6. Ocean storage

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Executive Summary

Captured CO_2 could be deliberately injected into the ocean at great depth, where most of it would remain isolated from the atmosphere for centuries. CO_2 can be transported via pipeline or ship for release in the ocean or on the sea floor. There have been small-scale field experiments and 25 years of theoretical, laboratory, and modelling studies of intentional ocean storage of CO_2, but ocean storage has not yet been deployed or thoroughly tested.

The increase in atmospheric CO_2 concentrations due to anthropogenic emissions has resulted in the oceans taking up CO_2 at a rate of about 7 $GtCO_2$/yr (2 GtC/yr). Over the past 200 years the oceans have taken up 500 $GtCO_2$ from the atmosphere out of 1300 $GtCO_2$ total anthropogenic emissions. Anthropogenic CO_2 resides primarily in the upper ocean and has thus far resulted in a decrease of *p*H of about 0.1 at the ocean surface with virtually no change in *p*H deep in the oceans. Models predict that the oceans will take up most CO_2 released to the atmosphere over several centuries as CO_2 is dissolved at the ocean surface and mixed with deep ocean waters.

The Earth's oceans cover over 70% of the Earth's surface with an average depth of about 3800 metres; hence, there is no practical physical limit to the amount of anthropogenic CO_2 that could be placed in the ocean. However, the amount that is stored in the ocean on the millennial time scale depends on oceanic equilibration with the atmosphere. Over millennia, CO_2 injected into the oceans at great depth will approach approximately the same equilibrium as if it were released to the atmosphere. Sustained atmospheric CO_2 concentrations in the range of 350 to 1000 ppm imply that 2300 ± 260 to 10,700 ± 1000 Gt of anthropogenic CO_2 will eventually reside in the ocean.

Analyses of ocean observations and models agree that injected CO_2 will be isolated from the atmosphere for several hundred years and that the fraction retained tends to be larger with deeper injection. Additional concepts to prolong CO_2 retention include forming solid CO_2 hydrates and liquid CO_2 lakes on the sea floor, and increasing CO_2 solubility by, for example, dissolving mineral carbonates. Over centuries, ocean mixing results in loss of isolation of injected CO_2 and exchange with the atmosphere. This would be gradual from large regions of the ocean. There are no known mechanisms for sudden or catastrophic release of injected CO_2.

Injection up to a few $GtCO_2$ would produce a measurable change in ocean chemistry in the region of injection, whereas injection of hundreds of $GtCO_2$ would eventually produce measurable change over the entire ocean volume.

Experiments show that added CO_2 can harm marine organisms. Effects of elevated CO_2 levels have mostly been studied on time scales up to several months in individual organisms that live near the ocean surface. Observed phenomena include reduced rates of calcification, reproduction, growth, circulatory oxygen supply and mobility as well as increased mortality over time. In some organisms these effects are seen in response to small additions of CO_2. Immediate mortality is expected close to injection points or CO_2 lakes. Chronic effects may set in with small degrees of long-term CO_2 accumulation, such as might result far from an injection site, however, long-term chronic effects have not been studied in deep-sea organisms.

CO_2 effects on marine organisms will have ecosystem consequences; however, no controlled ecosystem experiments have been performed in the deep ocean. Thus, only a preliminary assessment of potential ecosystem effects can be given. It is expected that ecosystem consequences will increase with increasing CO_2 concentration, but no environmental thresholds have been identified. It is also presently unclear, how species and ecosystems would adapt to sustained, elevated CO_2 levels.

Chemical and biological monitoring of an injection project, including observations of the spatial and temporal evolution of the resulting CO_2 plume, would help evaluate the amount of materials released, the retaining of CO_2, and some of the potential environmental effects.

For water column and sea floor release, capture and compression/liquefaction are thought to be the dominant cost factors. Transport (i.e., piping, and shipping) costs are expected to be the next largest cost component and scale with proximity to the deep ocean. The costs of monitoring, injection nozzles etc. are expected to be small in comparison.

Dissolving mineral carbonates, if found practical, could cause stored carbon to be retained in the ocean for 10,000 years, minimize changes in ocean *p*H and CO_2 partial pressure, and may avoid the need for prior separation of CO_2. Large amounts of limestone and materials handling would be required for this approach.

Several different global and regional treaties on the law of the sea and marine environment could be relevant to intentional release of CO_2 into the ocean but the legal status of intentional carbon storage in the ocean has not yet been adjudicated.

It is not known whether the public will accept the deliberate storage of CO_2 in the ocean as part of a climate change mitigation strategy. Deep ocean storage could help reduce the impact of CO_2 emissions on surface ocean biology but at the expense of effects on deep-ocean biology.

6.1. Introduction and background

6.1.1 Intentional storage of CO_2 in the ocean

This report assesses what is known about intentional storage of carbon dioxide in the ocean by inorganic strategies that could be applied at industrial scale. Various technologies have been envisioned to enable and increase ocean CO_2 storage (Figure 6.1). One class of options involves storing a relatively pure stream of carbon dioxide that has been captured and compressed. This CO_2 can be placed on a ship, injected directly into the ocean, or deposited on the sea floor. CO_2 loaded on ships could either be dispersed from a towed pipe or transported to fixed platforms feeding a CO_2 lake on the sea floor. Such CO_2 lakes must be deeper than 3 km where CO_2 is denser than sea water. Any of these approaches could in principle be used in conjunction with neutralization with carbonate minerals.

Figure 6.1. Illustration of some of the ocean storage strategies described in this chapter.

Research, development and analysis of ocean CO_2 storage concepts has progressed to consider key questions and issues that could affect the prospects of ocean storage as a response option to climate change (Section 6.2). Accumulated understanding of the ocean carbon cycle is being used to estimate how long CO_2 released into the oceans will remain isolated from the atmosphere. Such estimates are used to assess the effectiveness of ocean storage concepts (Section 6.3).

Numerical models of the ocean indicate that placing CO_2 in the deep ocean would isolate most of the CO_2 from the atmosphere for several centuries, but over longer times the ocean and atmosphere would equilibrate. Relative to atmospheric release, direct injection of CO_2 in to the ocean could reduce maximum amounts and rates of atmospheric CO_2 increase over the next several centuries (Figure 6.2; Kheshgi *et al.*, 1994; Kheshgi, 2004b). Direct injection of CO_2 in the ocean would not reduce atmospheric CO_2 content on the millennial time scale (Table 6.1; Figure 6.3; Hoffert *et al.*, 1979; Kheshgi *et al.*, 1994).

Table 6.1. Amount of additional CO_2 residing in the ocean after atmosphere-ocean equilibration for different atmospheric stabilization concentrations. The uncertainty range represents the influence of climate sensitivity to a CO_2 doubling in the range of 1.5K to 4.5K (Kheshgi *et al*., 2005; Kheshgi 2004a). This table considers the possibility of increased carbon dioxide storage in the terrestrial biosphere. Such an increase, if permanent, would allow a corresponding increase in total cumulative emissions. This table does not consider natural or engineered dissolution of carbonate minerals, which would increase ocean storage of anthropogenic carbon. The amount already in the oceans exceeds 500 $GtCO_2$ (= 440 $GtCO_2$ for 1994 (Sabine *et al*., 2004) plus CO_2 absorption since that time). The long-term amount of CO_2 stored in the deep ocean is independent of whether the CO_2 is initially released to the atmosphere or the deep ocean.

Figure 6.2. Simulated atmospheric CO_2 resulting from CO_2 release to the atmosphere or injection into the ocean at 3,000 m depth (Kheshgi and Archer, 2004). Emissions follow a logistic trajectory with cumulative emissions of 18,000 $GtCO_2$. Illustrative cases include 100% of emissions released to the atmosphere leading to a peak in concentration, 100% of emissions injected into the ocean, and no emissions (i.e., other mitigation approaches are used). Additional cases include atmospheric emission to year 2050, followed by either 50% to atmosphere and 50% to ocean after 2050 or 50% to atmosphere and 50% by other mitigation approaches after 2050. Ocean injection results in lower peak concentrations than atmospheric release but higher than if other mitigation approaches are used (e.g., renewables or permanent storage).

Figure 6.3. Equilibrium partitioning of CO_2 between the ocean and atmosphere. On the time scale of millennia, complete mixing of the oceans leads to a partitioning of cumulative CO_2 emissions between the oceans and atmosphere with the bulk of emissions eventually residing in the oceans as dissolved inorganic carbon. The ocean partition depends nonlinearly on CO_2 concentration according to carbonate chemical equilibrium (Box 6.1) and has limited sensitivity to changes in surface water temperature (shown by the grey area for a range of climate sensitivity of 1.5 to 4.5°C for CO_2 doubling) (adapted from Kheshgi *et al*., 2005; Kheshgi, 2004a). ΔpH evaluated from pCO_2 of 275 ppm. This calculation is relevant on the time scale of several centuries, and does not consider changes in ocean alkalinity that increase ocean CO_2 uptake over several millennia (Archer *et al*., 1997).

There has been limited experience with handling CO_2 in the deep sea that could form a basis for the development of ocean CO_2 storage technologies. Before they could be deployed, such technologies would require further development and field testing. Associated with the limited level of development, estimates of the costs of ocean CO_2 storage technologies are at a primitive state, however, the costs of the actual dispersal technologies are expected to be low in comparison to the costs of CO_2 capture and transport to the deep sea (but still non-negligible; Section 6.9). Proximity to the deep sea is a factor, as the deep oceans are remote to many sources of CO_2 (Section 6.4). Ocean storage would require CO_2 transport by ship or deep-sea pipelines. Pipelines and drilling platforms, especially in oil and gas applications, are reaching ever-greater depths, yet not on the scale or to the depth relevant for ocean CO_2 storage (Chapter 4). No insurmountable technical barrier to storage of CO_2 in the oceans is apparent.

Putting CO_2 directly into the deep ocean means that the chemical environment of the deep ocean would be altered immediately, and in concepts where release is from a point, change in ocean chemistry would be greater proximate to the release location. Given only rudimentary understanding of deep-sea ecosystems, only a limited and preliminary assessment of potential ecosystem effects can be given (Section 6.7).

Technologies exist to monitor deep-sea activities (Section 6.6). Practices for monitoring and verification of ocean storage would depend on which, as of yet undeveloped, ocean storage technology would potentially be deployed, and on environmental impacts to be avoided.
More carbon dioxide could be stored in the ocean with less of an effect on atmospheric CO_2 and fewer adverse effects on the marine environment if the alkalinity of the ocean could be increased, perhaps by dissolving carbonate minerals in sea water. Proposals based on this concept are discussed primarily in Section 6.2.

For ocean storage of CO_2, issues remain regarding environmental consequences, public acceptance, implications of existing laws, safeguards and practices that would need to be developed, and gaps in our understanding of ocean CO_2 storage (Sections 6.7, 6.8, and 6.10).

6.1.2 Relevant background in physical and chemical oceanography

The oceans, atmosphere, and plants and soils are the primary components of the global carbon cycle and actively exchange carbon (Prentice *et al.*, 2001). The oceans cover 71% of the Earth's surface with an average depth of 3,800 m and contain roughly 50 times the quantity of carbon currently contained in the atmosphere and roughly 20 times the quantity of carbon currently contained in plants and soils. The ocean contains so much CO_2 because of its large volume and because CO_2 dissolves in sea water to form various ionic species (Box 6.1).

The increase in atmospheric CO_2 over the past few centuries has been driving CO_2 from the atmosphere into the oceans. The oceans serve as an important sink of CO_2 emitted to the atmosphere taking up on average about 7 $GtCO_2$/yr (2 GtC/yr) over the 20 years from 1980 to 2000 with ocean uptake over the past 200 years estimated to be > 500 $GtCO_2$ (135 GtC) (Prentice *et al.,* 2001; Sabine *et al.*, 2004). On average, the anthropogenic CO_2 signal is detectable to about 1000 m depth; its near absence in the deep ocean is due to the slow exchange between ocean surface and deep –sea waters.

Ocean uptake of anthropogenic CO_2 has led to a perturbation of the chemical environment primarily in ocean surface waters. Increasing ocean CO_2 concentration leads to decreasing carbonate ion concentration and increasing hydrogen ion activity (Box 6.1). The increase in atmospheric CO_2 from about 280 ppm in 1800 to 380 ppm in 2004 has caused an average decrease across the surface of the oceans of about 0.1 *p*H units ($\Delta p\text{H} \approx -0.1$) from an initial average surface ocean *p*H of about 8.2. Further increase in atmospheric CO_2 will result in a further change in the chemistry of ocean surface waters that will eventually reach the deep ocean (Figure 6.4). The anthropogenic perturbation of ocean chemistry is greatest in the upper ocean where biological activity is high.

Figure 6.4. Simulated ocean pH changes from CO_2 release to the atmosphere. Modelled atmospheric CO_2 change and horizontally averaged ΔpH driven by a CO_2 emissions scenario: historic atmospheric CO_2 up to 2000, IS92a from 2000 to 2100, and logistic curve extending beyond 2100 with 18,000 $GtCO_2$ (Moomaw *et al*., 2001) cumulative emissions from 2000 onward (comparable to estimates of fossil-fuel resources – predominantly coal; Caldeira and Wickett, 2003). Since year 1800, the pH of the surface of the oceans has decreased about 0.1 pH units (from an initial average surface ocean pH of about 8.2) and CO_3^{2-} has decreased about 40 µmol kg^{-1}. There

are a number of pH scales used by ocean chemists and biologists to characterize the hydrogen ion content of sea water, but ΔpH computed on different scales varies little from scale to scale (Brewer *et al*., 1995).

Most carbon dioxide released to either the atmosphere or the ocean will eventually reside in the ocean, as ocean chemistry equilibrates with the atmosphere (Table 6.1, Figure 6.3). Thus, stabilization of atmospheric CO_2 concentration at levels above the natural level of 280 ppm implies long-term addition of carbon dioxide to the ocean. In equilibrium, the fraction of an increment of CO_2 released that will reside in the ocean depends on the atmospheric CO_2 concentration (Table 6.1; Figure 6.3; Kheshgi *et al*., 2005; Kheshgi, 2004a).

The capacity of the oceans to absorb CO_2 in equilibrium with the atmosphere is a function of the chemistry of sea water. The rate at which this capacity can be brought into play is a function of the rate of ocean mixing. Over time scales of decades to centuries, exchange of dissolved inorganic carbon between ocean surface waters and the deep ocean is the primary barrier limiting the rate of ocean uptake of increased atmospheric CO_2. Over many centuries (Kheshgi, 2004a), changes in dissolved inorganic carbon will mix throughout the ocean volume with the oceans containing most of the cumulative CO_2 emissions to the atmosphere/ocean system (Table 6.1; Figure 6.3). Over longer times (millennia), dissolution of $CaCO_3$ causes an even greater fraction of released CO_2 (85–92%) to reside in the ocean (Archer *et al*., 1997).

Box 6.1. Chemical properties of CO_2.

The oceans absorb large quantities of CO_2 from the atmosphere principally because CO_2 is a weakly acidic gas, and the minerals dissolved in sea water have created a mildly alkaline ocean. The exchange of atmospheric CO_2 with ocean surface waters is determined by the chemical equilibrium between CO_2 and carbonic acid H_2CO_3 in sea water, the partial pressure of CO_2 (pCO_2) in the atmosphere and the rate of air/sea exchange. Carbonic acid dissociates into bicarbonate ion HCO_3^-, carbonate ion CO_3^{2-}, and hydronium ion H^+ by the reactions (see Appendix A1.3):

$$CO_2\ (gas) + H_2O \leftrightarrow H_2CO_3\ (aqueous) \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+ \qquad (6.1)$$

Total dissolved inorganic carbon (DIC) is the sum of carbon contained in H_2CO_3, HCO_3^-, and CO_3^{2-}. The atmospheric concentration of CO_2 in equilibrium with surface water can be calculated from well-known chemical equilibria that depend on ocean total dissolved inorganic carbon, alkalinity, temperature and salinity (Zeebe and Wolf-Gladrow, 2001). The partial pressure of CO_2 in the ocean mixed layer equilibrates with the atmosphere on a time scale of about one year.

The ocean is a highly buffered system, that is the concentration of the chemical species whose equilibrium controls *p*H is significantly higher than the concentrations of H^+ or OH^-. The *p*H of sea water is the base–10 log of activity of H^+. Total Alkalinity (TAlk) is the excess of alkaline components, and is defined as the amount of strong acid required to bring sea water to the 'equivalence point' at which the HCO_3– and H_2CO_3 contributions are equal (Dickson, 1981).

The principal effect of adding CO_2 to sea water is to form bicarbonate ion, for example,

$$CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^-. \qquad (6.2)$$

In addition, some CO_2 undergoes simple reaction with water, for example,

$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$. (6.3)

In either case, Total Alkalinity does not change. The combined reactions lower both ocean *p*H, and carbonate ion concentration. For current ocean composition, CO_2 that is added to sea water is partitioned primarily into HCO_3^- with the net reaction resulting in the generation of H^+ and thus decreasing *p*H and making sea water more acidic; adding CO_2 thereby decreases the concentration of CO_3^{2-}.

Total Alkalinity is increased when, for example, alkaline minerals such as $CaCO_3$ are dissolved in sea water through the reaction,

$CaCO_3$ (solid) $\leftrightarrow Ca^{2+} + CO_3^{2-}$ (6.4)

which releases 2 mole-equivalents of Total Alkalinity and 1 mole of Dissolved Inorganic Carbon for each mole of $CaCO_3$ dissolved. Increasing TAlk more than DIC leads to a decrease in the partial pressure of CO_2 as seen in Figure 6.5. Because most Dissolved Inorganic Carbon is in the form of HCO_3^-, the main effect of dissolving $CaCO_3$ in surface waters is (see Kheshgi, 1995)

$CaCO_3$ (solid) + CO_2 (gas) + $H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$, (6.5)

thereby shifting CO_2 from the atmosphere to the oceans in equilibrium, neutralizing the effect of CO_2 on *p*H.

Figure 6.5. Composition diagram for ocean surface waters at 15°C (adapted from Baes, 1982). The white lines denote compositions with the same value of pCO_2 (in ppm); the black lines denote compositions with the same pH. The tan shaded region is undersaturated and the green shaded region is supersaturated with respect to calcite at atmospheric pressure (calcite solubility increases with depth). Surface water and average ocean compositions are also indicated. Adding CO_2 increases Dissolved Inorganic Carbon (DIC) without changing Total Alkalinity (TAlk); dissolving $CaCO_3$ increases both DIC and TAlk, with 2 moles of TAlk added for each mole of DIC added.

Ocean surface waters are super-saturated with respect to $CaCO_3$, allowing the growth of corals and other organisms that produce shells or skeletons of carbonate minerals. In contrast, the deepest ocean waters have lower *p*H and lower CO_3^{2-} concentrations, and are thus undersaturated with respect to $CaCO_3$. Marine organisms produce calcium carbonate particles in the surface ocean that settle and dissolve in undersaturated regions of the deep oceans.

Both biological and physical processes lead to the observed distribution of *p*H and its variability in the world ocean (Figure 6.6). As they transit from the Atlantic to Pacific Basins, deep ocean waters accumulate about 10% more dissolved inorganic carbon dioxide, primarily from the oxidation of sinking organic matter (Figure 6.7).

Figure 6.6. Observed variation in open ocean pH for the 1990s (shown on the total hydrogen scale; data from Key *et al*., 2004). In this figure the oceans are separated into separate panels. The three panels are on the same scale and coloured by latitude band to illustrate the large north-south changes in the pH of intermediate waters. Pre-industrial surface values would have been about 0.1 pH units greater than in the 1990s.

Figure 6.7. Natural variation in dissolved inorganic carbon at 3 km depth. Total dissolved inorganic carbon concentration at 3000 m depth (data from Key *et al*., 2004). Ocean carbon concentrations increase roughly 10% as deep ocean waters transit from the North Atlantic to the North Pacific due to the oxidation of organic carbon in the deep ocean.

6.2. Approaches to release of CO_2 into the ocean

6.2.1 Approaches to releasing CO_2 that has been captured, compressed, and transported into the ocean

6.2.1.1 Basic approach

The basic concept of intentional CO_2 storage in the ocean is to take a stream of CO_2 that has been captured and compressed (Chapter 3), and transport it (Chapter 4) to the deep ocean for release at or above the sea floor. (Other ocean storage approaches are discussed in Sections 6.2.2 and 6.2.3.) Once released, the CO_2 would dissolve into the surrounding sea water, disperse and become part of the ocean carbon cycle.

Marchetti (1977) first proposed injecting liquefied CO_2 into the waters flowing over the Mediterranean sill into the mid-depth North Atlantic, where the CO_2 would be isolated from the atmosphere for centuries. This concept relies on the slow exchange of deep ocean waters with the surface to isolate CO_2 from the atmosphere. The effectiveness of ocean storage will depend on how long CO_2 remains isolated from the atmosphere. Over the centuries and millennia, CO_2 released to the deep ocean will mix throughout the oceans and affect atmospheric CO_2 concentration. The object is to transfer the CO_2 to deep waters because the degree of isolation from the atmosphere generally increases with depth in the ocean. Proposed methods would inject the CO_2 below the thermocline[1] for more effective storage.

Depending on the details of the release and local sea floor topography, the CO_2 stream could be engineered to dissolve in the ocean or sink to form a lake on the sea floor. CO_2, dissolved in sea water at high concentrations can form a dense plume or sinking current along an inclined sea floor. If release is at a great enough depth, CO_2 liquid will sink and could accumulate on the sea floor as a pool containing a mixture of liquid and hydrate. In the short-term, fixed or towed pipes appear to be the most viable methods for oceanic CO_2 release, relying on technology that is already largely commercially available.

6.2.1.2 Status of development

To date, injection of CO_2 into sea water has only been investigated in the laboratory, in small-scale *in situ* experiments, and in models. Larger-scale *in situ* experiments have not yet been carried out.

An international consortium involving engineers, oceanographers and ecologists from 15 institutions in the United States, Norway, Japan and Canada proposed an *in situ* experiment to help evaluate the feasibility of ocean carbon storage as a means of mitigating atmospheric increases. This was to be a collaborative study of the physical, chemical, and biological changes associated with direct injection of CO_2 into the ocean (Adams *et al.*, 2002). The proposed CO_2 Ocean Sequestration Field Experiment was to inject less than 60 tonnes of pure liquid carbon dioxide (CO_2) into the deep ocean near Keahole Point on the Kona coast of the Island of Hawaii.This would have been the largest intentional CO_2 release into the ocean water column. The test was to have taken place in water about 800 m deep, over a period of about two weeks during the summer of 2001. Total project cost was to have been roughly US$ 5 million. A small steel pipeline, about 4 cm in diameter, was to have been deployed from a ship down to the injection depth, with a short section

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[1] The thermocline is the layer of the ocean between about 100 and 1000 m depth that is stably stratified by large temperature and density gradients, thus inhibiting vertical mixing. Vertical mixing rates in the thermocline can be about 1000 times less than in the deep sea. This zone of slow mixing would act as a barrier to slow degassing of CO_2 released in the deep ocean to the atmosphere.

of pipeline resting on the sea floor to facilitate data collection. The liquid CO_2 was to have been dispersed through a nozzle, with CO_2 droplets briefly ascending from the injection point while dissolving into the sea water. However, the project met with opposition from environmental organizations and was never able to acquire all of the necessary permits within the prescribed budget and schedule (de Figueiredo, 2002).

Following this experience, the group developed a plan to release 5.4 tonnes of liquefied CO_2 at a depth of 800 metres off the coast of Norway, and monitor its dispersion in the Norwegian Sea. The Norwegian Pollution Control Authority granted a permit for the experiment. The Conservative Party environment minister in Norway's coalition government, Børge Brende, decided to review the Norwegian Pollution Control Authorities' initial decision. After the public hearing procedure and subsequent decision by the Authority to confirm their initial permit, Brende said, 'The possible future use of the sea as storage for CO_2 is controversial. … Such a deposit could be in defiance of international marine laws and the ministry therefore had to reject the application.' The Norwegian Environment ministry subsequently announced that the project would not go ahead (Giles, 2002).

Several smaller scale scientific experiments (less than 100 litres of CO_2) have however been executed (Brewer *et al.*, 1999, Brewer *et al.*, 2005) and the necessary permits have also been issued for experiments within a marine sanctuary.

6.2.1.3 Basic behaviour of CO_2 released in different forms

The near-field behaviour of CO_2 released into the ocean depends on the physical properties of CO_2 (Box 6.2) and the method for CO_2 release. Dissolved CO_2 increases the density of sea water (e.g., Bradshaw, 1973; Song, *et al.*, 2005) and this affects transport and mixing. The near field may be defined as that region in which it is important to take effects of CO_2-induced density changes on the fluid dynamics of the ocean into consideration. The size of this region depends on the scale and design of CO_2 release (Section 6.2.1.4).

Box 6.2. Physical properties of CO_2.

