Marine baseline and monitoring strategies for Carbon Dioxide Capture and Storage (CCS)

Jerry Blackford[a*], Jonathan M. Bull[b], Melis Cevatoglu[b], Douglas Connelly[c], Chris Hauton[b], Rachael H. James[b], Anna Lichtschlag[c], Henrik Stahl[d], Steve Widdicombe[a], Ian C. Wright[c]

[a]Plymouth Marine Laboratory, Prospect Place, Plymouth, PL1 3DH, UK.
[b]Ocean and Earth Science, University of Southampton, National Oceanography Centre Southampton, Southampton, SO14 3ZH, UK.
[c]National Oceanography Centre, University of Southampton Waterfront Campus, Southampton SO14 3ZH, UK.
[d]Scottish Association for Marine Science, Oban, Argyll, PA37 1QA, UK.

*Corresponding author. E: jcb@pml.ac.uk; T: +44(0)1752 633468

Abstract

The QICS controlled release experiment demonstrates that leaks of carbon dioxide (CO_2) gas can be detected by monitoring acoustic, geochemical and biological parameters within a given marine system. However the natural complexity and variability of marine system responses to (artificial) leakage strongly suggests that there are no absolute indicators of leakage or impact that can unequivocally and universally be used for all potential future storage sites. We suggest a multivariate, hierarchical approach to monitoring, escalating from anomaly detection to attribution, quantification and then impact assessment, as required. Given the spatial heterogeneity of many marine ecosystems it is essential that environmental monitoring programmes are supported by a temporally (tidal, seasonal and annual) and spatially resolved baseline of data from which changes can be accurately identified. In this paper we outline and discuss the options for monitoring methodologies and identify the components of an appropriate baseline survey.

Keywords: Carbon dioxide capture and storage, monitoring, baselines, marine.

Highlights

- Development of a marine monitoring system suitable for operational CCS is achievable.
- Monitoring should be hierarchical, starting with anomaly detection.
- Comprehensive baselines are required to support monitoring.

1. Introduction, the regulatory environment and other drivers for monitoring.

Carbon dioxide capture and storage (CCS) in deep, sub-surface geological reservoirs has been proposed as a credible mitigation approach to climate change. The success of this mitigation approach, beyond the demonstration stage, depends on establishing that storage is long-term and integral for the vast majority of sequestered carbon dioxide, as well as environmentally safe. Regulations governing CCS vary internationally (see: http://www.iea.org/ccsdatabase/). Taking European regulations as an example, the EU directive (European Union, 2009) states that:

> " member states must ensure that the operator monitors the injection facilities, the storage complex and where appropriate the surrounding environment, for a number of specified purposes, including:
>
> 1. comparison of actual and modelled behaviour of CO_2 and formation water;
> 2. detecting significant irregularities, migration or leakage; and
> 3. detecting significant adverse effects for the environment."

and

> "Provisions are required concerning liability for damage to the local environment and the climate, resulting from any failure of permanent containment of CO_2. Liability for environmental damage (damage to protected species and natural habitats, water and land) ……. should be applied to the operation of storage sites…. . Liability for climate damage as a result of leakages …… requires surrender of emissions trading allowances for any leaked emissions."

A secondary driver for monitoring, especially for proposed onshore storage, stems from public concern regarding human health and ecosystems. Public opposition to CCS has led to costly delays and cancellations of some onshore projects (Feenstra et al., 2010; Van Noorden, 2010; Monastersky, 2013), whilst erroneous claims of leakage, (Beaubien et al., 2013), similarly generate adverse public responses. Scientifically credible and robust monitoring programmes at storage sites will provide public assurance and ensure an evidence based assessment of this greenhouse gas control strategy. Monitoring, whilst effectively detecting any leakage must minimise the incidence of false positives, ensuring that commercial operators are not subjected to regulatory sanction for leaking CO_2 or causing 'impacts' that are, in reality, the consequence of natural changes.

The QICS (Quantifying and Monitoring Potential Ecosystem Impacts of Geological Carbon Storage) project used a novel controlled release of CO_2 into shallow subsea sediments, coupled with modelling approaches to examine the detectability of moderate amounts of “leaking” CO_2 in sediments and water column, using a variety of methods (Blackford & Kita, 2013). Whilst we do not repeat the detailed results here (see Blackford et al. 2014 and other papers in this special issue), in summary CO_2 was detectable using acoustic, chemical and biological methods, but the signal was spatially restricted, moderated by ambient conditions, and sometimes only visible above certain thresholds. In particular only 15% of injected CO_2 was detectable at the seafloor, the remainder remains in the sediments as dissolved inorganic carbon, mineral phases or as a gas phase.

In this paper we use the insight gained during the QICS project (Blackford & Kita, 2013; Blackford et al., 2014; Taylor et al., this issue;), other associated studies and previously published work to assess and discuss the potential approaches to monitoring the marine environment at offshore storage sites, beyond that previously discussed (IEAGHG, 2012; Shitashima et al, 2013). Further, we propose a set of generic requirements for baseline surveys. Whilst we use the North Sea as a case study region, our findings can be generally applied to the majority of marine sites proposed for CCS, especially those on continental shelves with a water depth not exceeding ~300m.

2. The challenges for monitoring

Comparatively little quantified data has been published describing possible leakage scenarios due to high degrees of uncertainty, especially in predicting geological flow mechanisms and rates. Further, whilst there are some analogues (in the form of reservoir blowouts and leakage events) from offshore oil and gas exploration, there is no direct evidence of leakage from existing offshore storage sites. Given this, risk assessments have tended to investigate a range of theoretical leakage scenarios, starting from a minimum inconsequential leak up to a plausible maximum, providing that operational or geological mechanisms of leakage can be invoked in each case. Leakage from transportation can be easily constrained as pipeline flow rates are known (e.g., ~3 kilotonnes per day at the North Sea, Sleipner field), and it is assumed that such leaks could be operationally controlled in a matter of hours to days. Leakage from storage is more speculative, with fluxes estimated from <1 tonne per day, to 10-100 tonnes per day, to >1 kilotonne per day being associated with seepage, abandoned wells, geological discontinuities and catastrophic operational failures respectively (IEA, 2008; Klusman, 2003).

