

## **D2.3: Report summarizing all information from WP2 relevant for the creation of an 'Environmental Best Practice' for offshore CCS sites; lead beneficiary number 4 (NERC-NOC)**

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## D2.3: Report summarizing all information from WP2 relevant to seabed fluid and gas fluxes for the creation of an 'Environmental Best Practice' for the management of offshore CCS sites.

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### 1. Introduction

This report summarizes all relevant information from work carried out in ECO2 on identifying leakage of CO<sub>2</sub> across the seabed, attributing its source, and estimating fluxes of fluid and gas leakage from the seabed and into the water column. This information is based on studies at natural CO<sub>2</sub> seeps and existing sub-seafloor CO<sub>2</sub> storage sites, as well as modelling studies.

### 2. Objectives

The objectives of this report are as follows:

- Summarize information on detecting CO<sub>2</sub> release from the seabed into the water column
- Summarize information on estimating fluxes of fluids and gases across the seabed
- Summarize information on establishing the source of fluid and gas leakage
- Summarize information on the use of modelling techniques for predicting fluxes of CO<sub>2</sub> and other chemical species across the seabed under different leakage scenarios

### 3. Methodology

#### 3.1 Field studies

##### 3.1.1 Detection of leakage

Extensive work in the vicinity of the sub-seafloor CO<sub>2</sub> plume at the Sleipner CCS site found no evidence for leakage of CO<sub>2</sub> from the storage reservoir into the shallow sub-surface sediments. Analyses of bubbles seeping from abandoned exploration wells in the vicinity of Sleipner reveal that they consist principally of methane gas, which most likely comes from shallow depth, and is not related to the deep Utsira Formation that hosts the sequestered CO<sub>2</sub>.

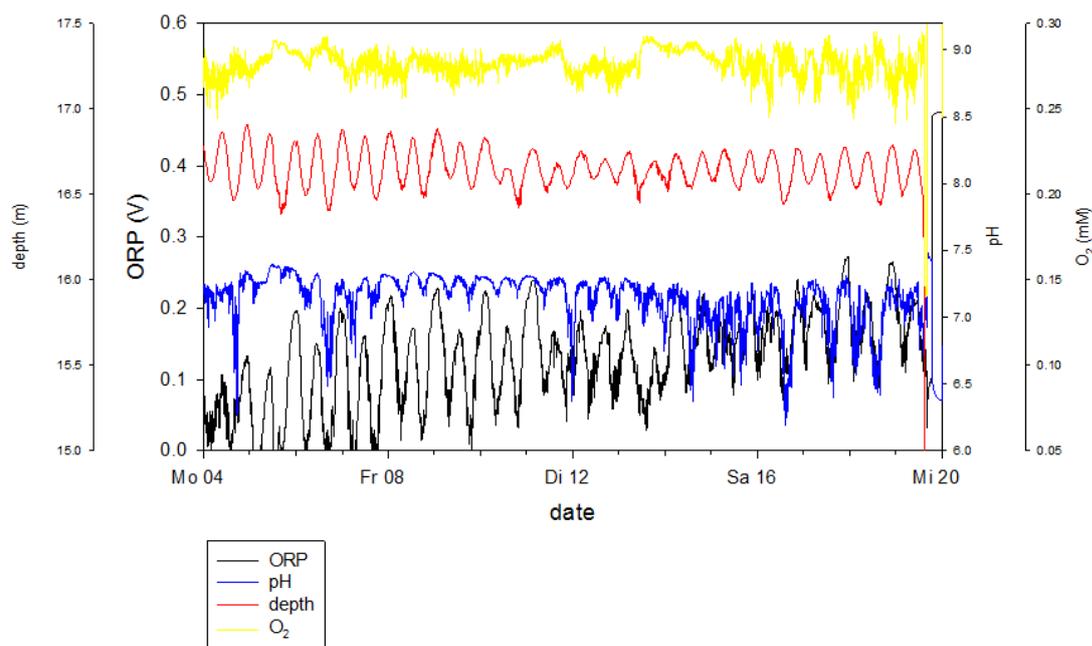
Field studies conducted at natural seafloor CO<sub>2</sub> seeps (Okinawa Trough, Jan Mayen, Panarea, Salt Dome Juist) have revealed that leakage of CO<sub>2</sub> across the seabed may be detected by:

- The presence of seafloor CO<sub>2</sub> bubble streams, wherever the CO<sub>2</sub> flux is sufficient to produce CO<sub>2</sub>-saturated sediment pore waters. Bubble streams may be readily detected using passive (e.g. via a ship's or AUV's echosounder) and active (e.g. hydrophones) acoustic techniques.
- Elevated partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) and acidity (lowered pH) and reduced oxidation-reduction potential (ORP) in the water column within a few metres of the sea bed. All of these variables can be measured using sensors with in-built logger systems, which can be deployed at the seafloor for periods of up to several months. An example of data produced by these systems is shown in Fig. 1.
- Elevated concentrations of dissolved inorganic carbon (DIC, the sum of the concentration of dissolved CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) in pore waters in near-surface sediments. Pore waters are also likely to have reduced pH, although if CO<sub>2</sub> seepage rates are low, dissolution of calcium carbonate, which is naturally present in most marine sediments, may buffer pore water pH.

