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Environmental risks and performance assessment of carbon dioxide (CO_2) leakage in marine ecosystems

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Abstract: This chapter describes the state of the current understanding of the potential for CO_2 leaked from carbon dioxide (CO_2) capture and storage (CCS) to impact the marine ecosystem. This is a complex problem as it requires an understanding of physical dispersion, the behaviour of plumes, marine chemistry, organism physiology and ecological relationships. Aside from predicting the likelihood of a leak event, the key issue is to understand the spread, persistence and impact of a hypothetical CCS derived leak and contrast this with, for example, trawling impacts and the global long-term consequences of climate change and the uptake of anthropogenically created atmospheric CO_2 (ocean acidification), which CCS seeks to mitigate. Excess CO_2 in the marine system is undoubtedly harmful to many organisms. In the vicinity of a leak event, it is likely that significant ecological alteration would occur. Initial research indicates that only persistent leaks of a significant proportion of reservoir capacities would cause widespread and unacceptable impacts. However, much more research is required to determine critical leak magnitudes, within sediment interactions and ecosystem recovery before any comprehensive risk assessment of CCS can be delivered.

Key words: carbon dioxide capture and storage, leakage, marine, environment, ecosystem, CO_2, pH.

13.1 Introduction

In this chapter we review existing knowledge on both the dynamics and dispersion of carbon dioxide (CO_2) emanating from a failure of CCS and on the potential environmental impacts that may result. From the marine perspective, two forms of CCS are pertinent, storage in geological reservoirs under shelf seas and deep sea sequestration. Deep sea CO_2 sequestration is a proposal by which CO_2 is injected into deep water where it forms semi-stable clathrates, although there is much debate as to the stability and longevity of this form of storage. Broadly speaking, from a marine environmental perspective, leaks from geological storage systems may take two forms, either a breakdown of infrastructure such as a pipeline, that would release CO_2 directly into the bottom of the water column, or a geological failure resulting in a percolation of CO_2 through various geological strata, the biochemically active sediment layers (benthos) and then into the (pelagic) water column.

Many scientific disciplines need to be integrated to form a full understanding of leak impacts, amounting to a significant research challenge. These are:

- fluid and gas dynamic processes that determine the micro to mesoscale dispersion of CO_2 both in water and within sediments;
- carbonate chemistry describing the behaviour and chemical impacts of dissolved CO_2 in seawater;
- marine hydrodynamics addressing dispersion and mixing on meso to macroscales;
- physiological and biochemical responses of marine processes, flora and fauna to changes in carbonate chemistry;
- ecological assessments of the impacts on communities, ecological functionality and resources.

Whilst some research specific to CO_2 discharge from CCS exists, focused either on the dynamics of direct sequestration to deep water or geological sequestration under shelf seas, research into ocean acidification also provides relevant insights especially into impacts. Ocean acidification is the process by which anthropogenic CO_2 released to the atmosphere is slowly absorbed into the world's oceans causing a shift in carbonate chemistry and a lowering of pH. This chemical response is identical to that which would occur from a CCS derived CO_2 leak, differing only in scale and magnitude. Prevention of ocean acidification and climate change is the objective of mitigation methods such as CCS. In summary, existing research can provide a first-order answer to questions about dispersion and impact, but further research is required to reduce the significant uncertainties and achieve cross-disciplinary integration.

The marine system faces many challenges over the coming decades. It is vulnerable to climate change, increased fishing pressures and pollution whilst at the same time it provides a vital component in the regulatory earth system and is of huge economic and societal importance. It is vital, therefore, that any risk assessment of CCS includes a risk assessment of the potential impacts on the marine ecosystem.

In this chapter, Section 13.2 details the physical and chemical behaviour of CO_2 in seawater and Section 13.3 details the potential range of ecological impacts. Section 13.4 discusses the options for monitoring the marine system for leaks, with the mitigation of CCS leaks briefly discussed in Section 13.5. Future trends are summarised in Section 13.6.

13.2 The physical and chemical behaviour of carbon dioxide (CO_2) in the marine system

13.2.1 Carbonate (CO_2) chemistry in the marine system

The behaviour of dissolved CO_2 in seawater (the carbonate system) is well constrained, equilibrium constants are extensively published and, although there are variations in particular constants emerging from different studies, a consistent, robust approach is generally possible (e.g. Zeebe and Woolf-Gladrow, 2001 amongst others). Four parameters of the carbonate system can be analytically determined: dissolved inorganic carbon (DIC), total alkalinity (TA), pH and the partial pressure of CO_2 in the water (pCO_2w). Knowledge of any two of these variables is sufficient, given appropriate meta data, to derive the other two and a number of biogeochemically important parameters such as bicarbonate and carbonate ion concentrations and carbonate saturation states (Zeebe and Woolf-Gladrow, 2001).

CO_2 added to seawater exists as dissolved gaseous CO_2, a proportion of which reacts to form carbonic acid (H_2CO_3) which then dissociates to form bicarbonate (HCO_3^-), releasing hydrogen ions to solution (equations 13.1 and 13.2). These hydrogen ions then combine with carbonate ions (CO_3^{2-}) to form more bicarbonate (equation 13.3).

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \qquad [13.1]$$

$$H_2CO_3 \Leftrightarrow HCO_3^- + H^+ \qquad [13.2]$$

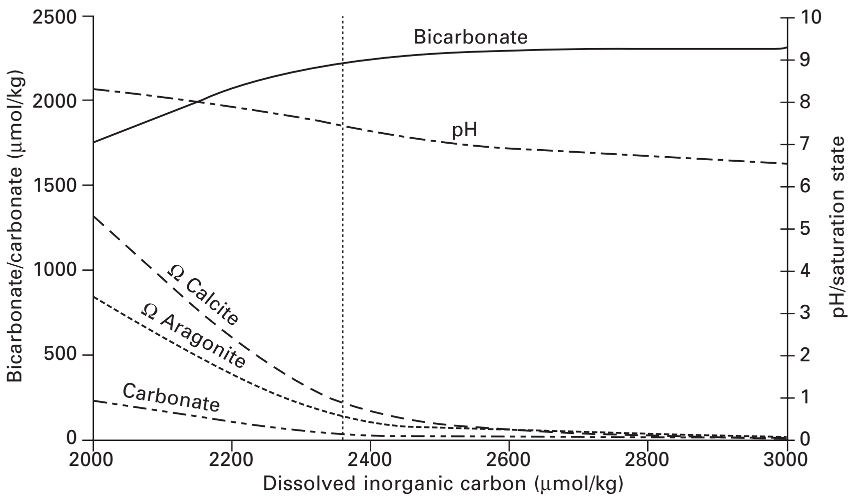
$$CO_3^{2-} + H^+ \Leftrightarrow HCO_3^- \qquad [13.3]$$

Hence, adding CO_2 to seawater results in an increase in bicarbonate ions, a decrease in carbonate ions and an increase in hydrogen ions or acidity (decreasing pH) (Fig. 13.1). Such changes are problematic for marine biogeochemical cycles and ecosystems as many biochemical and physiological processes are affected by pH, and bicarbonate and carbonate are substrates for some of the most fundamental marine processes such as photosynthesis and calcification. Calcification, the generation of hard shells by many types of marine flora and fauna (corals, coccolithophores, pteropods, molluscs, echinoderms, etc.), is a process that produces CO_2 and is therefore inhibited by excess CO_2 in the system (equation 13.4). Additionally the decrease in carbonate ions encourages dissolution of calcium carbonate (equation 13.5).

$$2HCO_3^- + Ca^{2+} \Leftrightarrow CaCO_3 + CO_2 + H_2O \qquad [13.4]$$

$$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-} \qquad [13.5]$$

Inhibition of shell formation obviously has consequences for the organism involved. The carbonate saturation state omega (Ω) represents the balance



13.1 Changes in key carbonate system parameters for rising concentrations of DIC. The present day status is approximated by the left-hand limit of the figure. The approximate maximum predicted perturbation likely from ocean acidification is marked by the dashed vertical line. CCS leakage could provoke perturbations beyond the right-hand limits of the figure but only for restricted volumes and durations. Left axis, bicarbonate and carbonate ion concentration (μmol kg^{-1}); right axis, pH and carbonate saturation state. (The saturation states are the product of the concentrations of the reacting ions divided by the product of those ions at equilibrium, hence saturation states below 1 indicate that mineral carbonate will dissolve into the surrounding seawater.) Calculations made for surface waters at 10 °C, a salinity of 36 psu, with an alkalinity of 2324 μmol kg^{-1}.

between dissolution and mineralisation, with values below 1 indicating net dissolution is thermodynamically favoured (Fig. 13.1).

