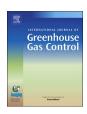
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## Monitoring of offshore geological carbon storage integrity: Implications of natural variability in the marine system and the assessment of anomaly detection criteria



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#### ABSTRACT

The design of efficient monitoring programmes required for the assurance of offshore geological storage requires an understanding of the variability and heterogeneity of marine carbonate chemistry. In the absence of sufficient observational data and for extrapolation both spatially and seasonally, models have a significant role to play. In this study a previously evaluated hydrodynamic-biogeochemical model is used to characterise carbonate chemistry, in particular pH heterogeneity in the vicinity of the sea floor. Using three contrasting regions, the seasonal and short term variability are analysed and criteria that could be considered as indicators of anomalous carbonate chemistry identified. These criteria are then tested by imposing a number of randomised DIC perturbations on the model data, representing a comprehensive range of leakage scenarios. In conclusion optimal criteria and general rules for developing monitoring strategies are identified. Detection criteria will be site specific and vary seasonally and monitoring may be more efficient at periods of low dynamics. Analysis suggests that by using high frequency, sub-hourly monitoring anomalies as small as 0.01 of a pH unit or less may be successfully discriminated from natural variability - thereby allowing detection of small leaks or at distance from a leakage source. Conversely assurance of no leakage would be profound. Detection at deeper sites is likely to be more efficient than at shallow sites where the near bed system is closely coupled to surface processes. Although this study is based on North Sea target sites for geological storage, the model and the general conclusions are relevant to the majority of offshore storage sites lying on the continental shelf.

#### 1. Introduction

The effectiveness of carbon dioxide capture and storage (CCS) as a greenhouse gas emissions reduction strategy (IPCC, 2005; IEA GHG, 2008) depends in part on a rigorous demonstration of storage integrity. Regulations governing CCS vary from country to country, but in general require the storage site operator to monitor the deep geological storage complex for leakage and perform an environmental impact assessment of any plausible leakage event at the surface (Dixon et al., 2015). Further, there may be a requirement to quantify leakage, should it occur, with a view to carbon accounting (IPCC, 2006). Primary monitoring of storage reservoirs will utilise seismic techniques capable of imaging CO<sub>2</sub> through a sedimentary overburden of the order of a kilometre thick. However such techniques have limitations in that the detection threshold may be of the order of 10<sup>3</sup>t CO<sub>2</sub> and are expensive to perform (Jenkins et al., 2015). Monitoring for emissions at the surface (land or sea floor) therefore provides an important secondary monitoring strategy which can be deployed more frequently and rapidly

to detect or respond to any anomalies which might indicate leakage (Blackford et al., 2015). Such surface monitoring is also necessary for environmental impact assessment and may have the potential to quantify  $\rm CO_2$  flow. Critically, a comprehensive monitoring program can provide assurance that no leakage is occurring, as is expected for appropriately sited and operated storage programs.

Globally many potential storage reservoirs are located offshore, for example in NW Europe, China, Japan, Korea, Australia, Brazil and the United States. Consequently the ability to detect or discount anomalous  ${\rm CO}_2$  emissions from offshore storage requires marine deployments of suitable instrumentation at or near the sea floor.

Offshore storage sites are predominantly coastally located, frequently under continental shelves with overlying water depths between 10 and 250 m (Bradshaw and Dance, 2005). Monitoring systems are likely to need a combination of fixed sea floor landers, situated near known risk points (e.g. the injection point) and autonomous underwater vehicles patrolling wider areas (Blackford et al., 2015). Deployment of sea floor instrumentation at these depths is routine, and

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methods of transferring data to land in near real time established. Nevertheless, developing instrumentation that can efficiently cover the area of the storage complex, which may be in excess of 100 km<sup>2</sup>, requires some technological development. Further an important consideration is what to measure? Research suggests that leakage events are complex and resulting signals heterogeneous in time and space. In particular tidal mixing may cause plumes of high CO<sub>2</sub> water to circulate a release point (Blackford et al., 2013, 2014; Maeda et al., 2015), following a tidal ellipse, and bubble plumes may be intermittent due to both the tidal cycle and evolution of sub surface pathways (Blackford et al., 2014; Bergès et al., 2015; Shitashima et al., 2015). Further the morphology of individual bubble plumes can cause considerable small scale heterogeneity in chemical signatures (Atamanchuk et al., 2015). It is likely therefore, that sensors mounted on fixed platforms or autonomous vehicles would be exposed to continuous oscillations between normal and release plume conditions. Current recommendations are for the combined deployment of at least two types of sensor: chemical, sampling for changes in carbonate chemistry (e.g. pH or pCO2) and other associated variables and acoustic, using either sonar or hydrophones to locate bubble plumes (Blackford et al., 2015). Further, it has been proposed that monitoring strategies should be hierarchical in approach, initially confined to identifying anomalies (or the lack thereof) only, thus maximising efficiency. Only if an anomaly is identified should more detailed surveys be performed to confirm, attribute and assess the phenomenon (Blackford et al., 2015; Shitashima et al., 2013; Romanak et al., 2012).

Economically efficient and reliable monitoring strategies are the goal for both site operators and regulators. This translates to minimising the deployment of instrument platforms, while maximising detection range, spatial and temporal coverage and accuracy. Alongside sensor development, a crucial component is knowing when a measured signal should be judged anomalous and worthy of further, more expensive, scrutiny. Understanding natural variability and heterogeneity in relation to likely signals of leakage is therefore vital.