The footprint of an active gas release for these scenarios at the sea floor may range from a point source to focused flows characterised by radii of 10-500 metres, to elongated narrow fractures of several hundreds of metres. It is generally agreed that the epicentre of leakage will be easily detectable; however, successful monitoring may depend on the ability to distinguish diffuse low flux leaks away from the epicentre of the leak. The experimental release, as well as CO_2 dispersion modelling of various scenarios (Dewar et al., 2013; Blackford et al., 2008; Blackford et al., 2013; Phelps et al., this issue), have revealed that chemical detectability directly scales with leakage flux, progressing from a few tens of metres radius in the case of one tonne per day to several kilometres in the case of one kilotonne per day. However, as marine systems are naturally dynamic, physically, chemically, and biologically, these perturbed signals will be increasingly difficult to recognise against the background heterogeneity at increasing distance from the leakage epicentre. This heterogeneity is manifest at many scales and is due to many processes (see section 3). Detectability is further compounded by the natural ocean circulation such that entrained CO_2 plumes would be highly mobile (Blackford et al., 2013; Mori et al., this issue). This is especially the case for tidally influenced coastal and shelf seas where the majority of global offshore storage is planned. Further, on cessation of leakage, mixing in shelf seas is such that the detectable signal is advected away from the leakage location and dispersed rapidly, reducing to below detection limits within hours for low level fluxes and weeks for worst case scenarios (Blackford et al., 2008; Blackford et al., 2014; Phelps et al., this issue).

Although CO_2 is highly soluble in seawater, initial seepage of CO_2 across the seafloor interface is observed to be in a non-hydrated gas bubble phase in shallow shelf sea environments. Individual bubble plumes cause small pockmarks (<25cm in radius), whilst concerted long term flow can cause large pockmarks (>10m in radius) (Cathles et al., 2010). The QICS experiment, in very shallow water, showed that only a relatively small proportion (<15%) of gas injected below the sea bed manifested as bubble plumes at the sea floor, at least in the initial stages of leakage, and showed that bubble size and rise height was highly sensitive to hydrostatic pressure (Blackford et al., 2014; Sellami et al., this issue; Dewar et al., this issue). Modelling (Dewar et al., 2013) shows that bubble size and plume dimensions reduce significantly at increasing water-depth. Consequently, direct leakage of dissolved CO_2 from seafloor sediments into the water column cannot be ruled out and should be considered by any monitoring strategy.

Primary monitoring of the robustness of geological storage will likely be based on time-lapse seismic monitoring of the deep geological storage complex, of the order of one kilometre or more below the sea floor, augmented by ‘down-hole’ sensors as appropriate. This will be used to monitor the dispersal and evolution of the CO_2 within the storage reservoir, and would detect large leakage fluxes beyond the reservoir formation. However, deep seismic monitoring may not resolve smaller, low flux leakage pathways through the cap rock and overburden, which would only be visible near or at the sea floor. This suggests that monitoring at the seabed (or land surface) during and after injection will be required for complete assurance. Hence, marine monitoring should be optimised to detect the smaller range of leakage, well under 100 tonnes per day, either from storage or from non-catastrophic transportation seeps.

3. Monitoring strategies:

The manifestation of leakage can be multifaceted, e.g., by gas flow in dynamic bubble streams, potential fluxes in a dissolved phase, numerous spatial distributions related to geological structures or well-head infrastructure, with finite potential for geochemical mitigation (e.g., carbonate buffering, Blackford et al., 2014; Lichtschlag et al., this issue) depending on sediment type. Further, it has been shown that detectable leakage footprints could be relatively small compared with the area requiring assessment (Dewar et al., 20013). Consequently a tiered and multivariate approach to monitoring, comprising some combination of geophysical, acoustic, chemical and biological observation is highly desirable. Given that natural background variability of sediment morphology, marine acoustics, chemistry and biology, is significant, especially in shelf seas, each monitoring approach will need to be supported by robust baseline surveys that characterise the spatial and temporal dynamics of all relevant processes in the region.

A hierarchical approach to monitoring in which the initial stage aims to detect anomalies using a minimum number of techniques across a wide area would be most cost effective. Only once an anomaly is detected are more detailed and resource intensive surveys required to confirm abnormal levels of CO_2, attribute the CO_2 to a source and subsequently if leakage is confirmed, quantify leakage and assess impacts. The stages for monitoring could be summarised thus:

I. For **detection of anomalies**, deep time-lapse seismic monitoring of the storage reservoir along with monitoring of reservoir pressure will need to be supported by seafloor based monitoring which may include passive acoustic and chemical monitoring, deployed on both site specific seafloor landers and Autonomous Underwater Vehicles (AUV) performing spatially resolving surveys.

II. For **attribution**, once an anomaly is detected, a full assay of carbonate chemistry (DIC, total alkalinity, pH, pCO_2, calcium ion concentration) for dissolved phase and/or direct sampling of gas bubbles can confirm if CO_2 is present. The carbon isotope composition of the CO_2 plume may help attribute the source of the CO_2, alternatively consideration is being given to tracers, both natural (Gilfillan et al., 2008) or added to the CO_2 injection stream prior to storage, that would uniquely identify the source. Otherwise detailed seismic imaging may be used to identify a leakage pathway and consider shallow natural gas deposits as an alternative source of the anomaly.

III. To **quantify leakage**, fluxes of dissolved CO_2 across the sediment-seawater interface can be estimated using benthic chambers (Tengberg et al., 2004), but several would need to be deployed to account for small scale heterogeneity. 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, with improved spatial coverage (IEAGHG, 2012). Passive acoustic techniques also show great promise in quantifying bubble streams (Blackford et al, 2014; Berges et al, submitted). Some direct sampling of gas by remote vehicles may be necessary to verify estimates. The legal and economic consequences of leakage suggest that quantification will require a high degree of accuracy, suggesting that multiple methods may need to be combined to reduce uncertainty.

IV. During and after confirmed leakage the **impact on the marine environment** and the timescale of its recovery will need to be assessed. Measurements of biological impactors such as pH or heavy metal mobilisation in sediment pore waters and the overlying water column can indicate severity of impact. Community composition analysis and microbial assays can be used directly to estimate the impact and recovery of the ecosystem. These methods would require direct sampling of the sediment, possibly augmented by video surveys for changes in faunal community structure.

4. Techniques for monitoring CO_2 leakage in the marine environment and their baseline requirements.

4.1 Deployment options

Given the need to cover the area of the storage reservoir, as well as accounting for possible lateral migration of CO_2 into the storage complex and further lateral movement as CO_2 passes through the overburden (amounting to a footprint of potentially several hundreds of square kilometres in area), an unmanned system that can be deployed for long durations is necessary. A candidate vehicle for primary marine monitoring is an AUV, (e.g. figure 1) which can be programmed to follow a pre-determined survey pattern at high resolution with an ambition for deployment to last up to 6 months (Wynn et al., 2014). AUVs can house a range of sensors relevant to CCS leakage monitoring (e.g., chemical, acoustic, imaging) but there is a trade-off between sensor power load and survey duration. Currently, passive sensing (e.g. chemical sensors and passive hydrophones) would allow deployments in order of months, whereas active sensing (e.g., acoustic sonar imaging on either the seafloor or sub-surface), would only allow deployments in the order of days. Real-time data telemetry is improving, with the imminent use of un-manned surface vehicles as “data gateways” with acoustic transmission from the AUV to the surface platform, and onward satellite telemetry transmission to shore station, offshore platform, or ship. Alternatively both Gliders and Float based systems are already configured for long term deployment and are being tested for use in offshore monitoring.