Dissolution of calcium carbonate is revealed by increased pore water calcium ion concentration ( $[Ca^{2+}]$ ), and increased total alkalinity (TA, where  $TA = [HCO_3^-] + 2[CO_3^{2-}] + \text{other minor components, including borate}$ ). Pore waters may also have elevated concentrations of metals (including iron and strontium) and dissolved silicon, because of enhanced dissolution of carbonate and silicate minerals.

The presence of bubble plumes at the seafloor may be readily detected by ship- or AUV-based echosounder surveys, or by deployment of hydrophones on the seafloor. Direct sampling of the gas is however needed to confirm if  $CO_2$  is present. Chemical monitoring of the water column close to the sea bed will also detect elevated  $CO_2$ , as well as changes in associated parameters including pH and ORP. This can be achieved by deploying sensors on the sea bed. Increased spatial resolution can be achieved by mounting the sensors on AUVs, but this requires flying the AUV close to the seafloor which may not be possible in some environments (e.g. if the seafloor is rugged).

Analysis of sediment pore water is not practicable for leakage detection, because it is expensive to collect sediment cores on a regular basis and they have limited spatial resolution. However, pore water analyses will be critical for attributing the source of  $CO_2$  leakage (Section 3.2).



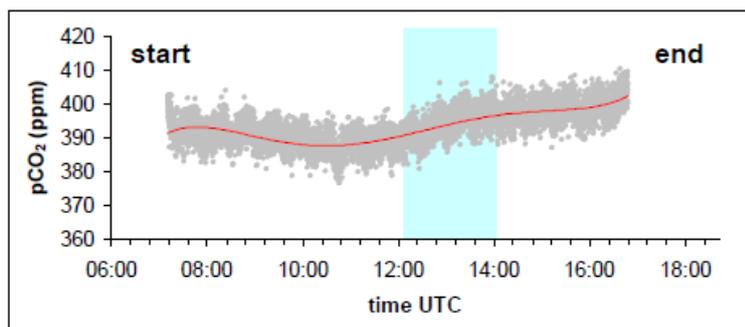
**Fig. 1:** Data obtained from pH, dissolved oxygen and ORP sensors deployed at the seafloor at a natural  $CO_2$  seep site (Panarea) as part of the ECO2 project. Leakage of  $CO_2$  reduces the pH of the bottom waters (seawater unaffected by  $CO_2$  seepage has pH  $\sim 8$ ); note that fluxes of  $CO_2$ -rich water are higher at low tide (shown by shallower water depths).

### 3.1.2 Baseline mapping of the natural variation in the $CO_2$ system

While changes in carbonate system parameters (including  $pCO_2$  and pH), ORP, and other variables, in pore waters in surface sediments and in the lowermost part of the water column are indicative of leakage of  $CO_2$  across the seabed, work done in ECO2 demonstrates that all of these parameters exhibit considerable natural variability, both temporally and spatially, in the marine environment (Fig. 2). This is mainly driven by variations in biological processes, including respiration, photosynthesis and nutrient supply, and by variations in physical processes, including seasonal stratification, currents and tides. Depending on size and geographical location, spatial differences

over an individual site may be limited, but large differences exist along latitudinal and depth gradients. Seasonal signals, whilst following a general pattern, vary between years both in terms of magnitude and timing. Consequently, geochemical data must be collected at least weekly and, at periods corresponding to intense biological activity, daily and even sub-hourly sampling is necessary to constrain variability.

Detailed Best Practise guidelines for establishing geochemical environmental baselines at CCS sites are provided in Chapter 6 of the Best Practice document (D14.1).



**Fig. 2:** Variation in bottom water  $p\text{CO}_2$  measured along a transect extending across the sub-seafloor  $\text{CO}_2$  plume at Sleipner (shown by the blue shaded region).  $p\text{CO}_2$  varies naturally as a function of the tidal cycle. Note that there is no indication of elevated levels in the vicinity of the sub-seafloor  $\text{CO}_2$  plume. Deployment of a seafloor observatory system close to the Sleipner site during ECO2 also revealed that over the course of one year, bottom water pH varies naturally by  $>0.5$  pH units.

### 3.1.3 Estimating $\text{CO}_2$ fluxes across the seabed

If carbon dioxide leaks from a sub-seafloor storage site it will dissolve in sediment pore waters, move upwards towards the seafloor and diffuse across the seabed. If the pore waters become  $\text{CO}_2$  saturated, or the  $\text{CO}_2$  migrates through open fractures or cracks, then  $\text{CO}_2$  may escape from the sediments as streams of bubbles. If the pressure at the seabed is high (i.e. water depths of  $> \sim 400\text{m}$ ), then  $\text{CO}_2$  may be in a liquid or hydrate phase.