13.2.2 Predicted changes in carbonate chemistry likely from ocean acidification and carbon capture and storage (CCS) leakage

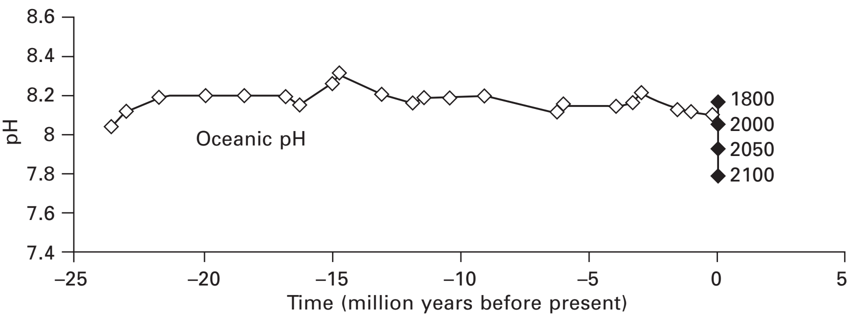
The marine system is highly buffered with respect to changes in CO_2, but only via slow millennial scale processes such as erosion. Consequently, the marine system has evolved with a very stable carbonate system for potentially over 20 million years (Pearson and Palmer, 2000), with global mean pH in the range 8.0–8.2. However, the comparatively short-term perturbations such as ocean acidification (the uptake of anthropogenic atmospheric CO_2 by the oceans) or leaks from CCS systems alter pH, ion concentrations and omega far beyond the ranges experienced over the evolutionary timescales of contemporary species.

Broad-scale predictions of the oceanic uptake of atmospheric CO_2 and the consequences for the marine carbonate system are tractable and reasonably robust. It is predicted that global mean ocean pH will fall significantly to pH 7.5 or less within the timeframe of 100–300 years (Caldeira and Wickett, 2003, 2005) dependent on emission scenarios and mitigation. This fall represents an extreme and rapid perturbation from estimated marine pH over at least 20 million years (Fig. 13.2).

Many marine organisms depend on synthesising calcium carbonate structures, and their ability to perform this synthesis depends at least partly on the carbonate saturation state (Ω). Because of the dependence of saturation state on temperature and pressure, under-saturation ($\Omega < 1.0$) is a property of deeper waters and the depth of the saturation horizon (where $\Omega = 1.0$ and waters, above remain over-saturated and hence conducive to calcifiers) is an important diagnostic of the marine environment. The temperature dependency creates a latitudinal variation in the saturation horizon depth such that this depth is significantly shallower in polar waters. Global predictions of saturation state predict that polar surface waters will become under-saturated within decades due to ocean acidification (Orr *et al*., 2005; Steinacher *et al*., 2008).

The impacts of ocean acidification will be experienced globally, although some regions will be more sensitive. Further, the perturbation will persist for thousands of years before the natural processes of weathering, ocean circulation and carbonate buffering return pH and omega to normal values (Archer, 2005).

In contrast, the perturbation in carbonate chemistry caused by a leak from CCS has the potential to exceed the perturbation expected from ocean acidification but only in the vicinity of the leak and within any plume of CO_2 rich water that is created. The natural mixing of seawater caused by tides, etc. would act to disperse and dilute the CO_2-rich plume, restricting the spatial



13.2 Past (white diamonds, data from Pearson and Palmer, 2000) and contemporary variability of marine pH (black diamonds with dates). Future predictions are model-derived values based on IPCC mean scenarios (reprinted from Blackford and Gilbert, 2007).

scale of impact. If the leak was temporary then the water chemistry would return to normal within a relatively short timeframe (days to months, rather than the millennia required to mitigate ocean acidification). Thus a CCS leak could provoke a pH decrease to ~6.0, but its spread and persistence are likely to be restricted. These issues are explored in the following sections.

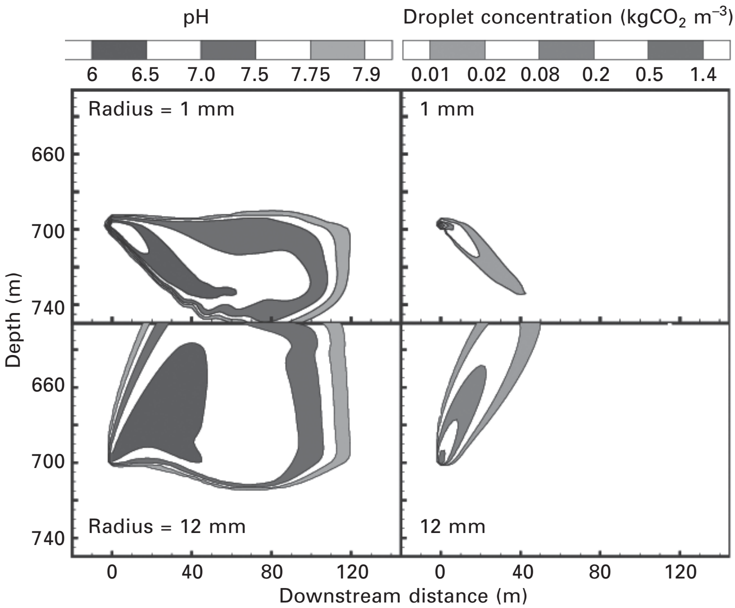
13.2.3 Fine-scale dynamics of (CO_2) droplets/plumes in marine systems

The initial behaviour of CO_2 injected into seawater is complex, as an understanding of fluid dynamics and bubble/droplet behaviour in the context of ocean turbulence on fine scales is required.

The fine-scale ocean can be defined as the volume where leaked CO_2 as a separate phase interacts with seawater, and it is important to take the turbulence generated by leaked CO_2 on ocean flow fields into account. The fine-scale dynamics of CO_2 leaked from the seabed into the water column depend on the physical-chemical properties of the CO_2/seawater system, the leakage depth and the form of leakage. CO_2 could potentially leak in two general ways, dilute leakage with a limited mass flux from natural dispersion through sediments and dense leakage with a high mass flux from fractures of geo-formation or failures of injection well and pipelines. Observations of small-field experiments (Brewer *et al.*, 2006) and natural leakage (Hall-Spencer *et al.*, 2008) demonstrate that leaked CO_2 enters the seawater column in the form of either bubbles or droplets. The bubbles/droplets are in a variety of sizes, ranging from millimetres to several centimetres, generated from the porous sediments or broken up from a CO_2 column leaked from fractures. CO_2 is more compressible than seawater at depths above 3000 m and soluble in seawater. CO_2 bubbles or droplets released above this depth could ascend, driven by buoyancy, as well as dissolve into seawater, causing the changes to the seawater carbonate system described above. The interaction of ascending CO_2 bubbles/droplets with ocean currents creates a bubble/droplet plume and a CO_2-enriched seawater plume in a turbulent ocean. A sample scenario of CO_2 droplet and CO_2-enriched plumes generated by a numerical model (Alendal and Drange, 2001) is shown in Fig. 13.3, for which the mass leakage (CO_2 injection) rate from a depth of 700 m is 1.0 kg/s and the initial droplet size is 12 and 1.0 mm in radius. For the fully developed plume, the spatial scale of dilution may vary from 10^2 to10^4 m and the associated temporal scale from hours to days.