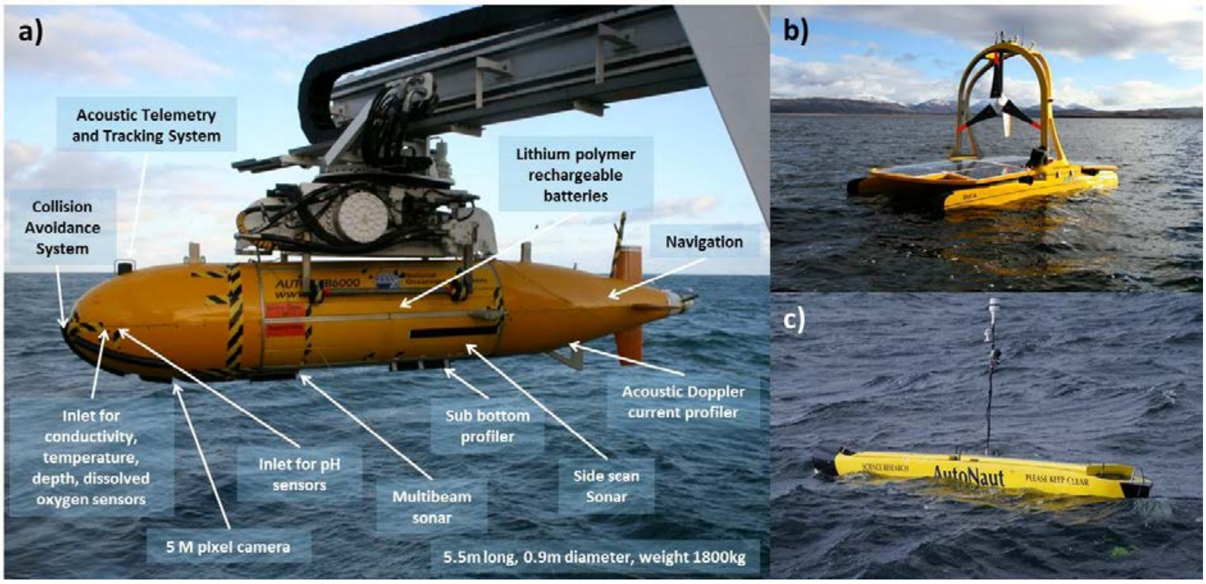

Figure 1, a) an example of an autonomous underwater vehicle system, with its associated power, navigation and sensor systems; b and c) examples of surface support unmanned vessels.

Other deployment options, for more detailed and site specific surveys, especially for relatively high risk leakage locations such as abandoned well bores, include seafloor lander based systems, ship based benthic core sampling and other instrumentation, remotely operated vehicles, and if the water is sufficiently shallow, diver sampling. All of these methods, whilst providing more technological capacity are resource intensive, limited in spatial and temporal range, and in the case of landers, vulnerable to accidental trawling.

4.2 Active acoustic methods

Acoustic methods that use active sonar (e.g., seismic reflection for the sub-surface; multibeam sonar for the water column and sea floor) are effective in detecting free gas in the surface sediments and for imaging the migration of CO_2 through those sediments to the sea floor (Cevatoglu et al., this issue), and in the water column. Seismic reflection methods are particularly sensitive to gas accumulation in the sub-surface as small increases in gas content lead to enhanced seismic reflectivity (Best et al., 2004; Hovland and Judd, 1988; Petersen et al., 2010; Rajan et al., 2012; Zhang et al., 2012; Cevatoglu et al., this issue) due to the large acoustic impedance contrast between gas-charged and non-gassy sediments. The presence of gas can also lead to characteristic acoustic turbidity and poor penetration on high frequency seismic reflection profiles (Fleischer et al., 2001; Cevatoglu et al., this issue).

Whilst active acoustic methods can efficiently survey a considerable area, there is uncertainty as to whether relatively small scale features will be detected in the sub-surface, and methods for inverting seismic reflection data to determine physical property information (e.g. gas concentration) are still being developed. Nonetheless, water column acoustic techniques are effective at identifying small pockmarks caused by individual bubble streams (Cevatoglu et al., this issue).

In terms of a baseline, sediments and sea floor systems in shelf seas can be spatially complex. Many features that could be used to identify leakage are commonly present as functions of natural phenomena. For example natural seabed fractures or pockmarks with or without gas release, resulting from shallow sediment biogenic gas production, could readily be mistakenly interpreted as evidence of storage leakage. Shallow gas (methane or hydrogen sulphide) is often naturally present in shallow sediments, and its geophysical manifestation may vary seasonally (Wever et al., 1988). A baseline survey is needed to broadly identify the seismic attributes of gassy sediments that may already be present within a proposed storage site.

Given that the spatial extent of the possible leakage area can be predicted by geological modelling, a systematic, spatially complete survey of the storage region is recommended, recording fissures, pock marks and geological discontinuities predating storage. Whilst spatial coverage is paramount, the possibility for variability driven by season, weather, tidal variation or biological activity should not be discounted.

4.3 Passive acoustic methods

Bubbles, when released from the sediments produce a sound whose pitch relates to the bubble size, and inversion of bubble streams recorded on calibrated hydrophones can be used to determine gas flux (Leifer & Tang, 2007; Leighton & White, 2012; Berges et al., this issue). If bubble streams exist, hydrophones may provide a detection distance significantly greater than achievable with chemical signals although it is currently not clear what the effective sensing distance is, given different bubble discharge rates through different seafloor substrate types.

However, shelf seas are acoustically complex domains containing both man-made noise (e.g. from marine traffic, oil/gas platforms, or even active sound-based seal deterrents) and natural noise from storms/waves and natural seeps (principally of methane), all potentially contributing to masking a specific acoustic signal. Indeed AUV surveys create their own acoustic noise, which need to be known when using them as a platform for passive hydrophone sensing. Furthermore the frequency range generated by bubbles can be sizeable. Anomaly detection with passive acoustics may be less impaired by background noise, however quantification of flow could be compromised by substantive noise pollution. Generating a baseline imparts some challenges as these sound generators may be fixed, mobile and/or intermittent and unpredictable. Thus, a sufficient baseline would require a spatially and temporally detailed survey of marine noise, across the range of frequencies associated with bubble streams.