The properties of CO_2 in sea water affect its fate upon release to the deep-sea environment. The conditions under which CO_2 can exist in a gas, liquid, solid hydrate, or aqueous phase in sea water are given in Figure 6.8 (see Appendix A1.2).

Figure 6.8. CO_2 phases in sea water. CO_2 is stable in the liquid phase when temperature and pressure (increasing with ocean depth) fall in the region below the blue curve; a gas phase is stable under conditions above the blue dashed line. In contact with sea water and at temperature and pressure in the shaded region, CO_2 reacts with sea water to from a solid ice-like hydrate $CO_2 \bullet 6H_2O$. CO_2 will dissolve in sea water that is not saturated with CO_2. The red line shows how temperature varies with depth at a site off the coast of California; liquid and hydrated CO_2 can exist below about 400 m (Brewer *et al.*, 2004).

At typical pressures and temperatures that exist in the ocean, pure CO_2 would be a gas above approximately 500 m and a liquid below that depth. Between about 500 and 2700 m depth, liquid CO_2 is lighter than sea water. Deeper than 3000 m, CO_2 is denser than sea water. The buoyancy of CO_2 released into the ocean determines whether released CO_2 rises or falls in the ocean column (Figure 6.9). In the gas phase, CO_2 is lighter than sea water and rises. In the liquid phase CO_2 is a highly compressible fluid compared to sea water. A fully formed crystalline CO_2 hydrate is denser than sea water and will form a sinking mass (Aya *et al.*, 2003); hydrate formation can thus aid ocean CO_2 storage by more rapid transport to depth, and by slowing dissolution. It may also create a nuisance by impeding flow in pipelines or at injectors.

Figure 6.9. Shallower than 2500 m, liquid CO_2 is less dense than sea water, and thus tends to float upward. Deeper than 3000 m, liquid CO_2 is denser than sea water, and thus tends to sink downwards. Between these two depths, the behaviour can vary with location (depending mostly on temperature) and CO_2 can be neutrally buoyant (neither rises nor falls). Conditions shown for the northwest Atlantic Ocean.

The formation of a solid CO_2 hydrate (Sloan, 1998) is a dynamic process (Figure 6.10; Brewer *et al.*, 1998, 1999, 2000) and the nature of hydrate nucleation in such systems is imperfectly understood. Exposed to an excess of sea water, CO_2 will eventually dissolve forming an aqueous phase with density higher than surrounding sea water. Release of dense or buoyant CO_2 – in a gas, liquid, hydrate or aqueous phase – would entrain surrounding sea water and form plumes that sink, or rise, until dispersed.

Figure 6.10. Liquid CO_2 released at 3600 metres initially forms a liquid CO_2 pool on the sea floor in a small deep ocean experiment (b, upper picture). In time, released liquid CO_2 reacts with sea water to form a solid CO_2 hydrate in a similar pool (b, lower picture).

CO_2 plume dynamics depend on the way in which CO_2 is released into the ocean water column. CO_2 can be initially in the form of a gas, liquid, solid or solid hydrate. All of these forms of CO_2 would dissolve in sea water, given enough time (Box 6.1). The dissolution rate of CO_2 in sea water is quite variable and depends on the form (gas, liquid, solid, or hydrate), the depth and temperature of disposal, and the local water velocities. Higher flow rates increase the dissolution rate.

Gas. CO_2 could potentially be released as a gas above roughly 500 m depth (Figure 6.8). Below this depth, pressures are too great for CO_2 to exist as a gas. The gas bubbles would be less dense than the surrounding sea water so tend to rise towards the surface, dissolving at a radial speed of about 0.1 cm hr^{-1} (0.26 to 1.1 μmol cm^{-2} s^{-1}; Teng *et al.*, 1996). In waters colder than about 9°C, a CO_2 hydrate film could form on the bubble wall. CO_2 diffusers could produce gaseous CO_2 bubbles that are small enough to dissolve completely before reaching the surface.

Liquid. Below roughly 500 m depth, CO_2 can exist in the ocean as a liquid. Above roughly 2500 m depth CO_2 is less dense than sea water, so liquid CO_2 released shallower than 2500 m would tend to rise towards the surface. Because most ocean water in this depth range is colder than 9°C, CO_2 hydrate would tend to form on the droplet wall. Under these conditions, the radius of the droplet would diminish at a speed of about 0.5 cm hr^{-1} (= 3 μmol cm^{-2} s^{-1}; Brewer *et al.*, 2002). Under these conditions a 0.9 cm diameter droplet would rise about 400 m in an hour before dissolving completely; 90% of its mass would be lost in the first 200 m (Brewer *et al.*, 2002). Thus, CO_2 diffusers could be designed to produce droplets that will dissolve within roughly 100 m of the depth of release. If the droplet reached approximately 500 m depth, it would become a gas bubble.

CO_2 is more compressible than sea water; below roughly 3000 m, liquid CO_2 is denser than the surrounding sea water and sinks. CO_2 nozzles could be engineered to produce large droplets that would sink to the sea floor or small droplets that would dissolve in the sea water before contacting the sea floor. Natural ocean mixing and droplet motion are expected to prevent concentrations of dissolved CO_2 from approaching saturation, except near liquid CO_2 that has been intentionally placed in topographic depressions on the sea floor.

Solid. Solid CO_2 is denser than sea water and thus would tend to sink. Solid CO_2 surfaces would dissolve in sea water at a speed of about 0.2 cm hr^{-1} (inferred from Aya *et al.*, 1997). Thus small quantities of solid CO_2 would dissolve completely before reaching the sea floor; large masses could potentially reach the sea floor before complete dissolution.

Hydrate. CO_2 hydrate is a form of CO_2 in which a cage of water molecules surrounds each molecule of CO_2. It can form in average ocean waters below about 400 m depth. A fully formed crystalline CO_2 hydrate is denser than sea water and will sink (Aya *et al.*, 2003). The surface of this mass would dissolve at a speed similar to that of solid CO_2, about 0.2 cm hr^{-1} (0.47 to 0.60 µm s^{-1}; Rehder *et al.*, 2004; Teng *et al.*, 1999), and thus droplets could be produced that either dissolve completely in the sea water or sink to the sea floor. Pure CO_2 hydrate is a hard crystalline solid and will not flow through a pipe; however a paste-like composite of hydrate and sea water may be extruded (Tsouris *et al.*, 2004), and this will have a dissolution rate intermediate between those of CO_2 droplets and a pure CO_2 hydrate.

6.2.1.4 Behaviour of injected CO_2 in the near field: CO_2-rich plumes

As it leaves the near field, CO_2 enriched water will reside at a depth determined by its density. The oceans are generally stably stratified with density increasing with depth. Parcels of water tend to move upward or downward until they reach water of the same density, then there are no buoyancy forces to induce further motion.

The dynamics of CO_2-rich plumes determine both the depth at which the CO_2 leaves the near-field environment and the amount of initial dilution (and consequently the amount of *p*H change). When CO_2 is released in any form into seawater, the CO_2 can move upward or downward depending on whether the CO_2 is less or more dense than the surrounding seawater. Drag forces transfer momentum from the CO_2 droplets to the surrounding water column producing motion in the adjacent water, initially in the direction of droplet motion. Simultaneously, the CO_2 dissolves into the surrounding water, making the surrounding water denser and more likely to sink. As the CO_2-enriched water moves, it mixes with surrounding water that is less enriched in CO_2, leading to additional dilution and diminishing the density contrast between the CO_2-enriched water and the surrounding water.

CO_2 releases could be engineered to produce CO_2 plumes with different characteristics (Chen *et al.*, 2003; Sato and Sato, 2002; Alendal and Drange, 2001; Crounse *et al.*, 2001; Drange *et al.,* 2001; Figure 6.11). Modelling studies indicate that releases of small droplets at slow rates produce smaller plumes than release of large droplets at rapid rates. Where CO_2 is denser than seawater, larger droplet sizes would allow the CO_2 to sink more deeply. CO_2 injected at intermediate depths could increase the density of CO_2-enriched sea water sufficiently to generate a sinking plume that would carry the CO_2 into the deep ocean (Liro *et al.*, 1992; Haugan and Drange, 1992). Apparent coriolis forces would operate on such a plume, turning it towards the right in the Northern Hemisphere and towards the left in the Southern Hemisphere (Alendal *et al.,* 1994). The channelling effects of submarine canyons or other topographic features could help steer dense plumes to greater depth with minimal dilution (Adams *et al.*, 1995).

Figure 6.11. Simulated CO_2 enriched sea water plumes (left panels; indicated by pH) and CO_2 droplet plumes (right panels; indicated by $kgCO_2\ m^{-3}$) created by injecting 1 cm and 12 cm liquid CO_2 droplets (top and bottom panels, respectively) into the ocean from fixed nozzles (elapsed time is 30 min; injection rate is 1.0 $kgCO_2\ s^{-1}$; ocean current speed is 5 cm s^{-1}; Alendal and Drange, 2001). By varying droplet size, the plume can be made to sink (top panels) or rise (bottom panels).

The concept of ocean injection from a moving ship towing a trailing pipe was developed in order to minimize the local environmental impacts by accelerating the dissolution and dispersion of injected liquid CO_2 (Ozaki, 1997; Minamiura *et al.*, 2004). A moving ship could be used to produce a sea water plume with relatively dilute initial CO_2 concentrations (Figures 6.12 and 6.13). In the upper ocean where CO_2 is less dense than seawater, nozzles engineered to produce mm-scale droplets would generate CO_2 plumes that would rise less than 100 m.

Figure 6.12. Simulated plumes (Chen *et al.*, 2005) created by injecting liquid CO_2 into the ocean from a fixed pipe (left panel) and a moving ship (right panel) at a rate of 100 kg s^{-1} (roughly equal to the CO_2 from a 500 MW_e coal-fired power plant). Left panel: injection at 875 m depth (12 m from the sea floor) with an ocean current speed of 2.3 cm s^{-1}. Right panel: injection at 1340 m depth from a ship moving at a speed of 3 m s^{-1}. Note difference in pH scales; maximum pH perturbations are smaller in the moving ship simulation.

Figure 6.13. Volume of water with a ΔpH less than the value shown on the horizontal axis for the simulations shown in Figure 6.12 corresponding to CO_2 releases from a 500 MW_e power plant. The fixed pipe simulation produces a region with ΔpH < –1, however, the moving ship disperses the CO_2 more widely, largely avoiding pH changes of this magnitude.

6.2.1.5 Behaviour of injected CO_2 in the far field

The far field is defined as the region in which the concentration of added CO_2 is low enough such that the resulting density increase does not significantly affect transport, and thus CO_2 may be considered a passive tracer in the ocean. Typically, this would apply within a few kilometres of an injection point in midwater, but if CO_2 is released at the sea floor and guided along topography, concentration may remain high and influence transport for several tens of kilometres. CO_2 is transported by ocean currents and undergoes further mixing and dilution with other water masses (Alendal and Drange, 2001). Most of this mixing and transport occurs along surfaces of nearly constant density, because buoyancy forces inhibit vertical mixing in a stratified fluid. Over time, a release of CO_2 becomes increasingly diluted but affects ever greater volumes of water.

Ocean general circulation models have been used to predict changes in ocean chemistry resulting from the dispersion of injected CO_2 for hypothetical examples of ocean storage (e.g., Orr, 2004). Wickett *et al.* (2003) estimated that injection into the deep ocean at a rate of 0.37 $GtCO_2$ yr^{-1} (= 0.1 GtC yr^{-1}) for 100 years would produce a ΔpH < –0.3 over a volume of sea water equivalent to 0.01% or less of total ocean volume (Figure 6.14). In this example, for each $GtCO_2$ released to the deep ocean, less than about 0.0001%, 0.001% and 0.01% of the ocean volume has Δ*p*H of less than –0.3, –0.2, and –0.1 *p*H units respectively. Caldeira and Wickett (2005) predicted volumes of water undergoing a range of *p*H changes for several atmospheric emission and carbon stabilization pathways, including pathways in which direct injection of CO_2 into the deep ocean was assumed to provide either 10% or 100% of the total atmospheric CO_2 mitigation effort needed to stabilize atmospheric CO_2 according to the WRE550 pathway. This assumed a CO_2 production scenario in which all known fossil-fuel resources were ultimately combusted. Simulations in which ocean injection provided 10% of the total mitigation effort, resulted in significant changes in ocean *p*H in year 2100 over roughly 1% of the ocean volume (Figure 6.15). By year 2300, injection rates have slowed but previously injected carbon has spread through much of the ocean resulting in an additional 0.1 *p*H unit reduction in ocean *p*H over most of the ocean volume compared to WRE550.

Figure 6.14. Estimated volume of pH perturbations at basin scale (Wickett *et al.*, 2003). Simulated fraction of global ocean volume with a ΔpH less than the amount shown on the horizontal axis, after 100 years of simulated injection at a rate of 0.37 $GtCO_2$ yr^{-1} (= 0.1 GtC yr^{-1}) at each of four

different points (two different depths near New York City and San Francisco). Model results indicate, for example, that injecting CO_2 at this rate at a single location for 100 years could be expected to produce a volume of sea water with a ΔpH < –0.3 units in 0.01% or less of total ocean volume (0.01% of the ocean is roughly 10^5 km^3). As with other simulations of direct CO_2 injection in the ocean, results for the upper ocean (e.g., 800 m) tend to be more site-specific than are results for the deep ocean (e.g., 3000 m).

Figure 6.15. Estimated volume of pH perturbations at global scale for hypothetical examples in which injection of CO_2 into the ocean interior provides 100% or 10% of the mitigation effort needed to move from a logistic emissions curve cumulatively releasing 18,000 $GtCO_2$ (=5000 GtC) to emissions consistent with atmospheric CO_2 stabilization at 550 ppm according to the WRE550 pathway (Wigley *et al*., 1996). The curves show the simulated fraction of ocean volume with a pH reduction greater than the amount shown on the horizontal axis. For the 10% case, in year 2100, injection rates are high and about1% of the ocean volume has significant pH reductions; in year 2300, injection rates are low, but previously injected CO_2 has decreased ocean pH by about 0.1 unit below the value produced by a WRE550 atmospheric CO_2 pathway in the absence of CO_2 release directly to the ocean. (Caldeira and Wickett, 2005).

6.2.1.6 Behaviour of CO_2 lakes on the sea floor

Long-term storage of carbon dioxide might be more effective if CO_2 were stored on the sea floor in liquid or hydrate form below 3000 metres, where CO_2 is denser than sea water (Box 6.2; Ohsumi, 1995; Shindo *et al.*, 1995). Liquid carbon dioxide could be introduced at depth to form a lake of CO_2 on the sea floor (Ohsumi, 1993). Alternatively, CO_2 hydrate could be created in an apparatus designed to produce a hydrate pile or pool on the sea floor (Saji *et al.*, 1992). To date, the concept of CO_2 lakes on the sea floor has been investigated only in the laboratory, in small-scale (tens of litres) *in situ* experiments and in numerical models. Larger-scale *in situ* experiments have not yet been carried out.

Liquid or hydrate deposition of CO_2 on the sea floor could increase isolation, however in the absence of a physical barrier the CO_2 would dissolve into the overlying water (Mori and Mochizuki, 1998; Haugan and Alendal, 2005). In this aspect, most sea floor deposition proposals can be viewed as a means of 'time-delayed release' of CO_2 into the ocean. Thus, many issues relevant to sea floor options, especially the far-field behaviour, are discussed in sections relating to CO_2 release into the water column (e.g., Section 6.2.1.5).

CO_2 released onto the sea floor deeper than 3 km is denser than surrounding sea water and is expected to fill topographic depressions, accumulating as a lake of CO_2 over which a thin hydrate layer would form. This hydrate layer would retard dissolution, but it would not insulate the lake from the overlying water. The hydrate would dissolve into the overlying water (or sink to the bottom of the CO_2 lake), but the hydrate layer would be continuously renewed through the formation of new crystals (Mori, 1998). Laboratory experiments (Aya *et al.*, 1995) and small deep ocean experiments (Brewer *et al.*, 1999) show that deep-sea storage of CO_2 would lead to CO_2 hydrate formation (and subsequent dissolution).

Predictions of the fate of large-scale CO_2 lakes rely on numerical simulations because no large-scale field experiments have yet been performed. For a CO_2 lake with an initial depth of 50 m, the time of complete dissolution varies from 30 to 400 years depending on the local ocean and sea floor environment. The time to dissolve a CO_2 lake depends on its depth, complex dynamics of the ocean bottom boundary layer and its turbulence characteristics, mechanism of CO_2 hydrate dissolution, and properties of CO_2 in solution (Haugan and Alendal, 2005). The lifetime of a CO_2 lake would be longest in relatively confined environments, such as might be found in some trenches or depressions with restricted flow (Ohgaki and Akano, 1992). (Strong flows have been observed in trenches (Nakashiki, 1997). Nevertheless, simulation of CO_2 storage in a deep trench (Kobayashi, 2003) indicates that the bottom topography can weaken vertical momentum and mass transfer, slowing the CO_2 dissolution rate. In a quiescent environment, transport would be dominated by diffusion. Double-diffusion in the presence of strong stratification may produce long lake lifetimes. In contrast, the flow of sea water across the lake surface would increase mass transfer and dissolution. For example, CO_2 lake lifetimes of >10,000 yr for a 50 m thick lake can be estimated from the dissolution rate of 0.44 cm yr^{-1} for a quiescent, purely diffusive system (Ohsumi, 1997). Fer and Haugan (2003) found that a mean horizontal velocity of 0.05 m s^{-1} would cause the CO_2 lake to dissolve >25 times more rapidly (12 cm yr^{-1}). Furthermore, they found that an ocean bottom storm with a horizontal velocity of 0.20 m s^{-1} could increase the dissolution rate to 170 cm yr^{-1}.

6.2.2 CO_2 storage by dissolution of carbonate minerals

Over thousands of years, increased sea water acidity resulting from CO_2 addition will be largely neutralized by the slow natural dissolution of carbonate minerals in sea-floor sediments and on land. This neutralization allows the ocean to absorb more CO_2 from the atmosphere with less of a change in ocean *p*H, carbonate ion concentration, and pCO_2 (Archer *et al.*, 1997, 1998). Various approaches have been proposed to accelerate carbonate neutralization, and thereby store CO_2 in the oceans by promoting the dissolution of carbonate minerals[2]. These approaches (e.g., Kheshgi, 1995; Rau and Caldeira, 1999) do not entail initial separate CO_2 capture and transport steps. However, no tests of these approaches have yet been performed at sea, so inferences about enhanced ocean CO_2 storage, and effects on ocean *p*H are based on laboratory experiments (Morse and Mackenzie, 1990; Morse and Arvidson, 2002), calculations (Kheshgi, 1995), and models (Caldeira and Rau, 2000).

Carbonate neutralization approaches attempt to promote Reaction 6.5 (see Box 6.1) in which limestone reacts with carbon dioxide and water to form calcium and bicarbonate ions in solution. Accounting for speciation of dissolved inorganic carbon in sea water (Kheshgi, 1995), for each mole of $CaCO_3$ dissolved there would be 0.8 mole of additional CO_2 stored in sea water in equilibrium with fixed CO_2 partial pressure (i.e., about 2.8 tonnes of limestone per tonne CO_2). Adding alkalinity to the ocean would increase ocean carbon storage, both in the near term and on millennial time scales (Kheshgi, 1995). The duration of increased ocean carbon storage would be limited by eventual $CaCO_3$ sedimentation, or reduced $CaCO_3$ sediment dissolution, which is modelled to occur through natural processes on the time scale of about 6,000 years (Archer *et al.*, 1997, 1998).

Carbonate minerals have been proposed as the primary source of alkalinity for neutralization of CO_2 acidity (Kheshgi 1995; Rau and Caldeira, 1999). There have been many experiments and observations related to the kinetics of carbonate mineral dissolution and precipitation, both in fresh water and in sea water (Morse and Mackenzie, 1990; Morse and Arvidson, 2002). Carbonate minerals and other alkaline compounds that dissolve readily in surface sea water (such as Na_2CO_3), however, have not been found in sufficient quantities to store carbon in the ocean on scales comparable to fossil CO_2 emissions (Kheshgi, 1995). Carbonate minerals that are abundant do not dissolve in surface ocean waters. Surface ocean waters are typically oversaturated with respect to carbonate minerals (Broecker and Peng, 1982; Emerson and Archer, 1990; Archer, 1996), but

[2] This approach is fundamentally different than the carbonate mineralization approach assessed in Chapter 7. In that approach CO_2 is stored by reacting it with non-carbonate minerals to form carbonate minerals. In this approach, carbonate minerals are dissolved in the ocean, thereby increasing ocean alkalinity and increasing ocean storage of CO_2. This approach could also make use of non-carbonate minerals, if their dissolution would increase ocean alkalinity.

carbonate minerals typically do not precipitate in sea water due to kinetic inhibitions (Morse and Mackenzie, 1990).

To circumvent the problem of oversaturated surface waters, Kheshgi (1995) considered promoting reaction (6.5) by calcining limestone to form CaO, which is readily soluble. If the energy for the calcining step was provided by a CO_2-emission-free source, and the CO_2 released from $CaCO_3$ were captured and stored (e.g., in a geologic formation), then this process would store 1.8 mole CO_2 per mole CaO introduced into the ocean. If the CO_2 from the calcining step were not stored, then a net 0.8 mole CO_2 would be stored per mole CaO. However, if coal without CO_2 capture were used to provide the energy for calcination, and the CO_2 produced in calcining was not captured, only 0.4 mole CO_2 would be stored net per mole lime (CaO) to the ocean, assuming existing high-efficiency kilns (Kheshgi, 1995). This approach would increase the ocean sink of CO_2, and does not need to be connected to a concentrated CO_2 source or require transport to the deep sea. Such a process would, however, need to avoid rapid re-precipitation of $CaCO_3$, a critical issue yet to be addressed.

Rau and Caldeira (1999) proposed extraction of CO_2 from flue gas via reaction with crushed limestone and seawater. Exhaust gases from coal-fired power plants typically have 15,000 ppmv of CO_2 – over 400 times that of ambient air. A carbonic acid solution formed by contacting sea water with flue gases would accelerate the dissolution of calcite, aragonite, dolomite, limestone, and other carbonate-containing minerals, especially if minerals were crushed to increase reactive surface area. The solution of, for example, Ca^{2+} and dissolved inorganic carbon (primarily in the form of HCO_3^-) in sea water could then be released back into the ocean, where it would be diluted by additional seawater. Caldeira and Rau (2000) estimate that dilution of one part effluent from a carbonate neutralization reactor with 100 parts ambient sea water would result, after equilibration with the atmosphere, in a 10% increase in the calcite saturation state, which they contend would not induce precipitation. This approach does not rely on deep-sea release, avoiding the need for energy to separate, transport and inject CO_2 into the deep ocean. The wastewater generated by this carbonate-neutralization approach has been conjectured to be relatively benign (Rau and Caldeira, 1999). For example, the addition of calcium bicarbonate, the primary constituent of the effluent, has been observed to promote coral growth (Marubini and Thake, 1999). This approach will not remove all the CO_2 from a gas stream, because excess CO_2 is required to produce a solution that is corrosive to carbonate minerals. If greater CO_2 removal were required, this approach could be combined with other techniques of CO_2 capture and storage.

Process wastewater could be engineered to contain different ratios of added carbon and calcium, and different ratios of flue gas CO_2 to dissolved limestone (Caldeira and Wickett, 2005). Processes involving greater amounts of limestone dissolution per mole CO_2 added lead to a greater CO_2 fraction being retained. The effluent from a carbonate-dissolution reactor could have the same *p*H, pCO_2, or $[CO_3^{2-}]$ as ambient seawater, although processing costs may be reduced by allowing effluent composition to vary from these values (Caldeira and Rau, 2000). Elevation in Ca^{2+} and bicarbonate content from this approach is anticipated to be small relative to the already existing concentrations in sea water (Caldeira and Rau, 2000), but effects of the new physicochemical equilibria on physiological performance are unknown. Neutralization of carbon acidity by dissolution of carbonate minerals could reduce impacts on marine ecosystems associated with *p*H and CO_3^{2-} decline (Section 6.7).

Carbonate neutralization approaches require large amounts of carbonate minerals. Sedimentary carbonates are abundant with estimates of 5×10^{17} tonnes (Berner *et al.*, 1983), roughly 10,000 times greater than the mass of fossil-fuel carbon. Nevertheless, up to about 1.5 mole of carbonate mineral must be dissolved for each mole of anthropogenic CO_2 permanently stored in the ocean

(Caldeira and Rau, 2000); therefore, the mass of $CaCO_3$ used would be up to 3.5 times the mass of CO_2 stored. Worldwide, 3 Gt $CaCO_3$ is mined annually (Kheshgi, 1995). Thus, large-scale deployment of carbonate neutralization approaches would require greatly expanded mining and transport of limestone and attendant environmental impacts. In addition, impurities in dissolved carbonate minerals may cause deleterious effects and have yet to be studied.

