit the subsurface properties and the experimental aims. At a number of sites, disturbance to the subsurface structure during site construction and pre-release tests affected the CO_2 flow pathways. While every reasonable attempt should be made to minimise disturbance, this can be difficult to avoid. The well bore was the primary source of unintentional leakage at CO_2 release experiments, which in some cases required corrective engineering. The location of seepage hotspots was hard to predict prior to CO_2 injection (Jones et al., 2014a). Sites with a number of adjacent experimental plots found CO_2 often cross-contaminated neighbouring plots (e.g. ZERT, Grimsrud Farm, ASGARD). Similarly, CO_2 breakout or injectivity often did not occur as predicted by modelling and the pre-injection knowledge of the site (Barrio et al., 2013, Spangler et al., 2010, Moni and Rasse, 2014). These complications should be considered when designing the surface monitoring array and baseline survey so that the monitoring infrastructure should cover an appropriate area, or be flexible to allow for relocation if needed.
CO_2 injection strategy	Where there has been only one CO_2 release experiment conducted at a site, most researchers would choose to modify their experimental design to improve the outcomes. For example, the period of injection would ideally have been longer at CO2 Field Lab and at QICS, to allow the experiment to reach steady state (Jones et al., 2014a) and to enhance the impact of CO_2 on sediment porewaters (Taylor et al., 2015b). This shows the value of conducting multiple releases at a site, such as at Ginninderra and ZERT, since the CO_2 injection strategy can be progressively modified. The isotopic signature of CO_2 can vary between canisters and suppliers, depending on the process from which it is sourced. As such, where multiple cylinders/deliveries of CO_2 are used for the experiment duration, and CO_2 isotopes are used as a monitoring tool, the isotopic signature should be recorded from each CO_2 cylinder used.
CO_2 fate	CO_2 flux at a single measurement point can vary due to a range of environmental factors. This is important to consider when interpreting results of CO_2 flux and using measured leakage rates to

	estimate total leakage quantities. It also highlights the importance of developing a robust understanding of the baseline, and factors that influence the baseline contribution. When reporting CO_2 flux, it should be clear whether the baseline has been subtracted from the measurements or not. Baseline should be subtracted before CO_2 flux values are used to estimate the proportion of leaked CO_2. Quantifying the proportion of injected CO_2 that was released to surface (atmosphere or seabed) has proven very challenging. Efforts have also been complicated by the need to integrate measured flux with (variable) background biological CO_2 flux measurements.
Additional monitoring	At a number of CO_2 release experiments baseline surveys were not conducted for long enough to characterise the main features of the site, and post-release monitoring was not conducted for long enough to observe the return to baseline conditions. Baseline information should include aspects such as seasonal variations in groundwater depth and speed, as well as typical background CO_2. It would be beneficial also to understand the short- and long-term effects of unusual weather patterns. Many CO_2 release projects have not accurately established the CO_2 arrival time to surface or into soil gas. If the arrival time is an important parameter to inform the intended work at the field experiment then sampling frequency should be particularly intense during the first days of the experiment.

Table 4: Common issues identified at CO_2 release experiments and recommendations for future sites to consider during design and operation of the experiment and monitoring procedure.

4.3 Research questions for future release experiments

The field experiments that we have examined here have allowed for testing of a range of monitoring techniques to identify and quantify CO_2 leakage, and for factors affecting CO_2 leakage to be investigated. However, knowledge gaps remain. Current sampling approaches are high intensity, and the quantification of any leakage, as required by guidelines and legislation for CCS (Dixon et al., 2015), has proven difficult. These experiments have therefore illustrated the need to develop more effective and low-cost detection and quantification techniques, and methods that are viable on the scale of the monitoring interval of CO_2 stores and over the time frame of the storage project. Release experiments present the opportunity to test promising candidate cost-effective techniques such as remote monitoring approaches (both airborne and ground-based (Bellante et al., 2013), acoustic methods (Bergès et al., 2015) and chemical tracers for quantitating CO_2 fate and leak rate (Myers et al., 2013, Roberts et al., 2017a). The latter have not yet been used to calculate CO_2 flux. As mentioned previously, the nature of the period of recovery following CO_2 release has been little explored in the experiments that we investigated, and this is important for obtaining and complying with legislative permits.

There has currently been little variation in the physical setting of the CO_2 experiments conducted to date, in terms of ecosystem, topography, and subsurface properties. The experiments that were available to be reviewed largely investigated the effect of CO_2 on grassland, crop or microbial species. Future experiments are being developed and conducted to address broader impacts, such as that at the Environmental Impact Test (EIT) facility developed by K-COSEM (Lee et al., 2016). Other ecosystems with larger or perennial species, natives versus introduced species could be investigated and research could explore how ecosystems might influence the soil structure or properties, and so CO_2 distribution and leakage.