This paper addresses the natural variability of marine chemistry relevant to  $\mathrm{CO}_2$  (carbonate chemistry), using the geological storage rich North Sea as an example to illustrate how seasonal and spatial heterogeneity affect detectability and the selection of appropriate anomaly detection criteria. Despite this region being one of the most intensely sampled in the marine world, there is a significant lack of observations characterising the carbonate system at or near the sea floor. Further, existing observations are generally not targeted at revealing variability at temporal and spatial scales relevant to leakage, i.e. over some 10 s of meters or the tidal cycle. For this reason we turn to coupled hydrodynamic biogeochemical models which provide comprehensive spatial and temporal fields of marine chemistry. Although such models are never perfect representations of reality, evaluation against available observations provides a degree of confidence in outputs.

The reaction kinetics of  $CO_2$  in seawater are well known (Zeebe and Wolf-Gladrow, 2001; Dickson, 2010). Adding  $CO_2$  to seawater leads to an increase in bicarbonate ions ( $HCO_3^-$ ) and hydrogen ions, ( $H^+$ , measured as a decrease in pH) and a decrease in carbonate ions ( $CO_3^{2-}$ ) according to the following equations.

$$CO_2\,+\,H_2O\,\rightarrow\,H_2CO_3\,\rightarrow\,HCO_3^-\,+\,H^+$$

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$

The reaction kinetics are controlled by temperature, pressure, salinity and alkalinity (the capacity of seawater to neutralise acid). Total dissolved  $CO_2$  in seawater ( $CO_2 + H_2CO_3 + HCO_3^- + CO_3^2^-$ ) is known as Dissolved Inorganic Carbon (DIC). pH ( $-log_{10}$  [H $^+$ ], although see Zeebe and Wolf-Gladrow, 2001, for a formal definition) or pCO $_2$  (the partial pressure of  $CO_2$  in seawater) are the most accessible parameters for routine, automated measurement. This paper takes pH (seawater scale) as the parameter of choice; qualitatively the same outcomes would apply if pCO $_2$  were considered.

In marine systems the concentration of DIC and/or the resulting pH and  $pCO_2$  vary according to a number of processes:

- Biological uptake of DIC occurs via photosynthesis and calcification (the formation of calcium carbonate shells etc.). Release of DIC occurs via respiration and dissolution of carbonate structures. These processes are decoupled in time and space and can be especially dynamic in coastal waters, rich in nutrients. There is variability on diurnal and seasonal cycles as well as in response to stochastic weather events and other external influences.
- External inputs, e.g. advection of oceanic or riverine water and rainfall with varying DIC, or alkalinity contents. Variability on ocean boundaries is dominantly seasonal while atmospheric and terrestrial influences are also driven by stochastic weather events.
- Changes in temperature associated with the annual cycle and the mixing or separation (stratification) of different water bodies. The primary signal is seasonal, along with gradients which may be vertical, horizontal (across fronts) or latitudinal.
- Exchange across the air-sea interface serves to equilibrate atmospheric and seawater partial pressures over monthly timescales, so both out gassing and uptake of CO<sub>2</sub> can occur depending on the sum of biological and physical processes. Over annual to decadal timescales the continued emission of anthropogenic CO<sub>2</sub> to the atmosphere is responsible for a gradual net uptake of CO<sub>2</sub> by the oceans, resulting in an increase in DIC and pCO<sub>2</sub> and a decline in ocean pH (ocean acidification).

There is sufficient observational evidence to demonstrate significant spatial, annual and short term variability of the marine carbonate system, including pH (Hofmann et al., 2011; Thomas et al., 2005, 2007; Bates, 2007) which reveal annual ranges of  $\sim$ 0.1 pH units in the open ocean to ranges of 1.0 pH units in near shore/estuarine systems. In the North Sea, away from the immediate coast the range of pH is 0.2–0.3 pH units, over an annual cycle (Clargo et al., 2015).

If leakage occurred at the sea floor the resulting pH change would scale with the release rate, but will dissipate with distance from the leak point. For a small leak a clearly anomalous pH signal may be restricted to a few metres from source (Dewar et al., 2013), consequently monitoring over an entire storage complex with limited resolution may well depend on identifying signals at some distance from the source that are similar to natural variability.

In this paper a previously evaluated marine system model of the North West European Shelf (Artioli et al., 2012; Blackford and Gilbert, 2007) is used to produce a three dimensional, 30 year time-series of marine pH (Section 2). The pH range and it's variability over relevant spatial and temporal scales are quantified along with a selection of criteria that could be useful indicators of anomalies (Section 3). These criteria are tested by applying a comprehensive range of pseudo leak signals to the model output, assessing how successful detection varies with the magnitude of the anomaly, its timing and the frequency of monitoring observations (Section 4). Finally the application of the outcomes to global offshore storage initiatives is discussed (Section 5).

#### 2. Model methodology

#### 2.1. The model system

The model system dynamically simulates the spatial and temporal evolution of DIC over the North West European Shelf and includes all of the processes that significantly alter DIC as outlined above. The model system has a long development history and has previously been used to examine carbonate chemistry in the region (Blackford and Gilbert, 2007; Wakelin et al., 2012; Artioli et al., 2012, 2014) and CCS leakage scenarios (Blackford et al., 2008). The model system (Fig. 1) comprises of a coupling between a 3D hydrodynamic model (POLCOMS, Holt and James, 2001), the ERSEM model of marine ecosystems (Baretta et al.,

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