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A B S T R A C T

Chemical tracers are proposed as an effective means of detecting, attributing and quantifying any CO₂ leaks to surface from geological CO₂ storage sites, a key component of Carbon Capture and Storage (CCS) technology. A significant proportion of global CO₂ storage capacity is located offshore, with some regions of the world having no onshore stores. To assure regulatory bodies and the public of CO₂ storage integrity it is important to demonstrate that robust offshore monitoring systems are in place. A range of chemical tracers for leakage have been tested at onshore pilot CCS projects worldwide, but to date they have not been trialled at injection projects or CO₂ release experiments located offshore. Here, for the first time, we critically review the current issues surrounding commercial scale use of tracers for offshore CCS projects, and examine the constraints and cost implications posed by the marine environment. These constraints include the logistics of sampling for tracers offshore, the fate of tracers in marine environments, tracer background levels, marine toxicity and legislative barriers – with particular focus on the Europe and the UK. It is clear that chemicals that form a natural component of the CO₂ stream are preferable tracers for ease of permitting and avoiding cost and risks of procuring and artificially adding a tracer. However, added tracers offer more reliability in terms of their unique composition and the ability to control and regulate concentrations. We identify helium and xenon isotopes (particularly ^{124,129}Xe), and artificial tracers such as PFCs and deuterated methane as the most suitable added tracers. This is due to their conservative behaviour, low environmental impact and relative inexpense. Importantly, we also find that SF₆ and C¹⁴ are not viable tracers for CCS due to environmental concerns, and many other potential tracers can be ruled out on the basis of cost. Further, we identify key challenges that are unique to using tracers for offshore monitoring, and highlight critical uncertainties that future work should address. These include possible adsorption or dispersion of tracer compounds during ascent through the overburden, longevity of tracers over the timeframes relevant for CCS monitoring, the permissible environmental effects of tracer leakage, and tracer behaviour in seabed CO₂ bubble streams and in dissolved CO₂. These uncertainties directly affect the selection of appropriate tracers, the injection program and concentrations necessary for their reliable detection, and appropriate sampling approaches. Hence offshore tracer selection and associated expense are currently poorly constrained. Further, there is limited experience of sampling for tracers in the marine environment; current approaches are expensive and must be streamlined to enable affordable monitoring strategies. Further work is necessary to address these unknowns so as to evaluate the performance of potential tracers for CO₂ leak quantitation and provide more accurate costings for effective offshore tracer monitoring programs.

1. Introduction

Effectively communicating and limiting the risk of leakage is paramount for Carbon Capture and Storage (CCS) to obtain a social license to operate. For the technology to be an effective climate change mitigation strategy the injected CO₂ must remain securely in the subsurface (Schaffer et al., 2013) with less than a 1% CO₂ loss to the surface over 1000 years (Hepple and Benson, 2005; IPCC, 2005). Legislation and

guidelines developed for CCS have set performance requirements to minimise leakage risk (Dixon et al., 2015), and to quantify and remediate any leaks that arise (Dixon et al., 2015; IEAGHG, 2012, 2015). The leakage of CO₂ would therefore impact on a number of stakeholders, incurring financial and environmental costs, and also challenge public acceptance of the technology. Hence, methods of monitoring are also necessary to verify that CO₂ is securely contained in the storage formation, and additionally has not leaked to into marine or terrestrial

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environments. Detecting and quantifying CO₂ leaks is challenging because CO₂ can be naturally present or generated in the subsurface, biosphere and atmosphere. Chemical tracers that ‘fingerprint’ CO₂ injected for CCS could allow it to be differentiated from these other natural or background sources (Stalker et al., 2009a).

The effective application of chemical tracers could provide valuable information about the migration and fate of CO₂. Assessment of monitoring options have found tracers to be a low cost and high returns technique (Ringrose et al., 2013) and one of the most promising for leak detection and quantification (IEAGHG, 2012). For these reasons, a portfolio of tracers has been proposed for CCS, and several have been developed and tested at CO₂ injection and release experiments and pilot CCS projects worldwide (Jenkins et al., 2015; Myers et al., 2013b). These have provided important learning for CCS monitoring, measurement and verification (MMV) programs (Stalker et al., 2015), but there is a dearth of experience using tracers at large CCS operations. Scaling up from pilot to commercial operations introduces issues of tracer selection and injection strategies, costs and environmental legislation. Lastly, there is significant uncertainty surrounding the behaviour of tracers in the range of environments with which they may interact (Stalker and Myers, 2014).

Most commercial CCS projects and all pilot projects worldwide are located onshore, whilst many future full-chain commercial scale offshore CCS projects are proposed (GCCSI, 2015). It is estimated that 40% of global CO₂ storage capacity is located offshore, and in some regions of the world the majority of storage capacity is located offshore (IEAGHG, 2008). This is the case in Western Europe, where, due to the location of the geological storage resource and availability of subsurface information, prospective stores are largely located below societally important shelf seas. Further, attempts to deploy CCS onshore in Europe have been challenged by public opposition. Since proximity to CO₂ pipelines and stores is of greatest concern to the public (Wallquist et al., 2012), largely due to fear of CO₂ leakage, offshore storage could have the added benefit of fewer issues around public acceptance of a project. However, public perception studies have found little evidence of this in practise (Mabon et al., 2015; Schumann et al., 2014), highlighting that the risk of CO₂ leakage and the potential resulting environmental impacts is a public concern (Blackford et al., 2014; Shackley et al., 2009). These concerns have contributed, along with economic and political factors, to the delay of CCS development offshore to date.

For CCS to gain a social license to operate it is important to demonstrate capability of identifying, locating, and quantifying CO₂ leaks to seabed. Further, testing cost-effective tracer monitoring strategies is important for the future industry to inform their monitoring programs. All CO₂ release experiments to date have been conducted onshore. The only sub-seabed CO₂ release site in the world currently is located offshore near to the town of Oban, located on the West coast of Scotland. The project conducted in 2012, known as QICS, 2017 (Quantifying and Monitoring Potential Ecosystem Impacts of Geological Storage (www.qics.co.uk)), mimicked small-scale CO₂ leakage into seabed sediments and aimed to investigate the environmental consequences of, and methods of detecting, the leak. In the experiment, CO₂ was continuously released 11 m below seabed (and ~10 m seawater) for 37 days. CO₂ bubble streams were observed at the seabed only a couple of hours after CO₂ injection started, but it took 34 days for dissolved CO₂ to reach pore waters near the seabed (Taylor et al., 2015a). A broad range of approaches were used to monitor the evolution of the seep and its impact on the marine environment, as well as to quantify the fate of the released CO₂ (Blackford et al., 2014). Overall, it is estimated that ~15% of the injected CO₂ reached seabed as a free phase (Blackford et al., 2014) and modelling finds that 14–63% dissolved in sediment pore waters (Taylor et al., 2015a) but there are considerable uncertainties associated with these numbers (Blackford et al., 2014). This illustrates the need to develop and test techniques to measure and quantify the fate of injected CO₂, and it has been proposed that chemical tracers could quantitate these processes further

(Blackford et al., 2015). As the project found significant potential for buffering by carbonate compounds in the seabed sediments, which suppressed the changes to chemical parameters (pH, conductivity and so on) that might be expected to arise from a CO₂ leak (Blackford et al., 2014), we must look to other approaches to identify a CO₂ leak. Chemical changes provided no information about CO₂ attribution and so chemical tracing using stable isotope composition (if CO₂ source is significantly different from background) or inert tracers may be more reliable for future experiments (Blackford et al., 2015). As such the QICS project highlighted the difficulties attributing and understanding the fate of injected CO₂ without chemical fingerprinting approaches, even with a very high intensity monitoring program.

The capability of tracer monitoring methods must be demonstrated before being applied to commercial scale CCS projects. As yet, there has been no attempt at testing or applying CO₂ tracers for leakage in the offshore marine environment, although the Peterhead CCS project (offshore Scotland, now cancelled) planned to use tracers to distinguish injected CO₂ from background in the case of CO₂ leaks being detected (IEAGHG, 2015; Jenkins et al., 2015). Offshore tracer programs will face considerably different challenges to those onshore. For example, the properties of the most suitable tracers might vary due to differences in the fate and impact of CO₂ (and tracers) that leak to seabed, and there will be practical and legal differences around injection and sampling strategy and permitting procedure.

Here, we first outline the different applications of chemical tracers for CCS, and how these have been applied or tested at pilot projects to date. We then consider the suitability of these tracers to offshore storage from practical and environmental perspectives, with particular focus on the European and UK setting, before assessing the cost of adding, sampling and analysing tracers in the marine environment compared to onshore settings. This enables identification of a suite of potential tracers for offshore CCS applications, and the current knowledge gaps that future research and experiments should address. This work lays the foundation for the design and implementation of effective tracer monitoring approaches for offshore CCS, and will directly inform future research focused on monitoring CO₂ storage offshore.

2. How chemical tracers have been used in CCS projects to date

2.1. Learning from experience

Tracing techniques are well established in the hydrocarbon and geothermal industry to provide information about reservoir connectivity and flow paths, or to estimate formation residual oil or connate water saturation. The most commonly used tracer compounds in these industries have been sulphur hexafluoride (SF₆) and perfluorocarbons (PFCs), which can be tailored to have certain properties.

The selection of tracers for CCS has been built on this industrial experience, but also presents new challenges on many aspects such as tracer purpose, desirable properties, tracer injection and sampling methods, analytical quantification, and the length of the monitoring program. For this reason, using tracers at CO₂ injection and release projects worldwide has been integral for developing knowledge and capability of selecting, injecting, sampling and analysing tracers for CCS, and these developments have recently been summarised in several comprehensive reviews (Mayer et al., 2015; Myers et al., 2013b; Stalker and Myers, 2014). For example, it has found that O-isotopes change significantly in the reservoir due to rapid equilibration of O-isotopes between CO₂ and water (Serno et al., 2016) and so are not reliable tracers for CO₂ attribution (Flude et al., 2016; Shevalier et al., 2014).

For controlled quantities of several tracers to be added to and mix with the CO₂ prior to injection into the subsurface, a slip-stream injection system (Stalker et al., 2009b) was designed at the Otway injection project, Australia, and the U-tube sampling device (Freifeld et al., 2005) allows multiple samples to be collected at reservoir intervals. Analysing tracers with extremely low background levels has

Table 1

The four principal purposes of chemical tracers for CCS. The tracer purpose determines the desirable properties of the tracer. Tracers are largely used to provide information about the CO₂ reservoir.