4.4 Geochemical methods

CO_2 dissolves rapidly in seawater forming an equilibrium between CO_2, carbonic acid, bicarbonate ions and carbonate ions and hence acidifying the system. The total of the dissolved components are referred to as dissolved inorganic carbon (DIC). Operational instrumentation that can measure resulting acidity (pH) or the partial pressure of CO_2 in seawater are readily available (e.g. Atamanchuk et al this volume and references therein), although there are still some significant challenges in calibration that require frequent assays against known standards (Dickson et al., 2007). Further, the speciation of CO_2 in seawater is very dependent on pressure, temperature and total alkalinity (TA); TA being simplistically the capacity of the seawater to neutralise acid (Zeebe & Wolf-Gladrow, 2005). Highest accuracy can be obtained by measuring at least two of the measurable quantities of the so-called carbonate system (pH, pCO_2, DIC, TA) along with temperature, depth and salinity. In complex shelf sea environments there is arguably a requirement to measure three of these parameters to quantify the system (Artioli et al., 2012; Kim & Lee, 2009). The most operationally achievable combination, pH and pCO_2, unfortunately provide the lowest accuracy in deriving the other components of the system, as necessary for quantification. Whilst automated methodologies for DIC and TA are being developed (e.g. Rérolle et al., 2013), they are not yet fully operational.

The biggest challenge for a sufficient chemical baseline is to record the spatial and temporal heterogeneity that characterises shelf seas driven by biological and physical processes such as respiration, photosynthesis and nutrient supply (figure 2). Depending on size and geographical location, spatial differences over an individual storage site may be limited, but large differences exist along latitudinal and depth gradients with the largest discontinuity being the presence or absence of seasonal stratification. 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 with intense biological activity, daily and even sub-hourly sampling will be necessary to constrain variability completely.

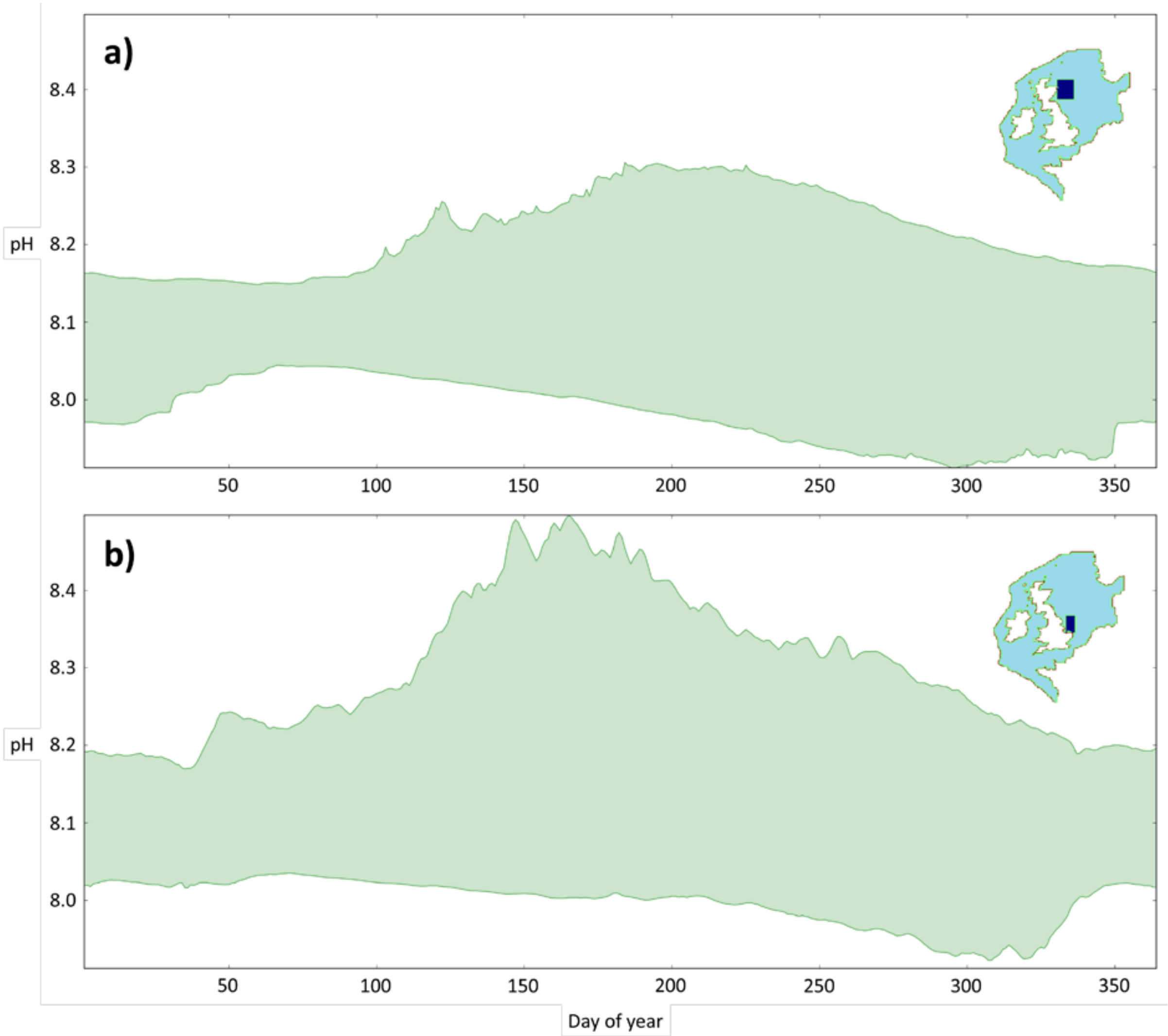

Figure 2. Climatology of modelled pH ranges in the North Sea a) northern region which seasonally stratifies, b) southern region which remains mixed throughout the year (see insets). Whilst any particular shelf sea region will have a unique pH range and spatial heterogeneity, the causative processes are common and likely to result in similar complexity.

Changes in DIC due to biological activities will often be associated with changes in oxygen and physical effects associated with changes in temperature. Synchronous measurements of temperature and oxygen (and possibly some other commonly recorded parameters) have the potential to increase the accuracy of anomaly identification (Romanak et al., 2012; Atamanchuck et al., this issue), although this has yet to be demonstrated for shelf sea environments. Hence, as part of any baseline, covariance relationships between geochemical parameters, established as deviations from these 'normal relationships', may be more powerful indicators than absolute changes from the mean value of a single measurement, especially if detection is dependent on recognising weak signals some distance from the release epi-centre.

Deep core sampling to assess carbonate content of the unconsolidated sediment layer across the storage complex is an important additional consideration. As noted in the QICS experiment (Blackford et al., 2014; Lichtschlag et al., this issue), the potential for carbonate buffering is significant, and measurable chemical parameters can be dramatically affected as a result. Carbonate content across North Sea seafloor sediments, for example, is variable (Pantin, 1991) and its quantification would indicate the potential for buffering of leaked CO_2 and pH signals (Tsukasaki et al., this issue), at least in the initial stages of a leak.