6.2.3 Other ocean storage approaches

Solid hydrate. Water reacts with concentrated CO_2 to form a solid hydrate (CO_2.6H2O) under typical ocean conditions at quite modest depths (Løken and Austvik, 1993; Holdren and Baldwin, 2001). Rehder *et al.* (2004) showed that the hydrate dissolves rapidly into the relatively dilute ocean waters. The density of pure CO_2 hydrate is greater than seawater, and this has led to efforts to create a sinking plume of released CO_2 in the ocean water column. Pure CO_2 hydrate is a hard crystalline solid and thus will not flow through a pipe, and so some form of CO_2 slurry is required for flow assurance (Tsouris *et al.*, 2004).

Water-$CaCO_3$-CO_2 emulsion. Mineral carbonate could be used to physically emulsify and entrain CO_2 injected in sea water (Swett *et al.* 2005); a 1:1 CO_2:$CaCO_3$ emulsion of CO_2 in water could be stabilized by pulverized limestone ($CaCO_3$). The emulsion plume would have a bulk density of 40% greater than that of seawater. Because the emulsion plume is heavier than seawater, the $CaCO_3$coated CO_2 slurries may sink all the way to the ocean floor. It has been suggested that the emulsion plume would have a *p*H that is at least 2 units higher than would a plume of liquid CO_2. Carbonate minerals could be mined on land, and then crushed, or fine-grained lime mud could be extracted from the sea floor. These fine-grain carbonate particles could be suspended in sea water upstream from the CO_2-rich plume emanating from the direct CO_2 injection site. The suspended carbonate minerals could then be transported with the ambient sea water into the plume, where the minerals could dissolve, increasing ocean CO_2 storage effectiveness and diminishing the *p*H impacts of direct injection.

Emplacement in carbonate sediments. Murray *et al.* (1997) have suggested emplacement of CO_2 into carbonate sediments on the sea floor. Insofar as this CO_2 remained isolated from the ocean, this could be categorized as a form of geologic storage (Chapter 5).

Dry ice torpedoes. CO_2 could be released from a ship as dry ice at the ocean surface (Steinberg,1985). One costly method is to produce solid CO_2 blocks (Murray *et al.*, 1996). With a density of 1.5 t m^{-3}, these blocks would sink rapidly to the sea floor and could potentially penetrate into the sea floor sediment.

Direct flue-gas injection. Another proposal is to take a power plant flue gas, and pump it directly into the deep ocean without any separation of CO_2 from the flue gas, however costs of compression are likely to render this approach infeasible.

6.3. Capacity and fractions retained

6.3.1 Capacity

The physical capacity for storage of CO_2 in the ocean is large relative to fossil-fuel resources. ; The degree to which this capacity will be utilized may be based on factors such as cost, equilibrium pCO_2, and environmental consequences.

Storage capacity for CO_2 in the ocean can be defined relative to an atmospheric CO_2 stabilization concentration. For example, roughly 2,300 to 10,700 $GtCO_2$ (above the natural pre-industrial background) would be added to the ocean in equilibrium with atmospheric CO_2 stabilization concentrations, ranging from 350 ppm to 1000 ppm, regardless of whether the CO_2 is initially released to the ocean or the atmosphere. (Table 6.1, Figure 6.3; Kheshgi *et al.*, 2005; Sorai and Ohsumi, 2005). The capacity of the ocean for CO_2 storage could be increased with the addition of alkalinity to the ocean (e.g., dissolved limestone).

6.3.2 Measures of fraction retained

Effectiveness of ocean CO_2 storage has been reported in a variety of ways. These different ways of reporting result in very different numerical values (Box 6.3).

Box 6.3. Measures of the fraction of CO_2 retained in storage

Different measures have been used to describe how effective intentional storage of carbon dioxide in the ocean is to mitigate climate change (Mueller *et al.*, 2004). Here, we illustrate several of these measures using schematic model results reported by Herzog *et al.* (2003) for injection of CO_2 at three different depths (Figure 6.16).

Figure 6.16. Fraction of carbon in the ocean from injection at three different depths and the atmosphere illustrated with results from a schematic model (Herzog *et al.*, 2003). Calculations assume a background 280 ppm of CO_2 in the atmosphere. Solid lines = retained fraction. Dashed lines = airborne fraction. Grey dashed line = airborne fraction for release to atmosphere.

Fraction retained (see Chapter 1) is the fraction of the cumulative amount of injected CO_2 that is retained in the storage reservoir over a specified period of time, and thereby does not have the opportunity to affect atmospheric CO_2 concentration (Mignone *et al.*, 2004). The retained fraction approaches zero (Figure 6.16) over long times, indicating that nearly all injected CO_2 will interact with the atmosphere (although a small amount would interact first with carbonate sediments).

Airborne Fraction is the fraction of released CO_2 that adds to atmospheric CO_2 content (Kheshgi and Archer, 2004). For atmospheric release, airborne fraction is initially one and decays to roughly 0.2 (depending on atmospheric CO_2 concentration) as the added CO_2 is mixed throughout the ocean, and decays further to about 0.08 as CO_2 reacts with sediments (Archer *et al.*, 1997). For deep-sea release, airborne fraction is initially zero and then approaches that of atmospheric release. Note that the asymptotic airborne fraction depends on the concentration of CO_2 of surface waters (Figure 6.3).

Fraction retained is used throughout this report to indicate how long the CO_2 is stored. In addition the following measures can be used to compare the effectiveness of ocean carbon storage with other options, for example:

- The **Net Present Value** (NPV) approach (Herzog *et al.*, 2003) considers temporary storage to be equivalent to delayed emission of CO_2 to the atmosphere. The value of delaying CO_2 emissions depends on the future costs of CO_2 emission and economic discount rates. There is economic value to temporary storage (i.e., delayed emission) if the cost of CO_2 emissions increases at a rate that is less than the discount rate (Herzog *et al.*, 2003).
- The **Global-Warming Potential** (GW_p) is a measure defined by the IPCC to compare the climatic effect of different greenhouse-gas emissions. It is computed by accumulating the radiative climate forcing of a greenhouse-gas emission over a specified time horizon. This measure has been applied to compare the radiative forcing from oceanic and atmospheric releases of carbon dioxide (Kheshgi *et al.*, 1994, Ramaswamy *et al.*, 2001). Haugan and Joos (2004) propose a modification to the GWP approach that compares the climate effects of the airborne fraction of a CO_2 release to the ocean with those from a release to the atmosphere.

Table 6.2 compares these measures for results from a schematic model at three depths.

Table 6.2. Evaluation of measures described in the text illustrated using schematic model results shown in Figure 6.16. For the Net Present Value measure, the percentage represents the discount rate minus the rate of increase in the cost of CO_2 emission. (If these are equal, the Net Present Value of temporary carbon storage is zero.) Two significant digits shown for illustration exceed the accuracy of model results.

Over several centuries, CO_2 released to the deep ocean would be transported to the ocean surface and interact with the atmosphere. The CO_2-enriched water would then exchange CO_2 with the atmosphere as it approaches chemical equilibrium. In this chemical equilibrium, most of the injected CO_2 remains in the ocean even though it is no longer isolated from the atmosphere (Table 6.1; Figure 6.3). CO_2 that has interacted with the atmosphere is considered to be part of the natural carbon cycle, much in the way that CO_2 released directly to the atmosphere is considered to be part of the natural carbon cycle. Such CO_2 cannot be considered to be isolated from the atmosphere in a way that can be attributable to an ocean storage project.

Loss of isolation of injected CO_2 does not mean loss of all of the injected CO_2 to the atmosphere. In chemical equilibrium with an atmosphere containing 280 ppm CO_2, about 85% of any carbon injected would remain the ocean. If atmospheric CO_2 partial pressures were to approach 1000 ppm, about 66% of the injected CO_2 would remain in the ocean after equilibration with the atmosphere (Table 6.1). Thus, roughly 1/5 to 1/3 of the CO_2 injected into the ocean will eventually reside in the atmosphere, with this airborne fraction depending on the long-term atmosphere-ocean CO_2 equilibrium (Kheshgi, 1995, 2004b). The airborne fraction is the appropriate measure to quantify the effect of ocean storage on atmospheric composition.

6.3.3 Estimation of fraction retained from ocean observations

Observations of radiocarbon, CFCs, and other tracers indicate the degree of isolation of the deep sea from the atmosphere (Prentice *et al.*, 2001). Radiocarbon is absorbed by the oceans from the atmosphere and is transported to the deep-sea, undergoing radioactive decay as it ages. Radiocarbon age (Figure 6.17) is not a perfect indicator of time since a water parcel last contacted the atmosphere because of incomplete equilibration with the atmosphere (Orr, 2004). Taking this partial equilibration into account, the age of North Pacific deep water is estimated to be in the range of 700 to 1000 years. Other basins, such as the North Atlantic, have characteristic overturning times of 300 years or more. This data suggests that, generally, carbon injected in the deep ocean would equilibrate with the atmosphere over a time scale of 300 to 1000 years.

Figure 6.17. Map of radiocarbon (^{14}C) age at 3500 m (Matsumoto and Key, 2004).

6.3.4 Estimation of fraction retained from model results

Ocean models have been used to predict the isolation of injected CO_2 from the atmosphere. Many models are calibrated using ocean radiocarbon data, so model-based estimates of retention of injected CO_2 are not completely independent of the estimates based more directly on observations (Section 6.3.3).

A wide number of studies have used three-dimensional ocean general circulation models to study retention of CO_2 injected into the ocean water column (Bacastow and Stegen, 1991; Bacastow *et al.*, 1997; Nakashiki and Ohsumi, 1997; Dewey *et al.*, 1997, 1999; Archer *et al.*, 1998; Xu *et al.*, 1999; Orr, 2004; Hill *et al.*, 2004). These modelling studies generally confirm inferences based on simpler models and considerations of ocean chemistry and radiocarbon decay rates. In ocean general circulation simulations performed by seven modelling groups (Orr, 2004), CO_2 was injected for 100 years at each of seven different locations and at three different depths. Model results indicate that deeper injections will be isolated from the atmosphere for longer durations. Figure 6.17 shows the effect of injection depth on retained fraction for the mean of seven ocean sites (Orr, 2004). Ranges of model results indicate some uncertainty in forecasts of isolation of CO_2 released to the deep ocean, although for all models the time extent of CO_2 isolation is longer for deeper CO_2 release, and isolation is nearly complete for 100 years following CO_2 release at 3000 m depth (Figure 6.18 and 6.19). However, present-day models disagree as to the degassing time scale for particular locations (Figure 6.19). There seems to be no simple and robust correlation of CO_2 retention other than depth of injection (Caldeira *et al.*, 2002), however, there is some indication that the mean fraction retained for stored carbon is greater in the Pacific Ocean than the Atlantic Ocean, but not all models agree on this. Model results indicate that for injection at 1500 m depth, the time scale of the partial CO_2 degassing is sensitive to the location of the injection, but at 3000 m, results are relatively insensitive to injection location. Model results have been found to be sensitive to differences in numerical schemes and model parameterizations (Mignone *et al.*, 2004).

Figure 6.18. Results are shown for seven ocean general circulation models at three different depths averaged over seven injection locations (Orr, 2004). The percentage efficiency shown is the retained fraction for an injection at a constant rate from 2000 to 2100. Models agree that deeper injection isolates CO_2 from the atmosphere longer than shallower injection. For release at 3000 m, most of the added carbon was still isolated from the atmosphere at the end of the 500 year simulations.

Figure 6.19. Comparison of storage results for three injection locations (at 3000 m depth) in ten ocean model simulations (Orr, 2004). Models differ on predictions of CO_2 fraction retained for release in different oceans.

These ocean general circulation model calculations did not consider interactions with $CaCO_3$ sediments or marine biota. Increased CO_2 concentrations in the ocean promote dissolution of $CaCO_3$ sediments, which would tend to increase predicted CO_2 retention. This has been modelled for the deep sea with results of greater retention for release in the Atlantic because of high $CaCO_3$ inventory in Atlantic sediments (Archer *et al.*, 1998).

Preliminary numerical simulations of ocean CO_2 injection predict increased oceanic retention of injected CO_2 with concurrent global warming due to weaker overturning and a more stratified ocean (Jain and Cao, 2005). Some evidence indicates recent increases in stratification in all major ocean basins (e.g., Joos, 2003; McPhaden and Zhang, 2002; Palmer *et al.*, 2004; Stramma *et al.*, 2004).

6.4. Site selection

6.4.1 Background

There are no published papers specifically on site selection for intentional ocean storage of CO_2; hence, we can discuss only general factors that might be considered when selecting sites for ocean storage. Among these considerations are environmental consequences, costs, safety, and international issues (including cross border transport). Because environmental consequences, costs, and social and political issues are addressed in other parts of this report, here we briefly consider site selection factors that enhance the fraction retained or reduce the costs.

6.4.2 Water column release

Large point sources of CO_2 located near deep water would generally be the most cost effective settings in which to carry out direct CO_2 injection (Figure 6.21; Section 6.9). While models indicate that site-specific differences exist, they do not yet agree on the ranking of potential sites for effectiveness of direct injection CO_2 operations (Orr, 2004).

Figure 6.20. Locations of ocean water at least 1 km and 3 km deep. Distance over land to water that is at least 3 km deep (Caldeira and Wickett, 2005). In general, land areas with the lightest colours would be the most-cost effective land-based settings for a CO_2-injection operation. However, each potential site would need to be evaluated prior to deployment.

6.4.3 CO_2 lakes on the sea floor

CO_2 lakes must be on the sea floor at a depth below 3000 m (Figures 6.20 and 6.21), because the liquid CO_2 must be denser than surrounding sea water (Box 6.2).

Figure 6.21. Relationship between depth and sea floor area.

Flow in ocean bottom boundary layers would need to be taken into account when selecting a site for a CO_2 lake. Bottom friction and turbulence can enhance the dissolution rate and vertical transport of dissolved CO_2 and lead to a short lifetime for the lake (Section 6.2.1.6). It has been suggested that CO_2 lakes would be preferentially sited in relatively restricted depressions or in trenches on sea floor (Ohsumi, 1995).

6.4.4 Limestone neutralization

The amounts of sea water and limestone required to neutralize the acidity of added CO_2 indicate that limestone neutralization would be most suitable for CO_2 point sources located near both the ocean and large deposits of limestone (Rau and Caldeira, 1999).

6.5. Injection technology and operations

6.5.1 Background

The development of ocean storage technology is generally at a conceptual stage; thus, we will only discuss general principles. There has been limited engineering analysis and experimental studies of these conceptual technologies for ocean storage (Nihous, 1997), and no field-testing. No operational experience exists. Various technology concepts have been proposed to improve isolation from the atmosphere or diminish environmental consequences of CO_2 injected into the ocean. Further research and development would be needed to make technologies available, but no major technical barriers are apparent.

6.5.2 Water column release

Dispersal of liquid CO_2 at a depth of 1000 m or deeper is technologically feasible. Since liquid CO_2 may be relatively easily transported to appropriate depths, the preferred release mode is thought at this time to be as a liquid or dense gas phase (achieved by compression beyond its critical point, 72.8 bar at 31°C). The pipes that would carry this CO_2 to the deep ocean would be similar to the pipes that have been used commercially on land to transport CO_2 for use in CO_2 enhanced oil recovery projects (Ozaki *et al.*, 1997). Models (Liro *et al.*, 1992, Drange and Haugan, 1992) predict that, with a properly designed diffuser, nearly all the CO_2 would dissolve in the ocean within a 100 m of the injection depth. Then, this CO_2-rich water would be diluted as it disperses, primarily horizontally along surfaces of constant density.

Water column injection schemes typically envision minimizing local changes to ocean chemistry by producing a relatively dilute initial injection through a series of diffusers or by other means. Dilution would reduce exposure of organisms to very low *p*H (very high CO_2) environments (Section 6.7).

One set of options for releasing CO_2 to the ocean involves transporting liquid CO_2 from shore to the deep ocean in a pipeline. This would not present any major new problems in design, 'according to petroleum engineers and naval architects speaking at one of the IEA Greenhouse Gas R&D Programme ocean storage workshops' (Ormerod *et al.*, 2002). The oil industry has been making great advances in undersea offshore technology, with projects routinely working at depths greater than 1000 m. The oil and the gas industry already places pipes on the bottom of the sea in depths down to 1600 m, and design studies have shown 3000 m to be technically feasible (Ormerod *et al.*, 2002). The 1 m diameter pipe would have the capacity to transport 70,000 tCO_2/day, enough for CO_2 captured from 3 GW_e of a coal-fired electric power plant (Ormerod *et al.*, 2002). Liro *et al.* (1992) proposed injecting liquid CO_2 at a depth of about 1000 m from a manifold lying near the ocean bottom to form a rising droplet plume. Nihous *et al.* (2002) proposed injecting liquid CO_2 at a depth of below 3000 m from a manifold lying near the ocean bottom and forming a sinking droplet plume. Engineering work would need to be done to assure that, below 500 m depth, hydrates do not form inside the discharged pipe and nozzles, as this could block pipe or nozzle flow.

CO_2 could be transported by tanker for release from a stationary platform (Ozaki *et al.*, 1995) or through a towed pipe (Ozaki *et al.*, 2001). In either case, the design of CO_2 tankers would be nearly identical to those that are now used to transport liquid petroleum gas (LPG). Cooling would be used, in order to reduce pressure requirements, with design conditions of –55 degrees C and 6 bar pressure (Ormerod *et al.*, 2002). Producing a dispersed initial concentration would diminish the magnitude of the maximum *p*H excursion. This would probably involve designing for the size of the initial liquid CO_2 droplet and the turbulent mixing behind the towed pipe (Tsushima *et al.*, 2002). Diffusers could be designed so that CO_2 droplets would dissolve completely before they reach the liquid-gas phase boundary.

CO_2 hydrate is about 15% denser than sea water, so it tends to sink, dissolving into sea water over a broad depth horizon (Wannamaker and Adams, 2002). Kajishima *et al.* (1997) and Saito *et al.* (2001) investigated a proposal to create a dense CO_2-seawater mixture at a depth of between 500 and 1000 m to form a current sinking along the sloping ocean bottom . Another proposal (Tsouris *et al.*, 2004; West *et al.*, 2003) envisions releasing a sinking CO_2-hydrate/seawater slurry at between 1000 and 1500 m depth. This sinking plume would dissolve as it sinks, potentially distributing the CO_2 over kilometres of vertical distance, and achieving some fraction of the CO_2 retained in deep storage despite the initial release into intermediate waters. The production of a hydrate/seawater slurry has been experimentally demonstrated at sea (Tsouris *et al.*, 2004). Tsouris *et al.* (2004) have carried out a field experiment at 1000 m ocean depth in which rapid mixing of sea water with CO_2 in a capillary nozzle to a neutrally buoyant composite paste takes place. This would enhance ocean retention time compared to that from creation of a buoyant plume. Aya *et al.* (2004) have shown that a rapidly sinking plume of CO_2 can be formed by release of a slurry combining cold liquid and solid CO_2 with a hydrate skin. This would effectively transfer ship released CO_2 at shallow ocean depth to the deep ocean without the cost of a long pipe. In all of these schemes the fate of the CO_2 is to be dissolved into the ocean, with increased depth of dissolution, and thus increased retention.

6.5.3 Production of a CO_2 lake

Nakashiki(1997) investigated several different kinds of discharge pipes that could be used from a liquid CO_2 tanker to create a CO_2 lake on the sea floor. They concluded that a 'floating discharge pipe' might be the best option because it is simpler than the alternatives and less likely to be damaged by wind and waves in storm conditions.

Aya *et al.* (2003) proposed creating a slurry of liquid CO_2 mixed with dry ice and releasing into the ocean at around 200 to 500 m depth. The dry ice is denser that the surrounding sea water and would cause the slurry to sink. An *in situ* experiment carried out off the coast of California found that a CO_2 slurry and dry ice mass with initial diameter about 8.0 cm sank approximately 50 metres within two minutes before the dry ice melted (Aya *et al.*, 2003). The initial size of CO_2 slurry and dry ice is a critical factor making it possible to sink more than 3000 m to the sea floor. To meet performance criteria, the dry ice content would be controlled with a system consisting of a main power engine, a compressor, a condenser, and some pipe systems.

6.6. Monitoring and verification

6.6.1 Background

Monitoring (Figure 6.22) would be done for at least two different purposes: (1) to gain specific information relating to a particular CO_2 storage operation and (2) to gain general scientific understanding. A monitoring program should attempt to quantify the mass and distribution of CO_2 from each point source and could record related biological and geochemical parameters. These same issues may relate to monitoring of potential leakages from subsea geologic storage, or for verification that such leakage does not occur. Monitoring protocols for submarine sewage disposal for example are already well established, and experience may be drawn from that.

Figure 6.22. Schematic of possible approaches for monitoring the injection of CO_2 into the deep ocean via a pipeline. The grey region represents a plume of high CO_2/low pH water extending from the end of the pipeline. Two sets of chemical, biological and current sensors and two underwater cameras are shown at the end of the pipeline. An array of moored sensors to monitor the direction and magnitude of the resulting plume can be seen around the pipe and are also located along the pipeline to monitor for possible leaks. A shore-based facility provides power to the sensors and for obtaining real-time data and an autonomous underwater vehicle maps the near-field distribution of the plume. A towed undulating pumping system monitors at distances of more than a few kilometres from the injection site. The towed system could provide much greater measurement accuracy and precision, but would also be able to provide measurements over large areas in a relatively short period of time. Moored systems are used to monitor the plume between mapping cruises. These moorings have surface buoys and make daily transmissions back to the monitoring facility via satellite. The very far-field distributions are monitored with hydrographic section cruises conducted every 2–5 years using standard discrete sampling approaches. These approaches provide the accuracy and precision required to detect the small CO_2 signals that add to background variations.

6.6.2 Monitoring amounts and distributions of materials released

6.6.2.1 Monitoring the near field

It appears that there is no serious impediment to verifying plant compliance with likely performance standards for flow through a pipe. Once CO_2 is discharged from the pipe then the specific monitoring protocols will depend upon whether the plume is buoyant or sinking. Fixed location injections present fewer verification difficulties than moving ship options.

For ocean injection from large point sources on land, verifying compliance involves above ground inspection of facilities for verification of flow and the CO_2 purity being consistent with environmental regulations (e.g., trace metal concentrations, etc.). For a power plant, flue gases could be monitored for flow rate and CO_2 partial pressure, thus allowing a full power plant carbon audit.

There are a variety of strategies for monitoring release of CO_2 into the ocean from fixed locations. Brewer *et al.* (2005) observed a plume of CO_2-rich sea water emanating from a small-scale experimental release at 4 km depth with an array of *p*H and conductivity sensors. Measurements of ocean *p*H and current profiles at sufficiently high temporal resolution could be used to evaluate the rate of CO_2 release, local CO_2 accumulation and net transport away from the site (Sundfjord *et al.*, 2001). Undersea video cameras can monitor the point of release to observe CO_2 flow. The very large sound velocity contrast between liquid CO_2 (about 300 m s^{-1}) and sea water (about 1,500 m s^{-1}) offers the potential for very efficient monitoring of the liquid CO_2 phase using acoustic techniques (e.g., sonar).

The placement of CO_2 directly in a lake on the sea floor can be verified, and the quantity and loss rate determined by a combination of acoustic, *p*H, and velocity measurements, and by direct inspection with underwater vehicles. Undersea vehicles, tethered or autonomous, could play a prominent role in monitoring and verification. Autonomous vehicles have been developed that can be programmed to efficiently follow a variety of complex trajectories over large areas (Simonetti, 1998), but accurate *p*H sensing in a rapidly changing pressure and temperature field has yet to be demonstrated. Deep-sea *p*H monitoring from tethered vehicles has been shown to be very precise (Brewer *et al.*, 2004), and these vehicles can routinely collect precisely located samples for later analysis.

6.6.2.2 Monitoring the far field

It will be possible to monitor the far field distributions of injected CO_2 using a combination of shipboard measurements and modelling approaches. The ability to identify *p*H plumes in the ocean has been well demonstrated (Figures 6.23). Current analytical techniques for measuring total CO_2 in the ocean are accurate to about ±0.05% (Johnson *et al.*, 1998). Thus, measurable changes could be seen with the addition of approximately 90 tonnes of CO_2/km^3. In other words, 1 $GtCO_2$ could be detected even if it were dispersed over 10^7 km^3 (i.e., 5000 km x 2000 km x 1 km), if the dissolved inorganic carbon concentrations in the region were mapped out with high-density surveys before the injection began.

Figure 6.23. Measurements showing the ability to measure chemical effects of a natural CO_2 plume. Profiles for pH were taken in June 1999 near the Axial Volcano at 46ºN 130ºW, in the ocean near Portland, Oregon, United States.

Variability in the upper ocean mixed layer would make it difficult to directly monitor small changes in CO_2 in waters shallower than the annual maximum mixed-layer depth. Seasonal mixing from the surface can extend as deep as 800 m in some places, but is less than 200 m in most regions of the ocean. Below the seasonal mixed layer, however, periodic ship-based surveys (every 2 to 5 years) could quantify the expansion of the injection plume.