Purpose	Monitoring interval	Period	Desired tracer properties
Reservoir characterisation	Reservoir	Site assessment	<ul style="list-style-type: none"> ● Must be soluble in dense phase CO₂ ● Must be conservative (unreactive) to inform on the transport and storage properties of the reservoir rock.
To validate the presence of the injected CO ₂ (i.e. CO ₂ attribution) or map the extent of the CO ₂ plume.	Reservoir. Possibly overburden units in the case of leakage.	Operation. Possibly post closure.	<ul style="list-style-type: none"> ● Must be soluble in dense phase CO₂ and/or CO₂ brine mixtures to track formation water displacement from CO₂ injection.
To evaluate CO ₂ migration and trapping mechanism within the storage reservoir.	Reservoir	Operation	<ul style="list-style-type: none"> ● Must significantly partition between different CO₂ phases present in the reservoir to provide information on the amount of CO₂ in these phases.
To verify CO ₂ containment within the storage reservoir	Vicinity of pilot site. <i>Onshore:</i> Shallow subsurface or groundwater, soil and atmosphere <i>Offshore:</i> Pore waters of shallow subsurface or seabed sediments, water column or sea surface.	Operation and post closure	<ul style="list-style-type: none"> ● Must be conservative. ● The flow properties of ‘early warning’ tracers must enable early arrival compared to migrating CO₂. ● Tracers for quantifying leakage must be distributed throughout the plume, and must partition into the free CO₂ phase. ● The total quantity of leaked CO₂ (to Earth surface) can be calculated from the leak rate if the time since seeping began is known. <p>$CO_2 \text{ seep rate} = \text{Tracer seep rate} \times \text{seepage area} \times (CO_2 \text{ tracer quantity ratio})$.</p> <ul style="list-style-type: none"> ● The minimum rate of detectable leakage is dependent on the minimum detection limit of the tracer and the dispersion of the tracer once it is leaking at the surface (Myers et al., 2013).

also been found to be challenging, and approaches have been improved to reduce analytical error (Stalker et al., 2015; Stalker and Myers, 2014).

2.2. Selecting tracers for CCS

There are established overarching criteria that should be fulfilled for any chemical to be considered for use as a tracer. In particular, potential tracers must be evaluated according to their occupational health, environmental safety, and suitability for the monitoring and analysis concerns (see Stalker et al. (2009a) and references therein). The chemicals should behave predictably in the media that they may interact with, at the appropriate conditions (temperatures, pressures, salinities), whether that is the storage reservoir and its fluids, sediments and soils of the overburden or the atmosphere or water column. To date there is limited understanding of the partitioning coefficients of many of the proposed tracer chemicals in CO₂ (super- and sub-critical) and water (brines) (Myers et al., 2013a). Ideally, they must also be relatively easy to procure in the desired quantities, and to sample and analyse at the required precision.

A suite of chemicals that could fulfil these criteria has been proposed for different CCS monitoring objectives. The chemicals could be:

- A chemical property of the CO₂ being injected.* This includes carbon or oxygen isotopes, which depend on the industrial source of the CO₂ (i.e. steel, cement, fossil fuel, biomass) and the capture method used (oxyfuel, post-combustion and so on) (Flude et al., 2016).
- A component inherent to the CO₂ stream delivered for injection.* These are trace impurities inherent from the CO₂ source, such as associated noble gases (He, Ne, Ar, Kr, and Xe) or their isotope signatures, CO from incomplete combustion, or impurities from the capture process.
- A natural component of the CO₂ store.* These are gases that are naturally found in the storage reservoir such as noble gases (³He, ⁴⁰Ar), remnant methane or other short chain hydrocarbons, or even residual trace chemicals in depleted hydrocarbon fields.
- A chemical component added to injected CO₂.* This may be additional CO₂ with particular carbon or oxygen isotope signatures, natural chemicals such as noble gases or methane, or artificial chemicals such as manufactured organic chemicals like fluorocarbon compounds (including chlorofluorocarbons, CFCs; perfluorocarbons,

PFCs; or halocarbons; HFCs), SF₆ or esters. There are two broad approaches to adding a tracer to the CO₂ stream. To tag the entire body of CO₂ the tracer(s) could be continuously injected into the CO₂ stream using a purpose-built facility. Otherwise the tracer(s) could be injected for a short time period (i.e. a pulse, or several pulses over given time periods), either into the injected CO₂ stream or as a concentrated slug during a brief pause in CO₂ injection.

Whether a tracer is ‘inherited’ (types a-c) or artificially introduced for the purpose of the study (type d) affects the cost and execution of the monitoring program. Relying on the inherent properties of the CO₂, the CO₂ stream or the reservoir should be the lowest-cost tracer program to deliver since there is no need for the added cost and complexity of adding a tracer to the injected fluids. However, the properties (i.e. the chemical or isotopic composition) of the injected CO₂ stream may vary with time due variation in the CO₂ capture source (e.g. addition of co-firing biomass, or change in source origin of the fuel) or due to changes in contributions in an industrial hub or cluster – a development model where CO₂ delivered to the storage site is an amalgam from several sources (Brownsort et al., 2016). The properties or quantities of potential tracer chemicals already in the storage reservoir (type c) may not be suitable or desirable for the purpose of a tracer program. An added tracer (type d) may be preferable where there are such uncertainties in the long-term reliability of inherent tracers in the injected CO₂, or when it is necessary to select for specific behavioural properties in order to fulfil the purpose of the tracer.

Different chemical tracers are suitable for different purposes, depending on which aspect of the CO₂ store they are intended to monitor. Consideration has to be taken for the pressure and temperature conditions, and therefore the partitioning behaviour of the tracer, from the injection point to surface. A suite of tracers with different properties provide more information and offer greater reliability than using one tracer chemical (Stalker et al., 2009a). For example, the solubility of noble gases relates to the molar mass, and so if several noble gases were injected as tracers, their relative fractions could be used to derive the extent of CO₂ dissolution. Longevity of the tracers before breakdown or conversion to secondary products can occur at certain temperature conditions, which needs to be considered as a part of the ranking of suitable tracers – since monitoring programs might need to continue for decades following site closure (Jenkins et al., 2015).

Specific factors determine which tracer(s) will be selected for pilot

or commercial scale operations, for what purpose, and appropriate injection strategy. Table 1 summarises the four principal purposes and relevant properties of tracers developed and tested at CCS pilot injection projects or CO₂ release experiments worldwide. It is important that the purpose of the tracer addition is defined from the project outset, otherwise the tracer program that is deployed may not address the intended objectives outlined in Table 1. The tracers tested at pilot projects to date have typically been a chemical property of the CO₂ used for injection (i.e. the isotopic signature of C or O that comprises the injected CO₂) or a chemical added to the injected CO₂ (type a and d, respectively). These tracers have been used to provide information on the CO₂ flow pathways and flow rate, or residual saturation or to indicate unequivocal CO₂ arrival (Myers et al., 2015; Ringrose et al., 2013; Van der meer, 2013). Tracers have also been trialled at several shallow controlled CO₂ release experiments onshore (Feitz et al., 2014a; Rillard et al., 2015; Spangler et al., 2010). However, as yet, there has been no attempt at testing or applying CO₂ tracers for leakage in the offshore marine environment. The Peterhead CCS project planned to use tracers to distinguish injected CO₂ from background in the case of CO₂ leaks being detected (IEAGHG, 2015), but this project was cancelled in 2015.

Table 1 also illustrates that for most purposes, tracers largely provide information about the CO₂ reservoir, in addition to allowing the detection of CO₂ leaks. The monitoring interval (the reservoir, overlying strata, and the Earth surface) affects the range of geologic media with which the tracer may interact, sampling methods, and other factors outlined in Table 2 that influence the desirable properties of the tracer chemical. It is clear from Table 2 that selecting tracers for monitoring CO₂ leakage is more challenging. The tracer must behave predictably with the range of geological media and fluids with which it interacts, and its dispersion and adsorption behaviour must be understood so that it is added in sufficient quantities to allow for tracer loss during transport to surface. Similarly, the tracer must behave predictably over the range of pressure, temperature, and CO₂ phase conditions that might be experienced during ascent to surface – whether to soil or seabed. Selecting and testing suitable tracers for monitoring CO₂ leakage is therefore arguably more challenging, especially since there is little previous experience of similarly broad applications in the hydrocarbon or geothermal industries, where tracer studies are relatively specific in both scale and scope.

Geochemical tracers should preferably be non-polluting. Whilst storage sites will be carefully selected to retain injected CO₂, operational risk of tracer leakage is greatest during transport and injection. In

the worst case of CO₂ leakage from the store, tracers should not exacerbate the environmental impact of the CO₂ leak. Polluting or harmful tracer chemicals may not be approved from permitting and regulatory bodies. Tracers perceived to fall into these categories can impact on public confidence in CCS operations, and so radiocarbon or radon are usually considered unsuitable as potential tracers (Nimz and Bryant Hudson, 2005). Several prospective tracers are potent greenhouse gases, and so could exacerbate the impact of the leak in terms of equivalent CO₂. Indeed, the use of SF₆ is particularly restricted in the European Union (Regulation No 517/2014 (2014b)) due to its Global Warming Potential (GWP), which is 23,500 times that of CO₂ (EU, 2014b) on a time horizon of 100 years (Myhre et al., 2013). The GWP of another group of proposed CCS tracers, cyclic perfluorocarbon (PFC) compounds, is expected to be high also (Martin et al., 2011; Watson and Sullivan, 2012), since the GWP of the cyclic PFC perfluorocyclobutane is 9540 (Myhre et al., 2013). The recent Kilgali Amendment (2016) to the UN Montreal protocol have enshrined an 85% reduction by 2036 in the use of related hydrofluorocarbon (HFC) compounds over a 2011–2013 baseline due to their high GWP.

Watson and Sullivan (2012) explored the GWP of CO₂ tagged with a cyclic PFC tracer, modelled to leak to surface at a rate of 0.001% per year. They found that the concentration of PFC needed to ensure reliable detection of the leak from 1 km away would add 20% to the GWP of the leak (compared to a leak of CO₂ with no PFC tracer). For some tracers, the GWP values are poorly constrained; for example, CD₄ takes longer to breakdown in the atmosphere and its GWP could be much greater than CH₄. Commercial scale CO₂ monitoring programs might require large quantities of tracer chemicals, and the GWP of a potential leak will need to be considered when selecting the tracers.

Pilot and commercial scale tracer programs may have different needs in terms of the purpose of the tracer, the length and intensity of the monitoring period, the budget and the relevant environmental legislation (Stalker and Myers, 2014). These differences (summarised in SI Table 1) mean that the criteria and approaches to selecting and using tracers developed at field trials may not be directly transferable to commercial scale CCS operations.

The purpose of tracers at field trials may be different to their purpose at deep geological stores; perhaps furthering fundamental understanding of CO₂ transport and fate in the subsurface, rather than to verify CO₂ containment or validate the CO₂ plume extent. At K12-B, offshore Netherlands, PFCs were used to assess the CO₂ sweep efficiency and migration rate during the re-injection of CO₂ at a natural gas field (Van der meer, 2013; Vandeweyer et al., 2011), while reactive

Table 2

Factors to consider when deciding the desirable properties of the tracer. The desirable properties depend on the tracer purpose, which also defines the monitoring interval for the tracer.