The physical properties of carbon dioxide (CO_2)/seawater system

Two physical properties, the phase diagram and solubility, are important for estimating the behaviour of CO_2 in fine-scale seawater. According to the

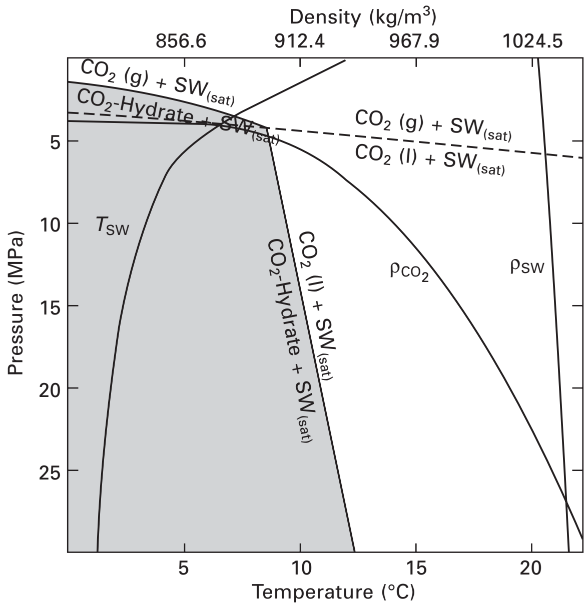


13.3 CO_2 droplet plume (right by droplet concentration) and CO_2-enriched seawater plume (left by pH) from numerical simulations: elapsed time is 30 min; injection rate is 1.0 kg CO_2 s^{-1}; ocean current speed is 5 cm s^{-1} (Alendal and Drange, 2001).

phase diagram, as shown in Fig. 13.4 (Nikolaus *et al*., 2008), leaked CO_2 can exist as a gas at depths roughly above 400m and as a liquid below that depth. A solid-like state, clathrate hydrate of CO_2, may form at the surface of CO_2 bubbles/droplets if the temperature of seawater is lower than 9 °C. This hydrate layer affects the dynamics of CO_2 and seawater, owing to the changes in features of the boundary layer and solubility. In general, CO_2 is more soluble in the deep ocean than in the shallower ocean because the solubility increases as pressure increases and temperature decreases. Another property which plays an important role in the development of CO_2-enriched seawater plumes is the increase of density of CO_2 solutions which provides a negative buoyancy causing high p_{CO_2} seawater to fall on to the seabed and affect benthic organisms.

Carbon dioxide (CO_2) bubble/droplet dynamics

To date, the research on transportation phenomena of an individual CO_2 bubble/droplet in seawater has been mostly focused on those at mid-ocean depths (Caldeira *et al*., 2005). Some ascending velocity data on droplets with and without hydrates have been obtained from both laboratory (Nikolaus *et al*., 2008) and small-scale *in situ* experiments (Brewer *et al*., 2002), while

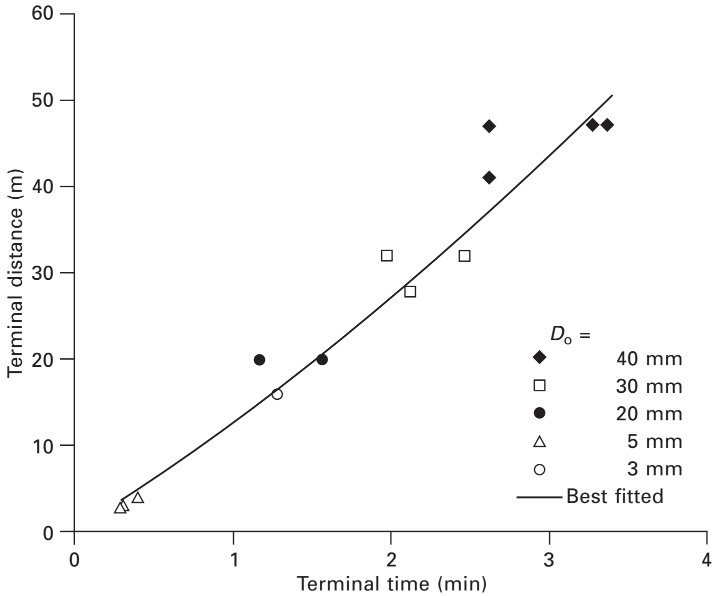


13.4 CO_2 phase diagram in the ocean (Nikolaus *et al.*, 2008).

a few data are available for CO_2 bubbles (Johnson *et al.*, 1969). Developed models calibrated against the data (Chen *et al.*, 2009) have been applied to simulate the dynamics of leaked CO_2 in seawater at various depths from 10 to 800 m (at temperatures from 5 to 25 °C) and for initial droplet/bubble sizes from 3.0 to 40.0 mm in diameter. A diagram of CO_2 terminal distance *vs* dissolution time obtained from model simulations shows that CO_2 droplets ascend at a mean speed of 11 cm/s and a mean shrinking rate of 7.0×10^{-3} mm/s in diameter approximately, if leaked from a deep-ocean (800~1000m) source. This speed and shrinking rate increase to 16 cm/s and 30×10^{-3} mm/s at middle-deep ocean (500~650 m) and finally reach 22 cm/s and 0.2 mm/s at shallow ocean (< 150 m), as shown in Fig. 13.5.

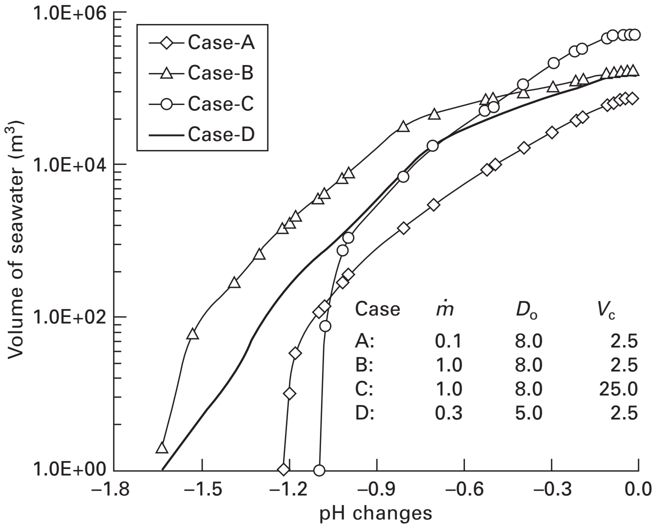
Fine-scale dynamics of carbon dioxide (CO_2) and CO_2-enriched seawater plumes

Recent observations of natural volcanic CO_2 vents (Hall-Spencer *et al.*, 2008) found that continuous leakage of CO_2 at a rate of 1.43×10^6 litre a day in an area of about 3000 m^2 lowers the pH of the water column at gradients of normal pH (8.1~8.2) to lowered pH (mean 7.8~7.9, minimum 7.4~7.5). It has been noted, however, that a purposeful field experiment on CO_2 plumes in the shallow ocean has not been carried out so far. An *in situ* experiment (Brewer *et al.*, 2006) at mid-ocean depths successfully



13.5 CO_2 bubble dissolution in shallow ocean, terminal distance vs time. The gradient of the curve is the mean velocity and the shrinking rate of bubble can be estimated by bubble size and associated terminal time (Chen *et al.*, 2009).

monitored the dispersion of CO_2 droplet plumes for more than 25 minutes from 1100 m to 750 m. A two-phase turbulent plume model calibrated by the data from the observation predicts that the pH change in seawater owing to CO_2 dissolution is directly proportional to the leakage mass flux ($\dot{m}$, kg/s/m^2) and inversely proportional to initial droplet/bubble size (D_o, mm) and ocean current speed (V_c, cm/s), as shown in Fig. 13.6. In the case of the mid-ocean, if $\dot{m} = 0.1$, $D_o = 8.0$, and $V_c = 2.5$, the maximum pH change is about –1.2 with a water volume less than 60 m^3 (case A). This pH change increases to –1.7 pH units when leakage mass flux increases to one (case B) and reduces to –1.0 pH units with water volume of 300 m^3 when ocean current increases to 25 (case C), respectively. The smaller the droplet size the larger the pH changes that could be produced (Case D and also the top panel of Fig. 13.3). The mean CO_2-enriched seawater volume developed from CO_2 leakage positioned in a turbulent ocean is also simulated. The results show that a fully-developed plume volume with pH changes greater than –0.1 could reach up to 1.0×10^6 m^3 within 30 minutes of onset of the source.