We do not have a direct means of measuring the evasion of carbon stored in the ocean to the atmosphere. In most cases of practical interest the flux of stored CO_2 from the ocean to atmosphere will be small relative to natural variability and the accuracy of our measurements. Operationally, it would be impossible to differentiate between carbon that has and has not interacted with the atmosphere. The use of prognostic models in evaluating the long-term fate of the injected CO_2 is critical for properly attributing the net storage from a particular site.

Given the natural background variability in ocean carbon concentrations, it would be extremely difficult, if not impossible, to measure CO_2 injected very far from the injection source. The attribution of a signal to a particular point source would become increasingly difficult if injection plumes from different locations began to overlap and mix. In some parts of the ocean it would be difficult to assign the rise in CO_2 to intentional ocean storage as opposed to CO_2 from atmospheric absorption.

6.6.3 Approaches and technologies for monitoring environmental effects

Techniques now being used for field experiments could be used to monitor some near field consequences of direct CO_2 injection (Section 6.7). For example, researchers (Barry *et al.*, 2004, 2005; Carman *et al.*, 2004; Thistle *et al.*, 2005) have been developing experimental means for observing the consequences of elevated CO_2 on organisms in the deep ocean. However, such experiments and studies typically look for evidence of acute toxicity in a narrow range of species (Sato, 2004; Caulfield *et al.,* 1997; Adams *et al.*, 1997; Tamburri *et al.*, 2000). Sub-lethal effects have been studied by Kurihara *et al.* (2004). Process studies, surveys of biogeochemical tracers, and ocean bottom studies could be used to evaluate changes in ecosystem structure and dynamics both before and after an injection.

It is less clear how best to monitor the health of broad reaches of the ocean interior (Sections 6.7.3 and 6.7.4). Ongoing long-term surveys of biogeochemical tracers and deep-sea biota could help to detect long-term changes in deep-sea ecology.

6.7. Environmental impacts, risks, and risk management

6.7.1 Introduction to biological impacts and risk

Overall, there is limited knowledge of deep-sea population and community structure and of deep-sea ecological interactions (Box 6.4). Thus the sensitivities of deep ocean ecosystems to intentional carbon storage and the effects on possibly unidentified goods and services that they may provide remain largely unknown.

Box 6.4. Relevant background in biological oceanography.

Photosynthesis produces organic matter in the ocean almost exclusively in the upper 200 m where there is both light and nutrients (e.g., PO_4, NO_3, NH_4^+, Fe). Photosynthesis forms the base of a marine food chain that recycles much of the carbon and nutrients in the upper ocean. Some of this organic matter ultimately sinks to the deep ocean as particles and some of it is mixed into the deep ocean as dissolved organic matter. The flux of organic matter from the surface ocean provides most of the energy and nutrients to support the heterotrophic ecosystems of the deep ocean (Gage and Tyler, 1991). With the exception of the oxygen minimum zone and near volcanic CO_2 vents, most organisms living in the deep ocean live in low and more or less constant CO_2 levels.

At low latitudes, oxygen consumption and CO_2 release can produce a zone at around 1000 m depth characterized by low O_2 and high CO_2 concentrations, known as the 'oxygen minimum zone'. Bacteria are the primary consumers of organic matter in the deep ocean. They obtain energy predominately by consuming dissolved oxygen in reactions that oxidize organic carbon into CO_2. In the oxygen minimum layer, sea water *p*H may be less than 7.7, roughly 0.5 *p*H units lower than average *p*H of natural surface waters (Figure 6.6).

At some locations near the sea floor, especially near submarine volcanic CO_2 sources, CO_2 concentrations can fluctuate greatly. Near deep-sea hydrothermal vents CO_2 partial pressures (pCO_2, expressed as a ppm fraction of atmospheric pressure, equivalent to μatm) of up to 80,000 ppm have been observed. These are more than 100 times the typical value for deep-sea water. Typically, these vents are associated with fauna that have adapted to these conditions over evolutionary time. For example, tube worms can make use of high CO_2 levels for chemosynthetic CO_2 fixation in association with symbiotic bacteria (Childress *et al.*, 1993). High CO_2 levels (up to a pCO2 of 16,000 ppm; Knoll *et al.*, 1996) have been observed in ocean bottom waters and marine sediments where there are high rates organic matter oxidation and low rates of mixing with the overlying seawater. Under these conditions, high CO_2 concentrations are often accompanied by low O_2 concentrations. Near the surface at night, respiratory fluxes in some relatively confined rock pools of the intertidal zone can produce high CO_2 levels. These patterns suggest that in some environments, organisms have evolved to tolerate relatively wide *p*H oscillations and/or low *p*H values.

Deep-sea ecosystems generally depend on sinking particles of organic carbon made by photosynthesis near the ocean surface settling down through the water. Most species living in the deep sea display very low metabolic rates (Childress, 1995), especially in oxygen minimum layers (Seibel *et al.*, 1997). Organisms living in the deep seawaters have adapted to the energy-limited environment by conserving energy stores and minimizing energy turnover. As a result of energy limitations and cold temperatures found in the deep sea, biological activities tend to be extremely low. For example, respiration rates of rat-tail fish are roughly 0.1% that of their shallow-water relatives. Community respiration declines exponentially with depth along the California margin, however, rapid turnover of large quantities of organic matter has been observed on the ocean floor (Mahaut *et al.*, 1995; Smith and Demopoulos, 2003). Thus, biological activity of some animals living on the deep sea floor can be as great as is found in relatives living on the sea floor in shallow waters.

Deep-sea ecosystems may take a long time to recover from disturbances that reduce population size. Organisms have adapted to the energy-limited environment of the deep sea by limiting investment in reproduction, thus most deep-sea species produce few offspring. Deep-sea species tend to invest heavily in each of their eggs, making them large and rich in yolk to provide the offspring with the resources they will need for survival. Due to their low metabolic rates, deep-sea species tend to grow slowly and have much longer lifespans than their upper-ocean cousins. For example, on the deep-sea floor, a bivalve less than 1 cm across can be more than 100 years old (Gage, 1991). This means that populations of deep-sea species will be more greatly affected by the loss of individual larvae than would upper ocean species. Upon disturbance, recolonization and community recovery in the deep ocean follows similar patterns to those in shallow waters, but on much longer time scales (several years compared to weeks or months in shallow waters, Smith and Demopoulos, 2003).

The numbers of organisms living on the sea floor per unit area decreases exponentially with depth, probably associated with the diminishing flux of food with depth. On the sea floor of the deepest ocean and of the upper ocean, the fauna can be dominated by a few species. Between 2000 and 3000 m depth ecosystems tend to have high species diversity with a low number of individuals, meaning that each species has a low population size (Snelgrove and Smith, 2002). The fauna living in the water column appear to be less diverse than that on the sea floor, probably due to the relative uniformity of vast volumes of water in the deep ocean.

Most ocean storage proposals seek to minimize the volume of water with high CO_2 concentrations either by diluting the CO_2 in a large volume of water or by isolating the CO_2 in a small volume (e.g., in CO_2 lakes). Nevertheless, if deployed widely, CO_2 injection strategies ultimately will produce large volumes of water with somewhat elevated CO_2 concentrations (Figure 6.15). Because large amounts of relatively pure CO_2 have never been introduced to the deep ocean in a controlled experiment, conclusions about environmental risk must be based primarily on laboratory and small-scale *in situ* experiments and extrapolation from these experiments using conceptual and mathematical models. Natural analogues (Box 6.5) can be relevant, but differ significantly from proposed ocean engineering projects.

Box 6.5. Natural analogues and Earth history.

There are several examples of natural systems with strong CO_2 sources in the ocean, and fluid pools toxic to marine life that may be examined to better understand possible physical and biological effects of active CO_2 injection.

Most natural environments that are heavily enriched in CO_2 (or toxic substances) host life forms that have adapted to these special conditions on evolutionary time scales. During Earth history much of the oceans may have hosted life forms specialized on elevated pCO_2, which are now extinct. This limits the use of natural analogues or Earth history to predict and generalize effects of CO_2 injection on most extant marine life.

- *Venting of carbon dioxide-rich fluids:* Hydrothermal vents, often associated with mid-ocean-ridge systems, often release CO_2 rich fluids into the ocean and can be used to study CO_2 behaviour and effects. For example, Sakai *et al.* (1990) observed buoyant hydrate forming fluids containing 86–91% CO_2 (with H_2S, and methane etc. making up the residual) released from the sea floor at 1335–1550 m depth from a hydrothermal vent field. These fluids would be similar to a heavily contaminated industrial CO_2 source. These fluids arise from the reaction of sea water with acid and intermediate volcanic rocks at high temperature; they are released into sea water of 3.8°C. A buoyant hydrate-coated mass forms at the sea floor, which then floats upwards dissolving into the ocean water. Sea floor venting of aqueous fluids, rich in CO_2 and low in *p*H (3.5–4.4), is also to be found in some hydrothermal systems (Massoth *et al.*, 1989; Karl, 1995).
  Near volcanic vents, deep-sea ecosystems can be sustained by a geochemical input of chemical energy and CO_2. While there has been extensive investigation of these sites, and the plumes emanating from them, this has not yet been in the context of analogues for industrial CO_2 storage effects. Such an investigation would show how a fauna has evolved to adapt to a high-CO_2 environment; it would not show how biota adapted to normal ocean water would respond to increased CO_2 concentrations.
- *Deep saline brine pools:* The ocean floor is known to have a large number of highly saline brine pools that are anoxic and toxic to marine life. The salty brines freely dissolve, but mixing into the overlying ocean waters is impeded by the stable stratification imparted by the high density of the dissolving brines.
  The Red Sea contains many such brine pools (Degens and Ross, 1969; Anschutz *et al.*, 1999), some up to 60 km^2 in area, filled with high-temperature hyper-saline, anoxic, brine. Animals cannot survive in these conditions, and the heat and salt that are transported across the brine-seawater interface form a plume into the surrounding bottom water. Hydrothermal sources

resupply brine at the bottom of the brine pool (Anschutz and Blanc, 1996). The Gulf of Mexico contains numerous brine pools. The largest known is the Orca Basin, where a 90 km^2 brine pool in 2250 m water depth is fed by drainage from exposed salt deposits. The salt is toxic to life, but biogeochemical cycles operate at the interface with the overlying ocean (van Cappellen *et al.*, 1998). The Mediterranean also contains numerous large hypersaline basins (MEDRIFF Consortium, 1995).
Taken together these naturally occurring brine pools provide examples of vast volumes of soluble, dense, fluids, hostile to marine life, on the sea floor. The number, volume, and extent of these pools exceed those for scenarios for CO_2 lake formation yet considered. There has been little study of the impact of the plumes emanating from these sources. These could be examined to yield information that may be relevant to environmental impacts of a lake of CO_2 on the ocean floor.

- *Changes over geological time:* In certain times in Earth's geological past the oceans may have contained more dissolved inorganic carbon and/or have had a lower *p*H.
  There is evidence of large-scale changes in calcifying organism distributions in the oceans in the geological record that may be related in changes in carbonate mineral saturation states in the surface ocean. For example, Barker and Elderfield (2002) demonstrated that glacial-interglacial changes in the shell weights of several species of planktonic foraminifera are negatively correlated with atmospheric CO_2 concentrations, suggesting a causal relationship.

Cambrian CO_2 levels (i.e., about 500 million years ago) were as high as 5000 ppm and mean values decreased progressively thereafter (see. Dudley, 1998; Berner, 2002). Two to three times higher than extant ocean calcium levels ensured that calcification of, for example, coral reefs was enabled in paleo-oceans despite high CO_2 levels (Arp *et al.*, 2001). High performance animal life appeared in the sea only after atmospheric CO_2 began to diminish. The success of these creatures may have depended on the reduction of atmospheric CO_2 levels (reviewed by Pörtner *et al.*, 2004, 2005).
CO_2 is also thought to have been a potential key factor in the late Permian/Triassic mass extinction, which affected corals, articulate brachiopods, bryozoans, and echinoderms to a larger extent than molluscs, arthropods and chordates (Knoll *et al.*, 1996; Berner, 2002; Bambach *et al.*, 2002). Pörtner *et al.* (2004) hypothesized that this may be due to the corrosive effect of CO_2 on heavily calcified skeletons. CO_2 excursions would have occurred in the context of large climate oscillations. Effects of temperature oscillations, hypoxia events and CO_2 excursions probably contributed to extinctions (Pörtner *et al.*, 2005, see 6.7.3).

Compared to the surface, most of the deep sea is stable and varies little in its physiochemical factors over time (Box 6.4). The process of evolutionary selection has probably eliminated individuals apt to endure environmental perturbation. As a result, deep-sea organisms may be more sensitive to environmental disturbance than their shallow water cousins (Shirayama, 1997).

Ocean storage would occur deep in the ocean where there is virtually no light and photosynthesizing organisms are lacking, thus the following discussion primarily addresses CO_2 effects on heterotrophic organisms, mostly animals. The diverse fauna that lives in the waters and sediments of the deep ocean can be affected by ocean CO_2 storage, leading to change in ecosystem composition and functioning. Thus, the effects of CO_2 need to be identified at the level of both the individual (physiological) and the ecosystem.

As described in Section 6.2, introduction of CO_2 into the ocean either directly into sea water or as a lake on the sea floor would result in changes in dissolved CO_2 near to and down current from a discharge point. Dissolving CO_2 in sea water (Box 6.1; Table 6.3) increases the partial pressure of

CO_2 (pCO_2, expressed as a ppm fraction of atmospheric pressure, equivalent to µatm), causes decreased *p*H (more acidic) and decreased CO_3^{2-} concentrations (less saturated). This can lead to dissolution of $CaCO_3$ in sediments or in shells of organisms. Bicarbonate (HCO_3^-) is then produced from carbonate (CO_3^{2-}).

Table 6.3. Relationships between ΔpH, changes in pCO_2, and dissolved inorganic carbon concentration calculated for mean deep-sea conditions. Also shown are volumes of water needed to dilute 1 tCO_2 to the specified ΔpH, and the amount of CO_2 that if uniformly distributed throughout the ocean would produce this ΔpH.

The spatial extent of the waters with increased CO_2 content and decreased *p*H will depend on the amount of CO_2 released and the technology and approach used to introduce that CO_2 into the ocean. Table 6.3 shows the amount of sea water needed to dilute each tonne of CO_2 to a specified Δ*p*H reduction. Further dilution would reduce the fraction of ocean at one Δ*p*H while increasing the volume of water experiencing a lesser Δ*p*H. Further examples indicating the spatial extent of ocean chemistry change from added CO_2 are represented in Figures 6.11, 6.12, 6.13, 6.14, and 6.15.

On evolutionary time scales most extant animal life has adapted to, on average, low ambient CO_2 levels. Accordingly, extant animal life may rely on these low pCO_2 values and it is unclear to what extent species would be able to adapt to permanently elevated CO_2 levels. Exposure to high CO_2 levels and extremely acidic water can cause acute mortality, but more limited shifts in CO_2, *p*H, and carbonate levels can be tolerated at least temporarily. Studies of shallow water organisms have identified a variety of physiological mechanisms by which changes in the chemical environment can affect fauna. These mechanisms should also apply to organisms living in the deep ocean. However, knowing physiological mechanisms alone does not enable full assessment of impacts at ecosystem levels. Long-term effects, for intervals greater than the duration of the reproduction cycle or the lifespan of an individual, may be overlooked, yet may still drastically change an ecosystem.

Species living in the open ocean are exposed to low and relatively constant CO_2 levels, and thus may be sensitive to CO_2 exposure. In contrast, species dwelling in marine sediments, especially in the intertidal zone, are regularly exposed to CO_2 fluctuations and thus may be better adapted to high and variable CO_2 concentrations. Physiological mechanisms associated with CO_2 adaptation have been studied mostly in these organisms. They respond to elevated CO_2 concentrations by transiently diminishing energy turnover. However, such responses are likely become detrimental during long-term exposure, as reduced metabolism involves a reduction in physical activity, growth, and reproduction. Overall, marine invertebrates appear more sensitive than fish (Pörtner *et al.*, 2005).

CO_2 effects have been studied primarily in fish and invertebrates from shallow waters, although some of these cover wide depth ranges down to below 2000 m or are adapted to cold temperatures (e.g., Langenbuch and Pörtner, 2003, 2004). Some *in situ* biological experiments used CO_2 in the deep ocean (See Box 6.6)

Box 6.6. *In situ* observations of the response of deep-sea biota to added CO_2.

In situ experiments concerning the sensitivity of deep and shallow-living marine biota to elevated carbon dioxide levels have been limited in scope. Significant CO_2 effects have been observed in experiments, consistent with the mechanisms of CO_2 action reported in Section 6.7.2. Some animals avoid CO_2 plumes, others do not.

Studies evaluating the behaviour and survival of deep-sea animals exposed to liquid CO_2 or to

CO_2-rich sea water have been performed on the continental slope and rise off California. Experiments in which about 20–70 kg of liquid CO_2 were released in small corrals on the sea floor at 3600 m depth were used to measure the response of animals that came in contact with liquid CO_2, and to the dissolution plume emanating from CO_2 pools (Barry *et al.*, 2004). Larger bottom-living animals collected from the sea floor were held in cages and placed at distances of 1–50 m from CO_2 pools. In addition, organisms living in the sediment were collected at a range of distances from CO_2 pools, both before CO_2 release and 1–3 months later.

The response of animals to direct contact with liquid CO_2 varied among species. Sea cucumbers (holothurians like Scotoplanes sp.) and brittle stars (ophiuroids, unidentified species) died immediately after contact with liquid CO_2 (Barry *et al.*, 2005). A few individuals (<5 individuals) of deep-sea fish (grenadiers, *Coryphaenoides armatus*) that approached CO_2 pools and made contact with the fluid turned immediately and swam out of view. Other deep-sea experiments (Tamburri *et al.* 2000) evaluating the behavioural response of animals to a saturated CO_2 / sea water solution have shown that some scavenger species (deep-sea hagfish) will not avoid acidic, CO_2-rich seawater if chemical cues from decaying bait are also present. In fact, hagfish would maintain contact with the CO_2-rich / bait-scented plume long enough to be apparently 'narcotized' by the CO_2.
Survival rates of abyssal animals exposed to CO_2 dissolution plumes in these experiments varied with the range of *p*H perturbation and the distance from the CO_2 source. Abyssal animals held in cages or inhabiting sediments that were near (<1 m) CO_2 pools, and which were exposed episodically to large *p*H reduction (1–1.5 *p*H units) experienced high rates of mortality (>80%). Animals affected included small (meio-)fauna (flagellates, amoebae, nematodes; Barry *et al.*, 2004) and larger (macro and mega-)fauna (Ampeliscid amphipod species, invertebrates like holothurians, echinoids, and fish like macrourids). Other fish like eelpout (zoarcids), however, all survived month-long exposure to episodic *p*H shifts of about –1.0 *p*H units. Animals held further (3–10 m) from CO_2 pools were exposed to mild episodic *p*H reductions (about 0.1 – 0.2 *p*H units) exhibited mortality rates were (about 20–50%) higher than at control sites (Barry *et al.*, 2005).

It is unknown whether mortality was caused primarily by short-term exposure to large *p*H / CO_2 shifts or by chronic, milder *p*H perturbations. Tidal variation in current direction resulted in a highly variable exposure to *p*H perturbations with the most intense exposure to dissolution plumes when the current was flowing directly towards the study animals. During other tidal periods there was often no *p*H reduction, increasing the difficulty of interpreting these experiments.

Three controlled *in situ* experiments were carried out at 2000 m in the Kumano Trough using a specially designed chamber (Figure 6.24; Ishida *et al.* 2005) to address the impact of 5,000 and 20,000 ppm rises in pCO_2 (with resulting *p*Hs of 6.8 and 6.3) on the abundance and diversity of bacteria and of small animals (nano- and meiobenthos). Significant impacts of elevated pCO_2 on meiobenthic organisms could not be found except for one case where the abundance of foraminifera decreased significantly within 3 days at 20,000 ppm. The abundance of nanobenthos decreased significantly in most cases, whereas the abundance of bacteria increased at 20,000 ppm (Figure 6.25).

Figure 6.24. Experimental chamber going to the sea floor. The bottom part houses a chamber that penetrates into the sediment. The top part houses electronics, pumps, valves, and water bags, that are used to control the CO_2 concentration inside the chamber, and to sample sea water in the chamber at designated times. At the time of recovery, the bottom of the chamber is closed, weights are released, and the system returns to the surface of the ocean using buoyancy provided

by the glass bulbs (yellow structures around the top).

Figure 6.25. Preliminary investigations into the change of bacteria, nanobenthos and meiobenthos abundance after exposure to 20,000 and 5,000 ppm CO_2 for 77 to 375 hr during three experiments carried out at 2,000 m depth in Nankai Trough, north-western Pacific. Error bars represent one standard deviation (Ishida *et al*. 2005).

In situ studies of short-term effects of elevated CO_2 concentrations on deep-sea megafauna have been conducted using CO_2 released naturally from the Loihi Seamount (Hawaii) at depths of 1200 to 1300 m (Vetter and Smith, 2005). A submersible was used to manipulate baited traps and bait parcels in Loihi's CO_2 plume to explore the effects of elevated CO_2 on typical deep-sea scavengers. Vent-specialist shrimp were attracted to the bait and proved to be pre-adapted to the high CO_2 levels found close to volcanic vents. Free swimming, amphipods, synaphobranchid eels, and hexanchid sharks avoided open bait parcels placed in the CO_2 plumes

6.7.2 *Physiological effects of CO_2*

6.7.2.1 Effects of CO_2 on cold-blooded water breathing animals

Hypercapnia is the condition attained when an organism (or part thereof) is surrounded by high concentrations of CO_2. Under these conditions, CO_2 enters the organisms by diffusion across body and especially respiratory surfaces and equilibrates with all body compartments. This internal accumulation of CO_2 will be responsible for most of the effects observed in animals (reviewed by Pörtner and Reipschläger, 1996, Seibel and Walsh, 2001, Ishimatsu *et al.*, 2004, 2005; Pörtner *et al.*, 2004, 2005). Respiratory distress, narcosis, and mortality are the most obvious short-term effects at high CO_2 concentrations, but lower concentrations may have important effects on longer time scales. The CO_2 level to which an organism has acclimated may affect its acute critical CO_2 thresholds, however, the capacity to acclimate has not been investigated to date.

6.7.2.2 Effects of CO_2 versus p*H*

Typically, tolerance limits to CO_2 have been characterized by changes in ocean *p*H or pCO_2 (see Shirayama, 1995; Auerbach *et al.*, 1997). However, changes in molecular CO_2, carbonate, and bicarbonate concentrations in ambient water and body fluids may each have specific effects on marine organisms (Pörtner and Reipschläger, 1996). In water breathers like fish or invertebrates CO_2 entry causes immediate disturbances in acid-base status, which need to be compensated for by ion exchange mechanisms. The acute effect of CO_2 accumulation is more severe than that of the reduction in *p*H or carbonate-ion concentrations. For example, fish larvae are more sensitive to low *p*H and high CO_2 than low *p*H and low CO_2 (achieved by addition of HCl with pCO_2 levels kept low by aeration; Ishimatsu *et al.*, 2004).

CO_2 added to sea water will change the hydrogen ion concentration (*p*H). This change in hydrogen ion concentration may affect marine life through mechanisms that do not directly involve CO_2. Studies of effects of lowered *p*H (without concomitant CO_2 accumulation) on aquatic organisms have a long history, with an emphasis on freshwater organisms (Wolff *et al.*, 1988). Observed consequences of lowered water *p*H (at constant pCO_2) include changes in production/productivity patterns in algal and heterotrophic bacterial species, changes in biological calcification/ decalcification processes, and acute and sub-acute metabolic impacts on zooplankton species, ocean bottom species, and fish. Furthermore, changes in the *p*H of marine environments affect: (1) the carbonate system, (2) nitrification (Huesemann *et al.*, 2002) and speciation of nutrients such as phosphate, silicate and ammonia (Zeebe and Wolf-Gladrow, 2001), and (3) speciation and uptake of essential and toxic trace elements. Observations and chemical calculations show that low *p*H conditions generally decrease the association of metals with particles and increase the proportion of biologically available free metals (Sadiq, 1992; Salomons and Forstner, 1984). Aquatic invertebrates take up both essential and non-essential metals, but final body concentrations of metals vary widely across invertebrates. In the case of many trace metals, enhanced bioavailability is likely to have toxicological implications, since free forms of metals are of the greatest toxicological significance (Rainbow, 2002).

6.7.2.3 Acute CO_2 sensitivity: oxygen transport in squid and fish

CO_2 accumulation and uptake can cause anaesthesia in many animal groups. This has been observed in deep-sea animals close to hydrothermal vents or experimental CO_2 pools. A narcotic effect of high, non-determined CO_2 levels was observed in deep-sea hagfish after CO_2 exposure *in situ* (Tamburri *et al.*, 2000). Prior to anaesthesia high CO_2 levels can exert rapid effects on oxygen transport processes and thereby contribute to acute CO_2 effects including early mortality.