Purpose/Factor	CO ₂ spread and interaction in the reservoir	CO ₂ leakage to surface
Geologic media	Reservoir	Reservoir, overburden, soils and sediments
Geologic fluids	Pore fluids (reservoir brines, perhaps residual hydrocarbons).	Pore fluids of the reservoir and overburden, soil gas, atmosphere, sediment pore water, seawater column.
Plume geometry	Larger horizontal than vertical extent in the long term.	Larger vertical extent than lateral extent – until the near surface. Possibly channelled along faults or permeability contrasts.
Changes to T & P conditions	Minimal away from the injection point.	Large changes from reservoir to surface.
CO ₂ phases	Dense phase and dissolved	Dense and light phases, and dissolved.
Environmental risk	Storage sites are selected for low likelihood of leakage, and CO ₂ and tracer should remain in storage formation. Though leak risk is low, the tracer would still preferably have minimal environmental impact, and must comply with environmental legislation.	Storage sites are selected for low likelihood of leakage, and CO ₂ and tracer should remain in storage formation. Though leak risk is low, the tracer would still preferably have minimal environmental impact, and must comply with environmental legislation. CO ₂ release experiments differ in that the CO ₂ and tracer are intended to reach surface. The long-term environmental impact of tracers must be minimal.
Sampling	Subsurface	Onshore: Shallow subsurface or groundwater, soil and atmosphere. Offshore: Pore waters of shallow subsurface or seabed sediments, water column or sea surface.
Background concentration	Preferably low, and preferably stable	Must be low, and stable.
Previous experience using tracers for this purpose	Moderate experience	Very little experience

esters were trialled at CO2CRC Otway site to determine residual CO₂ saturation (Myers et al., 2015). Tracer tests used by the hydrocarbon industry and tracer field trials for CCS are typically short-term compared to MMV programs at commercial CO₂ stores, which could be required to last for many decades. There is a risk that tracer chemicals might biodegrade or breakdown under certain conditions in the subsurface or at surface (land or seabed); CFCs in groundwaters can degrade within a couple of years (Horneman et al., 2008), HFCs (such as R-134a) degrade on the order of years to decades, and methane will quickly biodegrade through aerobic or anaerobic processes.

The overall cost of a tracer program will be affected by factors such as the tracer monitoring interval, the approach and intensity of sampling and analysis. For added tracers, the cost is dependent on the quantity of the tracer injected (which is a function of background values and the precision of available measurement approaches) and also the cost of procuring the tracer. The cost of a tracer program may not be prohibitive for pilot scale tests, but is of critical importance for large-scale CO₂ storage operations. Some chemicals are expensive to analyse; for example, analysing for noble gases is generally over twice the price per sample compared with SF₆ (IEAGHG, 2015). The possibility of routine analysis of certain tracers for storage site monitoring creates demand to develop and test rapid but precise means of analysis using low-cost, preferably real time instruments. The cost of procuring tracers should decrease with tracer demand (Nimz and Bryant Hudson, 2005), though this may not be the case for globally rare chemicals, such as ³He.

Determining the minimum concentrations or isotopic signature of tracers that must be injected to ensure reliable detection is challenging and is affected by several factors. These include the background concentration and its variability (in the subsurface formations, seabed or land surface), how conservative the tracer is, and the analytical approach required to measure the tracer. If background levels are very low, very small perturbations in concentration will be easily detected; PFCs are laudable because they exist in parts per trillion (ppt) concentrations in atmosphere and are detectable at pico (10⁻¹²) to femtogram (10⁻¹⁵) levels. For some chemicals, the precision of currently available analytical techniques can vary greatly depending on the method used, for example, detection limits for CD₄ by various analytical methods range from 0.0001 ppm to 10,000 ppm (Stalker et al., 2009a), and the method used will determine tracer injection concentration and analytical costs.

While background tracer concentrations are unlikely to vary significantly during the lifetime of a pilot project, they could feasibly change over the duration of commercial scale CCS monitoring programs, particularly if they are widely used as a tracer (Watson and Sullivan, 2012). For example, there was no detectable SF₆ in the atmosphere in the 1950's, however, in 2011 background levels were 7.28 parts per trillion and they continue to rise (Myhre et al., 2013). The possibility of changes to baseline concentrations introduces difficulty when assessing detection limits for future decades or centuries, and so the optimum injection concentrations of tracers for long term CO₂ storage monitoring.

Tracers for detecting and quantifying CO₂ leaks must be added in sufficient quantities to allow for reliable detection following possible dispersion, adsorption and loss during transport through the overburden. CO₂ release experiments have found that only a proportion of CO₂ makes it to surface (Barrio et al., 2013; Blackford et al., 2014; Roberts and Stalker, 2017). These experiments are typically shallow; the deepest CO₂ release experiment to date which intentionally released CO₂ to surface is the CO₂ Field Lab in Norway, which injected CO₂ at 20 m depth (Jones et al., 2014). Should CO₂ leak from a storage site, it must migrate through > ~1.5 km of overburden to reach the Earth surface. For commercial monitoring programs it is particularly important to establish whether a tracer might partition differently in subsurface systems that are saturated with brine or other fluids, of different rock composition (especially clay or organic matter content),

or at different subsurface conditions (Myers et al., 2012). Similarly, for CO₂ isotope tracers, the isotopic signature must be retained during CO₂ migration. The QUEST CCS project located in Edmonton, Canada, is using the inherent δ¹³C-CO₂ signature of captured CO₂ (−20.4‰) as a tracer. At the time of writing, QUEST, which commenced CO₂ injection in 2015, is the only large CCS project which planned to use tracers for the purpose of detecting leakage, in this case, the inherent chemical properties of injected CO₂ (type a). Shevalier et al. (2014) simulated potential CO₂ leakage from the QUEST reservoir into the overlying formation (via a leaky well-bore), and predicted that the δ¹³C signature of the leaked CO₂ should remain stable, enabling leakage to be identified and quantified. The inherent properties of the CO₂ injected at the Weyburn-Midale CO₂-EOR project, Canada, were used to determine if migration of dissolved CO₂ was responsible for an alleged CO₂ anomaly measured in soil gases and groundwaters nearby (Gilfillan et al., 2017). However, this chemical approach was not part of Weyburn's original monitoring program. Similar inherent noble gas techniques have been used to identify the migration of natural CO₂ from a CO₂ reservoir (Gilfillan et al., 2011), and track the fate of mantle derived CO₂ injected into a CO₂-EOR field in the USA (Györe et al., 2017; Györe et al., 2015).

3. Logistics of using tracers offshore

The challenges discussed in the previous section are relevant to both onshore and offshore storage projects. The field experience of using tracers for CCS to date has been solely at onshore projects. Some chemical tracers may behave markedly differently in the marine environment compared to terrestrial settings, making them more suited to a particular environment. Similarly, particular tracers may be easier to sample at the seabed, or have less harmful effects on marine ecosystems. These factors must be considered when selecting tracers for offshore storage, and the sampling program will need to be tailored to the individual tracer behaviour. In this section, issues specific to the design of offshore CCS tracer monitoring programs are considered, using the UK seas as an example, with a particular focus on tracers for detecting and quantifying CO₂ leaks into the marine environment.

3.1. Legal and regulatory issues

The marine environment is protected under international conventions and national legislation, and any offshore CCS activities must comply with these. For example, UK seas are protected by international treaties, such as the OSPAR Convention (Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR, 1992)) and EU Directives, and national and devolved legislation. Consents and permits must be obtained at these levels, many of which will require reporting for compliance.

There are two principal treaties that govern offshore CO₂ storage in Europe; the Directive on the Geological Storage of Carbon Dioxide (EU, 2009) (the "EU CCS Directive") and the 2007 OSPAR Guidelines for the Risk Assessment and management of Storage of CO₂ in Geological Formations (the "OSPAR FRAM", Annex 7 of the OSPAR Convention (OSPAR, 2007a)). Both emphasize the importance of monitoring and require a monitoring plan, particularly the OSPAR guidelines since the purpose of OSPAR is to protect the marine environment. However, neither is prescriptive regarding the use of tracers for CCS. The EU CCS Directive permits small quantities of incidental or added compounds. Article 12 (1) of the EU CCS directive (OSPAR, 2007a,b; EU, 2009) states that "a CO₂ stream may contain incidental associated substances from the source, capture or injection process and trace substances added to assist in monitoring and verifying CO₂ migration" provided that their concentration would not have any adverse effect on the storage site or infrastructure, would not pose significant risk to the environment or human health, and complies with legislation relevant to the site. Similarly, Annex II, Article 3(2) of the OSPAR convention states that CO₂ disposal streams "may contain incidental associated

substances derived from the source material and the capture, transport and storage processes used” OSPAR (2007a,b). Tracers that are a natural constituent of the CO₂ stream would therefore be acceptable. However, it is not clear whether OSPAR permits added tracers, which are not incidental substances, though added tracers were permitted to be injected in small quantities at the pilot K12-B well located in the Netherlands North Sea (Van der meer, 2013).

In UK law, the activity is permitted if there is no legislation that states otherwise. There are limitations for certain tracers, for example, although they were once used routinely. Radioactive tracers (such as radiocarbon and radon), chlorofluorocarbons, and sulphur hexafluoride are now restricted due to environmental and health and safety concerns (Myers et al., 2013b). For regulatory approval, information about the tracer chemicals and injection quantities must be stated, and to satisfy OSPAR additional information about the fate of injected chemical tracer in the marine environment needs to be provided, including ecotoxicology, bioaccumulation, and biodegradability. The hydrocarbon industry in the North Sea has used PFC tracers for decades and met the requirements of OSPAR, and, for example, PFC tracers injected with CO₂ at the K12-B CO₂ enhanced gas recovery project in the Dutch sector of the North Sea (Van der meer, 2013). However, these tracer tests are usually short duration pulsed injection tests that use smaller tracer quantities (i.e. kilograms) than would be used for leakage MMV programs, which could be injecting tracers continuously for much longer time periods, and so will use much larger quantities of tracer (tonnes (Watson and Sullivan, 2012)). These increased tracer volumes might introduce issues under OSPAR for artificial tracers, though this will be less of an issue for naturally occurring chemicals such as noble gases.

Finally, while the EU CCS Directive and OSPAR CCS Guidelines (OSPAR, 2007b) are exclusively for CCS, other EU Directives and OSPAR treaties will apply to the CO₂ storage activities, including the tracer program. For example, other relevant EU Directives include the Environmental Impact Assessment Directive 2014/52/EU, Integrated Pollution Prevention and Control Directive (Council Directive 96/61/EC), EU Water Framework Directive 2000/60/EC, Environmental Liability 2004/35/EC, and Waste Framework Directive 2008/98/EC. There are several Marine Protected Areas (OSPAR, 2016), and Special Protection Areas and Special Areas of Conservation (EU Habitats Directive 92/43/EEC) in areas of the UK seas that are prospective for carbon storage, which might introduce sensitivities for permitting. However, as hydrocarbon production is ongoing in several of these protected areas, it is unlikely that CCS activities would require significant additional permitting. Should the tracer be artificially added to the CO₂ stream prior to transportation, then full consent under the appropriate legislation related to transport of the CO₂ stream would be required.

Management of UK Controlled Waters (coastal waters up to 3 nautical miles from the mean low-water mark) is devolved to individual member nations. The UK Territorial Seas (coastal waters within maximum of 12 nautical miles from the mean low-water mark) are managed and owned by the Crown Estate. The UK government manages the Continental Shelf (coastal waters within 200 nautical miles from the mean low-water mark, or until the end of the continental shelf) which also includes the Exclusive Economic Zone (which defines boundaries on resource rights, 1982 United Nations Convention on the Law of the Sea). Consents and permitting of activities offshore UK may apply exclusively to, or across, these zones. For example, under the UK Energy Act (2008), which transposed the EU CCS Directive (EU, 2009) into UK law, any CO₂ storage operations offshore UK would require an Agreement for Lease and other relevant property grants from The Crown Estate, and a Carbon Storage Permit from the UK government. Further, permissions must be obtained from the devolved authority for activities in the Controlled Water zone (e.g. in Scotland, this would be from the Scottish Government under the Marine Scotland Act, (2010)).