The CO2 Field Lab and CO2-DEMO release experiments took place in disused quarries, but all remaining onshore experiments were located on relatively flat and exposed land, and so the effects of local topography have been little explored. Slight topographic variation at the ZERT site influenced the distribution of PFC tracers (which are denser than CO_2), and CO_2 leakage established at a surface depression at Ressacada Farm (Oliva et al., 2014). Topography is observed to influence the location and characteristics of natural CO_2 seeps due to corresponding changes in depth to the water table (Roberts et al., 2014), and also atmospheric dispersion of CO_2. Wind speed largely controls atmospheric CO_2 dispersion, and can also affect the accuracy

of CO_2 measurements. Topographic depressions or enclosed areas are usually more sheltered, and so can facilitate gravity-driven ponding of CO_2 to concentrations that are dangerous to human health (Roberts et al., 2011, Smets et al., 2010). While most onshore CO_2 storage projects are/were in relatively uniform topographic settings (e.g. Quest, Boundary Dam, and In Salah are all largely located in relatively flat environments), projects might be developed in more topographically variable terrains. As such, the effect of topography and annual weather conditions on the spread of CO_2 and tracers could be explored in more detail at future release experiments.

The hydraulic gradients at the sites are largely representative of groundwater flow systems in unconsolidated sandy aquifers with modest rainfalls (Lee et al., 2016). Only one experiment in the dataset, CO2-DEMO, injected CO_2 into lithified rock. Only three field experiments were excluded from our dataset and the analyses presented here, Plant Daniel and Cranfield were not included as these injected CO_2 deeper than ~40 m and did not intend to study the migration pathways of the injected CO_2. Future experiments could release CO_2 at greater depths, and into consolidated rock formations with the aim to monitor CO_2 fate and spread and for the CO_2 to leak to surface. While deeper wells are more expensive to drill, and deeper injection depths increase the risk that CO_2 will not reach the surface, the viability of these settings could be considered for future, longitudinal experiments.

The collective learning and common issues at these CO_2 release experiments are therefore extremely valuable for informing future research needs. Table 5 integrates the knowledge gaps discussed above together with other challenges identified in this review.

Variable	Suggestions for future experiments
Experiment set-up and site information	• **Environment**: More experiments need to be conducted offshore (only one offshore experiment conducted to date). A second sub-seabed CO_2 release experiment is planned as part of the H2020-funded STEMM-CCS project (reference 654462). For onshore experiments, sites should be more topographically varied and use ecosystems other than grassland. • **Subsurface properties**: Release into consolidated rock, or heterogeneous subsurface structure, or carbonate units.
CO_2 injection (for each experiment)	• **Injection depth**: inject CO_2 deeper to explore CO_2 migration in more consolidated or vertically heterogeneous units. • **Injection period**: inject CO_2 for longer periods (months). • **Properties:** Record $\delta^{13}C$ of all CO_2 injected (each vessel/cylinder delivered)
CO_2 Fate	• **Aim**: to quantify CO_2 leakage • Investigate how one or more of the following affects the spread and fate of CO_2 (and also use of possible tracers for CO_2): topography, rock type, water table depth (i.e. seasons).
Monitoring	• **Baseline surveys** should be detailed and collect information over a longer period than previous experiments. • Test cost-effective detection and quantification techniques, such as remote detection methods or chemical tracers for leakage. • **Post-release monitoring** should be detailed and collect information for longer periods so as to observe return to baseline conditions, and ecosystem recovery following CO_2 release/mitigation.

Table 5: Knowledge gaps that our synthesis has identified and that future CO_2 release experiments should seek to address.

5. Summary and Conclusions

Geological CO_2 storage sites are selected and engineered to minimize risk of leakage and maximise long-term storage potential, and are governed by legislation to this effect. Leakage to surface may not be anticipated, but effective site monitoring requires approaches that are capable of enabling any CO_2 leaks to be identified,

attributed, and quantified. In the absence of leakage from commercial CO_2 stores, field-scale shallow CO_2 release experiments provide opportunity to develop scientific understanding of the characteristics of CO_2 leaks that might arise from CCS projects, and methods of detecting them. We have collated a global dataset of experiments conducted between 2006 - 2017, drawing on information in the published domain complemented by correspondence with researchers from specific sites. The experimental procedure and results were then compared to establish the collective knowledge gained from these global efforts to date. We also determine whether current capabilities are fit for purpose, and if not, how future research can address the remaining knowledge gaps.

In this way, we examined 14 different CO_2 release projects, at which a total of 42 different CO_2 release experiments have been conducted. Other controlled release sites where injection depth was greater than 25 m were considered but not included in this paper. Collectively these experiments released 82.8 tonnes CO_2 over 994 days. Nine of the CO_2 release facilities intended that the injected CO_2 be released to surface, the majority of remaining experiments intended for CO_2 to remain in the shallow subsurface - usually to investigate groundwater interactions. The experiments show a range of test approaches, including CO_2 release duration, modes of release (horizontal, angled, vertical pipes), and injection depths.