Among invertebrates, this type of CO_2 sensitivity may be highest in highly complex, high performance organisms like squid (reviewed by Pörtner *et al.*, 2004). Blue-blooded squid do not possess red blood cells (erythrocytes) to protect their extracellular blood pigment (haemocyanin) from excessive *p*H fluctuations. Acute CO_2 exposure causes acidification of the blood, will hamper oxygen uptake and binding at the gills and reduce the amount of oxygen carried in the blood, limiting performance, and at high concentrations could cause death. Less oxygen is bound to haemocyanin in squid than is bound to haemoglobin in bony fish (teleosts). Jet-propulsion swimming of squid demands a lot of oxygen. Oxygen supply is supported by enhanced oxygen binding with rising blood *p*H (and reduced binding of oxygen with falling pH – a large Bohr effect[3]). Maximizing of oxygen transport in squid thus occurs by means of extracellular pH oscillations between arterial and venous blood. Therefore, finely controlled extracellular pH changes are important for oxygen transport. At high CO_2 concentrations, animals can asphyxiate because the blood cannot transport enough oxygen to support metabolic functions. In the most active open ocean squid (*Illex illecebrosus*), model calculations predict acute lethal effects with a rise in pCO_2 by 6500 ppm and a 0.25 unit drop in blood *p*H. However, acute CO_2 sensitivity varies between squid species. The less active coastal squid (*Loligo pealei*) is less sensitive to added CO_2.

In comparison to squid and other invertebrates, fish (teleosts) appear to be less sensitive to added CO_2, probably due to their lower metabolic rate, presence of red blood cells (erythrocytes containing haemoglobin) to carry oxygen, existence of a venous oxygen reserve, tighter epithelia, and more efficient acid-base regulation. Thus, adult teleosts (bony fish) exhibit a larger degree of independence from ambient CO_2. A number of tested shallow-water fish have shown relatively high tolerance to added CO_2, with short-term lethal limits of adult fish at a pCO_2 of about 50,000 to 70,000 ppm. European eels (*Anguilla anguilla*) displayed exceptional tolerance of acute hypercapnia up to 104,000 ppm (for review see Ishimatsu *et al.*, 2004, Pörtner *et al.*, 2004). The cause of death in fish involves a depression of cardiac functions followed by a collapse of oxygen delivery to tissues (Ishimatsu *et al.*, 2004). With mean lethal CO_2 levels of 13,000 to 28,000 ppm, juveniles are more sensitive to acute CO_2 stress than adults. In all of these cases, the immediate

[3] 'The Bohr Effect is an adaptation in animals to release oxygen in the oxygen starved tissues in capillaries where respiratory carbon dioxide lowers blood *p*H. When blood *p*H decreases, the ability of the blood pigment to bind to oxygen decreases. This process helps the release of oxygen in the oxygen-poor environment of the tissues.' modified after *ISCID Encyclopedia of Science and Philosophy*. 2004. International Society for Complexity, Information, and Design. 12 October 2004 <http://www.iscid.org/encyclopedia/Bohr_Effect>.

cause of death appears to be entry of CO_2 into the organism (and not primarily some other *p*H-mediated effect).

Fish may be able to avoid contact to high CO_2 exposure because they possess highly sensitive CO_2 receptors that could be involved in behavioural responses to elevated CO_2 levels (Yamashita *et al.*, 1989). However, not all animals avoid low pH and high concentrations of CO_2; they may actively swim into CO_2-rich regions that carry the odour of potential food (e.g., bait; Tamburri *et al.*, 2000, Box 6.6).

Direct effects of dissolved CO_2 on diving marine air breathers (mammals, turtles) can likely be excluded since they possess higher pCO_2 values in their body fluids than water breathers and gas exchange is minimized during diving. They may nonetheless be indirectly affected through potential CO_2 effects on the food chain (see 6.7.5).

6.7.2.4 Deep compared with. shallow acute CO_2 sensitivity

Deep-sea organisms may be less sensitive to high CO_2 levels than their cousins in surface waters, but this is controversial. Fish (and cephalopods) lead a sluggish mode of life with reduced oxygen demand at depths below 300 to 400 m. Metabolic activity of pelagic animals, including fish and cephalopods, generally decreases with depth (Childress, 1995; Seibel *et al.*, 1997). However, Seibel and Walsh (2001) postulated that deep-sea animals would experience serious problems in oxygen supply under conditions of increased CO_2 concentrations. They refer to midwater organisms that may not be representative of deep-sea fauna; as residents of so-called 'oxygen minimum layers' they have special adaptations for efficient extraction of oxygen from low-oxygen waters (Sanders and Childress, 1990; Childress and Seibel, 1998).

6.7.2.5 Long-term CO_2 sensitivity

Long-term impacts of elevated CO_2 concentrations are more pronounced on early developmental than on adult stages of marine invertebrates and fish. Long-term depression of physiological rates may, over time scales of several months, contribute to enhanced mortality rates in a population (Shirayama and Thornton, 2002, Langenbuch and Pörtner, 2004). Prediction of future changes in ecosystem dynamics, structure and functioning therefore requires data on sub-lethal effects over the entire life history of organisms.

The mechanisms limiting performance and long-term survival under moderately elevated CO_2 levels are even less clear than those causing acute mortality. However, they appear more important since they may generate impacts in larger ocean volumes during widespread distribution of CO_2 at moderate levels on long time scales. In animals relying on calcareous exoskeletons, physical damage may occur under permanent CO_2 exposure through reduced calcification and even dissolution of the skeleton, however, effects of CO_2 on calcification processes in the deep ocean have not been studied to date. Numerous studies have demonstrated the sensitivity of calcifying organisms living in surface waters to elevated CO_2 levels on longer time scales (Gattuso *et al.* 1999, Reynaud *et al.*, 2003, Feeley *et al.*, 2004 and refs. therein). At least a dozen laboratory and field studies of corals and coralline algae have suggested reductions in calcification rates by 15–85% with a doubling of CO_2 (to 560 ppm) from pre-industrial levels. Shirayama and Thornton (2002) demonstrated that increases in dissolved CO_2 levels to 560 ppm cause a reduction in growth rate and survival of shelled animals like echinoderms and gastropods. These findings indicate that previous atmospheric CO_2 accumulation may already be affecting the growth of calcifying organisms, with the potential for large-scale changes in surface-ocean ecosystem structure. Due to atmospheric CO_2 accumulation, global calcification rates could decrease by 50% over the next century (Zondervan *et al.*, 2001), and there could be significant shifts in global biogeochemical cycles. Despite the potential importance of biogeochemical feedback induced by global change, our understanding of these processes is still in its infancy even in surface waters (Riebesell, 2004). Much less can be said about potential ecosystem shifts in the deep sea (Omori *et al.*, 1998).

Long-term effects of CO_2 elevations identified in individual animal species affects processes in addition to calcification (reviewed by Ishimatsu *et al.*, 2004, Pörtner and Reipschläger, 1996, Pörtner *et al.*, 2004, 2005). In these cases, CO_2 entry into the organism as well as decreased water *p*H values are likely to have been the cause. Major effects occur through a disturbance in acid-base regulation of several body compartments. Falling *p*H values result and these affect many metabolic functions, since enzymes and ion transporters are only active over a narrow *p*H range. *p*H decreases from CO_2 accumulation are counteracted over time by an accumulation of bicarbonate anions in the affected body compartments (Heisler, 1986; Wheatly and Henry, 1992, Pörtner *et al.*, 1998; Ishimatsu *et al.* 2004), but compensation is not always complete. Acid-base relevant ion transfer may disturb osmoregulation due to the required uptake of appropriate counter ions, which leads to an additional NaCl load of up to 10% in marine fish in high CO_2 environments (Evans, 1984; Ishimatsu *et al.*, 2004). Long-term disturbances in ion equilibria could be involved in mortality of fish over long time scales despite more or less complete compensation of acidification.

Elevated CO_2 levels may cause a depression of aerobic energy metabolism, due to incomplete compensation of the acidosis, as observed in several invertebrate examples (reviewed by Pörtner *et al.* 2004, 2005). In one model organism, the peanut worm *Sipunculus nudus*, high CO_2 levels caused metabolic depression of up to 35% at 20,000 ppm pCO_2. A central nervous mechanism also contributed, indicated by the accumulation of adenosine in the nervous tissue under 10,000 ppm pCO_2. Adenosine caused metabolic depression linked to reduced ventilatory activity even more so when high CO_2 was combined with oxygen deficiency (anoxia; Lutz and Nilsson, 1997). Studies addressing the specific role of adenosine or other neurotransmitters at lower CO_2 levels or in marine fish during hypercapnia are not yet available.

The depression of metabolism observed under high CO_2 concentrations in marine invertebrates also includes inhibition of protein synthesis – a process that is fundamental to growth and reproduction. A CO_2 induced reduction of water *p*H to 7.3 caused a 55% reduction in growth of Mediterranean mussels (Michaelidis *et al.* 2005; for review see Pörtner *et al.* 2004, 2005). Fish may also grow slowly in high CO_2 waters. Reduced growth was observed in juvenile white sturgeon (Crocker and Cech, 1996). In this case, the stimulation of ventilation and the associated increase in oxygen consumption indicated a shift in energy budget towards maintenance metabolism, which occurred at the expense of growth. This effect was associated with reductions in foraging activity. A harmful influence of CO_2 on reproductive performance was found in two species of marine copepods (*Acartia steuri, Acartia erythrea*) and sea urchins (*Hemicentrotus purcherrimus, Echinometra mathaei*). While survival rates of adult copepods were not affected during 8 days at pCO_2 up to 10,000 ppm, egg production and hatching rates of eggs were significantly reduced concomitant to an increased mortality of young-stage larvae seen at water *p*H 7.0 (Kurihara *et al.*, 2004). In both sea urchin species tested, fertilization rates decreased with pCO_2 rising above1000 ppm (below water *p*H 7.6; Kurihara *et al.*, 2004). Hatching and survival of fish larvae also declined with water pCO_2 and exposure time in all examined species (Ishimatsu *et al.*, 2004).

6.7.3 From physiological mechanisms to ecosystems

CO_2 effects propagate from molecules via cells and tissues to whole animals and ecosystems (Figure 6.26; Table 6.4). Organisms are affected by chemistry changes that modulate crucial physiological functions. The success of a species can depend on effects on the most sensitive stages of its life cycle (e.g., egg, larvae, adult). Effects on molecules, cells, and tissues thus integrate into whole animal effects (Pörtner *et al.*, 2004), affecting growth, behaviour, reproduction, and development of eggs and larvae. These processes then determine the ecological success (fitness) of a species, which can also depend on complex interaction among species. Differential effects of chemistry changes on the various species thus affect the entire ecosystem. Studies of CO_2 susceptibility and affected mechanisms in individual species (Figure 6.26) support development of a cause and effect understanding for an entire ecosystem's response to changes in ocean chemistry, but need to be complemented by field studies of ecosystem consequences.

Table 6.4. Physiological and ecological processes affected by CO_2 (note that listed effects on phytoplankton are not relevant in the deep sea, but may become operative during large-scale mixing of CO_2). Based on reviews by Heisler, 1986, Wheatly and Henry, 1992, Claiborne *et al*., 2002, Langdon et al., 2003, Shirayama and Thornton, 2002, Kurihara *et al*., 2004, Ishimatsu *et al*., 2004, 2005, Pörtner *et al*. 2004, 2005, Riebesell, 2004, Feeley *et al*., 2004 and references therein.

Figure 6.26. Effects of added CO_2 at the scale of molecule to organism and associated changes in proton (H^+), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) levels in a generalized and simplified marine invertebrate or fish. The blue region on top refers to open water; the tan region represents the organism. Generalized cellular processes are depicted on the left and occur in various tissues like brain, heart or muscle; depression of these processes has consequences (depicted on the right and top). Under CO_2 stress, whole animal functions, like growth, behaviours or reproduction are depressed (adopted from Pörtner *et al*., 2005, – or + denotes a depression or stimulation of the respective function). Black arrows reflect diffusive movement of CO_2 between compartments. Red arrows reflect effective factors, CO_2, H^+, HCO_3^- that modulate functions. Shaded areas indicate processes relevant for growth and energy budget.

Tolerance thresholds likely vary between species and phyla, but still await quantification for most organisms. Due to differential sensitivities among and within organisms, a continuum of impacts on ecosystems is more likely than the existence of a well-defined threshold beyond which CO_2 cannot be tolerated. Many species may be able to tolerate transient CO_2 fluctuations, but may not be able to settle and thrive in areas where CO_2 levels remain permanently elevated. At concentrations that do not cause acute mortality, limited tolerance may include reduced capacities of higher functions, that is added CO_2 could reduce the capacity of growth and reproduction, or hamper resistance to infection (Burnett, 1997). It could also reduce the capacity to attack or escape predation, which would have consequences for the organism's food supply and thus overall fitness with consequences for the rest of the ecosystem.

Complex organisms like animals proved to be more sensitive to changing environmental conditions like temperature extremes than are simpler, especially unicellular, organisms (Pörtner, 2002). It is not known whether animals are also more sensitive to extremes in CO_2. CO_2 affects many physiological mechanisms that are also affected by temperature and hypoxia (Figure 6.26). Challenges presented by added CO_2 could lower long-term resistance to temperature extremes and thus narrow zoogeographical distribution ranges of affected species (Reynaud *et al.*, 2003, Pörtner *et al.*, 2005).

At the ecosystem level, few studies carried out in surface oceans report that species may benefit under elevated CO_2 levels. Riebesell (2004) summarized observations in surface ocean mesocosms under glacial (190 ppm) and increased CO_2 concentrations (790 ppm). High CO_2 concentrations caused higher net community production of phytoplankton. Diatoms dominated under glacial and elevated CO_2 conditions, whereas *Emiliania huxleyi* dominated under present CO_2 conditions. This example illustrates how species that are less sensitive to added CO_2 could become dominant in a high CO_2 environment, in this case due to stimulation of photosynthesis in resource limited phytoplankton species (Riebesell 2004). These conclusions have limited applicability to the deep sea, where animals and bacteria dominate. In animals, most processes are expected to be depressed by high CO_2 and low *p*H levels (Table 6.4).

6.7.4 Biological consequences for water column release scenarios

Overall, extrapolation from knowledge mostly available for surface oceans indicates that acute CO_2 effects (e.g., narcosis, mortality) will only occur in areas where pCO_2 plumes reach significantly above 5000 ppm of atmospheric pressure (in the most sensitive squid) or above 13,000 or 40,000 ppm for juvenile or adult fish, respectively. Such effects are thus expected at CO_2 increases with $\Delta p\mathrm{H} < -1.0$ for squid. According to the example presented in Figure 6.12, a towed pipe could avoid *p*H changes of this magnitude, however a fixed pipe without design optimization would produce a volume of several km^3 with this *p*H change for an injection rate of 100 kg s^{-1}. Depending on the scale of injection such immediate effects may thus be chosen to be confined to a small region of the ocean (Figures 6.13 and 6.14).

Available knowledge of CO_2 effects and underlying mechanisms indicate that effects on marine fauna and their ecosystems will likely set in during long-term exposure to pCO_2 of more than 400 to 500 ppm or associated moderate *p*H changes (by about 0.1–0.3 units), primarily in marine invertebrates (Pörtner *et al.* 2005) and, possibly, unicellular organisms. For injection at a rate of 0.37 $GtCO_2$ yr^{-1} for 100 years (Figure 6.14), such critical *p*H shifts would occur in less than 1% of the total ocean volume by the end of this period. However, baseline *p*H shifts by 0.2 to 0.4 *p*H-units expected from the WRE550 stabilization scenario already reach that magnitude of change. Additional long-term repeated large-scale global injection of 10% of the CO_2 originating from 18,000 $GtCO_2$ fossil fuel would cause an extension of these *p*H shifts from the surface ocean to significantly larger (deeper) fractions of the ocean by 2100 to 2300 (Figure 6.15). Finally, large-scale ocean disposal of all of the CO_2 would lead to *p*H decreases of more than 0.3 and associated long-term effects in most of the ocean. Expected effects will include a reduction in the productivity of calcifying organisms leading to higher ratios of non-calcifiers over calcifiers (Pörtner *et al.*, 2005). Reduced capacities for growth, productivity, behaviours, and reduced lifespan imply a reduction in population densities and productivities of some species, if not reduced biodiversity. Food chain length and composition may be reduced associated with reduced food availability for high trophic levels. This may diminish resources for local or global fisheries. The suggested scenarios of functional depression also include a CO_2 induced reduction in tolerance to thermal extremes, which may go hand in hand with reduced distribution ranges as well as enhanced geographical distribution shifts. All of these expectations result from extrapolations of current physiological and ecological knowledge and require verification in experimental field studies. The capacity of ecosystems to compensate or adjust to such CO_2 induced shifts is also unknown. Continued research efforts could identify critical mechanisms and address the potential for adaptation on evolutionary time scales.

6.7.5 Biological consequences associated with CO_2 lakes

Strategies that release liquid CO_2 close to the sea floor will be affecting two ecosystems: the ecosystem living on the sea floor, and deep-sea ecosystem living in the overlying water. Storage as a topographically confined 'CO_2 lake' would limit immediate large-scale effects of CO_2 addition, but result in the mortality of most organisms under the lake that are not able to flee and of organisms that wander into the lake. CO_2 will dissolve from the lake into the bottom water, and this will disperse around the lake, with effects similar to direct release of CO_2 into the overlying water. According to the scenarios depicted in Figures 6.11 and 6.12 for CO_2 releases near the sea floor, *p*H reductions expected in the near field are well within the scope of those expected to exert significant effect on marine biota, depending on the length of exposure**.**

6.7.6 Contaminants in CO_2 streams

The injection of large quantities of CO_2 into the deep ocean will itself be the topic of environmental concern, so the matter of possible small quantities of contaminants in the injected material is of additional but secondary concern. In general there are already stringent limits on contaminants in CO_2 streams due to human population concerns, and technical pipeline considerations. The setting of any additional limits for ocean disposal cannot be addressed with any certainty at this time.

There are prohibitions in general against ocean disposal; historical concerns have generally focused on heavy metals, petroleum products, and toxic industrial chemicals and their breakdown products.

A common contaminant in CO_2 streams is H_2S. There are very large sources of H_2S naturally occurring in the ocean: many marine sediments are anoxic and contain large quantities of sulphides; some large ocean basins (the Black Sea, the Cariaco Trench etc.) are anoxic and sulphidic. As a result ocean ecosystems that have adapted to deal with sulphide and sulphur-oxidizing bacteria are common throughout the worlds oceans. Nonetheless the presence of H_2S in the disposal stream would result in a lowering of local dissolved oxygen levels, and have an impact on respiration and performance of higher marine organisms.

6.7.7 Risk management

There is no peer-reviewed literature directly addressing risk management for intentional ocean carbon storage; however, there have been risk management studies related to other uses of the ocean. Oceanic CO_2 release carries no expectation of risk of catastrophic atmospheric degassing such as occurred at Lake Nyos (Box 6.7). Risks associated with transporting CO_2 to depth are discussed in Chapter 4 (Transport).

Box 6.7. Lake Nyos and deep-sea carbon storage.

About 2 million tonnes of CO_2 gas produced by volcanic activity were released in one night in 1986 by Lake Nyos, Cameroon, causing the death of at least 1700 people (Kling *et al.*, 1994). Could CO_2 released in the deep sea produce similar catastrophic release at the ocean surface?

Such a catastrophic degassing involves the conversion of dissolved CO_2 into the gas phase. In the gas phase, CO_2 is buoyant and rises rapidly, entraining the surrounding water into the rising plume. As the water rises, CO_2 bubbles form more readily. These processes can result in the rapid release of CO_2 that has accumulated in the lake over a prolonged period of magmatic activity.

Bubbles of CO_2 gas can only form in sea water shallower than about 500 m when the partial pressure of CO_2 in sea water exceeds the ambient total pressure. Most release schemes envision CO_2 release deeper than this. CO_2 released below 3000 m would tend to sink and then dissolve into the surrounding seawater. CO_2 droplets released more shallowly generally dissolve within a few 100 vertical metres of release.

The resulting waters are too dilute in CO_2 to produce partial CO_2 pressures exceeding total ambient pressure, thus CO_2 bubbles would not form. Nevertheless, if somehow large volumes of liquid CO_2 were suddenly transported above the liquid-gas phase boundary, there is a possibility of a self-accelerating regime of fluid motion that could lead to rapid degassing at the surface. The disaster at

Lake Nyos was exacerbated because the volcanic crater confined the CO_2 released by the lake; the open ocean surface does not provide such topographic confinement. Thus, there is no known mechanism that could produce an unstable volume of water containing 2 million tCO_2 at depths shallower than 500 m, and thus no mechanism known by which ocean carbon storage could produce a disaster like that at Lake Nyos.

It may be possible to recover liquid CO_2 from a lake on the ocean floor. The potential reversibility of the production of CO_2 lakes might be considered a factor that diminishes risk associated with this option.

6.7.8 Social aspects; public and stakeholder perception

The study of public perceptions and perceived acceptability of intentional CO_2 storage in the ocean is at an early stage and comprises only a handful of studies (Curry *et al.*, 2005; Gough *et al.*, 2002; Itaoka *et al.*, 2004; Palmgren *et al.*, 2004). Issues crosscutting public perception of both geologic and ocean storage are discussed in Section 5.8.5.

All studies addressing ocean storage published to date have shown that the public is largely uninformed about ocean carbon storage and thus holds no well-developed opinion. There is very little awareness among the public regarding intentional or unintentional ocean carbon storage. For example, Curry *et al.* (2005) found that the public was largely unaware of the role of the oceans in absorbing anthropogenic carbon dioxide released to the atmosphere. In the few relevant studies conducted thus far, the public has expressed more reservations regarding ocean carbon CO_2 storage than for geologic CO_2 storage.

Education can affect the acceptance of ocean storage options. In a study conducted in Tokyo and Sapporo, Japan (Iatoka *et al*, 2004), when members of the public, after receiving some basic information, were asked to rate ocean and geologic storage options on a 1 to 5 scale (1 = no, 5 = yes) the mean rating for dilution-type ocean storage was 2.24, lake-type ocean storage was rated at 2.47, onshore geologic storage was rated at 2.57, and offshore geologic storage was rated at 2.75. After receiving additional information from researchers, the mean rating for dilution-type and lake-type ocean storage increased to 2.42 and 2.72, respectively, while the mean ratings for onshore and offshore geologic storage increased to 2.65 and 2.82, respectively. In a similar conducted study in Pittsburgh, USA, Palmgren *et al.* (2004) found that when asked to rate ocean and geologic storage on a 1 to 7 scale (1 = completely oppose, 7 = completely favour) respondents' mean rating was about 3.2 for ocean storage and about 3.5 for geologic storage. After receiving information selected by the researchers, the respondents changed their ratings to about 2.4 for ocean storage and 3.0 for geologic storage. Thus, in the Itaoka *et al.* (2004) study the information provided by the researchers increased the acceptance of all options considered whereas in the Study of Palmgren *et al.* (2004) the information provided by the researchers decreased the acceptance of all options considered. The differences could be due to many causes, nevertheless, they suggest that the way information is provided by researchers could affect whether the added information increases or decreases the acceptability of ocean storage options.

Gough *et al.* (2002) reported results from discussions of carbon storage from two unrepresentative focus groups comprising a total of 19 people. These focus groups also preferred geologic storage to ocean storage; this preference appeared to be based, 'not primarily upon concerns for the deep-sea ecological environment', but on 'the lack of a visible barrier to prevent CO_2 escaping' from the oceans. Gough *et al.* (2002) notes that 'significant opposition' developed around a proposed ocean CO_2 release experiment in the Pacific Ocean (see Section 6.2.1.2).

6.8. Legal issues

6.8.1 International law

Please refer to Sections 5.8.1.1 (*Sources and nature of international obligations*) and 5.8.1.2 (*Key issues in the application of the treaties to* CO_2 *storage*) for the general position of both geological and ocean storage of CO_2 under international law. It is necessary to look at and interpret the primary sources, the treaty provisions themselves, to determine the permissibility or otherwise of ocean storage. Some secondary sources, principally the 2004 OSPAR Jurists Linguists' paper containing the States Parties' interpretation of the Convention (considered in detail in Section 5.8.1.3) and conference papers prepared for the IEA workshop in 1996, contain their authors' individual interpretations of the treaties.