Although analyses of carbonate system parameters can be used to identify CO_2 leakage, they do not provide any information about the source of the leak. If the stable isotopic composition of the leaked CO_2 is significantly different from background seawater (as in the QICS experiment, Lichtschlag et al., this issue), this may be a useful source tracer. In practice, it may be possible for inert tracers to be added to sequestered CO_2 (e.g., Gislason et al., 2010 providing an alternative target for chemical monitoring.

4.5 Biological methods

Whilst biological monitoring is primarily useful in impact assessment, it may also provide detection utility. For example in assessing ratios of sensitive to non-sensitive species, or observing unusual behaviours, such as the presence on the sea floor of animals (e.g., burrowing sea-urchins) that are normally buried within the sediments. There is also evidence that microbial populations can be sensitive to additional CO_2 (Ishida et al.,2013; Tait et al., this issue). Metagenomic analysis of microbial communities, which can quantify the abundance of genes relevant to CO_2 fixation pathways may also have utility in monitoring, in particular for verification or impact assessment. (Håvelsrud et al., 2013; Tait et al., this issue).

The challenge for biological monitoring of environmental impact lies in the accurate discrimination of human impacts from natural, and potentially long-term, environmental change. Within the context of the North Sea system there is good evidence that the duration of a particular monitoring programme, or the timescale of existing data, can have a powerful influence on the interpretation of recorded changes. In the short term, changes between sites might be interpreted as either the result of anthropogenic impacts (Buchanan & Warwick, 1974) or environmental temperature anomalies (Buchanan et al., 1978) that, when viewed in the long term, might be attributed to long term climate-driven changes in the organic flux to the sea bed (Buchanan & Moore, 1986), or a complex combination of changes in organic flux and the impacts of human activity (Frid et al., 1999). Benthic monitoring programmes of potential CCS sites, and associated reference sites, should resolve the long term signal and make use of existent data from similar sites in the region. Irrespective of the overall timespan of available data, any biological baseline programme should consider different temporal scales, employing a mix of quarterly, monthly and weekly repeat sampling during periods of intense biological activity, in order to capture the full nature of variability within the natural assemblage.

As argued (Underwood, 1994), it is insufficient to survey only one injection reservoir and one reference site before and during any injection project, as advocated in a: ‘ Before, After, Control, Impacted ‘BACI’ design’ (Green, 1979). Natural clinal changes within an entire system (e.g. shelf sea area) are inevitably not uniform and multiple reference sites are necessary to describe the mean field change across that system. Asymmetrical monitoring programmes, with multiple reference/control sites, are required to constrain the full variability within a system. Only by using large scale and replicated surveys with multiple reference sites will a monitoring programme be able to reliably discriminate anthropogenic pulse or press effects in the benthos that might result from CCS reservoir failure.

In response to recent EC legislative drivers, particularly the Marine Strategy Framework Directive (MFSD), a variety of numerical indices (e.g. Borja et al., 2009; Somerfield et al., 2008), based on faunal identity, abundances and biomass have been developed. These indices are proposed to be indicative of whether benthic communities are potentially compromised and in poor condition as a result of an anthropogenic stress (Rogers et al., 2008). Whilst the application of these indices could prove useful with respect to CCS, additional validation will be required using data from real or simulated leakage events. With growing understanding of the underlying physiological and ecological impacts of elevated CO_2 on marine organisms, it is becoming possible to develop novel indices of sensitivity, specific to CCS leakage and test these indices against existing community response data from mesocosm experiments and field release studies.

For a fully comprehensive baseline against which to perform an impact assessment, it would be advisable to fully constrain the biological system of the potential CCS reservoir, enabling a robust statistical assessment of suspected change. This would require an initial mapping of the benthic habitats found within the area of interest followed by the characterisation of the mega-, macro- and potentially meio- and micro- biota within each habitat. This approach could require a mixture of acoustic and visual sea bed imagery supported with appropriate faunal sampling.

Regarding monitoring for leakage detection, rather than impact assessment, it will not be economically feasible to conduct repeated physical sampling at multiple sites to the required level of detail. Automated monitoring platforms such as AUVs have demonstrated their potential for such large scale and long term repeat monitoring *via* collection of high definition still imagery. However, the use of autonomous platforms for data collection is not without its challenges. Using existing technologies a single AUV mission can generate of the order of 70000 still images of surficial macro- and megafauna. The complete biological interpretation of such a volume of raw data would represent a very significant resource commitment; though the emerging development of automated processing methodologies of such imagery will reduce cost.

4.6 Remote sensing of atmospheric CO_2

During the QICS project, which for practical reasons was situated in very shallow waters, CO_2 gas bubbles reached the sea surface. The resulting increase in atmospheric CO_2 could be clearly mapped using sensors deployed just above the sea surface, and could potentially be detected remotely via LiDAR technologies with some efficiency. However, it is well established that due to the high solubility of CO_2 in seawater, CO_2 bubbles, of the size generally predicted to be emitted from sediments, would dissolve within a few metres of leaving the sea floor (Dewar et al., 2013). The depth of water at sites ear-marked for CO_2 storage is certain to prevent free gas reaching the sea surface, and with relatively fast hydrodynamic mixing via tidal circulation and storm events spreading the dissolved plume, compared to the relatively slow equilibration across the air sea interface, this technique is viewed as impracticable for most shelf sea storage sites.

5. Baseline observation strategy,

Each property of the marine system relevant to monitoring varies on largely different temporal and spatial scales. Although some biological events can be measured in days, the dominant biological timescale is the seasonal evolution of communities. Chemical properties vary over the diurnal cycle as well as seasonally. Ambient noise is often random, depending on shipping traffic, while sediment physical properties may have little temporal variability. Inter-annual variability and decadal scale trends need also be considered. Spatially there is metre scale patchiness associated with benthic systems in terms of the biology, which would be beyond scope of CCS monitoring. Re-suspension, deposition and sediment characteristics tend to vary on scales of 10’s of kilometres, such that the characterisation of sediments across a storage site is entirely tractable. Optimal spatial and temporal criteria for baseline surveys relating to each category of monitoring approach are detailed in table 1. The particular choice of approaches will have some site specificity. We suggest that passive acoustics and geochemical methods will be the primary detection methodologies and therefore identify the most pressing aspects of baseline generation.