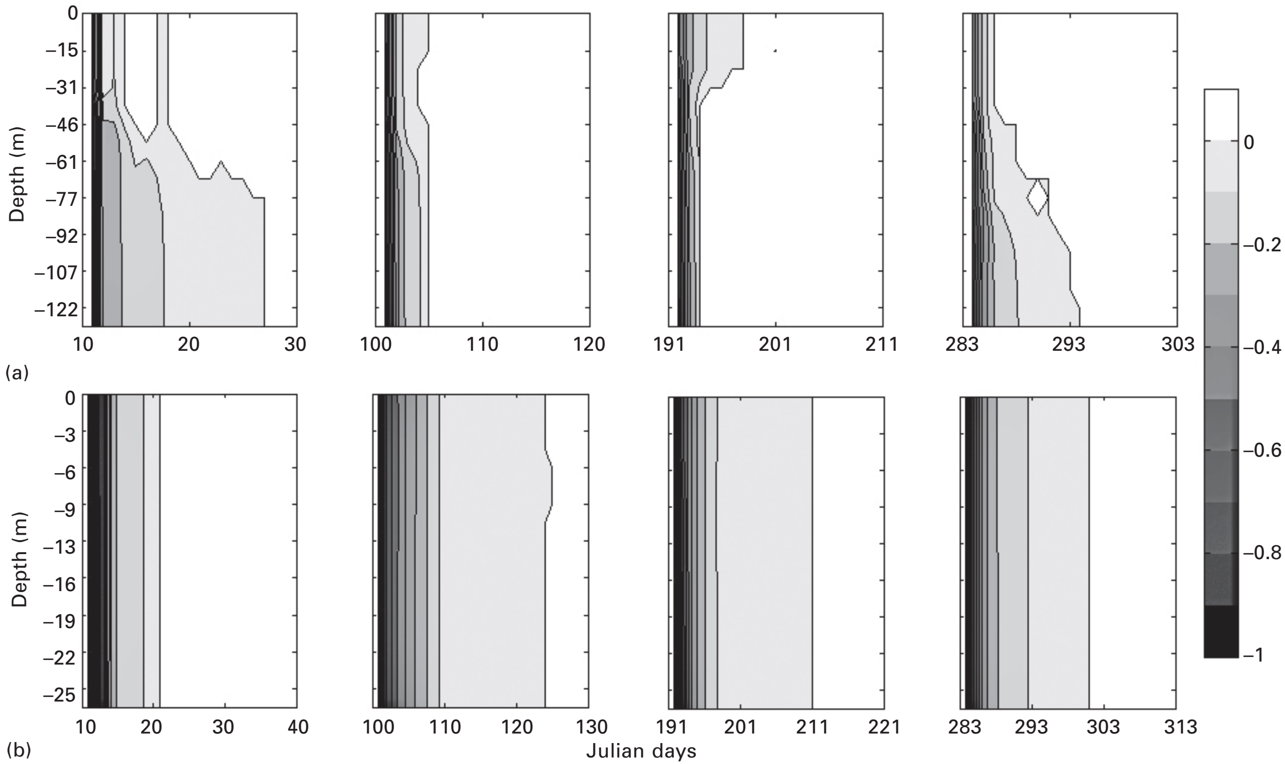
13.6 Full-developed CO_2-enriched plume properties indicated by plume volume vs pH changes (Chen *et al.*, 2007).

13.2.4 Regional scale modelling of carbon capture and storage (CCS) leakage, approaching ecosystem scales.

Shelf seas are typically subject to disruption from a variety of events such as fishing, dredging, eutrophication and pollution. A leak from a CCS installation would inevitably cause some disruption to the local ecosystem; however, the key question for risk assessment is to determine the spatial and temporal scales of disruption and assess whether the impact would be significant in ecological, regional or economic scales.

This contextual aspect has been partially addressed using coupled hydrodynamic–ecosystem models to quantify the possible spatial range and temporal persistence of perturbations arising from a failure of geological storage in shelf seas (Blackford *et al.*, 2008, 2009). In particular, this work has explored what size of leak event would be needed to produce an environmentally damaging response over a significant area.

Figure 13.7 illustrates a short-term leak scenario of $\sim 1.5 \times 10^5$ t CO_2 over one day, at four different times of the year at two sites in the North Sea. The north site is a deep water column (130 m) in the Forties field, the south site a shallow region (30 m) in the Viking field. The leak rate approximates to 50x the input rate at the Sleipner field, i.e. rather large. This leak rate provokes pH perturbations that exceed 0.5 pH units for about a day at the north site and up to five days at the south site. The duration of disturbance is



13.7 Temporary point–source leak scenario (x50 pipeline capacity): (a) South site, (b) North site. All perturbations below 0.01 pH unit have been masked for clarity. Perturbations below 0.2 pH units indicate little likely impact, those between 0.2 & 0.5 pH units indicate potential damage and those over 0.5 pH units indicate that significant damage is likely. These results illustrate the mean perturbation over an area of 50 km^2 (adapted from Blackford *et al.*, 2009).

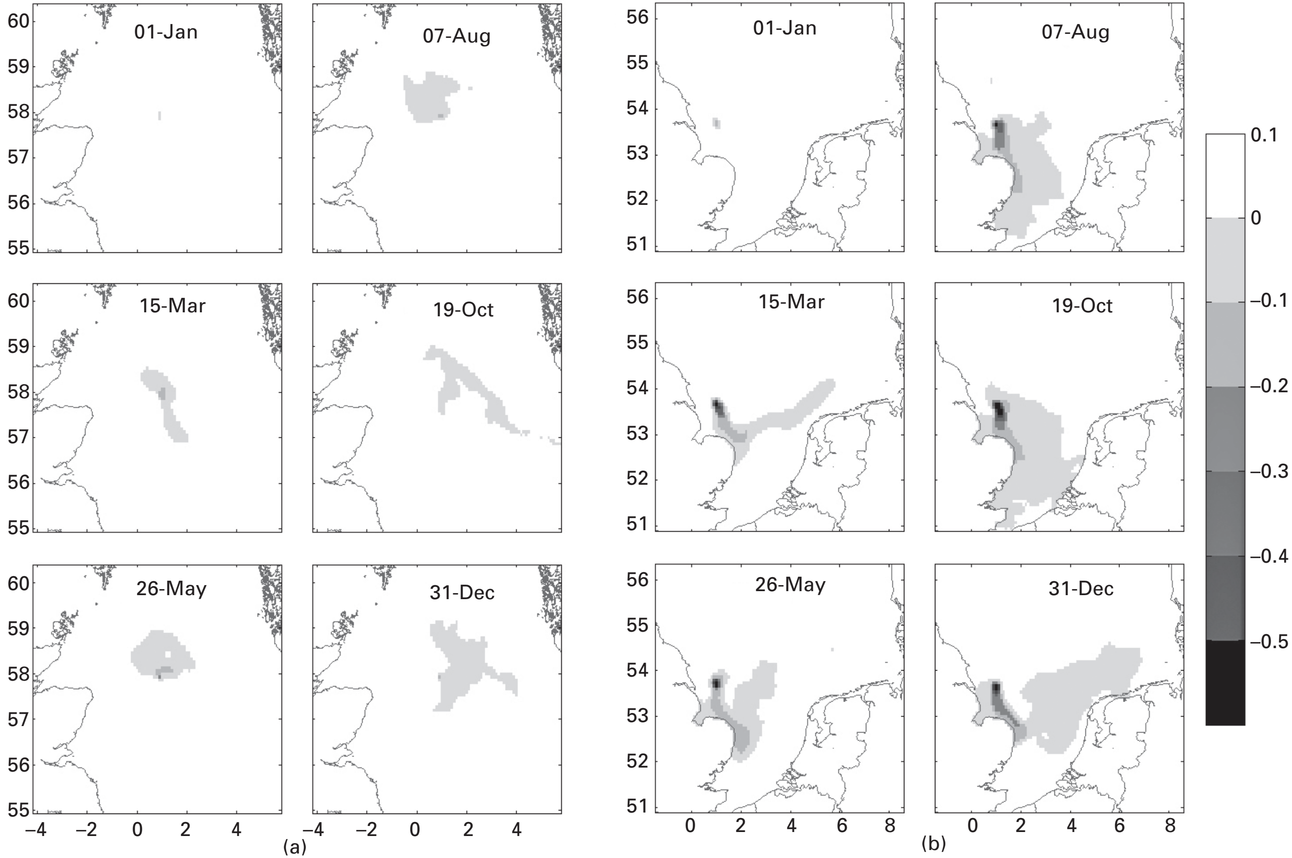
less than 10 days for the north site and as much as 20 days for the south site. The perturbation is the mean effect over an area of ~50 km^2. This scenario indicates the approximate scale of leakage required to provoke what may be serious environmental consequences on a regional scale, although there are few observations that quantify the consequences of a short sharp pH perturbation, such as simulated here. The difference between sites is simply driven by the relative depth of the water columns and the assumption of the initial distribution of dissolved CO_2.