3.2. Challenges of sampling for leakage

Tracer programs designed to monitor the performance security of the CO₂ store could sample fluids above or below surface. The presence of tracers in monitoring wells overlying the primary storage formation indicates CO₂ migration from the storage formation, and the presence of tracers in the near-surface (soil gas, ground waters, sediment pore-waters) or above surface (atmosphere, seabed or sea surface) unequivocally indicates CO₂ leakage to surface. In the subsurface, the CO₂ and tracers could be in dissolved or free phase, which will be gaseous at depths shallower than approximately 800 m below surface, depending on the geothermal gradient and the pressure conditions. As previously mentioned, the majority of offshore experience using chemical tracers for CCS or for CO₂-Enhance Oil Recovery (EOR) is based on sampling tracers in produced fluids, and so are not directly relevant to sampling for monitoring CO₂ leakage.

The sampling approach and logistics of sample analysis will be specific to the tracer(s) deployed, whether the project is offshore or onshore, the target environment being sampled, and other site-specific, and tracer-specific factors. For example, noble gases require copper apparatus rather than standard sampling materials due to problems of atmospheric contamination into and leakage of noble gases from the sample vessels as a result of the small atomic size and prevalence of certain noble gases in the atmosphere (Holland and Gilfillan, 2013). If combinations of tracers are used, then it will be advantageous if samples for all tracers could be collected using the same approach or during one sampling program.

Table 3 summarises the approaches that can be used for sampling tracers for CO₂ leakage monitoring in the range of environments, and also example project experiences. The various sampling horizons are shown in a schematic of CO₂ leakage in Fig. 1. Table 3 shows that there are appropriate techniques for monitoring or sampling for tracers in sediment pore waters, seabed, and the water column, however there is a dearth of experience in testing these techniques in field trials. These techniques also vary greatly in terms of the sampling style (e.g. invasive, localised, automated) and so the resource and logistical costs. Existing sampling techniques in the marine environment are largely high-intensity, high-cost procedures, that are significantly more expensive than onshore sampling strategies (see SI Table 2) due to access issues and other complexities associated with operating in the marine environment.

The sampling program will depend on the suite of monitoring tools at a site, and their purpose. The footprint of leaked CO₂ is likely to be very small compared with the area requiring assessment at a storage site (Blackford et al., 2015). Should tracers be the primary and sole method for detecting CO₂ leakage above a store, sampling (and analysis) for tracers would need to take place frequently and at regular intervals. As such, the tracer sampling program could be expensive and challenging. However, if tracers constitute a suite of leak detection monitoring techniques, sampling for tracers could take place in response to a potential leak detected by an alternative monitoring method, in which case the area for tracer sampling will be much more constrained. Regardless, there is a need to develop and test in situ approaches to routine sampling and analysis of tracers in seawater to streamline the site monitoring process. This effort could build on or work with advances in ocean sciences such as new techniques to continuously measure noble gas ratios in water (Aeschbach, 2016; Manning et al., 2016).

As the majority of offshore CO₂ storage operations in Europe will be in moderately shallow continental seas (keeping drilling and CO₂-transport costs down), free phase CO₂ leaks to seabed will be in the gaseous phase – although the CO₂ will be at a higher density than at the land surface due to the pressure exerted by the water column. Whilst the CO₂ density may be affected by tides, as was the case at QICS (Bergès et al., 2015), the CO₂ is unlikely to be in a liquid phase at the seabed, although this has been observed at deep-sea vents (Lupton

Table 3
The range of environments for sampling tracers for CO₂ leakage monitoring, the approaches used in these environments, and example project experiences. The method of sampling is dependent on the environment and the tracer properties. Baseline data would need to be collected, and repeat surveys will then determine any changes from background levels.

Loc.	Env.	Phases	Sampling methods	Example Project Experience	Cost
Onshore or Offshore	Subsurface – deep	Dissolved or free phase (dense or gas phase)	Samples obtained in situ (i.e. at reservoir pressure) from a monitoring or producing well (Myers et al., 2013). The sampling equipment may be tracer specific (for example, sampling helium requires copper apparatus). U-tube sampler: this device was developed to perform in situ gases and aqueous fluid sampling. This is a commercial wire line device that is permanently mounted during installation of the well apparatus.	Pilot projects: Otway: U-tube sampling over several intervals for CD ₄ , Kr, SF ₆ , reactive esters and also carbon compounds that were naturally in the CO ₂ stream (Myers et al., 2013). Frio Brine project: U-tube sampled for SF ₆ , PFCs and noble gases (McCallum et al., 2005). K12B (CCS-EOR). Two PFC tracers were added to injected CO ₂ and sampled at two producing wells (Van der meer, 2013). To date there is no experience using U-tube sampler offshore.	Onshore: £5–10 K per sample. No offshore experience (IEAGHG, 2015). Not including analytical costs.
Offshore	Subsided – shallow	Sediment pore waters	Sediment cores are the standard procedure for sampling sediment pore fluids. Scuba divers: can collect cores by hand for the pore fluids to be analysed in the lab. The Van Veen Grab: this is an industry standard benthic sampling device that can take longer cores and sample a 0.1 m ² area. Vibrocorer: this equipment can recover longer cores (1–5 m long) and sample from firmer substrate.	CCS projects Sleipner: Sediment and porewater samples (up to 20 cm length) were collected between 2001 and 2009 to monitor hydrocarbons and trace metals, with additional monitoring as part of ECO2 program between 2011 and 2013. Snohvit: Sediment and porewater samples (up to 40 cm length) were collected using multicore system as part of ECO ₂ program between 2011–2013. Peterhead: Sediment surveys were planned to measure hydrocarbons (total, and polyaromatic) and many other parameters. Also planned at ROAD and Tomakomai (IEAGHG, 2015). CO₂ release projects: QIGS: Scuba divers collected sediment cores 10–15 cm length (Taylor et al., 2015b) which detected CO ₂ arrival by changes in pH.	£5 K per day for survey (excludes cost of ship time)
	Above seafloor	Dissolved Free phase (gas)	Benthic Chambers: Benthic chamber lander equipment can measure in situ dissolved composition of seawater at the sediment-seawater interface. Scuba divers: Position a plastic funnel connected to a sampling flask over the rising bubbles. Acoustic hydrophones: hydrophones on the seafloor passive acoustic inversion technique	CCS projects: Sleipner: Deployed benthic chambers to measure CO ₂ and O ₂ fluxes (Linke, 2011) which showed no anomalous changes. CO₂ release projects: QIGS: Benthic chambers were deployed to measure release of dissolved carbon dioxide from the sediment into the water column, as well as geochemical fluxes and metal mobility (Taylor et al., 2015b). Scuba divers collected bubbles from bubble streams to determine flux of gaseous CO ₂ across the sea floor. Hydrophone data determined gas flux (Berges et al., 2015). Storforden: A localised CO ₂ release experiment offshore Norway used benthic chambers to explore the effects of CO ₂ on benthic biota (Ishida et al., 2013). To date, sampling for tracers have not been done by benthic chambers or scuba divers for CCS.	Acoustic hydrophones, if permanent, have high upfront cost.

(continued on next page)

Table 3 (continued)

Loc.	Env.	Phases	Sampling methods	Example Project Experience	Cost
			<p>Multibeam echosounders (MBES): These acoustic techniques map the seabed in detail. Time-lapse surveys could therefore detect changes to seafloor morphology that might indicate leakage (e.g. pockmarks) or bubble releases. Surveys can be conducted by ship or by underwater AUV/ROV systems.</p>	<p>CCS projects: Sleipner: ship-borne seabed imaging survey was conducted in 2006, and in 2011 an AUV mounted MBES survey was conducted as part of ECO2 project (IEAGHG, 2015). Snohvit: Repeat MBES surveys were acquired over 3 × 10 km area between 2011–2013 (IEAGHG, 2015). CO₂ release projects: QICS: Seven ship-mounted MBES surveys were conducted, which imaged pockmarks and bubbles streams (Cevatoglu et al., 2015). MBES does not sample tracers, but can observe any impacts that leaked tracers may have.</p>	<p>10 km² survey cost £100–200 K</p>
			<p>Underwater video or time-lapse photography: can record bubbles or changes to biota. Bacterial mounds could occur near leaks due to the CO₂ or due to co-released tracers such as CH₄ or reactive esters. Fluorescent or coloured tracers could be used to image CO₂ leaks. The camera equipment can be fixed, attached to an ROV/AUV, or, for transects, taken by scuba divers.</p>	<p>CCS projects: Sleipner: ROV collected video footage off seafloor when installing survey equipment. CO₂ release experiments: QICS: Underwater photographic surveys were conducted to observe marine fauna responses and bubble stream dynamics (Kita et al., 2015). Transects were taken by divers, and four cameras were fixed for time-lapse. This approach does not sample tracers, but can observe any impacts that leaked tracers may have.</p>	<p>£1–10 K (video-GPS equipment is a further ~£20 K to purchase)</p>
			<p>Conductivity, Temperature and Depth (CTD) probes: These probes take geochemical measurements from the water column and can be attached to survey ships or permanently attached to the platform. Water sampling: Usually done in combination with CTD probes, as the probes have sampling bottles attached. Analysis can be done on ship for parameters such as CO₂ and methane.</p>	<p>CCS projects: Sleipner: Between 2011–2013, CTD and water column sampling surveys were conducted at ~80 m water depth to measure CH₄ and poly aromatic hydrocarbons (IEAGHG, 2015). Snohvit: Depth profiles of CDT and water column samples at various sampling depths were conducted over a 12 × 8 km grid (IEAGHG, 2015). Peterhead: Permanent real-time CDT probes attached to the platform were planned at Peterhead (IEAGHG, 2015). There is experience sampling the water column for tracers such as CH₄ and organic compounds.</p>	<p>£1–10 K per survey (excluding ship time).</p>
			<p>Autonomous Underwater Vehicle (AUV) or Remotely Operated Vehicle (ROV) systems with chemical sensors or means of sampling.</p>	<p>CCS projects: Sleipner: Between 2011–2013, as part of the ECO2 project, water samples were collected by ROV (ECO2 Final Publishable Summary Report). CO₂ release projects: QICS: Wide-area mapping surveys of the water column were carried out by an AUV installed with pH and pCO₂ sensors (Shitashima et al., 2015). No experience for CCS. Method is used to collect water samples for ocean fertilization experiments, where SF₆ was used as a tracer (Martin et al., 1994).</p>	<p>> £10,000 per day for AUV survey (Chance et al., 2000)</p>
			<p>Surface Pumping Systems: collect water samples from the sea surface from the vessel.</p>		
			<p>Gas samples collected at the seawater-atmosphere interface.</p>		