Methodology	Variables	Temporal sampling interval	Spatial sampling scale	Notes
Active acoustics	Sea floor bathymetry, including pockmarks.	In shallow waters where the seafloor sediments are exposed to storm driven resuspension and biological sedimentation a seasonal discrimination, in the first instance. In deeper waters where sediments are disconnected from weather driven events an initial survey, followed by a repeat survey 1-2 years later.	The spatial extent of the storage reservoir in addition to allowing for lateral movement of migrating CO_2.	Assists identification of existent natural seeps.
	Free gas in surface sediments.	An initial survey, followed by a repeat survey 1-2 years later.		Useful for attribution.
Passive acoustics	All noise at relevant frequencies.	Seasonal in addition to targeted short term deployments to assess event driven noise.	Targeted to known fixed installations or shipping routes.	Necessary for quantification, not essential for detection.
	Acoustics of existent natural gas seeps.	Seasonal and targeted short term deployments to account for intermittent gas flow.	Spatial extent of the storage reservoir as well as allowing for lateral movement of migrating CO_2	Required for detection.
Geochemistry	Water column pH, pCO_2, temperature, salinity, pressure. TA or DIC and O_2 if possible.	Hourly measurements for at least part of the seasonal cycle, corresponding with periods of biological or physical activity. Weekly for entire annual cycle. Repeated for at least one subsequent year to assess inter-annual variability and then on an approximately decadal repeat to assess longer term trends.	For high frequency data, if the storage site is large or includes significant changes in water depth or other hydrodynamic properties, at least a pair of landers deployed across the site. Spatial extent of the storage site via AUV deployment.	Required for detection.
	Isotope composition ratios: e.g. C^{13}:C^{12}	Occasional (not dynamic)	Occasional (not dynamic)	Addresses attribution
Biology	Community structure, indicator species and related indices.	Weekly during periods of intense biological activity, otherwise monthly. Repeated for at least one subsequent year to assess inter-annual variability and then on an approximately decadal repeat to assess longer term trends.	Significant differences in water depth and-or different sediment types within the complex would need separate characterisation. Multiple replicates are required for statistical certainty.	Principally for impact assessment.

Table 1. An overview of the spatial and temporal criteria for baseline data acquisition, for the proposed range of monitoring methodologies, that could be considered.

Given the resource limitations, a risk-based approach to monitoring efficacy, and the overall economics of CCS deployment as a climate change mitigation strategy, the extent of monitoring programmes and initial baseline surveys are inevitably limited. Even in well sampled regions such as the North Sea there is a dearth of specific CO_2-related observations taken near the sea floor and at the higher frequencies necessary to fully characterise physically and biologically induced heterogeneity. To some extent regional modelling systems (e.g. Siddorn et al., 2007; Wakelin et al., 2012; Artioli et al., 2013), if they include the processes that impact the natural variability of CO_2 can provide interpolation between sparse chemical data. However the quality of such projections depends on having sufficient data with which to evaluate any model system. As individual storage sites are not independent of their wider environmental setting, in regions where multiple storage operations are planned, a regionally conceived, potentially international baseline survey approach could either save costs and/or improve baseline quality. The alternative – stand-alone baseline surveys specific to each and every storage site will increase cost, although geophysical characterisation of the storage complex must necessarily be site specific. Additionally it is likely that a comprehensive baseline acquisition will provide a resource of wider benefit to the marine community, beyond its utility for CCS, for example in support of the Marine Strategy Framework Directive in Europe (de-Jonge et al., 2006).

6. Summary

This paper offers some insights into the challenges facing an effective marine environment monitoring system for geological carbon storage and suggests potential strategies that may address these challenges. Primarily we suggest that monitoring needs to be multivariate, e.g. based on some combination of physical, chemical, acoustic and biological observations but also hierarchical. Due to the large areas that will require monitoring, a primary survey strategy to detect anomalies followed by more in depth surveys to confirm, attribute and assess impact from potential leakage is likely to be cost effective. For all monitoring approaches a detailed baseline is essential, otherwise the potential for false positive and false negative signals is high, given the natural heterogeneity of the marine system. The development of monitoring strategies and the acquisition of baseline data are both urgent, should ambition to bring CCS on-stream by 2020 be met.

This paper is focussed on sub-sea geological storage in relatively shallow shelf environments with water depths up to 300 m, sometimes significantly less. In deeper off shelf environments the phase chemistry of CO_2 is affected by temperature and pressure such that hydrate covered droplets rather than bubbles of CO_2 occur; in this case the physical, chemical, acoustic and biological responses typical of shallow seas would be unlikely to fully translate to the deep-sea.

In this discussion we make no comment on the likelihood of leakage, save to note that good monitoring practice will decrease the likelihood of events that significantly undermine storage or damage the environment. Of the technological developments required for anomaly detection, perhaps the most pressing is that of AUVs that can be deployed for long periods, along with sensors robust enough to deliver reliable data for several months, efficient data pipelines and strategies that can process and analyse these volumes of data efficiently and with low cost. As discussed, instrumentation for anomaly detection should be optimised to detect the smaller range of leakage, well under 100 tonnes per day, either from storage or from non-catastrophic transportation seeps.

Attribution is achievable via the application of tracer technology or by imaging leakage pathways from the storage complex. Quantification will be challenging (IEAGHG, 2012), especially given the legal and economic ramifications of leakage. It is unlikely that absolute quantification will be achievable; however applying a variety of methods to obtain a best estimate should reduce errors, as would repeat measurements across a range of environmental conditions. Impact assessment is not trivial but is relatively more established in the context of other impactors such as trawling, dumping and other pollution events. However, despite the outstanding challenges we suggest that the development of monitoring systems and a sufficient baseline is achievable within the time constraints required for effective mitigation of CO_2 emissions and subsequent climate change.

Acknowledgements

We gratefully acknowledge the funding provided by NERC for the QICS project under grant numbers: NE/H013962/1, NE/H013881/1, NE/H013873/1 and NE/H013911/1 and the additional funding provide by the Scottish Government. We also acknowledge the EU framework 7 grants ECO2 (project number 265847) and RISCS (project number 240837). We thank Dr Lee de Mora for figure 2.

References

Artioli, Y., Blackford, J. C., Butenschön, M., Holt, J. T., Wakelin, S. L., Allen, J. I., 2012. The carbonate system of the NW European shelf: sensitivity and model validation. Journal of Marine Systems, 102-104, 1–13.

Atamanchuk D., Tengberg A., Aleynik D., Fietzek P., Shitashima, K., Lichtschlag, A., Hall, Per O.J., Stahl H. Detection of CO_2 leakage from a simulated sub-seabed storage site using three different types of pCO_2 sensors. IJGGC submitted (this volume).

Beaubien S.E., Jones D.G., Gal F., Barkwith A.K.A.P., Braibant G., Baubron J.-C., Ciotoli G., Graziani S., Lister T.R., Lombardi S., Michel K., Quattrocchi F., Strutt M.H., 2013. Monitoring of near-surface gas geochemistry at the Weyburn, Canada, CO_2-EOR site, 2001–2011. International Journal of Greenhouse Gas Control 16S, S236–S262.

Berges, B.J.P., Leighton, T.G., White, P.R. Passive acoustic quantification of gas fluxes during controlled gas release experiments. IJGGC submitted (this volume).