A large-scale long-term leak scenario – perhaps representing some catastrophic failure of sequestration – is illustrated for the same two sites in Figs 13.8 and 13.9. Here, the leak rate is ~ 5x the input rate at Sleipner and is continuous over one year, the total injection of CO_2 amounting to ~5.5×10^6 t over one year. The results show, for both sites, an area of high perturbation centred over the release (approximately 50 km^2). In the north, this perturbation does not exceed 0.5 pH units; in the south, a perturbation sometimes exceeding 1.0 pH units is recorded. The area of maximum disturbance in both cases remains well constrained, although a plume of acidified water is seen to spread from the release point driven by the regional circulation. This plume can be extensive, although the majority of the plume area is acidified by significantly less than 0.1 pH units.

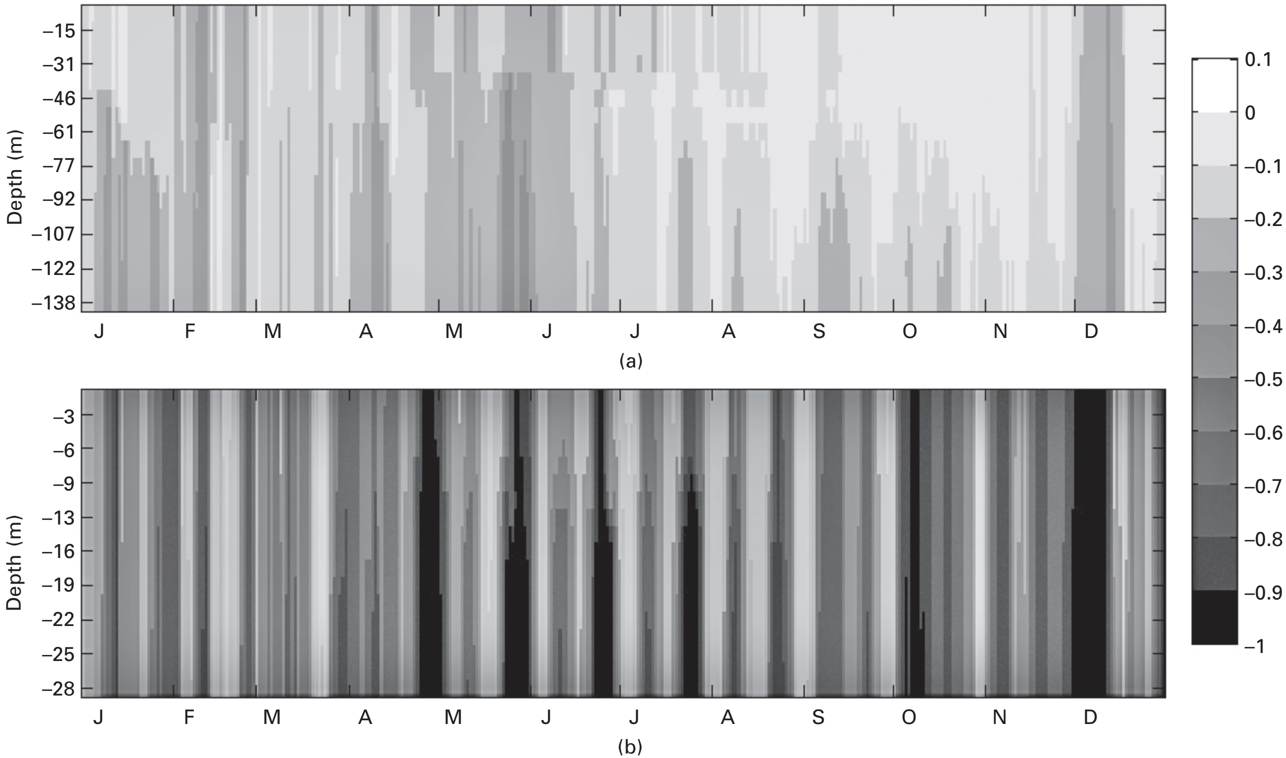
Examination of the chemical signal at the leak epicentre (Fig. 13.9) for both release sites clearly shows the influence of the tidal cycle in determining the instantaneous perturbation strength. Perturbation maxima are associated with neap (weak) tides and minima with springs and can differ by 0.4 or 0.8 pH units depending on site and wind strength. This suggests not only that the timing of leaks may be significant but also that a consideration of the siting of CCS systems in relation to tidal mixing patterns would be prudent.

A number of clear conclusions can be drawn from this work. First, it would require a very large or persistent leak to produce a perturbation in carbonate chemistry of sufficient magnitude to have ecological implications on a regional scale. Second, the key dispersion vector in the short to medium term is the strong tidally driven mixing in the region, rather than out-gassing of dissolved CO_2 to the atmosphere. Third, the spatial and temporal variability in tidal mixing can have a significant influence on the rate of dispersion and, consequently, the chemical signature at the leak epicentre.

Parameterising the likely magnitude and duration of a leak event is clearly difficult, as there is little evidence to base estimates on. Scenarios similar to the above using smaller CO_2 injection rates showed proportionally smaller perturbations at a regional scale. However, this model system has a horizontal resolution of ~7 km and does not resolve the fine-scale perturbation as described in the previous section.



13.8 Continuous point-source leak evolution: (a) North site, (b) South site, instantaneous snapshot times as stated. All perturbations below 0.01 pH unit have been masked for clarity. Damage potential is as described for Fig. 13.7 (adapted from Blackford *et al.*, 2009).



13.9 Continuous point-source leak as in Fig. 13.4 showing the evolution of pH perturbation at the leak location, indicating the mean state for an area of ~50 km^2 : (a) North site, (b) South site. Damage potential is as described for Fig. 13.7 (adapted from Blackford *et al.*, 2009).

13.3 Marine ecosystem impacts of carbon dioxide (CO_2) leakage

CO_2 sequestration in sub-seabed geological formations at depth, and thereby pressure, will result in the formation of hydrates. By contrast, shallow sea sequestration, such as proposed for the North Sea, will not; the gas would remain buried but in a liquid, or semi liquid state that would be buoyant if released. As such, CCS failure leakage scenarios are site specific and each is potentially different from another. Modelling studies have shown that in the case of leakage from sub-seabed CO_2 storage sites, any plume of acidified seawater will dissipate rapidly through continuous mixing by tides and currents (Blackford *et al.*, 2008). So, any exposure likely to be experienced by pelagic organisms may be brief. However, a leak that percolates up through the sediment or occurs near the sea floor could significantly alter the chemistry of the seawater both within and just above the seafloor. Consequently, the impacts of leakage could be severe for benthic organisms that have limited capacity to escape from an affected area. There is now a considerable body of evidence that describes the vulnerability of species and processes to exposure to excessive CO_2, which are described below. Whilst much of this experimental work has been performed in the context of ocean acidification impact research, the pH manipulations used are often a close mimic of the more extreme pH/CO_2 ranges that would occur with a CCS derived event as this enables scientists to better assess the functional response to decreasing pH.

The majority of the impact studies to date have concentrated on pH reductions due to atmospheric deposition of CO_2 and with no regard for the interactions between any contaminants that may be present in the water body. The failure of a CCS installation would, in some instances, result in the remobilization of CO_2 into the surrounding seas. However, the impact of the released CO_2 on the biota will vary depending on factors such as its industrial source, the process of liquefaction and residual gases such as H_2S, SO_x and NO_x. In addition, any residual chemicals associated with the original drilling activities as well as those occurring naturally, such as metals, minerals and previously unrecovered oil, could be released. Liquefied CO_2 is highly corrosive requiring that the pipework for the delivery system would need to have a protective coating to prevent corrosion. Many of the products used to prevent corrosion are themselves toxic thereby adding yet another confounding factor to any assessment of likely CCS leakage impact.

There is a rapidly growing body of published data indicating that exposure to elevated levels of dissolved CO_2 and the associated changes in carbonate chemistry (e.g. pH and carbonate saturation state) can have a considerable deleterious effect on many marine organisms and processes. In the following sections we identify the main impacts on an organism's basic biological functions, examine the consequences for animal health, survival and reproduction, and explore the implications for the maintenance of marine communities and processes.