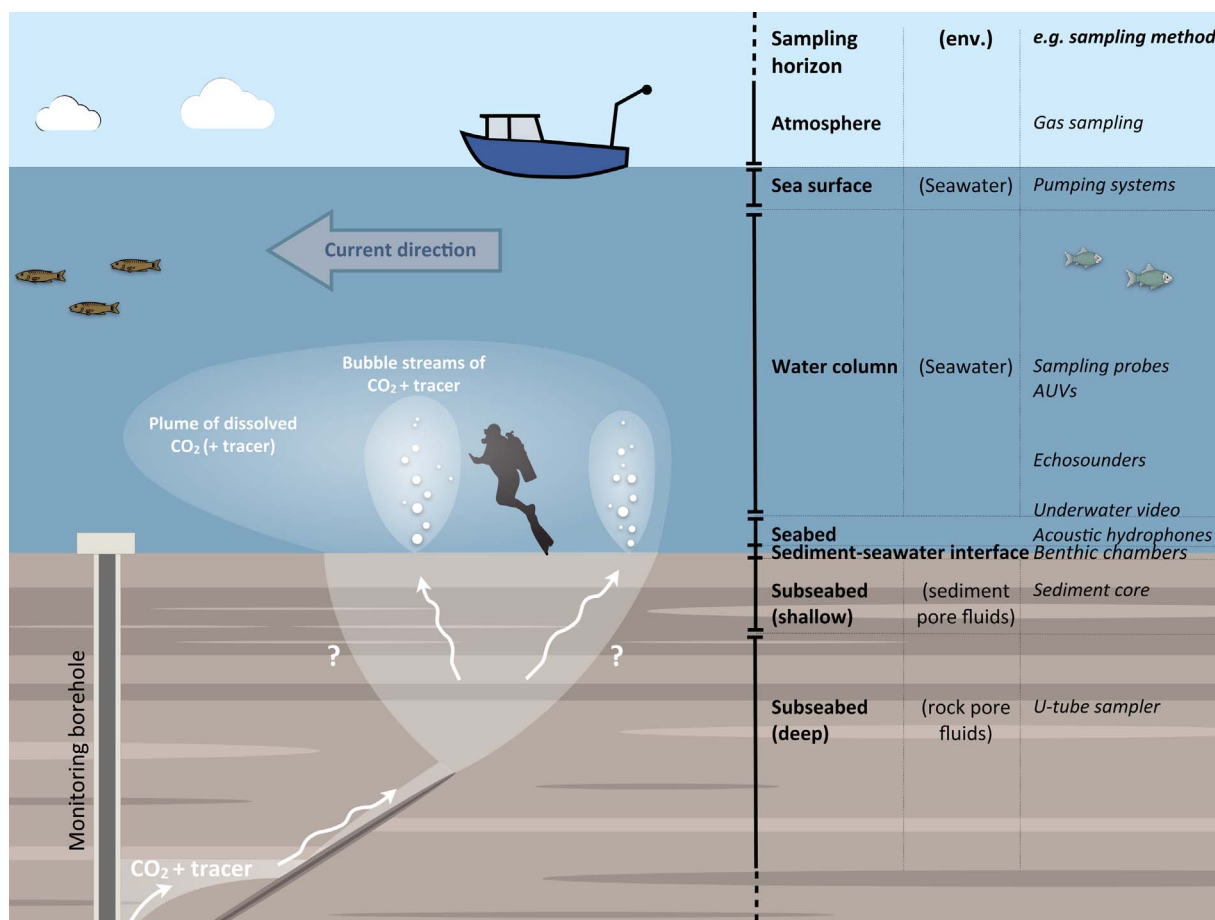


Fig. 1. Schematic of 7 sampling zones for monitoring for leaked CO₂ and tracers offshore, and their sampling environment and example methods. These methods are presented in more detail in Table 3. This is a schematic, and is not to scale; water depth in the North Sea could be ~100 m deep, and bubble plumes would soon dissolve in the water column. Leaking CO₂ and tracer is depicted in white, and a simplified schematic of leaking CO₂ in the subsurface is shown on the figure. CO₂ leaks to seabed as dissolved in porewaters, and also as a free phase as bubble plumes.

et al., 2006). Bubble streams of gas phase CO₂ quickly rise and dissolve into the seawater column (Sellami et al., 2015) unless the CO₂ emissions are very large (Caramanna et al., 2013) or occur in shallow waters. For sampling tracers, it may be important to target these bubble streams close to the seabed where they emerge, as differences in solubility of CO₂ and tracer at seabed conditions could mean that the tracer concentration increases or decreases as the bubbles rise. The behaviour of the tracer in bubble streams must be understood in order to derive the concentration of tracer in the leaked CO₂ from the bubble sampling height above seabed. This is particularly important for artificial tracers, such as SF₆ and many cyclic or fully-fluorinated PFCs, which are extremely hydrophobic. This may be problematic if CO₂ leaks to the seabed in its dissolved phase, since it is not clear how strongly hydrophobic tracer molecules would partition or behave, nor how they could be sampled. For example, in the absence of free phase CO₂, strongly hydrophobic chemicals like chain PFCs may form micelle-type structures if their concentration is high enough (Spiess, 2009). These hydrophobic structures could remain adsorbed on the sediment below seabed where they will be challenging to sample, or, should they reach seabed or the water column, it is not clear how sediment or seawater might reliably sampled for such compounds. Hence, it would be useful to develop a protocol for such sampling, such as an offshore equivalent of the passive sorbent packs used to sample PFC tracers at the onshore West Pearl Queen project (Jenkins et al., 2015; Wells et al., 2007).

Seabed or water column sampling programs will need to understand seabed currents, in a similar fashion to onshore programs that need to consider wind speeds and directions. On the UK continental shelf, where CO₂ stores are located, the current direction and strength vary

widely depending on location, season and climatic conditions such as the North Atlantic Oscillation. This results in the water column being relatively mixed all year round, particularly in the southern region (Blackford et al., 2015; Paramor et al., 2009). Elsewhere, currents may be weaker, more uniform, or the water column might become seasonally stratified, and the geometries of sampling programs must account for these factors so the CO₂-seawater plume is sampled. Should CO₂ leak to seabed in deep seas where currents are very weak it is possible that seawater containing dissolved CO₂ might accumulate at the seabed, as dissolved CO₂ will increase the density of the seawater (IEAGHG, 2012). The extent of these pools could aid leak quantitation, particularly if detectable levels of tracers are also dissolved into the seawater. Investigating tracers in bubble streams will illuminate how they partition when CO₂ dissolves into water, and hence which conservative tracers would be present in seawater containing dissolved CO₂.

In Western Europe, prospective stores are largely located below societally important shelf seas, and so sampling programs must also consider other sea users and their activities and how they may affect, or be affected by the monitoring program. For example, fishing trawlers could interrupt data collection or might damage or disturb equipment (Jenkins et al., 2015). It may also be necessary to establish a reliable means of locating sampling or monitoring equipment, since GPS devices cannot be used underwater and so would either need to be encased in a float, or other location techniques must be used.

3.3. Background tracer concentrations and tracer cost

For any tracer program, the baseline concentration or isotopic composition of tracer in the sampling horizon must be established prior to CO₂ injection. Carbon, oxygen (and their isotopes) and methane may vary with the seasons, ocean currents, with water depth, and other factors outlined in (Blackford et al., 2015). Thus, depending on the tracer to be used, baseline conditions and the co-variance of chemical processes may need to be established over a multi-year timeframe. These conditions will inform the suitability of certain tracers, since background levels in part determine the quantities of a tracer needed to be able to detect perturbations that will signal a CO₂ leak, and so whether inherent tracers will suffice or if added tracers are necessary (and if so, in what quantities). The background conditions therefore affect the cost of tagging CO₂ with a tracer and also the possible environmental effects of a leak if a tracer is not environmentally benign.

Background concentrations for most tracers are ~100 times lower in seawater than in the atmosphere, though the difference is more significant for methane, CD₄, and SF₆ (typical background concentrations in seawater and atmosphere for the tracers assessed in this work are shown in SI Table 3). The quantities of tracers required to detect a CO₂ leak will therefore depend on whether the CO₂ is stored onshore or offshore, and may also differ according to whether samples will be collected at seabed, seawater column or at the sea surface. In addition, some tracer concentrations are site specific, for example, radiocarbon and oxygen isotopes are well mixed in the atmosphere but are more variable in the oceans (Galbraith et al., 2011) and also vary with water depth, seasons, and factors such as ocean stratification (Schmidt et al., 1999). Methane is naturally produced or generated in subsurface and surface environments, and known to vary seasonally in concentration and isotopic properties (Yu et al., 2015), and so CH₄ alone isn't a reliable tracer for the unique identification of CO₂ from a breached storage site. Cyclic PFCs used in tracer experiments have background concentrations in the low ppqv (parts per quadrillion by volume) range (Martin et al., 2011). However, since most PFCs have atmospheric lifetimes of tens of thousands of years, their background levels are rising slowly (though still < 1 ppqv per annum) as a result of their industrial use (Simmonds et al., 2002) and so the calculated concentrations of PFC necessary to detect leakage must consider the impact of these long term changes (Watson et al., 2007). Since cyclic PFCs are virtually insoluble, it is assumed that concentrations in the ocean are zero.

Fig. 2 (and the table inset) shows how much it will cost – at a minimum – to purposefully tag 1 Mt of CO₂ with a range of potential tracers. These cost estimates assume there is no tracer loss during CO₂ transport to seabed/land surface; if tracer loss during CO₂ ascent is likely, then the tracer injection concentrations (and so cost) will need to increase, perhaps significantly. Other aspects of these estimates are conservative; it is assumed that 10 times the detectable perturbation above background levels are required for reliable tracer detection in the atmosphere or seawater. The cost per litre does not account for price reduction from bulk demand, which is likely since tonnes of the tracer chemical will be needed over the duration of CO₂ injection. It is also assumed that standard sensitive analytical approaches are used. If analytical approaches are developed to be more sensitive, then the tracer injection concentrations could be reduced. Based on these assumptions, we find that it is cheaper to tag injected CO₂ with tracers to monitor for leakage into the marine environment compared to terrestrial leakage due to differences in background concentrations of tracers in seawater and atmosphere.