Best, A.I., Tuffin, M.D.J., Dix, J.K., Bull, J.M., 2004. Tidal height and frequency dependence of acoustic velocity and attenuation in shallow gassy marine sediments. *Journal of Geophysical Research*, 109 (B8).

Blackford, J.C., Jones, N., Proctor, R. Holt, J., 2008. Regional scale impacts of distinct CO_2 additions in the North Sea, Marine pollution bulletin, vol. 56, 1461-1468.

Blackford, J.C., Torres R., Cazanave P., Artioli Y., 2013. Modelling Dispersion of CO_2 Plumes in Sea Water as an Aid to Monitoring and Understanding Ecological Impact. *Energy Procedia*, *37*, *3379-3386.*

Blackford, J.C., Kita J., 2013. A Novel Experimental Release of CO_2 in the Marine Environment to Aid Monitoring and Impact Assessment *Energy Procedia*, *37*, *3387-3393.*

Blackford J., Stahl H., Bull J.M., Bergès B.J.P., Cevatoglu M., Lichtschlag A., Connelly D., James R.H., Kita J., Long D., Naylor M., Shitashima K., Smith D., Taylor P., Wright I., Akhurst M., Chen B., Gernon T.M., Hauton C., Hayashi M., Kaieda H., Leighton T.G., Sato T., Sayer M.D.J., Suzumura M., Tait K., Vardy M.E., White P.R., Widdicombe S., 2014. Detection and impacts of leakage from sub-seafloor Carbon Dioxide Storage, Nature Climate Change, 10.1038/nclimate2381.

Borja A., Rodriguez J.G., Black K., Bodoy A., Emblow C., Fernandes T.F., Forte J., Karakassis I., Muxika I., Nickell T.D., Papageorgiou N., Pranovi F., Sevastou K., Tomassetti P., Angel D., 2009. Assessing the suitability of a range of benthic indices in the evaluation of environmental impact of fin and shellfish aquaculture located in sites across Europe. Aquaculture 293: 231-240.

Buchanan, J. B., Sheader, M., Kingston, P. F., 1978. Sources of variability in the benthic macrofauna off the south Northumberland coast. Journal of the Marine Biological Association of the UK 58: 191-209.

Buchanan, J. B.,Moore, J. J., 1986. A broad review of variability and persistence in the Northumberland benthic fauna: 1971–85. Journal of the Marine Biological Association of the UK 66: 641-657.

Buchanan, J. B., Warwick, R. M., 1974. An estimate of benthic macrofaunal production in the offshore mud of the Northumberland coast. Journal of the Marine Biological Association of the UK 54: 197-222.

Cathles L.M., Su Z., Chen D., 2010. The physics of gas chimney and pockmark formation, with implications for assessment of seafloor hazards and gas sequestration. Marine and Petroleum Geology 27, 82–91.
Cevatoglu, M., Bull, J.M., Vardy, M.E., Gernon, T.M., and Wright, I.C., and Long, D., submitted. Gas migration pathways, controlling mechanisms and changes in sediment physical properties observed in a controlled sub-seabed CO_2 release experiment. IJGGC submitted (this volume).
Dewar, M., Wei, W., McNeil, D., Chen, B., 2013. Small scale modelling of the physiochemical impacts of CO_2 leaked from sub-seabed reservoirs or pipelines within the North Sea and surrounding waters. *Mar Prod Bull*, 73, 504-515.
Dewar M., Sellami N., Chen B.. Dynamics of rising CO_2 bubbles in the QICS field experiment, Part 2 – Modelling. IJGGC submitted (this volume).
Dickson, A.G., Sabine, C.L., Christian, J.R., 2007. Guide to Best Practices for Ocean CO_2 Measurements Special Publication 3. PICES, p. 191.
European Union, 2009. Directive 2009/31/EC of the European Parliament and of the Council of 23 April 2009 on the geological storage of carbon dioxide and amending Council Directive 85/337/EEC, European Parliament and Council Directives 2000/60/EC, 2001/80/EC, 2004/35/EC, 2006/12/EC, 2008/1/EC and Regulation (EC) No 1013/2006 (EU CO_2 Storage Directive).
Feenstra, C.F.J., Mikunda T., and Brunsting S., 2010. What happened in Barendrecht? Case study on the planned onshore carbon dioxide storage in Barendrecht, the Netherlands. ECN and Global CCS Institute. http://www.globalccsinstitute.com/publications/what-happened-barendrecht.
Fleischer, P., Orsi T. H., Richardson M. D., Anderson A. L., 2001. Distribution of free gas in marine sediments: A global overview, *Geo Mar. Lett.*, **21**, 103–122.
Frid, C.L.J., Clark, R.A., Hall, J.A., 1999. Long-term changes in the benthos on a heavily fished ground off the NE coast of England. Marine Ecology Progress Series 188: 13-20
Gilfillan, S.M.V., Wilkinson, M., Haszeldine, R.S., Shipton, Z., Nelson, S.T. and Poreda, R.J., 2011. He and Ne as tracers of natural CO_2 migration up a fault from a deep reservoir, *International Journal of Greenhouse Gas Control*, 5, no. 6, p. 1507-1516.
Gislason, S.R., Wolff-Boenisch, D., Stefansson, A., Oelkers, E.H., Gunnlaugsson, E., Sigurardottir, H., Sigfusson, B., Broecker, W.S., Matter, J.M., Stute, M., Axelsson, G. & Fridriksson, T. 2010. Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project. Int. J. Greenhouse Gas Control 4(3), 537-545.
Green, R. H., 1979. Sampling design and statistical methods for environmental biologists. Wiley Interscience, Chichester, England.
Håvelsrud O.E., Haverkamp T.H.A., Kristensen T., Jakobsen K.S., and Rike A.G., 2013. Metagenomics in CO_2 monitoring. Energy Procedia 37, 4215 – 4233.
Hovland, M., and Judd, A.G., 1988. Seabed pockmarks and seepages: impact on geology, biology and the marine environment, 293, pp, Graham and Trotman, London.
IEAGHG, “Quantification Techniques For CO_2 Leakage”, 2012/02, January 2012.
IEA Greenhouse Gas R&D programme (IEA GHG) Assessment of Sub-sea ecosystem impacts, 2008/8, August 2008.
Ishida, H. , Golmen L., West J., Krüger M., Coombs P., Berge J., Magi M. Kita J., 2013. The Benthic Chamber experiment in Storfjorden (Norway) 2005 – effects of CO_2 on microbes, nanobenthos and meiofauna. Mar Poll Bull. 2013.
Jonge V.N. de-, Elliott, M., Brauer V.S., 2006. Marine monitoring: Its shortcomings and mismatch with the EU Water Framework Directive’s objectives, Marine Pollution Bulletin, 53, 5-19.
Kim, H.-C., Lee, K., 2009. Significant contribution of dissolved organic matter to seawater alkalinity. Geophys. Res. Lett. 36, L20603.