McCullagh (1996) considered the international legal control of ocean storage, and found that, whilst the UN Framework Convention on Climate Change (UNFCCC) encourages the use of the oceans as a reservoir for CO_2, the UN Convention on the Law of the Sea (UNCLOS) is ambiguous in its application to ocean storage. Whilst ocean storage will reduce CO_2 emissions and combat climate change, to constitute an active use of sinks and reservoirs as required by the UNFCCC, ocean storage would need to be the most cost-effective mitigation option. As for UNCLOS, it is unclear whether ocean storage will be allowable in all areas of the ocean, but provisions on protecting and preserving the marine environment will be applicable if CO_2 is deemed to be 'pollution' under the Convention (which will be so, as the large quantity of CO_2 introduced is likely to cause harm to living marine resources). In fulfilling their obligation to prevent, reduce and control pollution of the marine environment, states must act so as not to transfer damage or hazards from one area to another or transform one type of pollution into another, a requirement that could be relied upon by proponents and opponents alike.

Churchill (1996) also focuses on UNCLOS in his assessment of the international legal issues, and finds that the consent of the coastal state would be required if ocean storage occurred in that state's territorial sea (up to12 miles from the coast). In that state's Exclusive Economic Zone (up to 200 miles), the storage of CO_2 via a vessel or platform (assuming it constituted 'dumping' under the Convention) would again require the consent of that state. Its discretion is limited by its obligation to have due regard to the rights and duties of other states in the Exclusive Economic Zone under the Convention, by other treaty obligations (London and OSPAR) and the Convention's general duty on parties not to cause damage by pollution to other states' territories or areas beyond their national jurisdiction. He finds that it is uncertain whether the definition of 'dumping' would apply to use of a pipeline system from land for ocean storage, but, in any event, concludes that the discharge of CO_2 from a pipeline will, in many circumstances, constitute pollution and thus require the coastal state to prevent, reduce and control such pollution from land-based sources. But ocean storage by a pipeline from land into the Exclusive Economic Zone will not fall within the rights of a coastal or any other state and any conflict between them will be resolved on the basis of equity and in the light of all the relevant circumstances, taking into account the respective importance of the interests involved to the parties as well as to the international community as a whole. He finds that coastal states do have the power to regulate and control research in their Exclusive Economic Zones, although such consent is not normally withheld except in some cases.

As for the permissibility of discharge of CO_2 into the high seas (the area beyond the Exclusive Economic Zone open to all states), Churchill (1996) concludes that this will depend upon whether the activity is a freedom of the high sea and is thus not prohibited under international law, and finds that the other marine treaties will be relevant in this regard.

Finally, the London Convention is considered by Campbell (1996), who focuses particularly on the 'industrial waste' definition contained in Annex I list of prohibited substances, but does not provide an opinion upon whether CO_2 is covered by that definition 'waste materials generated by manufacturing or processing operations', or indeed the so-called reverse list exceptions to this prohibition, or to the general prohibition under the 1996 Protocol.

6.8.2 National laws

6.8.2.1 Introduction

CO_2 ocean storage, excluding injection from vessels, platforms or other human-made structures into the subseabed to which the Assessment made in Section 5.8 applies, is categorized into the following two types according to the source of injection of the CO_2 (land or sea) and its destination (sea): (1) injection from land (via pipe) into the seawater; (2) injection from vessels, platforms or other human-made structures into sea water (water column, ocean floor).

States are obliged to comply with the provisions of international law mentioned above in Section 6.8.1, in particular treaty law to which they are parties. States have to implement their international obligations regarding CO_2 ocean storage either by enacting relevant national laws or revising existing ones. There have been a few commentaries and papers on the assessment of the legal position of ocean storage at national level. However, the number of countries covered has been quite limited. Summaries of the assessment of the national legal issues having regard to each type of storage mentioned above to be considered when implementing either experimental or fully-fledged ocean storage of CO_2 are provided below.

With regard to the United States, insofar as CO_2 from a fossil-fuel power plant is considered industrial waste, it would be proscribed under the Ocean Dumping Ban Act of 1988. The Marine Protection, Research, and Sanctuaries Act of 1972 (codified as 33 U.S.C. 1401–1445, 16 U.S.C. 1431–1447f, 33 U.S.C. 2801–2805), including the amendments known as the Ocean Dumping Ban Act of 1988, has the aim of to regulating intentional ocean disposal of materials, while authorizing related research. The Ocean Dumping Ban Act of 1988 placed a ban on ocean disposal of sewage sludge and industrial wastes after 31 December 1991.

The US Environmental Protection Agency (US EPA) specified protective criteria for marine waters, which held *p*H to a value between 6.5 and 8.5, with a limit on overall excursion of no more than 0.2 *p*H units outside the naturally occurring range (see: Train, 1979). Much of the early work on marine organisms reflected concerns about the dumping of industrial acid wastes (e.g., acid iron wastes from TiO_2 manufacture) into marine waters. For the most part, however, these studies failed to differentiate between true *p*H effects and the effects due to CO_2 liberated by the introduction of acid into the test systems.

6.8.2.2 Injection from land (via pipe) into seawater

States can regulate the activity of injection within their jurisdiction in accordance with their own national rules and regulations. Such rules and regulations would be provided by, if any, the laws relating to the treatment of high-pressure gases, labour health and safety, control of water pollution, dumping at sea, waste disposal, biological diversity, environmental impact assessment etc. It is, therefore, necessary to check whether planned activities of injection fall under the control of relevant existing rules and regulations.

6.8.2.3 Injection from vessels, platforms or other human-made structures into sea water (water column, ocean floor)

It is necessary to check whether the ocean storage of CO_2 is interpreted as 'dumping' of 'industrial waste' by relevant national laws, such as those on dumping at sea or waste disposal, because this could determine the applicability of the London Convention and London Protocol (see Section 6.8.1). Even if ocean storage is not prohibited, it is also necessary to check whether planned activities will comply with the existing relevant classes of rules and regulations, if any, mentioned above.

6.9. Costs

6.9.1 Introduction

Studies on the engineering cost of ocean CO_2 storage have been published for cases where CO_2 is transported from a power plant located at the shore by either ship to an offshore injection platform or injection ship (Section 6.9.2), or pipeline running on the sea floor to an injection nozzle (Section 6.9.3). Costs considered in this section include those specific to ocean storage described below and include the costs of handling of CO_2 and transport of CO_2 offshore, but not costs of onshore transport (Chapter 4).

6.9.2 Dispersion from ocean platform or moving ship

Costs have been estimated for ship transport of CO_2 to an injection platform, with CO_2 injection from a vertical pipe into mid- to deep ocean water, or a ship trailing an injection pipe (Akai *et al.*, 2004; IEA-GHG, 1999; Ozaki, 1997; Akai *et al.*, 1995; Ozaki *et al.*, 1995). In these cases, the tanker ship transports liquid CO_2 at low temperature (–55 to –50ºC) and high pressure (0.6 to 0.7 MPa).

Table 6.5 shows storage costs for cases (Akai *et al.*, 2004) of ocean storage using an injection platform. In these cases, CO_2 captured from three power plants is transported by a CO_2 tanker ship to a single floating discharge platform for injection at a depth of 3000 m. The cost of ocean storage is the sum of three major components: tank storage of CO_2 onshore awaiting shipping; shipping of CO_2; and the injection platform pipe and nozzle. The sum of these three components is 11.5 to 12.8 US$/t$CO_2$ shipped 100 to 500 km. Assuming an emission equal to 3% of shipped CO_2 from boil-off and fuel consumption, the estimated cost is 11.9 to 13.2 US$/t$CO_2$ net stored.

Table 6.5. Ocean storage cost estimate for CO_2 transport and injection at 3000 m depth from a floating platform. Scenario assumes three pulverized coal-fired power plants with a net generation capacity of 600 MW_e each transported either 100 or 500 km by a CO_2 tanker ship of 80,000 m^3 capacity to a single floating discharge platform.

Liquid CO_2 could be delivered by a CO_2 transport ship to the injection area and then transferred to a CO_2 injection ship, which would tow a pipe injecting the CO_2 into the ocean at a depth of 2,000 to 2,500 m. Estimated cost of ocean storage (Table 6.6) is again the sum of three major components: tank storage of CO_2 onshore awaiting shipping; shipping of CO_2; and the injection ship, pipe and nozzle (Table 6.6; Akai *et al.*, 2004). The sum of these three components is 13.8 to 15.2 US$/t$CO_2$ shipped 100 to 500 km. Assuming an emission equal to 3% of shipped CO_2 from boil-off and fuel consumption, the estimated cost is 14.2 to 15.7 US$/t$CO_2$ net stored.

Table 6.6. Ocean storage cost estimate for CO_2 transport and injection at 2000–2500 m depth from a moving ship.

6.9.3 Dispersion by pipeline extending from shore into shallow to deep water

Compared with the ship transport option (6.9.2), pipeline transport of CO_2 is estimated to cost less for transport over shorter distances (e.g., 100 km) and more for longer distances (e.g., 500 km), since the cost of ocean storage via pipeline scales with pipeline length.

The cost for transporting CO_2 from a power plant located at the shore through a pipeline running on the sea floor to an injection nozzle has been estimated by IEA-GHG (1994) and Akai *et al.* (2004). In the recent estimate of Akai *et al.* (2004), CO_2 captured from a pulverized coal fired power plant with a net generation capacity of 600 MW_e is transported either 100 or 500 km by a CO_2 pipeline for injection at a depth of 3000 m at a cost of 6.2 US$/t$CO_2$ net stored (100 km case) to 31.1 US$/t$CO_2$ net stored (500 km case).

There are no published cost estimates specific to the production of a CO_2 lake on the sea floor; however, it might be reasonable to assume that there is no significant difference between the cost of CO_2 lake production and the cost of water column injection given this dominance of pipeline costs.

6.9.4 Cost of carbonate neutralization approach

Large-scale deployment of carbonate neutralization would require a substantial infrastructure to mine, transport, crush, and dissolve these minerals, as well as substantial pumping of seawater, presenting advantages for coastal power plants near carbonate mineral sources.

There are many trade-offs to be analyzed in the design of an economically optimal carbonate-neutralization reactor along the lines of that described by Rau and Caldeira (1999). Factors to be considered in reactor design include water flow rate, gas flow rate, particle size, pressure, temperature, hydrodynamic conditions, purity of reactants, gas-water contact area, etc. Consideration of these factors has led to preliminary cost estimates for this concept, including capture, transport, and energy penalties, of 10 to 110 US$/t$CO_2$ net stored (Rau and Caldeira, 1999).

6.9.5 Cost of monitoring and verification

The cost of a monitoring and verification program could involve deploying and maintaining a large array of sensors in the ocean. Technology exists to conduct such monitoring, but a significant fraction of the instrument development and production is limited to research level activities. No estimate of costs for near-field monitoring for ocean storage have been published, but the costs of limited near-field monitoring would be small compared to the costs of ocean storage in cases of the scale considered in 6.9.2-3. Far field monitoring can benefit from international research programs that are developing global monitoring networks.

6.10. Gaps

The science and technology of ocean carbon storage could move forward by addressing the following major gaps:

- *Biology and ecology:* Studies of the response of biological systems in the deep sea to added CO_2, including studies that are longer in duration and larger in scale than yet performed.
- *Research facilities:* Research facilities where ocean storage concepts (e.g., release of CO_2 from a fixed pipe or ship, or carbonate-neutralization approaches) can be applied and their effectiveness and impacts assessed *in situ* at small-scale on a continuing basis for the purposes of both scientific research and technology development.

- *Engineering:* Investigation and development of technology for working in the deep sea, and the development of pipes, nozzles, diffusers, etc., which can be deployed in the deep sea with assured flow and be operated and maintained cost-effectively.
- *Monitoring:* Development of techniques and sensors to detect CO_2 plumes and their biological and geochemical consequences.

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Tables

Table 6.1. Amount of additional CO_2 residing in the ocean after atmosphere-ocean equilibration for different atmospheric stabilization concentrations. The uncertainty range represents the influence of climate sensitivity to a CO_2 doubling in the range of 1.5 to 4.5°C (Kheshgi *et al*., 2005; Kheshgi 2004a). This table considers the possibility of increased carbon storage in the terrestrial biosphere. Such an increase, if permanent, would allow a corresponding increase in total cumulative emissions. This table does not consider natural or engineered dissolution of carbonate minerals, which would increase ocean storage of anthropogenic carbon. The amount already in the oceans exceeds 500 $GtCO_2$ (= 440 $GtCO_2$ for 1994 (Sabine *et al*., 2004) plus CO_2 absorption since that time). The long-term amount of CO_2 stored in the deep ocean is independent of whether the CO_2 is initially released to the atmosphere or the deep ocean.

Atmospheric CO_2 stabilization concentration (ppm)	Total cumulative ocean + atmosphere CO_2 release ($GtCO_2$)	Amount of anthropogenic CO_2 stored in the ocean in equilibrium ($GtCO_2$)
350	2880 ± 260	2290 ± 260
450	5890 ± 480	4530 ± 480
550	8350 ± 640	6210 ± 640
650	10,460 ± 750	7540 ± 750
750	12,330 ± 840	8630 ± 840
1000	16,380 ± 1000	10,730 ± 1000

Table 6.2. Evaluation of measures described in the text illustrated using schematic model results shown in Figure 6.16. For the Net Present Value measure, the percentage represents the discount rate minus the rate of increase in the cost of CO_2 emission. (If these are equal, the Net Present Value of temporary carbon storage is zero.) Two significant digits shown for illustration exceed the accuracy of model results.

Measure		Atmospheric release	Injection Depth		
			1000 m	2000 m	3000 m
Effective Retained Fraction	at 20 years	0	0.96	1.00	1.00
	at 100 years	0	0.63	0.97	1.00
	at 500 years	0	0.28	0.65	0.85
Airborne Fraction	at 20 years	0.61	0.03	6×10^{-6}	7×10^{-10}
	at100 years	0.40	0.19	0.02	$9. \times 10^{-4}$
	at 500 years	0.24	0.20	0.12	0.06
Net Present Value (constant emissions cost)	5% per year	0	0.95	1.00	1.00
	1% per year	0	0.72	0.95	0.99
	0.2% per year	0	0.41	0.72	0.85
Global Warming Potential	20 year horizon	1	0.01	1×10^{-6}	6×10^{-10}
	100 year horizon	1	0.21	0.01	$4. \times 10^{-4}$
	500 year horizon	1	0.56	0.20	0.06

Table 6.3. Relationships between ΔpH, changes in pCO_2, and dissolved inorganic carbon concentration calculated for mean deep-sea conditions. Also shown are volumes of water needed to dilute 1 tCO_2 to the specified ΔpH, and the amount of CO_2 that, if uniformly distributed throughout the ocean, would produce this ΔpH.

pH change ΔpH	Increase in CO_2 partial pressure ΔpCO_2 (ppm)	Increase in dissolved inorganic carbon ΔDIC (μmol kg^{-1})	Seawater volume to dilute 1 tCO_2 to ΔpH (m^3)	$GtCO_2$ to produce ΔpH in entire ocean volume
0	0	0	—	—
–0.1	150	30	656,000	2000
–0.2	340	70	340,000	3800
–0.3	580	100	232,000	5600
–0.5	1260	160	141,000	9200
–1	5250	400	54,800	24,000
–2	57,800	3,260	6800	190,000
–3	586,000	31,900	700	1,850,000

Table 6.4. Physiological and ecological processes affected by CO_2 (note that listed effects on phytoplankton are not relevant in the deep sea, but may become operative during large-scale mixing of CO_2). Based on reviews by Heisler, 1986, Wheatly and Henry, 1992, Claiborne *et al*., 2002, Langdon *et al*., 2003 Shirayama and Thornton, 2002, Kurihara *et al*., 2004, Ishimatsu *et al*., 2004, 2005, Pörtner *et al*. 2004, 2005, Riebesell, 2004, Feeley *et al*., 2004 and references therein.

Affected processes	Organisms tested
Calcification	Corals
	Calcareous benthos and plankton
Acid-base regulation	Fish
	Sipunculids
	Crustaceans
Mortality	Scallops
	Fish
	Copepods
	Echinoderms/gastropods
	Sipunculids
N-metabolism	Sipunculids
Protein biosynthesis	Fish
	Sipunculids
	Crustaceans
Ion homeostasis	Fish, crustaceans
	Sipunculids
Growth	Crustaceans
	Scallops
	Mussels
	Fish
	Echinoderms/gastropods
Reproductive performance	Echinoderms
	Fish
	Copepods
Cardio-respiratory functions	Fish
Photosynthesis	Phytoplankton
Growth and calcification	
Ecosystem structure	
Feedback on biogeochemical cycles (elemental stoichiometry C:N:P, DOC exudation)	

Table 6.5. Ocean storage cost estimate for CO_2 transport and injection at 3000 m depth from a floating platform. Scenario assumes three pulverized coal fired power plants with a net generation capacity of 600 MW_e each transported either 100 or 500 km by a CO_2 tanker ship of 80,000 m^3 capacity to a single floating discharge platform.

Ship transport distance	100 km	500 km
Onshore CO_2 Storage (US$/t$CO_2$ shipped)	3.3	3.3
Ship transport to injection platform(US$/t$CO_2$ shipped)	2.9	4.2
Injection platform, pipe and nozzle (US$/t$CO_2$ shipped)	5.3	5.3
Ocean storage cost (US$/t$CO_2$ shipped)	11.5	12.8
Ocean storage cost (US$/t$CO_2$ net stored)	11.9	13.2

Table 6.6. Ocean storage cost estimate for CO_2 transport and injection at 2000–2500 m depth from a moving ship.

Ship transport distance	100 km	500 km
Onshore CO_2 Storage (US$/t$CO_2$ shipped)	2.2	2.2
Ship transport to injection ship(US$/t$CO_2$ shipped)	3.9	5.3
Injection ship, pipe and nozzle (US$/t$CO_2$ shipped)	7.7	7.7
Ocean storage cost (US$/t$CO_2$ shipped)	13.8	15.2
Ocean storage cost (US$/t$CO_2$ net stored)	14.2	15.7

Figures

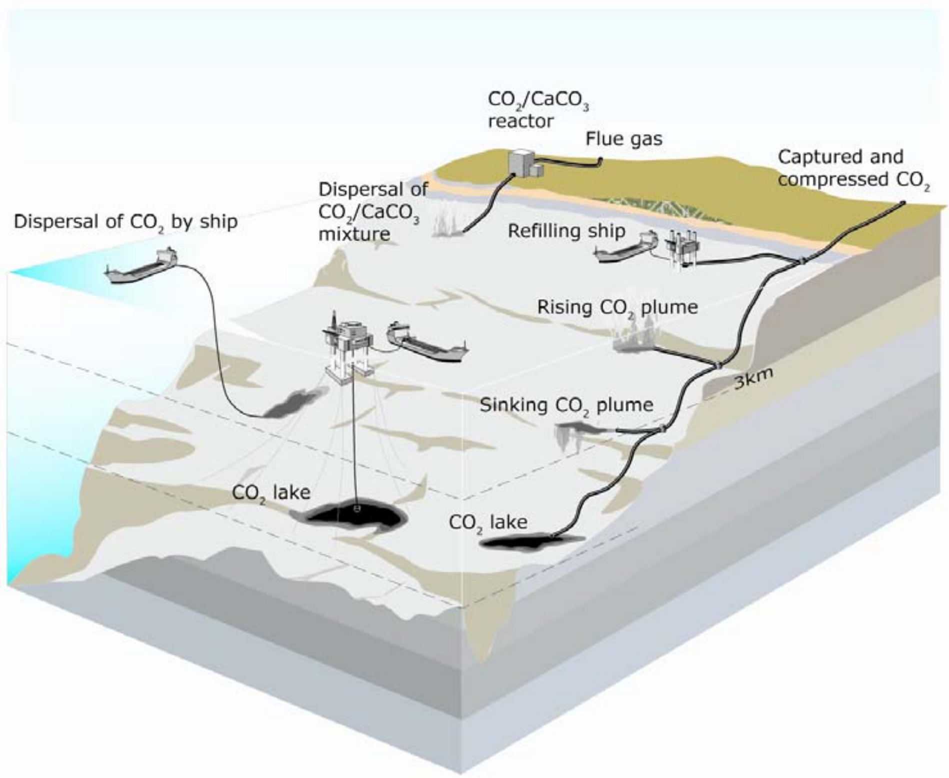

Figure 6.1. Illustration of some of the ocean storage strategies described in this chapter.

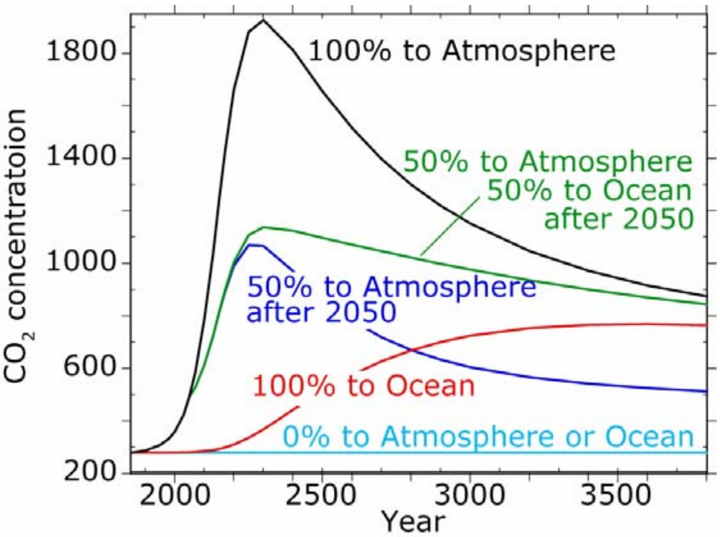

Figure 6.2. Simulated atmospheric CO_2 resulting from CO_2 release to the atmosphere or injection into the ocean at 3,000 m depth (Kheshgi and Archer, 2004). Emissions follow a logistic trajectory with cumulative emissions of 18,000 $GtCO_2$. Illustrative cases include 100% of emissions released to the atmosphere leading to a peak in concentration, 100% of emissions injected into the ocean, and no emissions (i.e., other mitigation approaches are used). Additional cases include atmospheric emission to year 2050, followed by either 50% to atmosphere and 50% to ocean after 2050 or 50% to atmosphere and 50% by other mitigation approaches after 2050. Ocean injection results in lower peak concentrations than atmospheric release but higher than if other mitigation approaches are used (e.g., renewables or permanent storage).

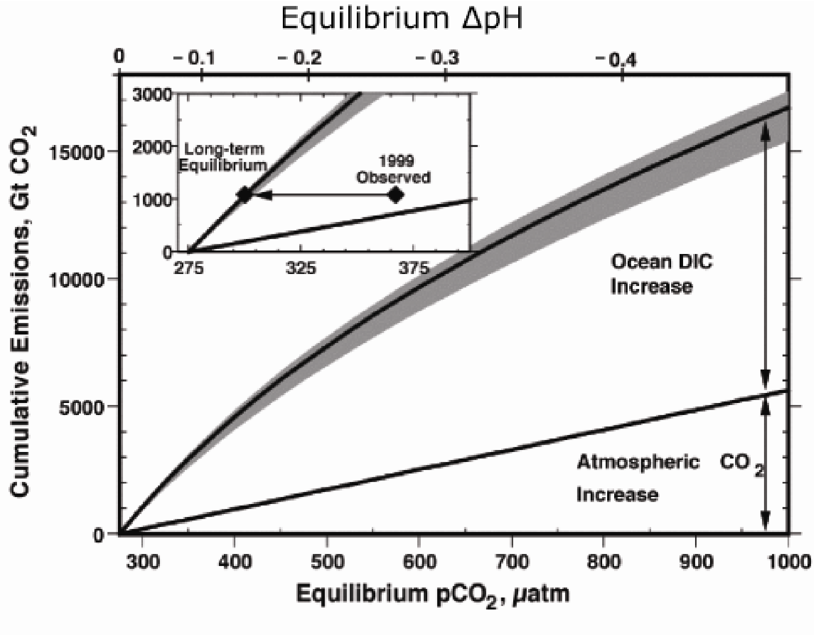

Figure 6.3. Equilibrium partitioning of CO_2 between the ocean and atmosphere. On the time scale of millennia, complete mixing of the oceans leads to a partitioning of cumulative CO_2 emissions between the oceans and atmosphere with the bulk of emissions eventually residing in the oceans as dissolved inorganic carbon. The ocean partition depends nonlinearly on CO_2 concentration according to carbonate chemical equilibrium (Box 6.1) and has limited sensitivity to changes in surface water temperature (shown by the grey area for a range of climate sensitivity of 1.5 to 4.5°C for CO_2 doubling) (adapted from Kheshgi *et al*., 2005; Kheshgi, 2004a). ΔpH evaluated from pCO_2 of 275 ppm. This calculation is relevant on the time scale of several centuries, and does not consider changes in ocean alkalinity that increase ocean CO_2 uptake over several millennia (Archer *et al*., 1997).