The released  $\text{CO}_2$  can undergo complex chemical interactions in the sediments and/or water column. For this reason,  $\text{CO}_2$  fluxes cannot (usually) be defined by a single carbonate system parameter, such as pH or  $p\text{CO}_2$ ; the carbonate system must be fully quantified. To do this, at least two of the measureable quantities (TA, DIC, pH,  $p\text{CO}_2$ ), along with temperature, depth and salinity, are required. In complex shelf sea environments, there is arguably a need to measure three of these parameters to fully quantify the system. Operational (off-the-shelf) sensors that can measure pH and  $p\text{CO}_2$  in seawater directly are readily available and have been tested extensively in ECO2, although there are still some significant challenges in calibration that currently preclude long-term (more than a few weeks) deployment. However, this combination of sensors unfortunately provides the lowest accuracy in deriving the other components of the carbonate system. Whilst automated methodologies for DIC and TA are being developed, they are not yet fully operational.

Various methodologies for estimating  $\text{CO}_2$  fluxes across the seabed were evaluated as part of the field studies carried out by ECO2. Brief descriptions of the methods, and their strengths and weaknesses, are provided below.

<b>Method</b>	Measurement of bubble fluxes using accumulation chambers combined with video observations (Fig. 3a).
<b>Description</b>	Gas bubbles are captured at the seabed in an accumulation chamber of known volume (volumes of between 0.1 and 11 L were captured in ECO2). The accumulation chamber can be deployed by divers or ROV. Fluxes are calculated by monitoring the time taken to completely fill the chamber; this can be done by divers, or via video observations (ROV).
<b>Strengths</b>	<ul style="list-style-type: none"> <li>• Simple and reliable method</li> <li>• Fluxes are obtained directly</li> </ul>
<b>Weaknesses</b>	<ul style="list-style-type: none"> <li>• Limited spatial coverage, so difficult/ time consuming to quantify leakage over wide areas, or requires extrapolation between sampling points which may incur significant error if fluxes are heterogeneous</li> <li>• Sampling can be time consuming if the flux rates are low</li> <li>• Divers can only be deployed at shallow depths</li> <li>• At deeper water depths, requires a ship and ROV, so can be expensive</li> <li>• Limited temporal coverage; fluxes may vary widely over time</li> <li>• Gas samples are required to confirm the CO<sub>2</sub> content of the gas bubbles</li> </ul>

<b>Method</b>	Benthic chamber (Fig. 3b and 3c)
<b>Description</b>	A benthic chamber usually consists of an incubation chamber, syringe sampling devices, and an electronics housing, mounted on a support frame. The chamber is usually deployed by an ROV or a video-guided launch system (although it can be deployed by divers at shallow depths), and is gently pushed slightly into the sediments to create a seal with the seafloor. A one-way valve on the lid of the chamber releases excess water. Concentrations of some solutes, including pH and pCO <sub>2</sub> , ORP and dissolved oxygen, can be continuously measured using sensors, and the concentration of other components, including DIC, alkalinity and nutrients can be measured via retrieval of discrete samples at pre-programmed intervals from within the incubation chamber. The change in the concentration of these variables over the incubation period allows the flux of dissolved solutes across the seabed to be calculated.
<b>Strengths</b>	<ul style="list-style-type: none"> <li>• Quick and simple to deploy</li> <li>• May be used at any water depth</li> <li>• Robust and reliable, well tested technique</li> <li>• Allows measurement of all carbonate system parameters, so the CO<sub>2</sub> flux can be accurately quantified</li> </ul>
<b>Weaknesses</b>	<ul style="list-style-type: none"> <li>• Limited spatial coverage (sediment surface area is usually about 0.25 m<sup>2</sup>) so difficult/ time-consuming to quantify leakage over wide areas, or requires extrapolation between sampling points which may incur errors</li> <li>• Limited temporal coverage; a chamber can only be deployed for up to 24 hours, and fluxes may vary widely over time</li> <li>• Sediment disturbance during deployment may lead to an overestimation of fluxes</li> <li>• Difficult to obtain accurate fluxes in permeable (e.g. sandy) sediments, as chambers exclude the natural hydrodynamics</li> <li>• Video-guided launch system requires a ship with a co-axial cable</li> </ul>