Artificial tracers are, on the whole, the cheapest tracers, owing to their very low background concentrations and low cost to procure. Cyclic PFCs are very low cost tracers, as have such low background values in seawater and atmosphere they are detectable to ppq levels. Even though the price of PFCs such as 1,3-PDMCH or PMCP (both used at K12-B, Van der Meer (2013)) is ~two orders of magnitude greater

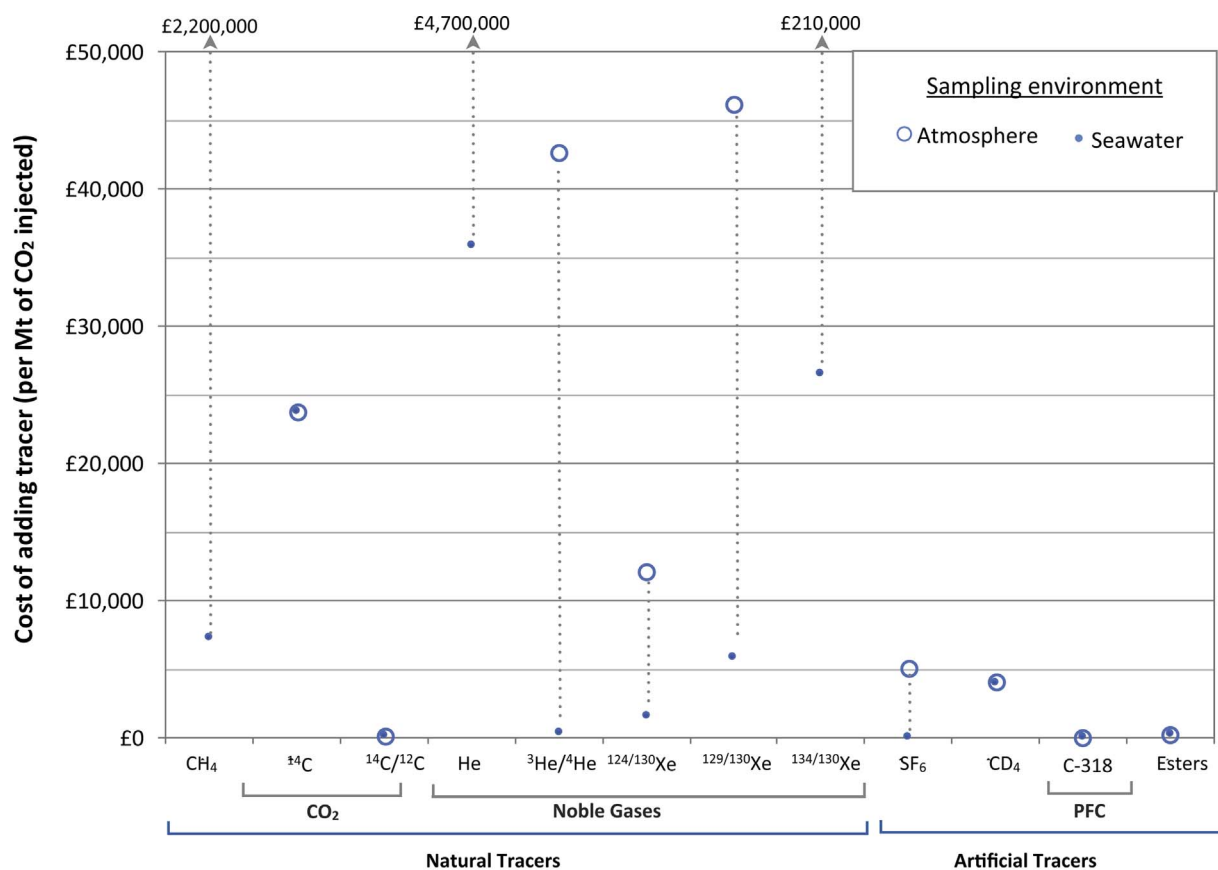
than the price of C-318 (octafluorocyclobutane) – there is little difference in the minimum cost of tagging 1Mt(CO₂) at concentrations that would reliably indicate leakage, because the background levels of C-318 are higher. Two of the cheapest tracers for monitoring leaks in the marine environment are SF₆ and ¹⁴C/¹²C(CO₂), however both of these tracers have restricted use. A suite of noble gas tracers could affordably be used for monitoring offshore including ³He/⁴He, ¹²⁴Xe/¹³⁰Xe and ¹²⁹Xe/¹³⁰Xe would each cost < £15 K/Mt(CO₂), whereas for onshore monitoring the cost of using these isotopes is at least an order of magnitude higher, and so cost could restrict their use as tracers onshore (see table inset Fig. 2).

Many of the tracers considered would cost more than £50,000 per 1 Mt(CO₂) at a minimum, which could be too expensive, depending on the CCS project and other monitoring options available. Even the most inexpensive tracers to implement would still cost ~several thousand pounds per annum to procure in the quantities required to co-inject with CO₂ at commercial scale CO₂ stores. As such, chemical tracers inherent in the captured CO₂ stream are clearly more economically favourable. The CO₂ stream injected at Sleipner contains 2–3% methane (Chadwick, 2013). In such high concentrations, the methane could act as an early warning tracer for onshore or offshore sites. Similarly, if the injected CO₂ contained 0.35% Ar which is feasible for oxyfuel combustion capture, this could be a suitable tracer for identifying offshore leakage. Importantly, these concentrations of CH₄ and Ar would be compatible with the purity required for the design parameters for CO₂ transport (DOE/NETL, 2012).

Chemical tracers have been used at many offshore hydrocarbon fields and so there may be residual tracers in depleted fields prospective for CO₂-EOR or for CO₂ storage (see Table 4). These are likely to be PFC compounds, though some chemicals could have been used that are now out-dated such as R134a (an HFC) and CFCs. While these tracers will have been flushed out of the formations during production, some traces may remain and so the background concentration in such formations cannot be assumed to be zero. Past tracer activities at these sites and in adjacent hydrocarbon fields (that may be connected) would need to be determined prior to CO₂ injection and the commencement of the tracer survey.

Tracers that are a natural constituent of the CO₂ stream, such as noble gases or methane, may also already exist in subsurface reservoirs (see Table 4). For depleted hydrocarbon fields, background levels (concentration or isotopic composition) might be spatially and temporally variable due to drilling and production activities (Flude et al., 2016). For example, the injection of seawater to maintain reservoir pressure is common during hydrocarbon production, and the seawater will have introduced noble gases with a seawater signature (Flude et al., 2016). As such, the background levels of natural tracers in the reservoir formation must be sampled as part of establishing baseline conditions prior to CO₂ injection.

Finally, chemical tracers could also be used to detect the leakage of formation brines displaced by CO₂ injection-induced pressure perturbations to the surface. Whilst, these deep brines may not contain dissolved anthropogenic CO₂, and hence would not need to be quantified as CO₂ leaks as required by the EU CCS Directive (EU, 2009), the chemicals dissolved in these brines, along with their low pH could have significant environmental impacts (Jones et al., 2015). Inherent chemicals in formation brines enable their attribution, should they leak to seabed. For example, deep saline formations may have characteristic ^{δ13}C values, and noble gas isotope compositions would have stronger radiogenic and terrigenous components than seawater (Flude et al., 2016). The composition will be unique for each storage reservoir, and likely to vary spatially, so would need to be established as best possible as part of baseline monitoring (Blackford et al., 2015; Jones et al., 2015).



Cost per Mt(CO ₂)	Marine environment (seawater)	Terrestrial environment (atmosphere)
£1-100	¹⁴ C/ ¹² C in CO ₂ , PFCs, SF ₆	¹⁴ C/ ¹² C in CO ₂ , PFCs
£100-1,000	Esters, ³ He/ ⁴ He	Esters
£1,000-10,000	^{124,129} Xe/ ¹³⁰ Xe, CD ₄ , CH ₄	CD ₄ , SF ₆
£10,000 - 100,000	¹⁴ C in CO ₂ , He, ¹³⁴ Xe/ ¹³⁰ Xe	¹⁴ C in CO ₂ , ^{124,129} Xe/ ¹³⁰ Xe, ³ He/ ⁴ He
£100,000 - 1,000,000	^{80,83,86} Kr/ ⁸⁴ Kr, ¹³² Xe/ ¹³⁰ Xe, ¹³ C/ ¹² C	^{134, 132} Xe/ ¹³⁰ Xe

Fig. 2. The minimum cost of adding tracers to 1Mt of injected CO₂. Costs are expressed to two significant figures. Tracers that would cost more than 5p/t(CO₂), (£50 K per Mt(CO₂)) are not shown on the graph, but are included in the table inset (up to £1 M per Mt(CO₂)). C-318 is PFC perfluorocyclobutane (see main text for how this compares to PFCs used as tracers). Since cyclic PFCs are virtually insoluble, it is assumed that the concentration of C-318 in the ocean is zero. The price per litre of tracers were sourced from chemical suppliers and do not account for price reduction from bulk demand. It is assumed that there is no loss or adsorption of tracer during ascent to seabed, and so these costs are a minimum estimate. These calculations were based on the minimum concentration of tracer (per tonne of injected CO₂) needed to give a clearly detectable shift in isotopic ratio or concentration using current analytical techniques. In order for a leak to be reliably detectable, we assume that there must be a shift in concentration greater than ten times the background values in atmosphere or seawater. If current analytical techniques would not be able to detect such change, then we assume that there must be a shift in concentration that is ten times greater than the limit of detection (for that tracer). For isotope tracers, we assume a shift in the isotope ratio that is at least ten times greater than the limits of current analytical precision. The full calculations, including details for tracers omitted from this table are included in SI Table 3.

3.4. Issues of tracer behaviour

Adsorption of tracers onto organic compounds during ascent through the overburden could be problematic for monitoring offshore CO₂ leaks (Stalker and Myers, 2014). Should tracers adsorb onto substances such as clays and organic matter as they migrate toward the seabed, or should they interact or exchange with other fluids, then the ability to identify or quantify potential CO₂ leaks using tracers is compromised. The majority of seafloor sediments of seas in Europe comprise of terrigenous sediment, which contains more clays and organic matter than deeper seafloor sediments located further from land. The overburden of prospective stores offshore UK contain some organic rich units, for example the Carboniferous coal measures in the Central Southern North Sea (Durucan et al., 2014), and the prospective unconventional hydrocarbon shales located offshore NE Scotland (Monaghan, 2014). Thus, organic rich units may lie above the caprock,

which in the North Sea is often an organic rich clay or shale unit. Therefore, tracers selected to monitor CO₂ leaks must not preferentially adsorb onto organic matter, shales or clays (of the seal, overburden or seabed), in order to ensure that the tracers reach the seabed with the leaked CO₂.

Lab and field experiments have found that the arrival times of noble gases vary with molecular mass (Kilgallon, 2015; Rillard et al., 2015). These experiments have considered water unsaturated environments, where CO₂ and noble gases have arrived as a free phase. Seabed sediments will be water saturated and the majority of leaked CO₂ might arrive to seabed as a dissolved constituent of porewaters, as observed at QICS (Taylor et al., 2015a). Differences in the behaviour or arrival times of CO₂ and noble gases, or other tracer chemicals need to be explored under water saturated conditions.

Table 4

A summary of the potential tracers for CCS, and their properties, environmental impact, cost and ease of sampling in the marine environment. Tracers for leakage would ideally exist in the CO₂ stream or the reservoir at measurable or predictable levels high enough to allow for reliable detection of a leak. Tracers CH₄ and CD₄ behave conservatively in the deep subsurface, but in the near surface are prone to biological interference, and so we classify their behaviour as uncertain (U). Some potential tracers have restricted usage because they are atmospheric pollutants, as indicated by the 100 year GWP. SF₆ and PFCs are the strongest greenhouse gas pollutants. CD₄ is assumed to have the same GWP as CH₄, though it is likely that CD₄ is higher because the C-D bond takes longer to breakdown than the C-H bond. Where it is unknown whether there is much experience in sampling in tracers in seawater, this is denoted by '?'. Only noble gases (He, Ar, Kr, Xe), CO₂ isotopes and CD₄ have no known biological impact. Esters and methane may provide a food source for marine organisms and so are considered to have a possible biological impact.