13.3.1 Organism physiology

A number of recent efforts have been made to review the available evidence from experimental observations and describe the likely impacts of exposure to CO_2 acidified seawater (including elevated dissolved CO_2, H^+ and HCO_3^- concentrations, plus reduced CO_3^{2-} concentration) on the physiology, performance and survival of marine organisms (Seibel and Walsh, 2001, 2003; Pörtner *et al.*, 2005; Pörtner, 2008; Pörtner and Farrell, 2008; Widdicombe and Spicer, 2008). These studies conclude that exposure to acidified seawater in the pH range 6.0–7.8 has the potential to disrupt a number of intracellular and extracellular physiological processes, across a range of taxonomic groups: echinoderms (Kurihara and Shiriyama, 2004; Kurihara *et al.*, 2004, 2007; Miles *et al.*, 2007; Wood *et al.*, 2008), molluscs (Michaelidis *et al.*, 2005; Berge *et al.*, 2007; Bibby *et al.*, 2007, 2008; Gazeau *et al.*, 2007; Beesley *et al.*, 2008), crustaceans (Metzger *et al.*, 2007; Pane and Barry, 2007; Spicer *et al.*, 2007) and sipunculids (Langenbuch and Pörtner, 2002, 2004; Langenbuch *et al.*, 2006).

The primary effect of exposure to acidified seawater is to decrease the pH of the body fluids (i.e. blood or haemolymph); known as acidosis. For many marine animals, the response to this extracellular acidosis is to increase the amount of bicarbonate ions within the body fluids to create near full or partial pH compensation. This is achieved predominantly through active ion transport processes in the gills (see Widdicombe and Spicer, 2008; and refs therein). However, recent studies have shown that for some invertebrates there is only partial, or no, compensation in hypercapnia (too much CO_2 in the blood) induced disturbance of extracellular acid-base balance, e.g. the mussel *Mytilus edulis* (Zange *et al.*, 1990), the crabs *Callinectes sapidus* (Wood and Cameron, 1985) and *Chionoecetes tanneri* (Pane and Barry, 2007) and the sea urchin *Psammechinus miliaris* (Miles *et al.*, 2007). To ensure the effective maintenance of intracellular pH, extracellular pH needs to be maintained 0.5–0.8 pH units above intracellular pH (Pörtner *et al.*, 2004). Consequently, any lack of regulatory capacity is important because countless cellular functions and regulations depend upon maintaining a specific intracellular pH (Putnam and Roos, 1997). Additionally, the maintenance of extracellular pH is also important for the function of respiratory proteins, with both pCO_2 (i.e. a specific CO_2 effect; Mangum and Burnett, 1986) and acidity having pronounced effects on oxygen binding by respiratory pigments; hemoglobins (Weber, 1980), hemocyanins (Mangum 1997), but particularly the annelid pigments erythrocruorin and chlorocruorin (Weber, 1980).

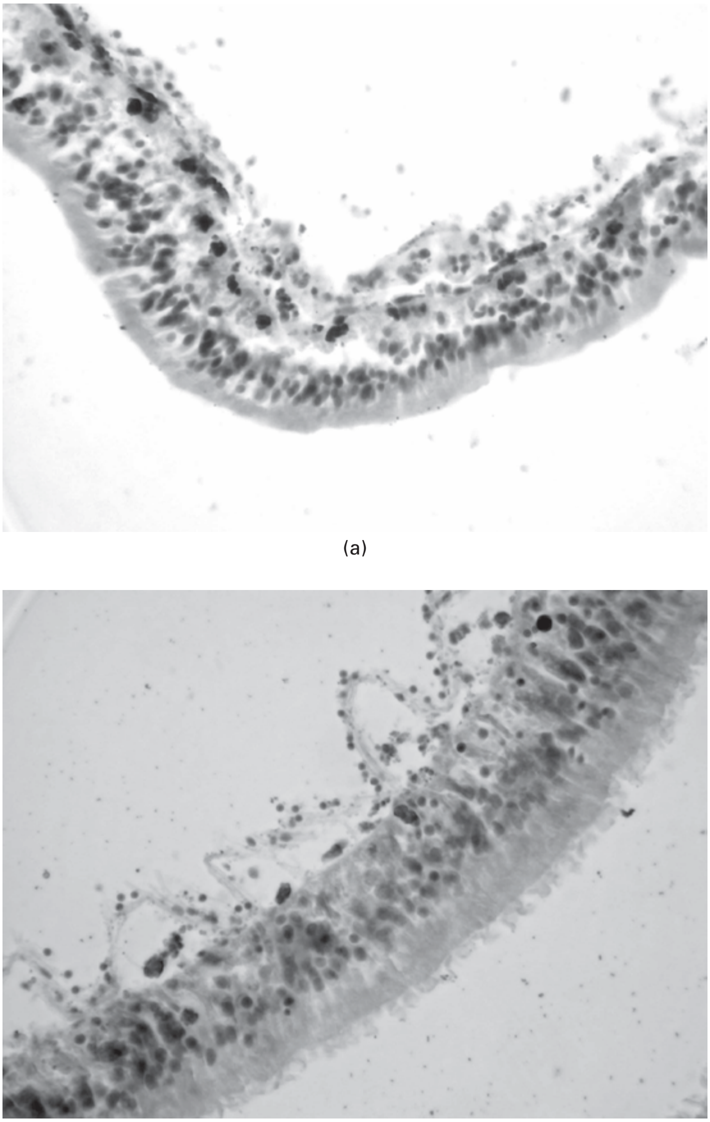
13.3.2 Organism health and survival

There is a growing body of research evidence to indicate that a reduced pH environment has a negative effect on animal growth, performance and health. Impacts on general health status reported have included immunosuppression in *Mytilus edulis* (Bibby *et al*., 2008) and narrowing of thermal tolerance in the edible crab *Cancer pagurus* with increasing CO_2 concentrations (Metzger *et al*., 2007). Wood *et al*. (2008) observed muscle wastage in the brittle star *Amphiura filiformis* which was associated with stimulation of calcium deposition for new arm growth. The capacity to upregulate calcium production in reduced pH environments receives support from studies by Gil-Martens *et al*. (2006) who observed bone remodelling and increased bone volume in salmon smolts maintained in a reduced pH environment; however, and again in support of the studies by Wood *et al*. above, there was evidence of reduced soft tissue growth. Beesley *et al*. (2008) observed that within seven days of exposure to reduced pH the lysosomes in mussel blood cells were exhibiting reduced membrane stability which is indicative of a decline in health status. Cardiac output was shown to decrease in yellowtail finfish (*Seriola quinqueradiata*) at reduced pH (Ishimatsu *et al*., 2005). Sea urchins (*Echinocardium incordata*) maintained at pH 6.8 for 30 days experienced disruption of the basement membrane of the gut epithelium and changes in the morphology of the mucous-rich apical cytoplasm (Fig. 13.10, PML unpublished data). There is also an extensive literature on the effects of some of the types of chemical contaminants associated with CCS installation leakage listed above to indicate that they also have an adverse effect on the same cellular processes (Sprague and Logan, 1979; Morse *et al*., 1982; Cranford and Gordon, 1991,1992; Olsgard and Gray, 1995; Fernley *et al*., 2000; Barlow and Kingston. 2001; Taban *et al*., 2004; Armsworthy, 2005). By contrast, there is a distinct lack of information on the consequences of any interactions between these two factors on animal health which may be additive or synergistic or both.

13.3.3 Impact on growth and reproduction

A general feature of many studies investigating the effects of a reduced pH environment for a range of organisms is that the greatest impacts are seen in eggs followed by larvae and early life stages with adults being the least affected (Haugan, 2004). In addition, Kikkawa *et al*. (2008) hypothesized that active species are more sensitive to elevated levels of CO_2 than inactive ones. By contrast, Seibel and Walsh (2003) hypothesized that deep sea animals with low metabolic rates are more sensitive to high CO_2 conditions.