<b>Method</b>	Water column mapping (Fig. 3d)
<b>Description</b>	<p>The distribution of carbonate system parameters, and temperature and salinity, in the water column may be mapped using:</p> <ul style="list-style-type: none"> <li>• Sensors deployed on an AUV or ROV (usually pH and pCO<sub>2</sub>, depth, temperature and salinity)</li> <li>• Acquisition of water samples from conductivity-temperature-depth (CTD) profiling at high spatial resolution</li> <li>• Acquisition of water samples using an in situ multiphase pump. This system pumps water directly to the ship, for immediate analysis of pCO<sub>2</sub> by membrane inlet mass spectrometry, and TA by titration. This system also allows in situ analysis of pH, ORP, and pCO<sub>2</sub> using sensors</li> <li>• Deployment of sensors (pH and pCO<sub>2</sub>, temperature and salinity) on fixed moorings</li> </ul> <p>Fluxes of CO<sub>2</sub> across the seabed and into the water column can be derived by combining these data with oceanographic current data.</p>
<b>Strengths</b>	<ul style="list-style-type: none"> <li>• Quick and simple to deploy (except the multiphase pump)</li> <li>• Robust and reliable</li> <li>• Sensors have low power consumption and are relatively low cost</li> <li>• AUV/ROV surveys allow wide areas of the seafloor to be mapped in a relatively short period of time</li> <li>• Allows the area of the seafloor/ volume of the water column affected by CO<sub>2</sub> leakage to be defined</li> <li>• Collection of water samples allows measurement of DIC and TA, which provide the highest accuracy for quantifying the carbonate system</li> <li>• Deployment of sensors on moorings allows temporal monitoring of the CO<sub>2</sub> plume, and its response to changing currents</li> </ul>
<b>Weaknesses</b>	<ul style="list-style-type: none"> <li>• AUV/ ROV and water column surveys are not suitable for long term monitoring; they can only provide a “snap-shot” at one moment in time</li> <li>• CTD/ water sample profiles are time consuming to collect and as analyses of carbonate system parameters are ex situ, the CO<sub>2</sub> plume may be missed</li> <li>• The multiphase pump system requires a ship with a co-axial cable, and is a relatively costly and time-consuming technique</li> <li>• Moorings have a restricted footprint</li> <li>• Derivation of CO<sub>2</sub> fluxes is complex, and may be impossible if current patterns are highly variable</li> <li>• Most CO<sub>2</sub> leakage is confined to an area close to the seafloor (see Chapter 5), which is difficult to survey with an AUV, especially if the seafloor is rugged</li> </ul>

<b>Method</b>	Video observations of bubbles streams from the seafloor
<b>Description</b>	<p>Video of bubble streams, collected either by ROV or by divers, is used to monitor bubble rise velocity, bubble shape and size, and the height of bubble rise. These data are input to bubble models (Chapter 5), to calculate the bubble flux across the seabed and to predict the dispersal and behaviour of the CO<sub>2</sub> in the water column. These data may also be used to ground-truth and validate data from ship-based hydroacoustic surveys.</p>
<b>Strengths</b>	<ul style="list-style-type: none"> <li>• Gives precise and detailed CO<sub>2</sub> bubble behaviour data</li> <li>• Useful for modelling the fate of CO<sub>2</sub> bubbles in the water column and for interpreting hydroacoustic survey results</li> </ul>
<b>Weaknesses</b>	<ul style="list-style-type: none"> <li>• Can only be deployed by ROV or divers</li> </ul>