Tracer	Type		Env. Impact					Logistics			
	in CO ₂ stream?	in storage reservoir?	Conservative?	GWP _(100y)	Biological impact	Bio-degradable	Use restricted	Cost	Experience sampling down-well	Experience sampling seawater	
Natural	C-14 (CO ₂)	Y**	N	N	1	Possible	–	Y	Acceptable	Y	Y
	C-13 (CO ₂)	Y	Y	N	1	No	–	N	Restrictive	Y	Y
	O-18 (CO ₂)	Y	Y	N	1	No	–	N	Restrictive	Y	Y
	CH ₄	N	Y	U	36	Possible	Y	N	Acceptable	Y	Y
	Other impurities	Y	Y	–	–	Possible	–	–	–	–	–
	Noble gases	Y	Y	Y	None	No	N	N	Acceptable for He, ³ He, and ¹²⁴ Xe/ ¹²⁹ Xe/ ¹³⁴ Xe/ ¹³⁰ Xe	Y	Y
Artificial	HFC: R-134a	N	N [†]	Y	1300 ± 10	–	U	Y	–	Y	N
	SF ₆	N	N [†]	Y	22,850	–	U	Y	Acceptable	Y	U
	Reactive esters	N	N	N	None	Possible	N	N	Acceptable	Y	N
	CD ₄	N	N	U	> 36	Possible	Y	N	Acceptable	Y	Yes
	PFCs	N	N [†]	Y	9540	Possible	Y	N	Acceptable	Y	U

* Possible residual component of depleted hydrocarbon reservoirs if tracers used during hydrocarbon production.

** Particularly in CO₂ produced from biomass combustion.

3.5. Environmental effects

Whilst the injected CO₂ and any co-injected chemicals are intended to remain in the subsurface for geological timescales, it will be preferable if added geochemical tracers have as low an impact on the environment as possible. Using tracers for detecting CO₂ leaks offshore requires consideration of issues of marine toxicity and bioaccumulation of the tracer or its possible breakdown products. Indeed, compounds with greater longevity may be more reliable as a monitoring tool, but their environmental impacts might be longer-term. Tracers would ideally have minimal long-term effect on marine biological communities, however, any short-term changes caused by tracers co-released with CO₂ might aid leak detection by multibeam echosounder or underwater video time-lapse surveys. Positive and negative effects on seafloor ecosystems could be detected by mobile monitoring methods such as Automatic Underwater Vehicles (AUVs), which might be the most cost-effective methods for regional monitoring (Blackford et al., 2015). If the CO₂ leak is into shelf seas (rather than the deep sea) these sensors could detect decreased ecosystem productivity (i.e. fewer biological species due to toxic tracer effects), or increased productivity (e.g. changes to biological communities or presence of bacterial mounds due to methanophile activity as observed at methane seeps in the North Sea (ECO2, 2016), or the unintended breakdown of organic compounds which could provide a food source). These effects would preferably be short-lived, with minimal bioaccumulation in marine species. PFCs exist as either chain or cyclic compounds. While bioaccumulation effects can be problematic for chain PFCs, the cyclic compounds that are relevant as tracers have no bioaccumulative potential and are non-toxic, to the extent that they are used as a blood substitute (Simmonds et al., 2002; Spiess, 2009). Tracers such as radiocarbon (C¹⁴) and radon, the radioactive noble gas, could have a harmful effect on marine species and so would not be considered for use as added tracers, though it could form an inherent component of CO₂ captured from biomass sources (Suess, 1955). Deuterated methane on the other hand is not classified as harmful or a marine pollutant, and will not bioaccumulate (Linde,

2015), but its utility is limited by its propensity to biodegrade (Myers et al., 2013b).

If the tracer has a high GWP, it will contribute to the indirect environmental impact of a CO₂ leak. The GWP of some potential tracers are shown in Table 4. Estimates for PFCs are based on the cyclic PFC perfluorocyclobutane (C318) because its GWP is known (Myhre et al., 2013) and cyclic PFCs that would be suitable as tracers for CCS are expected to have similar polluting properties (Martin et al., 2011; Watson and Sullivan, 2012). If tracers concentrate into the free-phase CO₂ during ascent, then the climate change impact of the leak will be accentuated, and the quantities of any leaked pollutant tracers will need to be reported to comply with environmental regulation. The greenhouse gas contribution of leaked tracers may also have financial implications in regions where carbon tax is applied. Fig. 3 presents the CO₂ equivalent (CO₂e) emissions that pollutant tracers contribute to a 1000 t CO₂ leak, assuming no tracer loss during ascent, for offshore and onshore. Based on these assumptions, the effect for most tracers is negligible (less than 1 millionth of the impact of the CO₂ leak) either due to the small tracer injection concentrations, or because some tracers have no GWP, such as noble gases and esters (which are not included in Fig. 2). Fig. 3 shows that, for marine settings, the most significant climate pollutant tracers would be SF₆ and CH₄, though CH₄ could dissolve or breakdown in the water column before being emitted as a pollutant. Although PFCs are strong climate pollutants (Table 4), they would need to be present in the leaked CO₂ in such small quantities to be detected that there is negligible contribution to the GWP of a leak. CH₄ and SF₆ (and to a lesser extent, R-134a) have much greater climate change impact when used as tracers for onshore CCS as their atmospheric background concentrations are higher than in seawater. Given the restrictions on SF₆, this chemical is not suitable as a tracer for leakage. The GWP of CD₄ is not known (we use the GWP of CH₄ in these calculations), however it is likely to be much greater than CH₄ because C-D bonds take longer to breakdown in the atmosphere (Gierczak et al., 1997), though it is likely that CD₄ will microbially degrade in the water column before it reaches atmosphere. In fact, should the CO₂-tracer mix

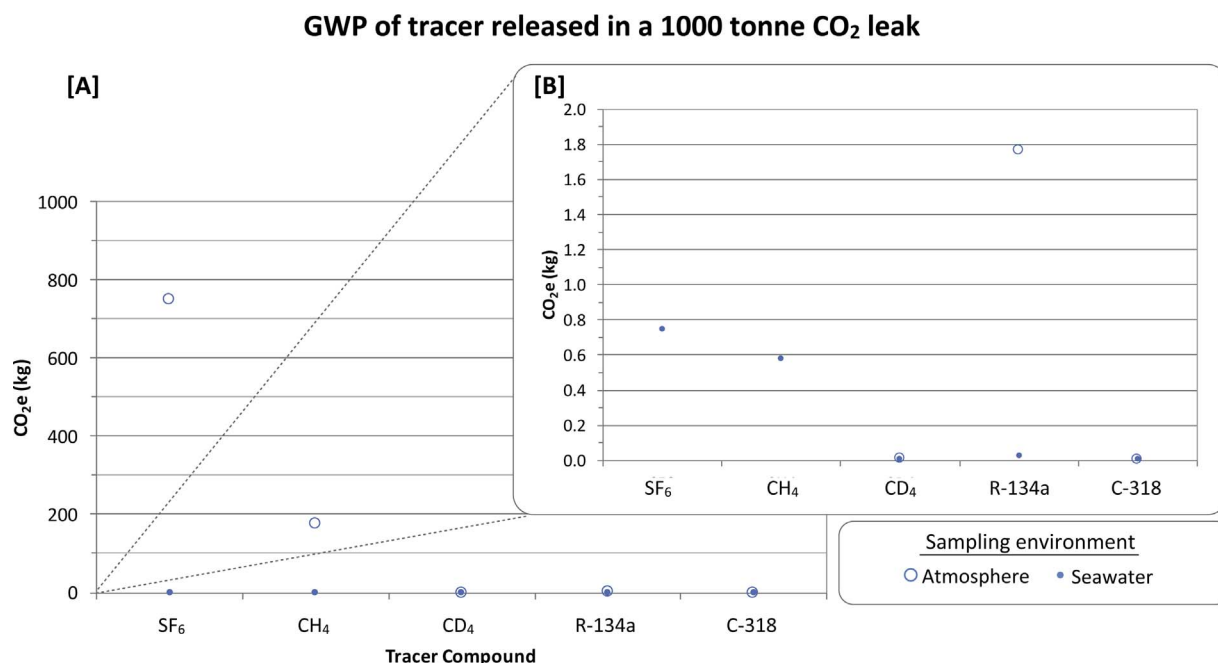


Fig. 3. CO₂ equivalent (CO₂e) emissions of pollutant tracers contribute to a 1000 t CO₂ leak, assuming no tracer loss during ascent, for offshore and onshore settings. CO₂e is a measure used to compare the emissions from various greenhouse gases based upon their global warming potential (GWP). Tracers that have no GWP are not included in this figure. Graphs (a) and (b) show the same data but the results are displayed on different scales. The minimum quantities of tracer per tonne were calculated from the minimum detectable concentrations above seawater and atmospheric background levels. These calculations assume that the tracer mimics CO₂ behaviour during ascent to seabed or atmosphere. The greatest polluters for onshore CO₂ leaks are SF₆ and CH₄, but the greatest polluters for offshore leaks are PFCs – assuming that they will release to atmosphere. Here, CD₄ is assumed to have the same GWP as CH₄, though it is likely that CD₄ is higher because the C-D bond takes longer to breakdown than the C-H bond.

dissolve into the water column, the seawater may act as a buffer to prevent the CO₂ and associated tracer gases from entering the atmosphere, depending on the time period for ocean-atmosphere exchange for tracers. This buffering could allow time for the tracer to biodegrade or be metabolized, and so the climate change consequences of CO₂ leakage to seabed may be much lower than for leakage to land surface.

Sampling approaches will need to have minimal disturbance to the marine environment. A network of Marine Protection Areas across the North Atlantic is recognized by OSPAR. In these areas additional measures have been instituted to protect species, habitats, ecosystems or ecological processes of the marine environment. There may therefore be restrictions on the use of echosounders, or sampling approaches (e.g. ship or AUVs) or their frequency due to their potential disruption to sea-life, which could have important consequences on the permissible sampling strategy above a store.

3.6. Addition of the tracer

Addition of a permitted tracer for both continuous or pulsed injection can be undertaken both onshore at the CO₂ terminal or at the injection point offshore, though the latter option is preferable for several reasons. Trace compounds can affect the design and performance of the transport pipelines, for example, a CO₂ stream containing 1% (by volume) argon would require additional compression, and for 1% (by volume) methane pipelines would have to be strengthened to resist ductility issues (DOE/NETL, 2012). There is also uncertainty around the partitioning or fugitive leakage of tracer compounds during CO₂ transport, and, finally, tracers could introduce additional permitting or regulatory complication. Tracer tests performed at offshore hydrocarbon fields usually add the tracers at the well-head, but these are not typically slip-streamed into the injection gas.