We have identified a number of common perils and pitfalls, which future experiments should seek to learn from and avoid. The main issues include leakage of CO_2 along the wellbore or pipeline, which in some instances required action to remediate, and disturbing the subsurface during construction of the experimental site in such a manner that these changes influence CO_2 spread and leakage. Many experiments also faced challenges around determining the appropriate area of monitoring, which rarely matches the models.

Our comprehensive synthesis has shown how the collective experience at the field experiments conducted to date have advanced current knowledge of near surface flow pathways, environmental impacts, and methods of detecting CO_2 leaks. The importance of establishing baseline conditions for an appropriate time period cannot be underestimated, since this is important for estimating CO_2 impacts, fate, flux rates and total CO_2 leakage. Crucially, quantification of any leakage has proven difficult, despite intensive monitoring using multiple approaches at a number of the sites. Further work is needed for any leaks to be quantified to the degree of confidence acceptable for relevant legislation. Cost-effective approaches for doing so include remote sensing methods or mobile devices, or the use of chemical methods such as isotopic tracers, and shallow CO_2 release experiments provide excellent opportunity to trial these methods. Tests in more consolidated rock environments and carbonate hosted environments are recommended, to diversify observations. Further, only one of the projects that we reviewed was located offshore (QICS), highlighting the need for more activity on CO_2 leakage into the marine environment.

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8. Data Availability

The detailed dataset of variables outlined in Table 1 are provided via the UKCCSRC Data and Information Archive. https://doi.org/10.5285/86bdbd9f-b595-41e2-9e3c-516c01fda449.

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Table 2. Compilation of controlled CO_2 release experiments around the world conducted to date. Half of the sites have conducted more than one release experiment ('No. of exp'), some of them preliminary tests, and the experiment phases often differed in the length ('inj. length (days)') and rate of CO_2 injection ('Max inj. rate t(CO_2)pa'). The style of the injection also varies between sites, injecting CO_2 as a gas (g) or dissolved in water (diss), and via an inclined, vertical (v) or horizontal (h) well, and at a steady, incremental (incr.) or variable (var.) injection rate.

N	**Name or Acronym**	Country	No. of exp	Year(s)	Inj. depth (min-max, m)	CO_2 phase	Well orientation (degrees from vertical)	Inj. style	Inj. length (min-max, days)	Max inj. rate t(CO_2)pa	Surface leakage? (time*)	% of CO_2 leaked (method of derivation)
1	**ASGARD**	UK	4	2006 - 2010	0.6	g	45°	Steady	14-16	3.1	Y (<24 h)	34% (measured)
2	**QICS**	UK	1	2012	12	g	90° (h)	Incr.	36	72.53	Y (<3 h)	15% as bubbles (measured)
3	**CO_2 Field Lab**	Norway	1	2011	20	g	45°	Incr	5	153.3	Y (24 h)	5% (measured)
4	**Grimsrud Farm**	Norway	4	2012	0.85	g	90° (h)	Steady	75	1.93	Y (<12 d)	82% (measured)
5	**Vrøgum**	Denmark	6	2012	5-10	g	45°	Incr	2-72	4.3-10.51	N	
6	**CO2DEMO**	France	1***	2010-2014	3.7	g	0° (v)	Steady	<1	3.06	Y (14 h)	78% (measured)
7	**CIPRES**	France	2	2013	25	diss	0° (v)	Steady	2	4.38	N	
8	**SIMEx**	France	1	2013	13-16	g	0° (v)	Var.	0.1	550.6	N	
9	**Brandenburg**	Germany	1	2011	18	g	0° (v)	Steady	0		N	
10	**PISCO2**	Spain	1	2012	1.6	g	90° (h)	Steady	46	0.96	Y (3 d)	82.3% (modelled)
11	**Ginninderra**	Australia	4	2010	2	g	90° (h)	Incr / steady	56-80	21.8-79.6	Y (<24 h)	54% (measured)
12	**Ressacada Farm**	Brazil	1	2013	3	g	0° (v)	Incr	12	1.31	Y (10 d)	
13	**ZERT****	USA	13	2007-2014	1.1-2.5	g	90° (h)	Steady / var.	7-10	0.95-110.4	Y (<24 h)	49% (measured)
14	**Brackenridge**	USA	2	2011-2012	6	diss	0° (v)	Steady	2		N	

* time lag, in days (d) or hours (h), between the start of CO_2 injection and detecting CO_2 leakage at the land or seabed surface.

**An experiment was conducted at ZERT in Autumn 2006 where CO_2 was released from a vertical pipe for 10 days to simulate leakage from well failure. All subsequent experiments were from a horizontal buried pipe, designed to simulate leakage via a line source such as a fault or fracture. Unless explicitly stated, in this paper, the ZERT facility refers to the horizontal injection experiments.

*** The CO_2-DEMO project followed the CO_2-VADOSE project at the same site. The deeper CO_2-VADOSE experiment did not observe CO_2 release to surface. The site was subsequently modified to ensure that surface release would occur for the CO_2-DEMO project. We refer only to the CO_2-DEMO release experiment here.