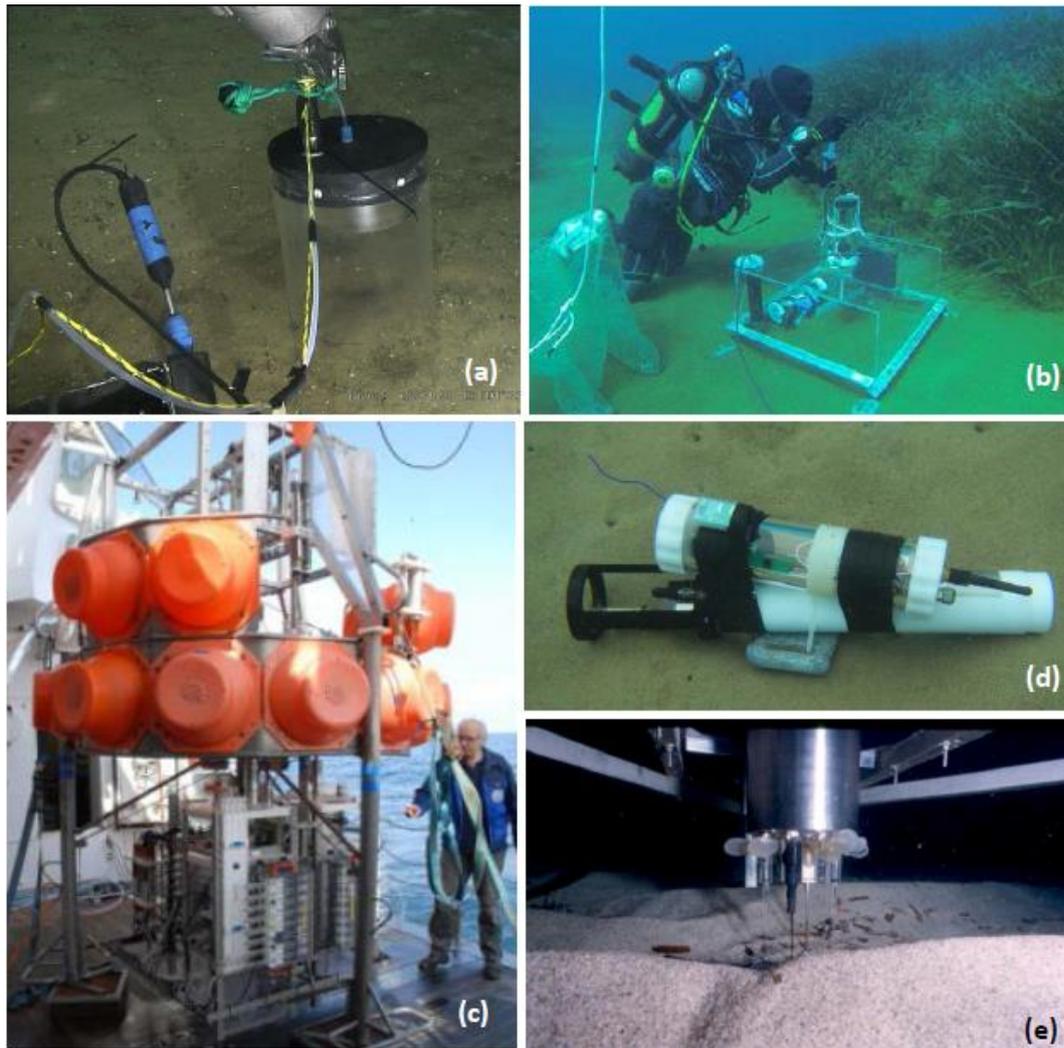
	<ul style="list-style-type: none"> <li>• Set-up is time consuming</li> <li>• For accurate calibration of the model, the CO<sub>2</sub> content of the bubbles as they emerge at the seafloor needs to be confirmed by sampling. This requires an ROV</li> <li>• Utilizable only in the absence of strong currents</li> </ul>
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<b>Method</b>	Composition of sediment pore waters (Fig. 3e)
<b>Description</b>	Samples of near-surface sediments are collected by e.g. box, gravity, piston or vibro coring, or by ROV or video-guided coring. Pore waters are separated from the sediment (usually using Rhizons, pressurized filtration, or centrifugation), and the concentrations of various solutes are determined as a function of sediment depth. Concentrations of some solutes (pCO <sub>2</sub> , pH, dissolved oxygen, H <sub>2</sub> S) can be determined in situ, using microprofiling sensor systems. Fluxes are determined from the solute concentration gradients, using Fick's 1 <sup>st</sup> law of diffusion and/or numerical transport-reaction models.
<b>Strengths</b>	<ul style="list-style-type: none"> <li>• Ex situ analysis permits accurate determination of all carbonate system parameters</li> <li>• Sediment coring and pore water extraction are robust and reliable techniques</li> <li>• Sediment cores can be collected in all environmental settings, except very hard ground</li> <li>• Microprofiling systems provide µm-resolution, allowing fluxes to be quantified precisely</li> </ul>
<b>Weaknesses</b>	<ul style="list-style-type: none"> <li>• Spatial footprint is small, making it difficult/ time-consuming to quantify leakage over wide areas, or requires extrapolation between sampling points which may incur errors</li> <li>• Coring can only provide a 'snap-shot' at one moment in time; temporal resolution can only be improved by conducting multiple sampling campaigns, which is expensive/ time-consuming</li> <li>• Microprofiling systems are fragile, and cannot be used in coarse sediments</li> </ul>

Work done in ECO2 demonstrates not only that natural fluxes of CO<sub>2</sub> across the seabed are highly variable in space and time (see Section 3.1.2), but CO<sub>2</sub> leakage is too. For example, at one site at Panarea, the CO<sub>2</sub> flux across the seafloor ranged from 0.1 to 5.4 L min<sup>-1</sup> at STP (1 bar and 298.5 K) over a few hours in an area of diffuse flow. On longer timescales (2-3 years), CO<sub>2</sub> fluxes varied by up to 2 orders of magnitude. As the spatial and temporal resolutions of many of the methodologies described above are relatively small, it is clear that accurate quantification of CO<sub>2</sub> fluxes across the seafloor, especially if leakage occurs over a wide area, remains a considerable challenge.

### 3.2 Source of fluid and gas leakage

Once an anomaly has been detected in the vicinity of a sub-seafloor site, more detailed surveys are required to attribute the source of fluid and/or gas leakage.



**Fig. 3:** Techniques for estimating fluxes of fluids and gas across the seabed tested during ECO2. (a) Accumulation chamber, deployed by an ROV, for measurement of gas fluxes. (b) Small benthic chamber, deployed by divers at a shallow site at Panarea. (c) Large benthic chamber system, deployed using a video guided launch. (d)  $p\text{CO}_2$  sensor, for measurement of  $p\text{CO}_2$  concentrations at the seafloor. (e) Microprofiling system for *in situ* analysis of various pore water constituents, including pH, ORP,  $p\text{CO}_2$  and dissolved oxygen.