Reduced egg production has also been reported in copepods and decreased hatching success in gastropods (Raven *et al*., 2005). Also in copepods, Kurihara



(a)

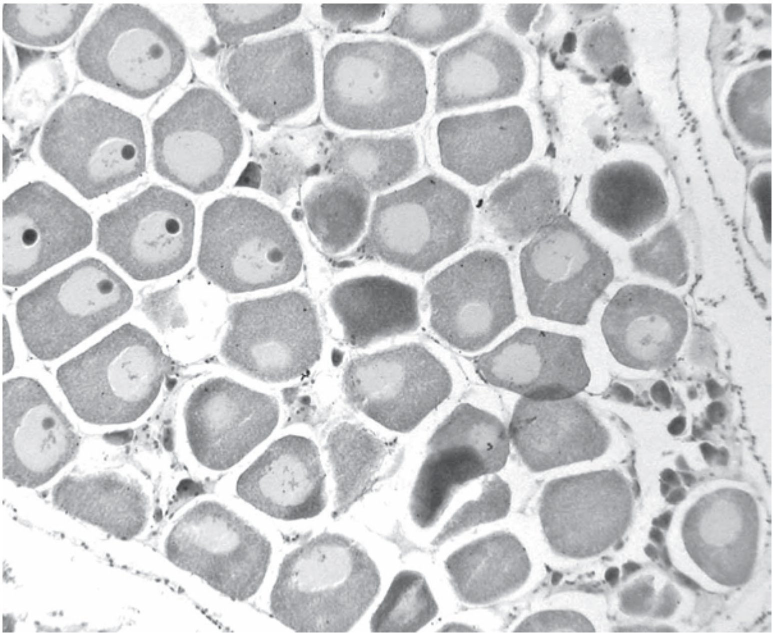
(b)

13.10 (a) Section of intestinal wall in sea urchin from reference treatment group at pH 8.0. (b) Section of intestinal wall in sea urchin maintained at pH 6.8 showing disruption of basement membrane on coelomic surface and enlarged and disrupted apical surface on luminal surface.

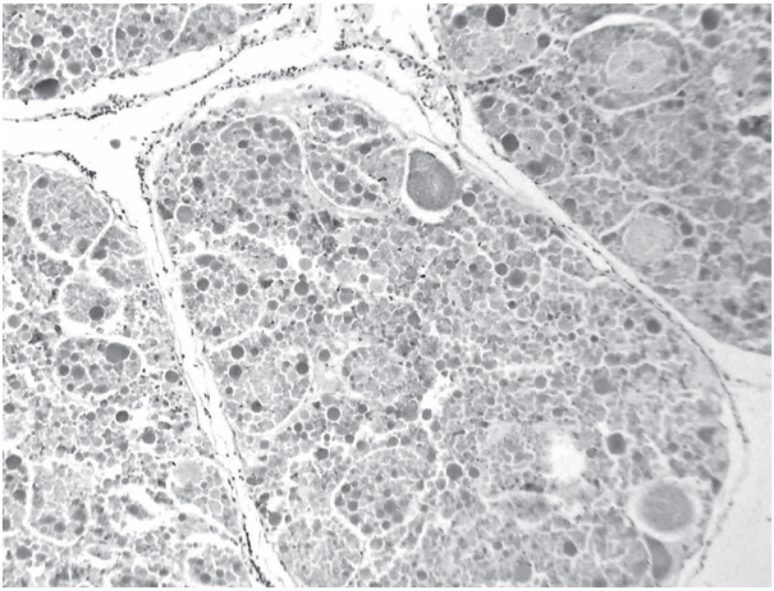
and colleagues (2004) noted decreased hatching rate and increased nauplius mortality at lowered pH (range 6.40–7.48). Other reported impacts have included a reduction in sperm motility broadcast in spawning invertebrates such as sea urchins (Havenhand *et al*., 2008) and Pacific oysters resulting in reduced fertilization success. Developmental impairment has been observed in sea urchins (Kurihara and Shirayama, 2004) and oysters (Kurihara *et al*., 2007); weakening of the shell structure (Green *et al*., 2004; Shirayama and Thornton, 2005; Haugan *et al*., 2006), dissolution of the protective armour of coccolithophors (Reibesell *et al*., 2000), forminiforera and pteropods. Slower growth in corals has been reported which could impact on reproductive success in those species where reproductive maturity is related to size and not age (Sakai, 1998a,b). Growth was also shown to be reduced in mussels following reduced pH exposure (Michaelidis *et al*., 2005; Berge *et al*., 2006), sea urchins and gastropods (Shirayama and Thornton, 2005). Abnormal larval development including altered skeletal proportions and symmetry was reported in brittle stars by Dupont *et al*. (2008) following exposure in reduced pH (7.7 and 7.9) after between five and six days with an associated marked increase in mortality. Increased larval mortality was also observed of bivalves during settling (Green *et al*., 2004; Raven, *et al*., 2005) and in sea bream (Kikkawa *et al*., 2004) following exposure of the eggs to seawater at reduced pH (pH 5.9 and pH 6.2). Whilst some capacity to regulate slight changes in pH (0.5 pH units over 8 days) was demonstrated in the sea urchin *Psammechinus miliaris*, more severe conditions resulted in high mortality rates (Miles *et al*., 2007). Egg maturation was shown to be severely disrupted in brittlestars (*Ophiura ophiura*) maintained at pH 6.5 as compared to reference treatment animals maintained at pH 8.0 (Fig. 13.11, PML unpublished data)

13.3.4 Community structure and diversity

The world's oceans contain enormous biological diversity (May, 1994; Reaka-Kudla, 1997), and most of this biodiversity, 98 % of all marine species, is made up of invertebrates either residing in (infauna) or on (epifauna) sediments (Snelgrove, 1999). This incredible diversity results from complex interactions between the underlying physical and environmental conditions, such as depth, temperature, organic supply and granulometry, and the biological interactions operating between and within benthic organisms, such as predation and competition (May, 1994). To date, there have been very few published studies describing the impact of CCS leakage on these important processes and the consequences for the diversity and structure of intact marine communities. Widdicombe *et al*. (2009) conducted a mesocosm experiment to quantify the direct effects of short (two weeks) and long (20 weeks) term exposure to acidified seawater on the structure and diversity of macrofaunal and nematode assemblages in two different sediment types; one muddy and one sandy. (A mesocosm is a medium sized enclosed experimental facility that aims to mimic the natural environment by maintaining a community of animals under close to natural conditions.) The experiment showed that



(a)



(b)

13.11 (a) Section of reproductive tissue in brittlestars from reference treatment group at pH 8.0 showing late maturing eggs. (b) Section of reproductive tissue from brittlestars maintained at pH 6.5 showing severe disruption of late maturing eggs.

communities were made up of species with different tolerances to high CO_2. Consequently, exposure to acidified seawater significantly altered community structure and reduced diversity for both macrofaunal and nematode assemblages. However, the impact on nematodes was seen to be less severe than the impact on macrofauna.

Two other studies have addressed the impacts of high CO_2 on biological interactions. The first, by Bibby *et al.* (2007), showed that the intertidal gastropod *Littorina littorea* produce thicker shells in the presence of predation (crab) cues but this response was disrupted at low seawater pH. This result demonstrated that CCS leakage could have indirect biological effects by disrupting the capability of organisms to express induced defences, hence, increasing their vulnerability to predation. In the second, Dashfield *et al.* (2008) used a mesocosm experiment to determine whether the presence of an important bioturbating species, the burrowing urchin *Echinocardium cordatum*, might influence the response of a nematode community to seawater acidification. They found that the urchin was vulnerable to elevated levels of CO_2, and its removal resulted in a significant change in the nematode community. A further concern is that any change in community structure or diversity could lead to a reduction in a number of key ecosystem functions, in particular the cycling of nitrogen, especially as shelf seas are known to host a disproportionately large fraction of productivity (Field *et al.*, 1998).

13.3.5 Nitrogen cycling

Of the very few studies that have been conducted to specifically examine the impact of CCS leakage on nitrogen cycling, all have reported significant effects. Huesemann *et al.* (2002) demonstrated that rates of ammonium oxidation to nitrite or nitrate (nitrification) were reduced by approximately 50 % at pH 7, by more than 90 % at pH 6.5 and were completely inhibited at pH 6. Whilst not directly measuring nitrification rates, the results of Widdicombe and Needham (2007) and Widdicombe *et al.* (2009) support the assumption that reduced seawater pH will inhibit the microbial oxidation of ammonium. In sediments the majority of nitrate used to fuel denitrification comes from nitrification rather than from the overlying water, particularly within the burrows of benthic species. Consequently, seawater acidification will inhibit the production of nitrate within the sediment and result in a greater sediment uptake of nitrate from the overlying water (Widdicombe and Needham, 2007; Widdicombe *et al.*, 2009). In addition, many benthic species have been shown to modify the exchange of nitrogen between the sediment and the overlying water (e.g. Widdicombe and Austen, 1998; Olsgard *et al.*, 2008). Deleterious effects on these organisms will have significant effects on nutrient flux rates. From the limited evidence available to date, it could be hypothesized that CCS leakage would significantly alter rates of nutrient cycling, either directly through impacts on bacteria or indirectly through changes in the structure and function of infaunal bioturbators (the animals whose burrowing and feeding behaviour has the effect of mixing the sediments).