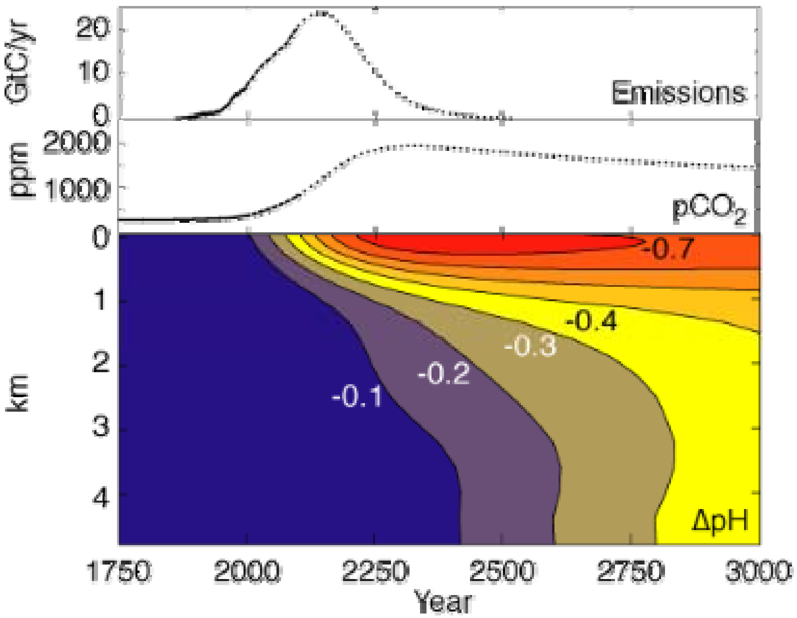

Figure 6.4. Simulated ocean pH changes from CO_2 release to the atmosphere. Modelled atmospheric CO_2 change and horizontally averaged ΔpH driven by a CO_2 emissions scenario: historic atmospheric CO_2 up to 2000, IS92a from 2000 to 2100, and logistic curve extending beyond 2100 with 18,000 $GtCO_2$ (Moomaw *et al*., 2001) cumulative emissions from 2000 onward (comparable to estimates of fossil-fuel resources – predominantly coal; Caldeira and Wickett, 2003).

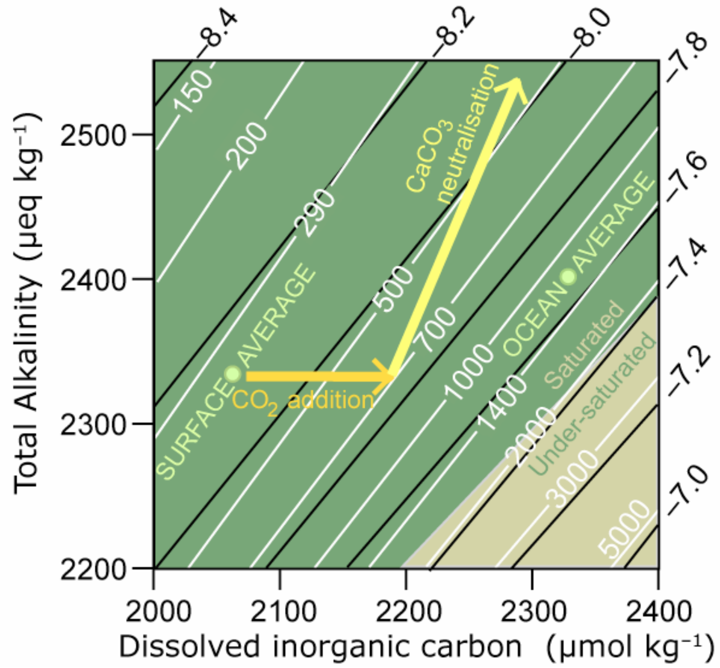

Figure 6.5. Composition diagram for ocean surface waters at 15°C (adapted from Baes, 1982). The white lines denote compositions with the same value of pCO_2 (in ppm); the black lines denote compositions with the same pH. The tan shaded region is undersaturated and the green shaded region is supersaturated with respect to calcite at atmospheric pressure (calcite solubility increases with depth). Surface water and average ocean compositions are also indicated. Adding CO_2 increases Dissolved Inorganic Carbon (DIC) without changing Total Alkalinity (TAlk); dissolving $CaCO_3$ increases both DIC and TAlk, with 2 moles of TAlk added for each mole of DIC added.

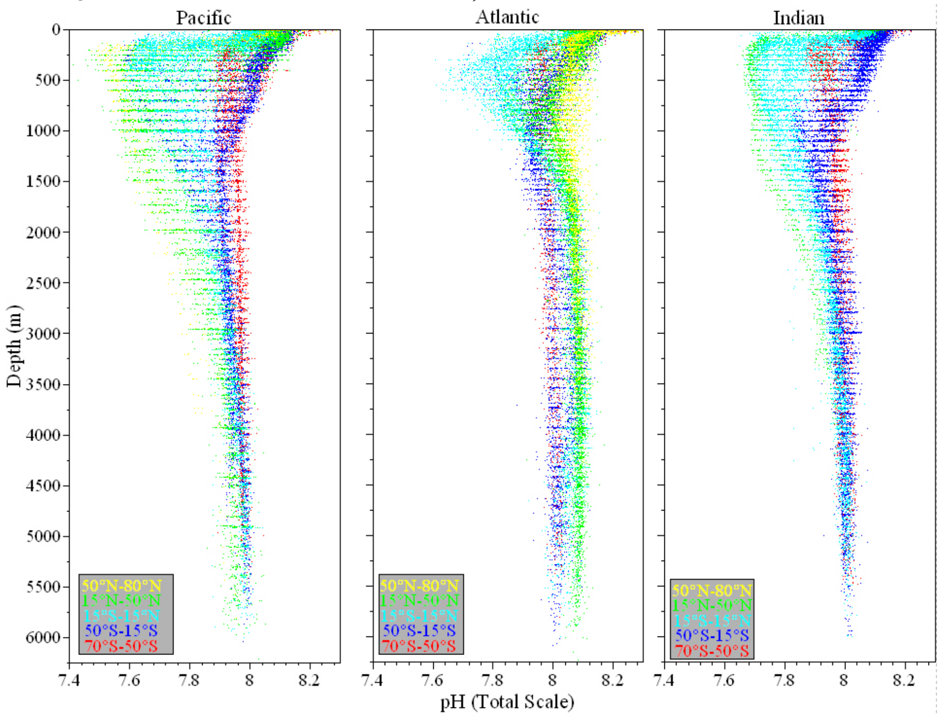

Figure 6.6. Observed variation in open ocean pH for the 1990s (shown on the total hydrogen scale; data from Key *et al*., 2004). In this figure the oceans are separated into separate panels. The three panels are on the same scale and coloured by latitude band to illustrate the large north-south changes in the pH of intermediate waters. Pre-industrial surface values would have been about 0.1 pH units greater than in the 1990s.

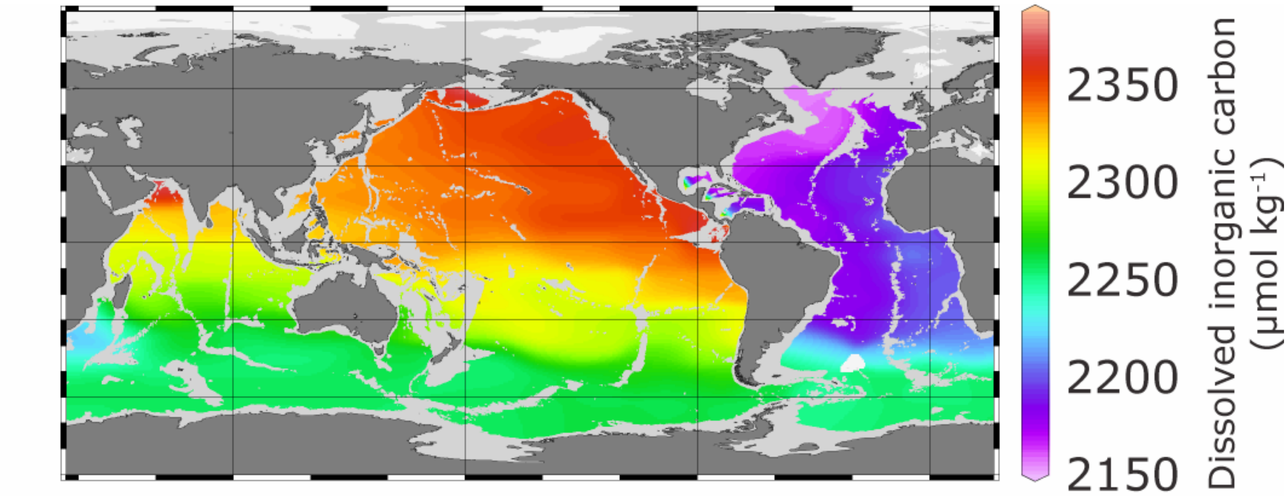

Figure 6.7. Natural variation in dissolved inorganic carbon at 3 km depth. Total dissolved inorganic carbon concentration at 3000 m depth (data from Key *et al.*, 2004). Ocean carbon concentrations increase roughly 10% as deep ocean waters transit from the North Atlantic to the North Pacific due to the oxidation of organic carbon in the deep ocean.

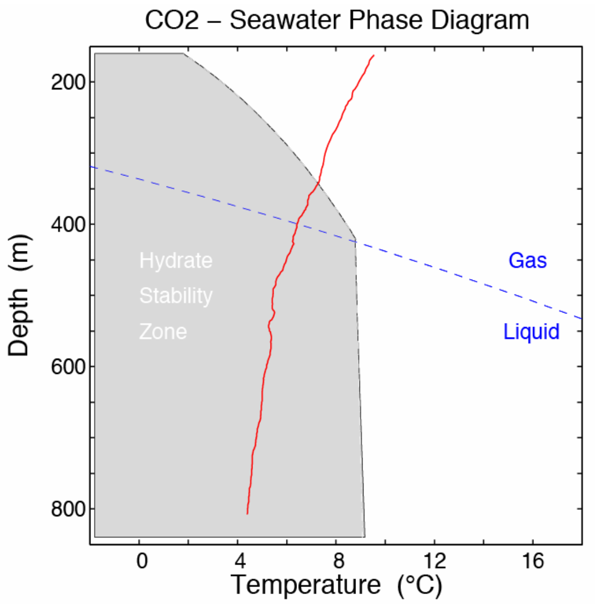

Figure 6.8. CO_2 phases in sea water. CO_2 is stable in the liquid phase when temperature and pressure (increasing with ocean depth) fall in the region below the blue curve; a gas phase is stable under conditions above the blue dashed line. In contact with sea water and at temperature and pressure in the shaded region, CO_2 reacts with sea water to from a solid ice-like hydrate CO_2•$6H_2O$. CO_2 will dissolve in sea water that is not saturated with CO_2. The red line shows how temperature varies with depth at a site off the coast of California; liquid and hydrated CO_2 can exist below about 400 m (Brewer *et al.*, 2004).

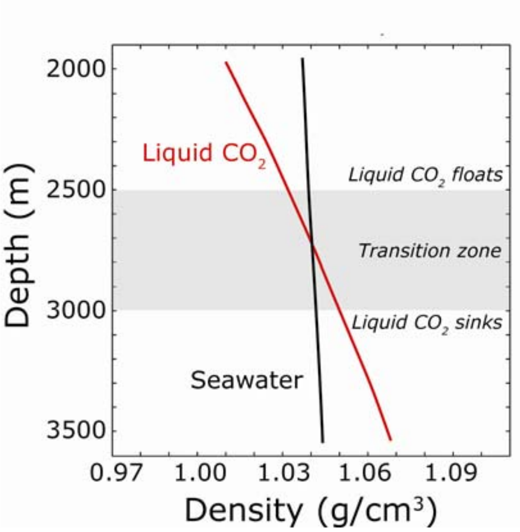

Figure 6.9. Shallower than 2500 m, liquid CO_2 is less dense than sea water, and thus tends to float upward. Deeper than 3000 m, liquid CO_2 is denser than sea water, and thus tends to sink downwards. Between these two depths, the behaviour can vary with location (depending mostly on temperature) and CO_2 can be neutrally buoyant (neither rises nor falls). Conditions shown for the northwest Atlantic Ocean.

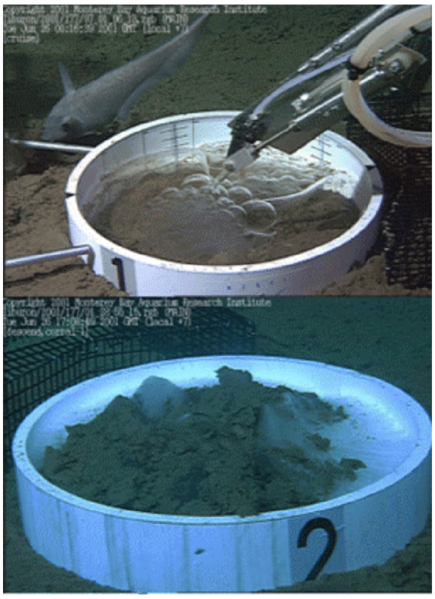

Figure 6.10. Liquid CO_2 released at 3600 metres initially forms a liquid CO_2 pool on the sea floor in a small deep ocean experiment (b, upper picture). In time, released liquid CO_2 reacts with sea water to form a solid CO_2 hydrate in a similar pool (b, lower picture).

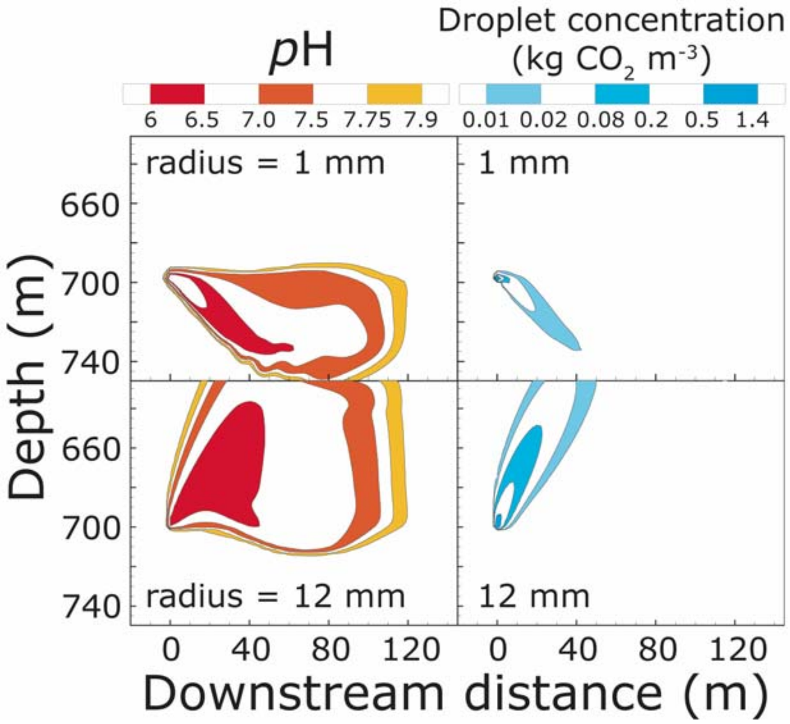

Figure 6.11. Simulated CO_2 enriched sea water plumes (left panels; indicated by pH) and CO_2 droplet plumes (right panels; indicated by kgCO_2 m^{-3}) created by injecting 1 cm and 12 cm liquid CO_2 droplets (top and bottom panels, respectively) into the ocean from fixed nozzles (elapsed time is 30 min; injection rate is 1.0 kgCO_2 s^{-1}; ocean current speed is 5 cm s^{-1}; Alendal and Drange, 2001). By varying droplet size, the plume can be made to sink (top panels) or rise (bottom panels).

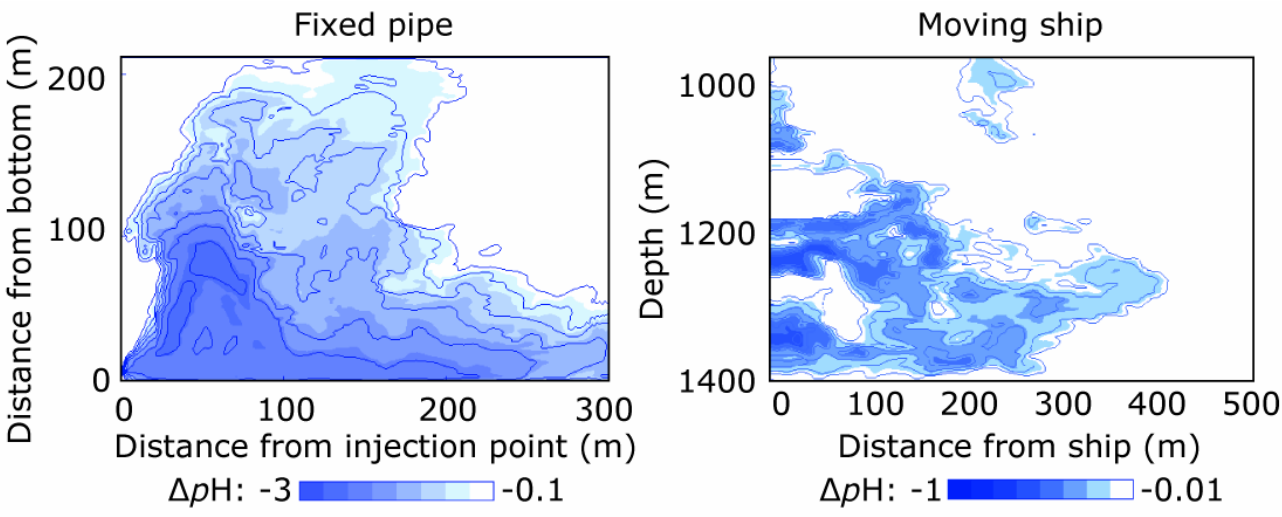

Figure 6.12. Simulated plumes (Chen *et al.*, 2005) created by injecting liquid CO_2 into the ocean from a fixed pipe (left panel) and a moving ship (right panel) at a rate of 100 kg s^{-1} (roughly equal to the CO_2 from a 500 MW$_e$ coal-fired power plant). Left panel: injection at 875 m depth (12 m from the sea floor) with an ocean current speed of 2.3 cm s^{-1}. Right panel: injection at 1340 m depth from a ship moving at a speed of 3 m s^{-1}. Note difference in pH scales; maximum pH perturbations are smaller in the moving ship simulation.

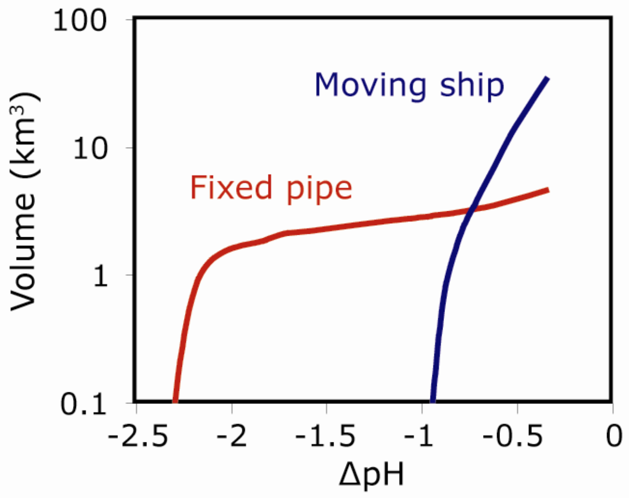

Figure 6.13. Volume of water with a ΔpH less than the value shown on the horizontal axis for the simulations shown in Figure 6.12 corresponding to CO_2 releases from a 500 MW_e power plant. The fixed pipe simulation produces a region with ΔpH < –1, however, the moving ship disperses the CO_2 more widely, largely avoiding pH changes of this magnitude.

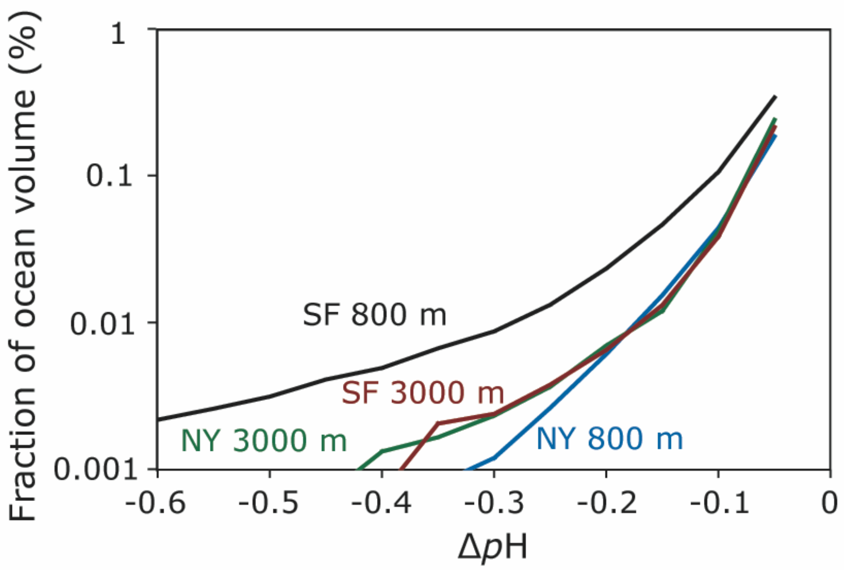

Figure 6.14. Estimated volume of pH perturbations at basin scale (Wickett *et al*., 2003). Simulated fraction of global ocean volume with a ΔpH less than the amount shown on the horizontal axis, after 100 years of simulated injection at a rate of 0.37 $GtCO_2$ yr^{-1} (= 0.1 GtC yr^{-1}) at each of four different points (two different depths near New York City and San Francisco). Model results indicate, for example, that injecting CO_2 at this rate at a single location for 100 years could be expected to produce a volume of sea water with a ΔpH < –0.3 units in 0.01% or less of total ocean volume (0.01% of the ocean is roughly 10^5 km^3). As with other simulations of direct CO_2 injection in the ocean, results for the upper ocean (e.g., 800 m) tend to be more site-specific than are results for the deep ocean (e.g., 3000 m).

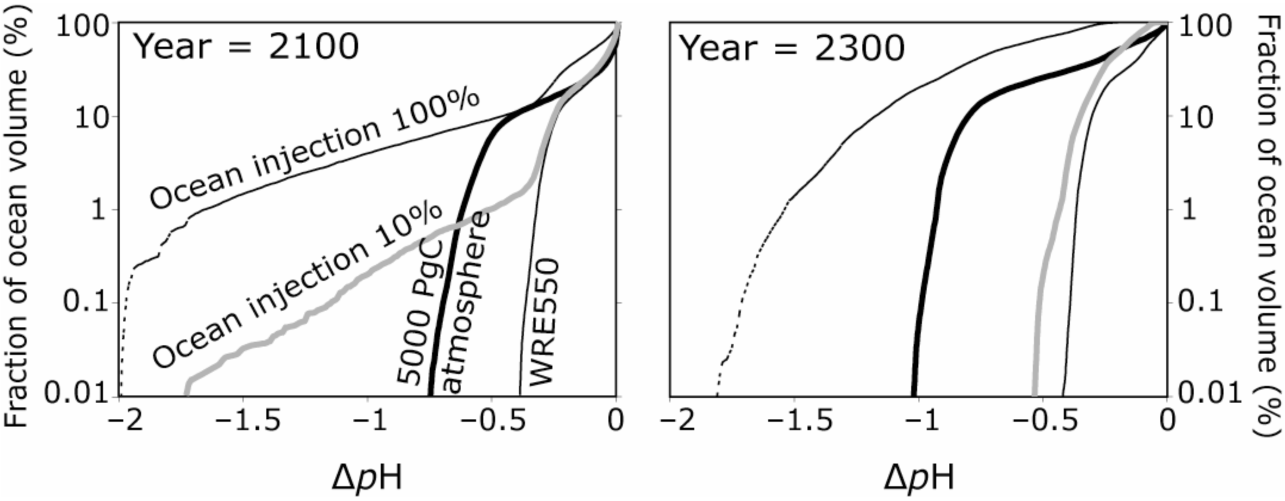

Figure 6.15. Estimated volume of pH perturbations at global scale for hypothetical examples in which injection of CO_2 into the ocean interior provides 100% or 10% of the mitigation effort needed to move from a logistic emissions curve cumulatively releasing 18,000 $GtCO_2$ (=5000 GtC) to emissions consistent with atmospheric CO_2 stabilization at 550 ppm according to the WRE550 pathway (Wigley *et al*., 1996). The curves show the simulated fraction of ocean volume with a pH reduction greater than the amount shown on the horizontal axis. For the 10% case, in year 2100, injection rates are high and about1% of the ocean volume has significant pH reductions; in year 2300, injection rates are low, but previously injected CO_2 has decreased ocean pH by about 0.1 unit below the value produced by a WRE550 atmospheric CO_2 pathway in the absence of CO_2 release directly to the ocean. (Caldeira and Wickett, 2005).