### 3.2.1 Chemical and isotopic composition of formation fluids, and other precursor fluids, at CCS storage sites

Natural tracers of leakage from a sub-seafloor reservoir may include solutes or gases in displaced reservoir formation fluids, or displaced sediment pore waters, that have a significantly different concentration compared to seawater. Detection of leakage of these types of fluids may be critical, as they are likely to precede leakage of the  $\text{CO}_2$  itself. Moreover, unlike  $\text{CO}_2$ , the composition of some of the chemical species in these fluids and gases will not change during transport (i.e. they are unreactive), so they represent unambiguous tracers of reservoir leakage, or displacement of pore waters.

The chemical and isotopic composition of reservoir fluids from the Sleipner and Snøhvit  $\text{CO}_2$  storage reservoirs (respectively, the Utsira and Tubåen formations) were determined as part of ECO2, and are summarised in Table 1.

Species	Units	Utsira	Tubåen	North Atlantic
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		Formation	Formation	Seawater
<i>Carbonate system parameters</i>				
pH		7.0	6.1	8.1
TA	μmol/kg	17700	7730	2340
DIC	μmol/kg	17380	6630	2170
<i>Cations</i>				
Li	μmol/kg	387	na	25
B	μmol/kg	1490	na	410
Na	mmol/kg	482	1960	460
Mg	mmol/kg	22.9	20.8	52
K	mmol/kg	5.82	19.4	10
Ca	mmol/kg	9.84	124	10.1
Fe	nmol/kg	390	915000	~0.1
Ba	μmol/kg	3.7	1070	0.15
<i>Anions</i>				
Cl	mmol/L	529	2520	540
SO <sub>4</sub>	μmol/L	10	708	28000
<i>Isotopes</i>				
<sup>87</sup> Sr/ <sup>86</sup> Sr		0.709237	na	0.70918

**Table 1:** Average chemical composition of Utsira and Tubåen formation fluids. Data for Tubåen supplied by Statoil. The average composition of North Atlantic seawater is also shown for comparison. na = not available.

No evidence for leakage from the CO<sub>2</sub> storage reservoir at Sleipner or Snøhvit was found during ECO2. If formation fluids were to leak from the reservoir, Li is likely to be the best tracer of Sleipner formation fluids. This is because the Li concentration of Sleipner formation fluids is some 15 times higher than bottom seawater, and Li is relatively unreactive with the overlying sediments. While other solutes, such as Fe and sulphate are also significantly enriched (or depleted) in the formation fluids relative to seawater, these species are reactive so their concentration is likely to be modified during transport through the overlying sediments.

While the Na and Cl content (salinity) of Sleipner formation fluids is close to that of seawater, the Snøhvit formation fluids have very high Cl levels, ~4 times higher than seawater. Due to charge balance constraints, concentrations of the major cations (Na, Ca) are also higher than seawater. As Cl and Na are relatively inert, and easy to measure, they are likely to be the most effective tracers for leakage of Tubåen formation fluids.

In shelf sea environments, the supply of organic carbon to the seabed is relatively high and sediment pore waters usually become anoxic within a few cm's below the sediment-seawater interface as the rate of oxygen utilization by organic carbon remineralisation exceeds the rate at which oxygen can be replenished by diffusion from seawater. Concentrations of many reduced species (including hydrogen sulphide, ammonium, iron and manganese) are consequently much higher, and concentrations of oxidised species (including sulphate and nitrate) are much lower, in these sediment pore waters compared to seawater. Similarly, ORP is much lower. Thus, the chemical composition of pore waters from shallow sub-surface sediments displaced due to leakage from sub-seafloor CO<sub>2</sub> storage reservoirs may be expected to be distinct from bottom seawater.

No evidence for displacement of sediment pore waters was discovered in the vicinity of the sub-seafloor CO<sub>2</sub> plume at Sleipner during ECO2. However, upward advection of sediment pore waters

was observed at the Hugin fracture, a seafloor fracture that lies some 25 km to the north of Sleipner, which was discovered during ECO2. These pore waters are characterised by low concentrations of dissolved oxygen and sulphate, and high concentrations of hydrogen sulphide, compared to bottom seawater, which is consistent with displacement of pre-existing pore waters. However, it is important to note that these may also be characteristics of the deep fluid source; if seepage has occurred at this site for some considerable period of time, then the pre-existing pore waters are likely to have already been displaced. Similarly, although upwelling of O<sub>2</sub>-poor, low ORP pore waters is observed at natural CO<sub>2</sub> seeps (Fig. 1), this is unlikely to be the result of displacement of pre-existing pore waters if leakage is long-lived.