13.4 Leak monitoring options

Monitoring the marine environment for CO_2 leakage could follow one or a combination of three methods, surveying for physical disruption to the sediment surface caused by geological seepage, detection of the chemical signal in the water column or detection of biological impacts. The stochastic nature of a leak event, the difficulty of predicting when, where and how much CO_2 and the shape of the dispersion plume, poses severe problems for an economical and efficient monitoring system. Based on existing research, it is impossible to gauge an appropriate spatial temporal distribution of monitoring that would guarantee a high certainty of detecting an event. Two developments can assist; firstly, a refinement of the range of possible leak scenarios, looking towards both geological and engineering research; and secondly, a refinement of the existing marine models, described here, that would better characterize the behaviour and dispersal of CO_2 and the likely chemical signature that would result. Given this information, it would be possible to estimate the optimal density of observations required.

Leakage from systems hardware, principally delivery pipelines, would most efficiently be detected via pressure sensors within the pipelines, essentially existent technology. Monitoring within the marine environment requires some knowledge of the base-state. Whilst regions like the North Sea are fairly well characterized, they are extremely heterogenous and dynamic with respect to sediments, implying that physical detection of sediment surface disruption would be problematic. Conversely, the technology to examine sediment topology, sidescan sonar, exists, is affordable, and can cover large areas efficiently.

The pelagic marine carbonate system is influenced by both physical and biological processes that impart variability on daily and seasonal scales, again with some spatial heterogeneity (Blackford and Gilbert, 2007). More recently, processes specific to benthic systems have been identified which need taking into account (Thomas *et al.*, 2008). These natural fluctuations are reasonably well characterized. Detection of leak driven perturbation sufficient to perturb the system beyond its natural variability could in theory be achieved by monitoring the carbonate system. Detection of leaks that are not large enough to perturb the system beyond its natural range is more problematic, as a range of physical and biological measurements would be required to determine the cause of the fluctuation. A lot of research has been devoted to developing carbonate system measurements in recent years (e.g.

Hardman-Mountford *et al*., 2008). Measurement of pCO_2 is operationally routine and affordable; however, pCO_2 has a very high variability and may not be the most sensitive indicator of change. pH is tightly buffered, with a natural variability of around 0.3–0.5 units. However, the accuracy required in pH measurement has prevented as yet a fully operational system being developed, although this is a likely development for the near future. To date, no operational deployable system for measuring DIC exists.

Monitoring for biological impact is problematic as we are as yet unable to characterize with any certainty the biological response to CO_2, given the high degree of species-specific variability in response and the high heterogeneity of shelf seas.

One clear challenge is to determine the optimal density of monitoring systems; too sparse a grid would imply that leak events could be missed, a high-resolution grid would have major cost implications. One solution maybe to employ autonomous underwater vehicles or remotely operated underwater vehicles with operational sonar and carbonate system monitors, coupled with fixed monitoring arrays around specific definable leak risk sites. A crucial component of operational systems is the automation of processing and data transfer; however, such systems are becoming routine in marine applications. (Hardman-Mountford *et al*., 2008). An added bonus of routine monitoring is that the observations will have significant value for understanding the basic behaviour and variability of the marine system and evaluating models.

13.5 Mitigation of leaks

Significant leakage from pipeline infrastructure can be simply prevented by judicious use of sensors, valves and automated shutdown systems, which is already standard practice. The mitigation of leaks from reservoirs through the caprock presents a considerable problem which could probably only be limited by depressurizing the reservoir. Once a significantly large CO_2 stream reaches the ecosystem, it is difficult to envisage an effective and achievable strategy that would limit impacts. Hence, rather than post-event mitigation, the minimization of risk using comprehensive pre-deployment risk assessment provides the best option for mitigation. The main elements of this risk assessment should include investigations of caprock integrity, an understanding of CO_2 movement through geological strata, an understanding of the likely sea floor footprint of a leak and the siting of sequestration in regions of naturally high oceanic mixing, away from ecological or economically sensitive areas.

13.6 Future trends

The general consensus is that excess CO_2, whether injected, leaked or absorbed into the marine environment, will cause potentially serious and harmful impacts to components of the ecosystem in the vicinity of the incursion. Further, it is likely that, if the CO_2 incursion is sufficiently large (in magnitude, duration or spatial scale), ecosystem functionality, regionally or globally important biogeochemical cycles and marine resources could be deleteriously affected. Hence Ocean Acidification (OA) – the global uptake of atmospherically borne anthropogenic CO_2 emissions – is considered to be a serious threat to the integrity of the marine system. Regarding CO_2 leaking from CCS facilities, and ignoring any consideration of leakage probability, it is reasonable to presume that impacts to marine chemistry at the epicentre of a leak may well be larger than what could be generated by OA and that impacts would be noted. However, the experimental and theoretical evidence suggests that the mixing (and dispersion) inherent in shelf seas coupled with the likely scales of any leakage event means that impacts from CCS leakage would be spatially constrained. Thus such events, should they occur, must be put into context. Clearly, as trawling and dredging and similar activities demonstrate, shelf seas can tolerate serious disruption to restricted areas. Some evidence suggests that only a very large (10^4 t CO_2 per day), long-term leak (Blackford *et al.*, 2008) would be capable of causing damage at a regionally significant scale. One of the key challenges, therefore, is to refine our understanding of the spread and dispersion of injected CO_2 in a variety of situations, relating to tidal patterns, currents and weather, which together drive the mixing of shelf waters. Whilst the theoretical elements are in place, but not yet coupled, there is a lack of observational evidence by which models could be verified.

There are also a number of remaining areas of limited knowledge. The first of these is the impact on sediment chemistry and biota of CO_2 percolating from below; many experimental manipulations have, for practical reasons, assessed benthic impacts by adding CO_2 to the overlying water. Given that marine sediments exhibit strong vertical chemical and biological gradients, it is likely that direction of the CO_2 source would be an important consideration. A second area of limited knowledge is the possible contamination of leaked CO_2 and the integrated effect of CO_2 and pollutants. Initial experiments indicate the potential for one to exacerbate the impacts of the other, but much more work remains to be done. A third area requiring consideration relates to the potential short to medium term nature of some leakage scenarios and consequently the ability of individuals and systems to recover from perturbations.

13.7 Sources of further information and advice

- A readable description of the chemistry and ecological implications of adding CO_2 to marine systems, in the context of ocean acidification, can be found in the Royal Society report of 2005 by Prof John Raven *et al.*:

'Ocean acidification due to increasing atmospheric carbon dioxide'. This can be downloaded from: http://www.co2storage.org.uk/Technical/Ocean/Ocean_acidificatiion_Jun_05_Roy_Soc.pdf (accessed January 2010),

- A more detailed description of the chemistry of CO_2 in sea water can be found in Dickson, A.G., Sabine, C.L. and Christian, J.R. (eds) 2007. *Guide to Best Practices for Ocean CO_2 Measurements*. PICES special publication 3, 191pp. This can be sourced from http://cdiac.ornl.gov/oceans/Handbook_2007.html (accessed January 2010).
- The Parliamentary Office of Science and Technology has released two 'Postnotes' describing succinctly the issues around CCS.
  - CARBON CAPTURE AND STORAGE (CCS) http://www.parliament.uk/documents/upload/POSTpn238.pdf (accessed January 2010)
  - CO2 CAPTURE, TRANSPORT AND STORAGE http://www.parliament.uk/documents/upload/POSTpn335.pdf (accessed January 2010)
- The Intergovernmental panel on Climate Change released a report on CCS 'CCS, IPCC Special Report, Working Group III, September 2005', which is available from Cambridge University Press (http://www.cambridge.org/ipcc), The Edinburgh Building, Shaftesbury Road, Cambridge, CB2 2RU England. A summary for policy makers can be sourced from: http://www.ipcc.ch/publications_and_data/publications_and_data_reports.htm.

The knowledge base has not yet enabled a comprehensive report on the potential ecosystem impacts of a leak from CCS; please refer to this chapter and the references cited below.

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