4. Selecting the most effective tracers for detecting CO₂ leaks offshore and current knowledge gaps

We have presented the most detailed review of tracer use for offshore CO₂ storage to date, examining the challenges of designing tracer programs for monitoring offshore CO₂ stores, and the issues and uncertainties surrounding the selection of appropriate tracers for detecting and quantifying CO₂ leaks. It is clear that chemicals that form a natural component of the CO₂ stream are preferable tracers for offshore CCS, due to the relative ease of permitting and avoidance of the cost and risks of procuring and artificially adding a tracer. Such inherent tracers include noble gas isotopes such as ⁴He and ¹²⁴Xe, or ¹⁴C isotopes or CH₄ in the injected CO₂. However, added tracers may offer more reliability in terms of their unique composition and the ability to control and regulate their concentration. By far the cheapest added tracers for monitoring leaks in the marine environment are PFCs. However uncertainties around sampling these chemicals in the marine environment, their increasing background concentrations and their potent GWP make them less favourable; though it might be possible to design PFCs with lower GWPs (Bera et al., 2010). Other low-cost tracers are SF₆ and ¹⁴C/¹²C(CO₂), however these chemicals have potential usage restrictions due to their environmental effects, and so are not suitable as tracers. Should the addition of artificial tracers be unfavourable (for example, for permitting reasons or issues of longevity) then helium and xenon isotopes (particularly ^{124,129}Xe) are the most promising tracers for several reasons, including their relative inexpense (due to the low concentrations needed), well understood behaviour, and the proven experience of sampling noble gases in seawater. While CD₄ is a promising tracer for similar reasons, there are uncertainties around its longevity in the marine environment. There are similar issues with CH₄, which might contribute to the environmental impact of a leak, and also occurs naturally in the subsurface and so is not unique. For this reason, we argue that CH₄ is not an appropriate added tracer, but recognise that it could be a useful tracer if inherent in the injected CO₂ or acquired from the storage formation (in the case that a depleted gas reservoir is

used for storage). Should chemicals with high GWP be used as tracers in high quantities (for example, due to potential for significant tracer loss during ascent through the overburden), then the permissible rate of leakage in terms of the effectiveness of CCS for mitigating climate change may need to be adjusted for certain programs, even if the tracer is inherent (such as for CH₄). This may have only minor implications for offshore CCS, where lower tracer concentrations can be detected in seawater compared to the atmosphere due to differences in background levels and where the water column could delay or prevent the release of tracers to atmosphere.

This work has highlighted a number of uncertainties which must be addressed in order to constrain the reliability and cost of tracer programs offshore. Firstly, fundamental questions remain on CO₂ and tracer behaviour, such as how much CO₂ will dissolve into porewaters during ascent to surface, adsorb or partition in seabed sediments, or partition in bubble streams at the seabed. Noble gases are promising inherent tracers, but it is important to establish if they will follow the CO₂ flow paths in water-saturated environments, and resolve the controls on differences in their arrival time (compared to each other and CO₂). The potential for rapid isotopic exchange and buffering between CO₂, sediments and porewaters must be explored in order to establish whether these processes would mask the isotopic composition of the injected CO₂ during CO₂ ascent to seabed. It is also important to establish how the tracer will partition when CO₂ dissolves into water. If tracers preferentially partition into the CO₂ phase, and the majority of CO₂ dissolves into porewaters during ascent, then tracers could concentrate into the gas phase and reach much higher concentrations than those injected. Many of these issues are also relevant to onshore CCS, and hence their resolution will affect how leaks are identified and estimates of leakage quantities are made.

Secondly, issues that are site specific or dependent on the monitoring program will need to be addressed for any offshore CO₂ storage project. For tracers inherent to the CO₂ stream, the background concentrations of these tracers in the reservoir must be established, as will the composition of the tracer in the CO₂ stream (as along with any variation in background concentrations in other monitoring horizons). For artificial tracers, it must first be established if the OSPAR Convention permits the addition of chemicals to the CO₂ stream for use as tracers, and identify the factors that might affect the sensitivity to particular tracer chemicals or sampling approaches (such as marine conservation areas). A tracer's longevity, biodegradation and bioaccumulative potential in the marine environment and the consequent environmental impacts must be established to understand environmental impacts and for compliance with OSPAR.

Finally, methods of sampling and detecting tracers at the seabed and in the seawater column must be developed and tested, including means of establishing baseline conditions (at the seabed and also the subsurface). Current procedures are expensive and reducing these costs will be important for CCS operators. Sampling strategies must take into account seabed currents and dispersion/mixing in the water column, and also have minimal disruption to marine life – particularly in protected areas. Similarly, consideration should be given to what combinations of tracers might be most useful, and how these chemicals might need to be sampled, or how tracers might fit with other monitoring approaches in a monitoring program. If particular tracers cause changes that are easily discriminated over short timescales, for example by encouraging particular biological communities (like methanophiles in response to CH₄ tracer) or causing fluorescence, then these effects could assist the recognition of a CO₂ leak using echosounders or time-lapse video – but seabed permanence will affect how persistent these changes are (Jenkins et al., 2015).

These uncertainties need to be addressed through a combination of laboratory and field experiments, along with numerical modelling. Given that there have been no field investigations of CO₂-tracer leaks into the marine environment to date, a subseabed CO₂-tracer release experiment that builds on the experiences and outcomes from QICS

(Blackford et al., 2014) would offer opportunity to (i) further improve knowledge of the fate and interactions of CO₂ leaks in the marine environment and (ii) to test and develop tracers for commercial scale CCS, their impacts, and methods of sampling, particularly for sub-critical CO₂ migration. For the latter, to ensure that the investigations are relevant for commercial scale CCS monitoring programs, the subseabed experiment must consider the following:

- For permitting reasons, the long term local and wider environmental impacts that the selected tracers have must be minimal, since the intention of a marine CO₂ release experiment is for CO₂ to reach seabed.
- The timeframe of a CO₂ release experiment will be much shorter than the monitoring timeframe relevant to CO₂ storage (decades), but the tracers tested must have appropriate potential longevity at subsurface and marine conditions to allow forensic examination of any unusual issues following the experimental monitoring period. Similarly, the quantities of CO₂ released at a field experiment will be much less than those injected into CO₂ stores, which should be considered when selecting suitable tracers and when calculating tracer costs and strategy. The injection rate at a CO₂ release experiment should be selected to be a reasonable representation of a leaking CO₂ store.
- The CO₂ at a shallow release experiment is migrating from a single injector source in gas phase, when it is least soluble. Should a storage site leak, the CO₂ will be migrating in its dense phase, and remain in this phase until depths shallower than ~800 m. The CO₂ phase may affect tracer partitioning or behaviour, and so should be considered when selecting tracers appropriate for testing for CCS.
- At a release experiment, the thickness of overburden that CO₂ must flow through to reach seabed will be much less than for CO₂ that leaks from a storage site. For example, at QICS, the thickness of the overburden was at least ~100 times smaller than for commercial stores, and so the potential for tracer loss or adsorption during CO₂ transport will be much reduced.
- For ease of access and sampling and to minimise project costs the water depths for a CO₂ release experiment will most likely be shallower than water depths above offshore CO₂ stores. The pressure conditions at seabed will be less in shallower waters, which may have a small effect on the properties of the CO₂ and tracer. The proximity to shore may also introduce differences in permitting and consent compared to those that apply to CCS sites further offshore. Further, depending on the positioning of a CO₂ store, the seabed above it may be subject to different seabed currents, or even differences in seawater stratification than at a shallower site, which will affect bubble pathways and CO₂ dispersion in the water column – and therefore sampling strategy.
- It will be important to be able to discriminate whether or not any changes to seafloor ecosystem is from the CO₂ or from the tracer – or the cumulative effect of both. It may be necessary to have two controls, where only CO₂ is released, and where no CO₂ is released. It will also be important to establish baseline conditions over a reasonable time period; perhaps over several years to have multiple seasons.
- A research-specific artificial experiment where sampling methods are being developed and tested will collect samples with greater intensity than a monitoring program above an offshore CO₂ store, which will need to cover a greater area, at greater water depth (for example, water depth at QICS was 10 m, whereas seawater depth at Sleipner is ~100 m). Questions such as the minimum effective sampling frequency or optimal sampling geometries should be explored for scale-up.
- The project team may solely access the seabed at a release experiment, and so marine sampling apparatus (such as benthic chambers) will be regularly checked and are unlikely to be disturbed by other sea users and marine activities. Long-term tracer sampling programs

must be coordinated to consider other users of the marine environment, particularly where these may damage sampling programs.

To establish the injected tracer concentrations necessary for reliable detection at or above the seabed from a sub-seabed release experiment, laboratory experiments could be performed to test the diffusion and adsorption behaviour of prospective tracer (for example using a sediment column following the approach of Plampin et al. (2014)). These experiments could then inform models of tracer loss during CO₂ transport to seabed. Lab experiments could also be used to examine tracer behaviour in bubble streams and to trial sampling approaches. Such work would inform the design of the CO₂ tracer release experiment, which will provide valuable learning on how effective tracers can be for detecting and quantifying CO₂ leaks in the marine environment.

5. Conclusions and recommendations for using tracers for monitoring leakage from offshore CO₂ stores

It is important that monitoring systems for CCS are fit for purpose and able to detect and to quantify CO₂ leaks. A robust monitoring regime will provide assurance to regulatory bodies and the public that the CO₂ store is not leaking (Feitz et al., 2014b). Chemical tracers have been identified as a cost-efficient CCS monitoring strategy but to date no offshore tracer programs have been trialled. In order to assess potential tracers for offshore CCS monitoring we have examined the current experience of using tracers onshore and the practise of using tracers in the offshore hydrocarbon industry.

It is clear that chemicals that form a natural component of the CO₂ stream, such as noble gas isotopes or radiogenic carbon, are preferable tracers for ease of permitting and avoiding cost and risks of procuring and artificially adding a tracer. However, added tracers offer more reliability in terms of their unique composition and the ability to control and regulate concentrations. We identify helium and xenon isotopes (particularly ^{124,129}Xe), and artificial tracers such as PFCs and deuterated methane are the most suitable added tracers. This is due to their conservative behaviour, low environmental impact and relative in-expense. We find that SF₆ and C¹⁴ are not viable tracers for CCS due to environmental concerns, and many other potential tracers can be ruled out on the basis of cost. CH₄ is not be a reliable added tracer to identify leaked CO₂, but it could be a useful tool to consider if CH₄ is inherent in the injected CO₂ or in the reservoir, particularly if it causes detectable changes to the seabed environment.

Background concentrations of most tracers in the marine environment are lower than in the atmosphere, and so, should the measurement approaches be sensitive enough, lower tracer concentrations could be required for reliable detection offshore compared to onshore. However, marine sampling and measurement approaches are currently labour intensive, expensive and hence require streamlining in order to contribute to an affordable and fit for purpose monitoring program in marine environments. It seems preferable tracer surveys to complement other monitoring tools, whereby tracer surveys to unequivocally identify and quantify leakage occur in response to potential leaks detected by an alternative monitoring method.

Key uncertainties which will hamper the design of offshore tracer programs include the possible adsorption or dispersion of tracer compounds during ascent through the overburden, the longevity of tracers over timeframes of CCS monitoring programs and the permissible environmental effects of tracer leakage. The partitioning of tracer as CO₂ dissolves into porewaters and CO₂ bubble streams at the seabed must also be established, and it remains unclear how tracer behaviour in seawater will affect sampling procedures. Thus, there is further work to be done to constrain these uncertainties, and provide more robust estimates of costs, and means of sampling, detecting and quantifying any CO₂ leaks to seabed from an offshore CO₂ storage site.

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Dataset can be accessed on this link <http://dx.doi.org/10.5285/e54b24cb-3f6a-4c41-a685-f8940f094589>.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ijggc.2017.07.021>.

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