### 3.2.2 Isotopic fingerprints of CO<sub>2</sub> leakage

If the carbon isotopic composition (expressed as the ratio of <sup>13</sup>C to <sup>12</sup>C) of the injected CO<sub>2</sub> is significantly different from the <sup>13</sup>C/<sup>12</sup>C ratio of dissolved inorganic carbon in background pore waters, then analysis of the carbon isotopic composition of the pore waters may be used to attribute the source of CO<sub>2</sub>. Though not addressed in ECO2, addition of natural or artificial tracers to the CO<sub>2</sub> injection stream prior to storage would also allow the source to be identified. Non-reactive ('conservative') tracers include sulfurhexafluoride (SF<sub>6</sub>), trifluoromethyl sulphur pentafluoride (SF<sub>5</sub>CF<sub>3</sub>), and perfluorocarbons (PFCs). These tracers have very low analytical detection limits and low background levels in the marine environment, making them relatively easy to detect, and they have different solubilities, allowing transport, dilution and phase partitioning processes to be differentiated. Reactive tracers, such as <sup>14</sup>C, can additionally provide information about geochemical interactions along leakage pathways. However, although these tracers have been used successfully in many terrestrial CCS projects, it is important to note that they have not been applied offshore, and there is a fundamental lack of knowledge about their behaviour in the marine environment.

### 3.3 Numerical Modelling

Based on likely leakage rates of CO<sub>2</sub> from reservoir depth to the sediment surface provided by 2-phase flow simulations (Table 2), predictions of CO<sub>2</sub>, pH and other solute fluxes across the seabed and the footprint of leakage at the seafloor for various leakage scenarios were made in ECO2 using the numerical, non-steady-state transport-reaction model C.CANDI (Calcite, Carbon And Nutrient Diagenesis). Briefly, C. CANDI simulates a large suite of sub-seafloor reaction kinetics, including microbial degradation of organic matter via the terminal electron acceptors oxygen, nitrate, manganese, iron, sulphate and methanogenesis, the associated redox chemistry of solutes and sediments, acid-base equilibria, and mineral reactions including carbonate dissolution, silicate weathering, gas hydrate formation and dissociation. Simulated transport processes include sediment burial, bioturbation, bioirrigation, solute diffusion, and fluid advection. As part of ECO2, the thermodynamic capabilities of C. CANDI were extended to incorporate a wide range of CO<sub>2</sub> concentrations, and all relevant pressure-temperature-salinity conditions found at sub-seafloor CO<sub>2</sub> storage sites. Thus, C.CANDI is capable of predicting the impact of CO<sub>2</sub> on biogeochemical processes in the sub-seafloor, the resulting changes in solute fluxes across the seabed and their temporal evolution. The resulting effects on benthic fauna can also be parameterised.

Leakage scenario	Maximum CO <sub>2</sub> leakage	Footprint (at seafloor)
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	rate (at seafloor)	
1) Chimney reactivation	150 tonnes/day	500 m diameter circle
2) Fault	15 tonnes/day	200 x 2000 m <sup>2</sup> fracture zone
3) Blowout	150 tonnes/day	50 m diameter circle
4) Well bore	20 tonnes/year	Few metres diameter

**Table 2:** Description of four representative leakage scenarios from Sleipner and Snøhvit investigated in ECO2.

The model reveals that the time taken for CO<sub>2</sub> to break through the sediment overburden into the water column is principally controlled by physical, rather than biogeochemical, parameters. The key parameters are: (1) The permeability (porosity) of the sediments and the leakage structure (e.g., a fault, a seismic chimney, or a leaking well). (2) The size of the leakage structure. (3) The distance between the source of the CO<sub>2</sub> and the leakage structure. For large leakage structures (e.g. seismic chimneys), located within a few kilometres of the CO<sub>2</sub> source, breakthrough of CO<sub>2</sub> is estimated to occur 20-50 years after the start of leakage; at lower leakage rates (e.g. through abandoned wells), CO<sub>2</sub> will not be released at the seafloor for several hundreds of years after the leak has occurred.

Maximum CO<sub>2</sub> leakage rate at the seafloor is similarly principally controlled by physical parameters, specifically permeability (porosity), the size of the leakage structure, and the rate of CO<sub>2</sub> release from the sub-seafloor reservoir. Leakage through consolidated sediments is mainly governed by diffusion (Darcy dispersion), whereas leakage through seismic chimneys is mainly controlled by convection in the chimney structure. Diffusion promotes dissolution of CO<sub>2</sub> in sediment pore waters (for example, two-phase non-Darcy modelling suggests that up to 60% of leaked CO<sub>2</sub> could dissolve in sediment pore waters within 30 days of the start of leakage, in a water depth of 15 m), whereas convection minimises the opportunity for dissolution of CO<sub>2</sub> beneath the seafloor. (Under the same circumstances, less than 20% of the leaked CO<sub>2</sub> is dissolved.) Hence flow rates across the seabed are highest at seismic chimney structures, and during blow-out events, which are characterised by catastrophic release of CO<sub>2</sub> from the storage reservoir. The leakage rate of CO<sub>2</sub> from an abandoned well is, by contrast, relatively low. Importantly, the C. CANDI simulations suggest that biogeochemical processes within the sediments, including consumption of dissolved CO<sub>2</sub> by weathering of carbonate and silicate minerals, have relatively little impact on CO<sub>2</sub> leakage across the seabed. Dissolution of calcium carbonate ( $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$ ) will delay breakthrough of CO<sub>2</sub> across the seabed by up to a few decades, depending on the proportion of CaCO<sub>3</sub> in the sediments, and the reaction rate.