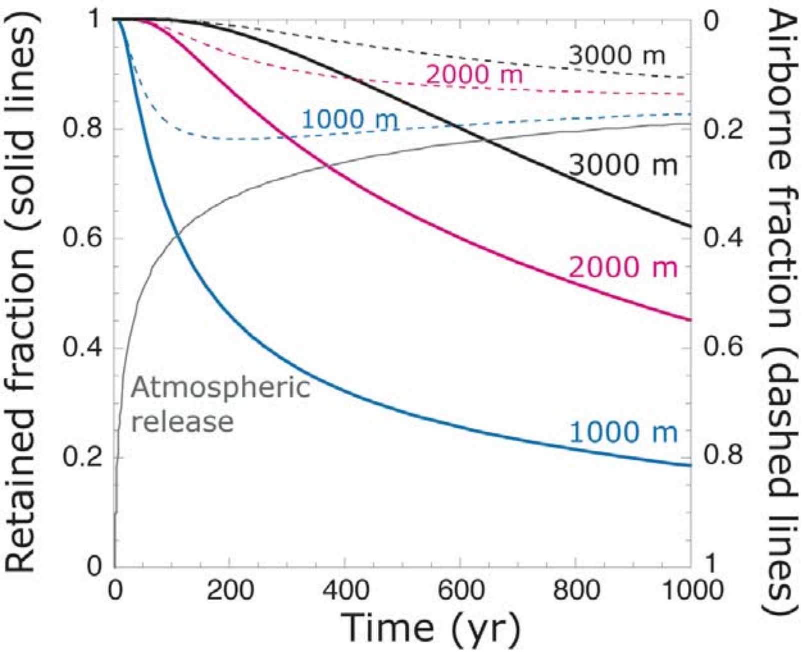

Figure 6.16. Fraction of carbon in the ocean from injection at three different depths and the atmosphere illustrated with results from a schematic model (Herzog *et al*., 2003). Calculations assume a background 280 ppm of CO_2 in the atmosphere. Solid lines = retained fraction. Dashed lines = airborne fraction. Grey dashed line = airborne fraction for release to atmosphere.

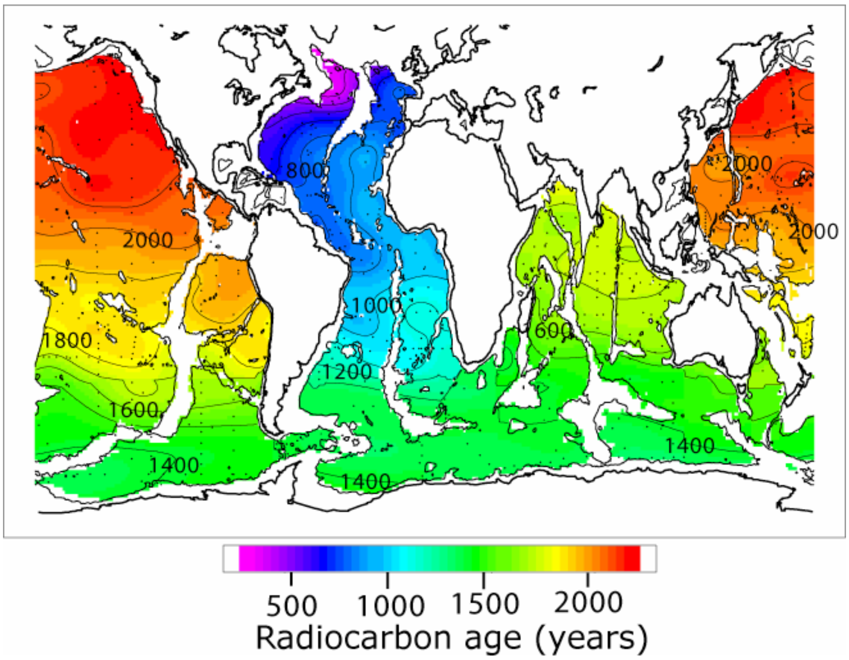

Figure 6.17. Map of radiocarbon (^{14}C) age at 3500 m (Matsumoto and Key, 2004).

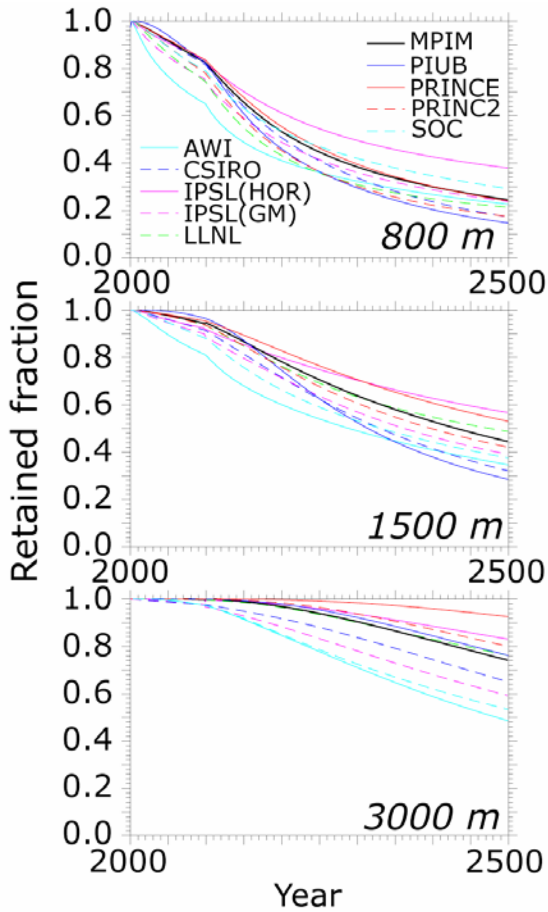

Figure 6.18. Results are shown for seven ocean general circulation models at three different depths averaged over seven injection locations (Orr, 2004). The percentage efficiency shown is the retained fraction for an injection at a constant rate from 2000 to 2100. Models agree that deeper injection isolates CO_2 from the atmosphere longer than shallower injection. For release at 3000 m, most of the added carbon was still isolated from the atmosphere at the end of the 500 year simulations.

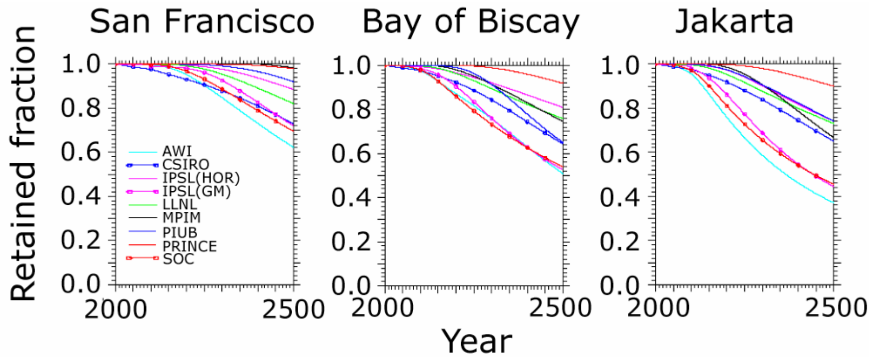

Figure 6.19. Comparison of storage results for three injection locations (at 3000 m depth) in ten ocean model simulations (Orr, 2004). Models differ on predictions of CO_2 fraction retained for release in different oceans.

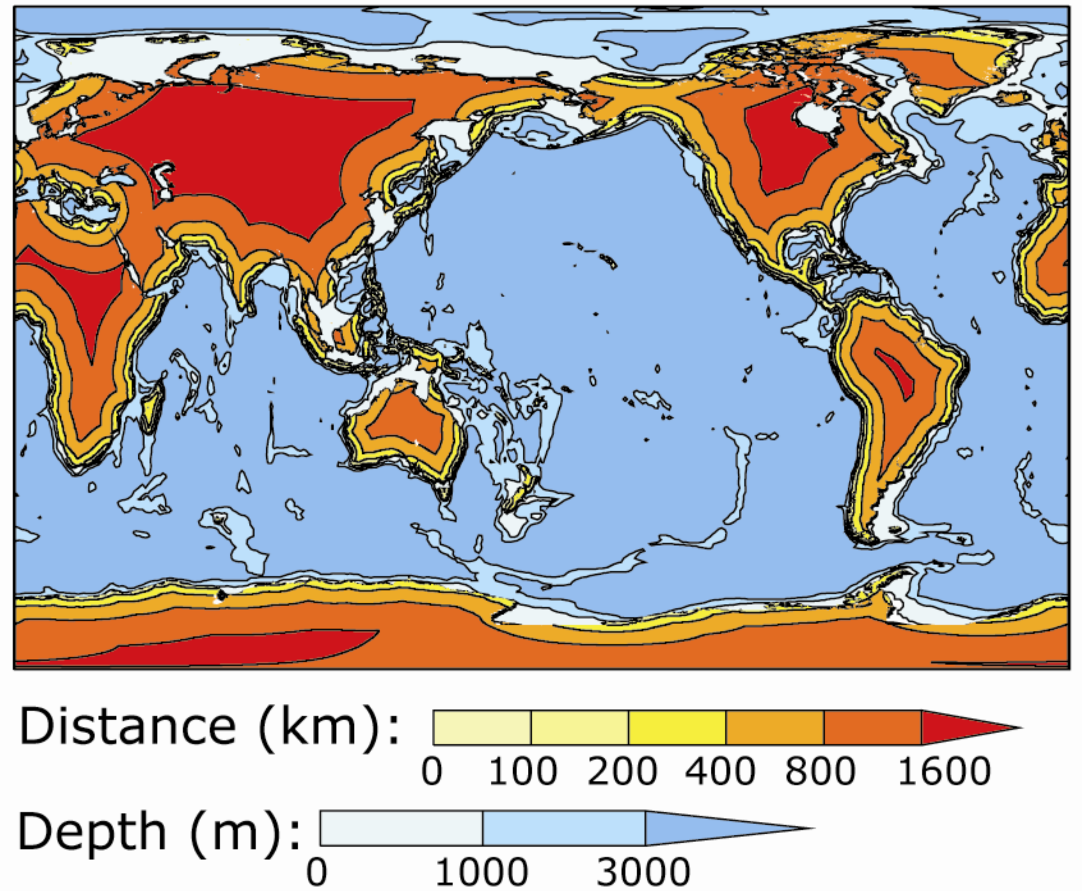

Figure 6.20. Locations of ocean water at least 1 km and 3 km deep. Distance over land to water that is at least 3 km deep (Caldeira and Wickett, 2005). In general, land areas with the lightest colours would be the most-cost effective land-based settings for a CO_2-injection operation. However, each potential site would need to be evaluated prior to deployment.

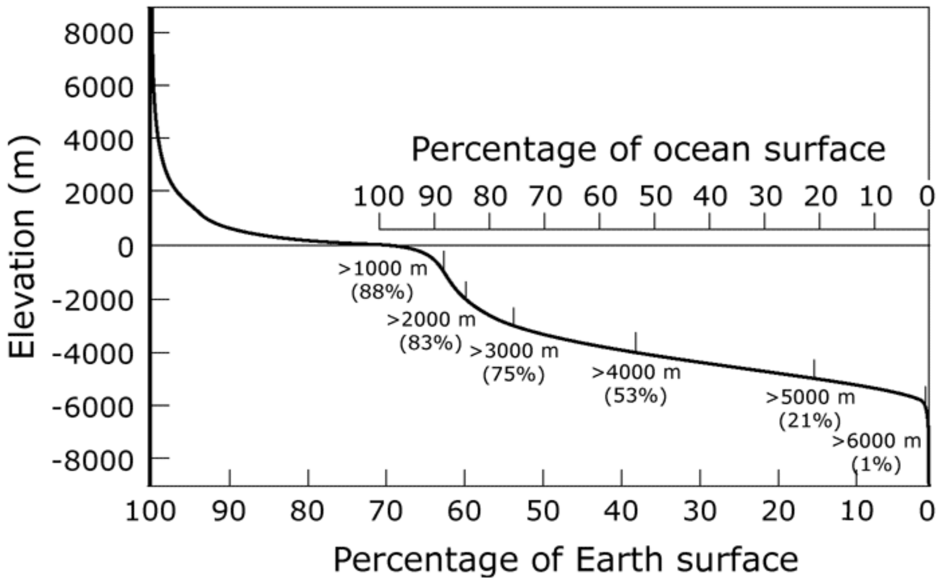

Figure 6.21. Relationship between depth and sea floor area.

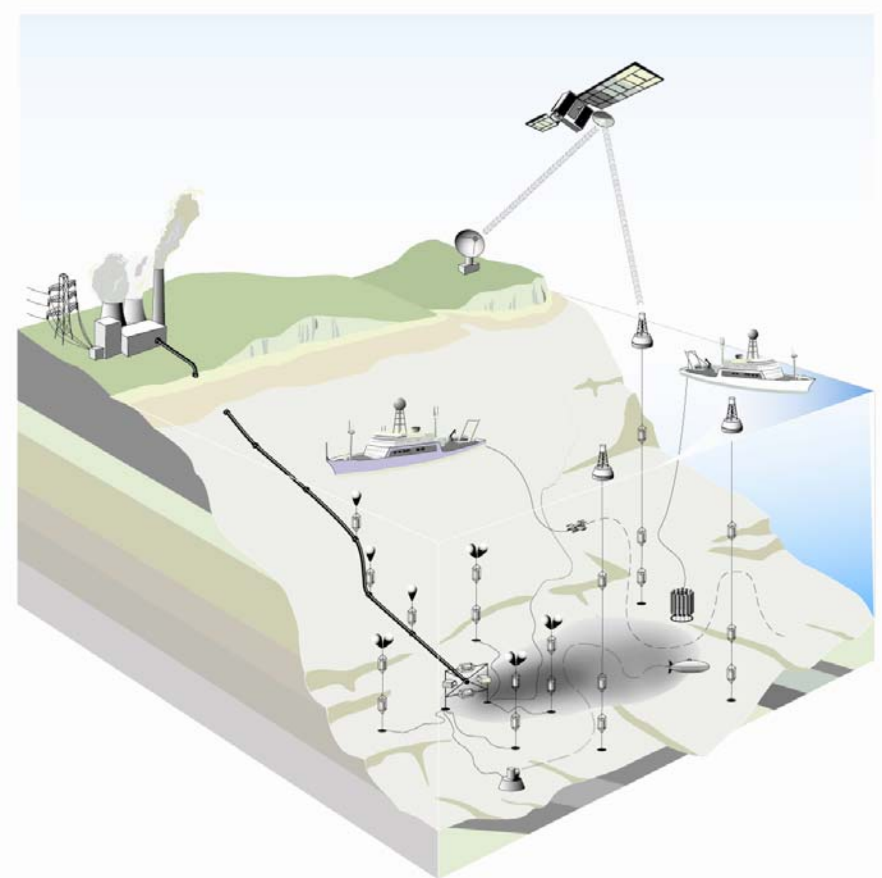

Figure 6.22. Schematic of possible approaches for monitoring the injection of CO_2 into the deep ocean via a pipeline. The grey region represents a plume of high CO_2/low pH water extending from the end of the pipeline. Two sets of chemical, biological and current sensors and two underwater cameras are shown at the end of the pipeline. An array of moored sensors to monitor the direction and magnitude of the resulting plume can be seen around the pipe and are also located along the pipeline to monitor for possible leaks. A shore-based facility provides power to the sensors and for obtaining real-time data and an autonomous underwater vehicle maps the near-field distribution of the plume. A towed undulating pumping system monitors at distances of more than a few kilometres from the injection site. The towed system could provide much greater measurement accuracy and precision, but would also be able to provide measurements over large areas in a relatively short period of time. Moored systems are used to monitor the plume between mapping cruises. These moorings have surface buoys and make daily transmissions back to the monitoring facility via satellite. The very far-field distributions are monitored with hydrographic section cruises conducted every 2–5 years using standard discrete sampling approaches. These approaches provide the accuracy and precision required to detect the small CO_2 signals that add to background variations.

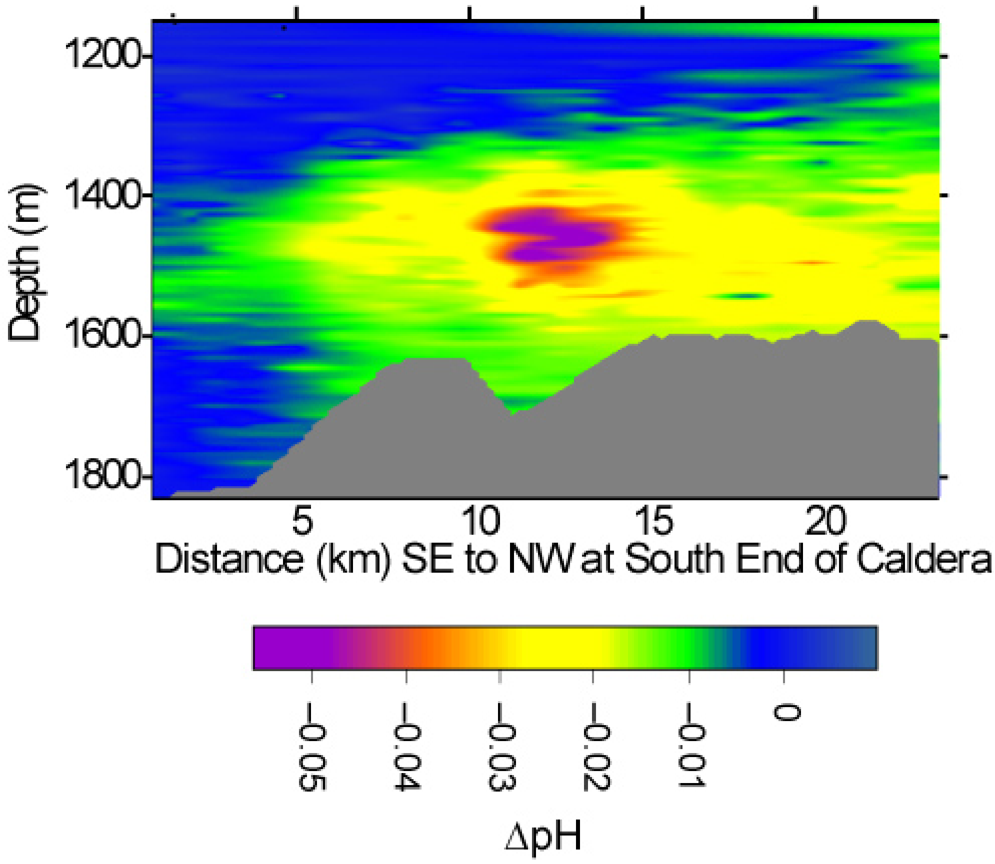

Figure 6.23. Measurements showing the ability to measure chemical effects of a natural CO_2 plume. Profiles for pH were taken in June 1999 near the Axial Volcano at 46ºN 130ºW, in the ocean near Portland, Oregon, United States.

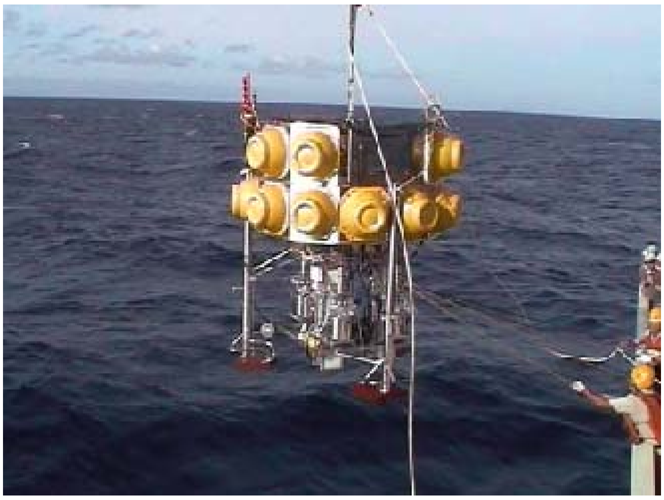

Figure 6.24. Experimental chamber going to the sea floor. The bottom part houses a chamber that penetrates into the sediment. The top part houses electronics, pumps, valves, and water bags, that are used to control the CO_2 concentration inside the chamber, and to sample sea water in the chamber at designated times. At the time of recovery, the bottom of the chamber is closed, weights are released, and the system returns to the surface of the ocean using buoyancy provided by the glass bulbs (yellow structures around the top).

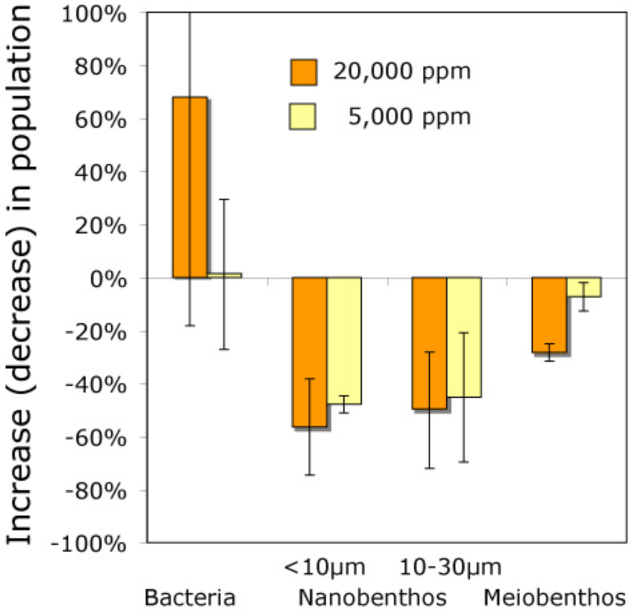

Figure 6.25. Preliminary investigations into the change of bacteria, nanobenthos and meiobenthos abundance after exposure to 20,000 and 5,000 ppm CO_2 for 77 to 375 hr during three experiments carried out at 2,000 m depth in Nankai Trough, north-western Pacific. Error bars represent one standard deviation (Ishida *et al*. 2005).

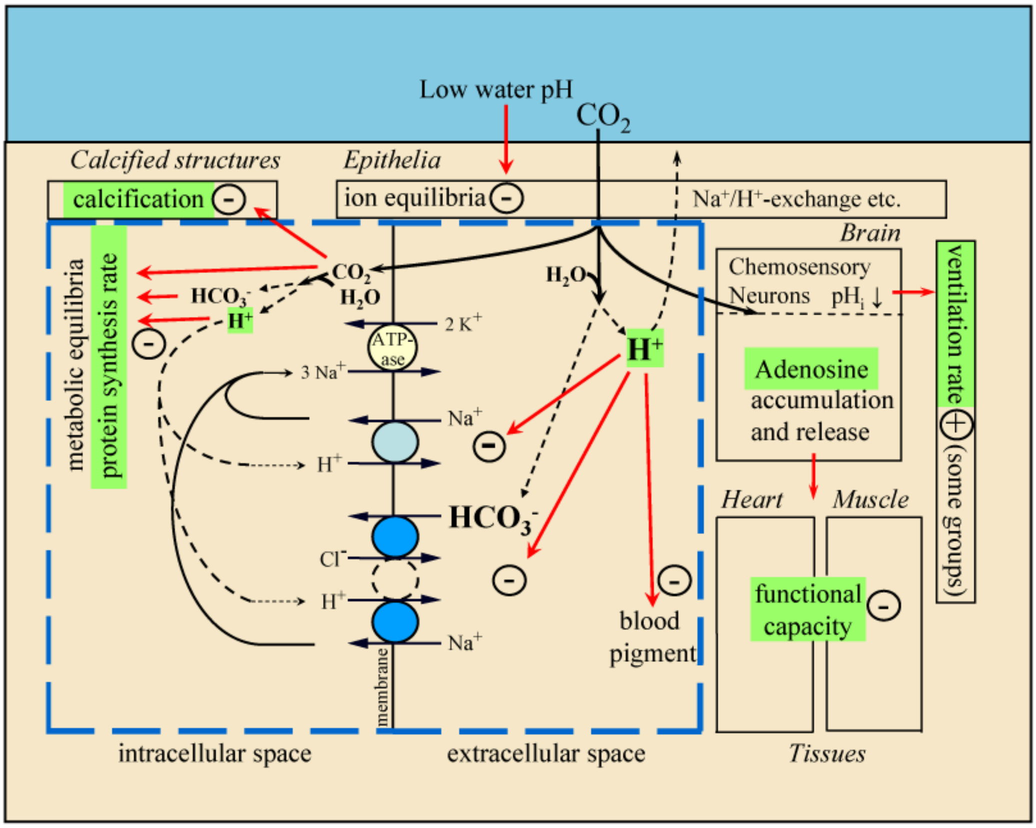

Figure 6.26. Effects of added CO_2 at the scale of molecule to organism and associated changes in proton (H^+), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) levels in a generalized and simplified marine invertebrate or fish. The blue region on top refers to open water; the tan region represents the organism. Generalized cellular processes are depicted on the left and occur in various tissues like brain, heart or muscle; depression of these processes has consequences (depicted on the right and top). Under CO_2 stress, whole animal functions, like growth, behaviours or reproduction are depressed (adopted from Pörtner *et al*., 2005, – or + denotes a depression or stimulation of the respective function). Black arrows reflect diffusive movement of CO_2 between compartments. Red arrows reflect effective factors, CO_2, H^+, HCO_3^- that modulate functions. Shaded areas indicate processes relevant for growth and energy budget.