Klusman, R.W., 2003. A geochemical perspective and assessment of leakage potential for a mature carbon dioxide-enhanced oil recovery project and as a prototype for carbon dioxide sequestration; Rangely field, Colorado. *AAPG Bulletin* 87, 1485–1507.
Leifer, I., Tang, D., 2007. The acoustic signature of marine seep bubbles. J. Acoust. Soc. Am. 121, EL35–EL40.
Leighton, T.G. and White, P.R., 2012. Quantification of undersea gas leaks from carbon capture and storage facilities, from pipelines and from methane seeps, by their acoustic emissions, Proceedings of the Royal Society A, 468, 485-510.
Lichtschlag A., James R.H., Stahl H., Connelly D. Effect of a controlled sub-seabed release of CO_2 on the biogeochemistry of shallow marine sediments, their pore waters, and the overlying water column. IJGGC submitted (this volume).
Monastersky, R., 2013. Seabed scars raise questions over carbon-storage plan. *Nature* 504, 339–340.
Pantin, H M., 1991. The sea-bed sediments around the United Kingdom: their bathymetric and physical environment: grain size, mineral composition and associated bedforms. *British Geological Survey Research Report*, SB/90/1.
Petersen, C.J., Bünz, S., Hustoft, S., Mienert, J., Klaeschen, D., 2010. High-resolution P-Cable 3D seismic imaging of gas chimney structures in gas hydrated sediments of an Arctic sediment drift. Marine and Petroleum Geology 27, 1981-1994.
Phelps J.J.C., Blackford J.C., Holt J.T., Polton J.A. Modelling Large-Scale CO_2 Leakages in the North Sea. IJGGC submitted (this volume).
Rajan, A., Mienert, J., Bünz, S., 2012. Acoustic evidence for a gas migration and release system in Arctic glaciated continental margins offshore NW-Svalbard. Marine and Petroleum Geology 32, 36-49.
Rérolle, V.M.C.; Floquet, C.F.A.; Harris, A.J.K.; Mowlem, M.C.; Bellerby, R.R.G.J.; Achterberg, E.P., 2013. Development of a colorimetric microfluidic pH sensor for autonomous seawater measurements. *Analytica Chimica Acta*, 786. 124-131.
Rogers S.I., Somerfield P.J., Schratzberger M., Warwick R., Maxwell T.A.D., Ellis J.R., 2008. Sampling strategies to evaluate the status of offshore soft sediment assemblages. Marine Pollution Bulletin, 56, 880-894 .
Romanak, K.D., Bennett, P.C., Yang, C.B., Horvorka, S.D., 2012. Process-based approach to CO_2 leakage detection by vadose zone gas monitoring at geologic CO_2 storage sites. Geophys. Res. Lett. 39, L15405.
Sellami N., Dewar M., Stahl H., Chen B. Dynamic of rising CO_2 bubbles from the QICS project in Ardmucknish bay, Part 1 – Experimental Data Analysis. IJGGC submitted (this volume).
Shitashima, K., Maeda, Y., Ohsuki, T., 2013. Development of detection and monitoring techniques of CO_2 leakage from seafloor in sub-seabed CO_2 storage. Appl. Geochem. 30, 114-124.
Siddorn, J.R., Allen, J.I., Blackford, J.C., Gilbert, F.J., Holt, J.T., Holt, M.W., Osborne, J.P., Proctor, R., Mills, D.K., 2007, Modelling the hydrodynamics and ecosystem of the North-West European continental shelf for operational oceanography, Journal of Marine Systems, 65, 417-429.
Somerfield P.J., Clarke K.R., Warwick R.M., Dulvy N.K., 2008. Average functional distinctness as a measure of the composition of assemblages. ICES Journal of Marine Science 65, 1462-1468.
Tait K., Stahl H., Taylor P., Widdicombe S. Rapid response of the active microbial community to CO_2 exposure from a controlled sub-seabed CO_2 leak in Ardmucknish Bay, Oban, Scotland. IJGGC submitted (this volume).
Taylor P., Stahl H., Blackford J., Vardy M.E., Bull J.M., Akhurst M., Hauton C., James R., Lichtschlag A., Long D., Montgomery J., Aleynik D., Toberman M., Naylor M., Connelly D., Smith D., Sayer M.D.J., Widdicombe S., Wright I.C. . Introduction to a novel in situ sub-seabed CO_2 release experiment for quantifying and monitoring potential ecosystem impacts from geological carbon storage. IJGGC submitted (this volume).

Tengberg A., Stahl H., Gust G., Müller V., Arning U., Andersson H., Hall P.O.J., 2004. Intercalibration of benthic flux chambers I. Accuracy of flux measurements and influence of chamber hydrodynamics. Progress in Oceanography 60, 1–28.
Tsukasaki A., Suzumura M., Lichtschlag A., Stahl H. and James R.H. Phosphorus behaviour in sediments during a controlled sub-seabed CO_2 release experiment. IJGGC submitted (this volume).
Underwood, A.J., 1994. On Beyond BACI: Sampling Designs that Might Reliably Detect Environmental Disturbances. Ecological Applications, 4, 3-15.
Van Noorden, R., 2010. Carbon sequestration: Buried trouble *Nature* 463, 871-873.
Wakelin, S. L., Holt, J. T., Blackford, J. C., Allen, J. I., Butenschön, M., Artioli, Y., 2012. Modelling the carbon fluxes of the northwest European continental shelf: validation and budgets. Journal of Geophysical Research, 117, C05020.
Wever, T.F., Abegg, F., Fielder, H.M, Fechner, G., and Stender, I.H., 1998. Shallow gas in the marine sediments of Eckernforde Bay, Germany, Continental Shelf Research, 18, 1715-1740.
Wynn, R.B., Huvenne, V.A.I., Le Bas, T.P., Murton, B.J., Connelly, D.P., Bett, B.J., Ruhl, H.A., Morris, K.J., Peakall, J., Parsons, D.R., Sumner, E.J., Darby, S.E., Dorrell, R.M., Hunt, J.E.,2014. Autonomous Underwater Vehicles (AUVs): their past, present and future contributions to the advancement of marine geoscience. Mar. Geol., 352, 451-468.
Zeebe, R.E., Wolf-Gradow, D., 2001. CO_2 in Seawater: Equilibrium, Kinetics, Isotopes. Elsevier Science Publishers.
Zhang, Z., McConnell, D.R., Han, D.-H., 2012. Rock physics-based seismic trace analysis of unconsolidated sediments containing gas hydrate and free gas in Green Canyon 955, Northern Gulf of Mexico. Marine and Petroleum Geology 34, 119-133.