At greater water depths (> ~400m), formation of CO<sub>2</sub> hydrate will occur within the sediments. The efficient reduction in sediment permeability due to CO<sub>2</sub> hydrate formation has been successfully quantified in ECO2, and demonstrates that CO<sub>2</sub> leakage at the seafloor at storage sites such as Snøhvit will be significantly reduced. Self-sealing of leakage pathways as a result of gas hydrate formation is well known at natural methane seeps, as well as CO<sub>2</sub> seeps (e.g. in the Okinawa Trough).

Although some of the hypothetical leakage structures modelled for the Sleipner and Snøhvit scenarios are very large (up to 500m diameter; Table 2), these structures are only partially percolated by leaking CO<sub>2</sub>, so the footprint of CO<sub>2</sub> leakage can be far smaller than the diameter of the structure itself, and is usually <0.2 km<sup>2</sup>. The footprint of leakage from an abandoned well is likely to be significantly less, on the order of a few meters.

## 4. Summary

Work done in ECO2 on seabed fluids and gas fluxes demonstrates that:

- Leakage of CO<sub>2</sub> across the seabed may be signaled by: (i) The presence of CO<sub>2</sub> bubble streams from the seafloor; (ii) Elevated pCO<sub>2</sub> and acidity (lowered pH) and reduced ORP in the water column close to the seabed; (iii) Elevated concentrations of dissolved inorganic carbon in pore waters of sediments close to the seafloor. The presence of bubble streams may be readily detected using passive and active seismic techniques, over a wide survey area. Changes in pCO<sub>2</sub> and related parameters close to the seabed may be detected in situ by deployment of various sensors, either at the seafloor, or on an AUV/ROV (which may restrict the survey to depths a few meters above the seafloor).
- Carbonate system parameters, ORP, and other variables, in pore waters in surface sediments and in the lowermost part of the water column, exhibit considerable natural variability, both temporally and spatially, in the marine environment. It is important to adequately constrain this variability, on a site by site basis, by constructing a full baseline study, to adequately isolate any leakage signal.
- Estimating fluid and gas fluxes across the seabed is a considerable challenge, especially if the leakage footprint is large. Gas bubble fluxes are best estimated by timing the collection of gas at the seafloor, and video observations, but this provides limited spatial and temporal coverage. Passive acoustic techniques (hydrophones) show great promise in quantifying bubble streams, over wide areas of the seafloor and for extended periods of time, but sampling is necessary to confirm the bubble CO<sub>2</sub> content. Fluxes of dissolved CO<sub>2</sub> across the seabed may be estimated using benthic chambers. These are relatively robust and reliable, but they have limited spatial and temporal coverage, and estimation of fluxes is difficult in permeable (sandy) sediments. Fluxes of dissolved CO<sub>2</sub> may also be derived from measurement of pore water profiles of carbonate system parameters, combined with transport-reaction modelling. As sensor technologies improve, *in situ* measurements of carbonate system parameters combined with eddy correlation methods could also be used to provide direct flux measurements.
- Potential precursors for CO<sub>2</sub> leakage include displaced reservoir formation fluids and pore waters in sediments in the shallow sub-surface. The chemical composition of reservoir formation fluids varies from site to site. The best tracer of Utsira formation fluids (Sleipner) is lithium, whereas the best tracer of Tubåen formation fluids (Snøhvit) is chloride. Shallow sub-surface pore waters in shelf seas are characterised by low ORP, sulphate and nitrate, and high hydrogen sulphide, ammonium, iron and manganese.
- If the carbon isotopic composition (expressed as the ratio of <sup>13</sup>C to <sup>12</sup>C) of the injected CO<sub>2</sub> is significantly different from the <sup>13</sup>C/<sup>12</sup>C ratio of dissolved inorganic carbon in background pore waters, then analysis of the carbon isotopic composition of the pore waters may be used to attribute the source of CO<sub>2</sub>. Though not addressed in ECO2, addition of natural or artificial tracers to the CO<sub>2</sub> injection stream prior to storage would also allow the source to be identified although, as yet, there is a fundamental lack of knowledge about the behaviour of these tracers in the marine environment.
- Modelling studies may be used to predict the flux and footprint of CO<sub>2</sub> leakage across the seabed, under different leakage scenarios. Both the leakage rate and the time taken for CO<sub>2</sub> to break through the subseafloor sediments into the overlying water column are principally

determined by physical parameters, especially permeability (porosity), the rate of CO<sub>2</sub> release from the storage reservoir, the size of the leakage structure and the distance from the source of the leak to the leakage structure. Dissolution of CO<sub>2</sub> in pore waters and its subsequent reaction with carbonate and silicate minerals within the sediments acts to delay the breakthrough of CO<sub>2</sub> across the seabed. At deeper water depths, formation of CO<sub>2</sub> hydrate in sediments will significantly reduce the flux of CO<sub>2</sub> across the sediment-seawater interface.