Ocean Storage of CO₂

E. Eric Adams¹ and Ken Caldeira²

INTRODUCTION

Other articles in this issue discuss the motivation for carbon dioxide (CO₂) capture and storage as a method to help combat global climate change (Oelkers and Cole 2008; Broecker 2008). In particular, storage in underground reservoirs is highlighted (Benson and Cole 2008; Oelkers et al. 2008). Here we describe the possibilities for CO₂ storage in the deep ocean, focusing on direct-injection strategies that could be applied on an industrial scale.

There are several reasons for considering the deep ocean as a sink for anthropogenic CO₂. First, the ocean has a vast uptake capacity. It currently contains an estimated 40,000 Gt C (billion tons of carbon), mostly in the form of dissolved inorganic ions. This compares with about 800 Gt C contained in the atmosphere and 2000 Gt C in the land biosphere. Thus, the amount of carbon that would cause a doubling of the atmospheric concentration would only change the ocean concentration by about 2%. Second, we are already discharging CO₂ indirectly into the surface ocean when we emit it to the atmosphere. Because emissions are large, the atmosphere and ocean are currently out of chemical equilibrium, causing a net flux of about 8 Gt C per year (2 Gt C per year) to the oceans. Over a period of centuries, 70–80% of present-day emissions will ultimately reside in the ocean. Discharging CO₂ directly into the deep ocean would accelerate this natural process, thus reducing peak atmospheric concentrations and protecting ocean surface waters with a slower rate of CO₂ increase. Figure 1 presents the results of simulations for the reduction in atmospheric CO₂ concentration that could be achieved using several release–uptake scenarios in which known fossil fuel reserves are burned and CO₂ is released. The atmospheric concentration would increase to ~2000 ppm in 300 years (similar to Figure 1), and ocean

Fig 1

Simulated atmospheric CO₂ concentration (ppm) resulting from release of 18,000 Gt CO₂ to the atmosphere, to the ocean at 3000 m below sea level, or to a combination of both. Adapted from Kheshgi and Archer (2004), with permission from the American Geophysical Union.

KEYWORDS: ocean carbon sequestration, CO₂ ocean storage, environmental impact, climate change

¹ Department of Civil and Environmental Engineering
Massachusetts Institute of Technology, Room 48-216b
Cambridge, MA 02139, USA
E-mail: eeadams@mit.edu

² Department of Global Ecology, Carnegie Institution
Stanford University, 260 Panama St., Stanford, CA 94305, USA
E-mail: kcaldeira@stanford.edu

releaseing all CO₂ to the atmosphere, as happens now, introducing half to the deep ocean would reduce the peak concentration by a factor of about two. However, the ocean and atmosphere systems are closely coupled, so even if all anthropogenic CO₂ were injected directly into the oceans, some would return to the atmosphere through degassing.

Over the past 200 years, oceans have taken up over 500 Gt of CO₂ from the atmosphere, compared with over 1300 Gt CO₂ emitted to the atmosphere (IPCC 2005). As a result, the pH of the surface ocean (the upper few hundred meters that are in greatest contact with the atmosphere) has dropped by about 0.1 pH units from the preindustrial value of about 8.2. This causes concern for the health of coral reefs and other organisms that use calcium carbonate in their skeletons or shells. Figure 2 presents model results for ocean pH if known fossil fuel reserves are burned and CO₂ is released. The atmospheric concentration would increase to ~2000 ppm in 300 years (similar to Figure 1), and ocean
surface pH would drop by more than 0.7 units (Caldeira and Wickett 2003). By injecting some of the CO$_2$ into the deep ocean, the time until it disperses to surface water is extended, allowing the change in pH to be distributed more uniformly with depth.

**Figure 2** Model simulations of long-term changes in ocean pH, averaged horizontally, as a result of the CO$_2$ emissions shown in the top panel. pCO$_2$ is the atmospheric concentration of CO$_2$. Reproduced from Caldeira and Wickett (2003), with permission from Macmillan Publishers Ltd.

**CAPACITY**

Oceans occupy more than 70% of the Earth’s surface and have an average depth of about 3.8 km. Considering the saturation concentration of CO$_2$ in seawater, this storage capacity is orders of magnitude greater than the capacity needed to absorb the CO$_2$ produced by burning all of the world’s fossil fuel resources, equivalent to an estimated 5000 to 10,000 Gt C. However, a more realistic capacity estimate requires understanding ocean biogeochemistry and the expected environmental impact.

CO$_2$ exists in seawater in various forms as part of the carbonate system:

\[ \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-} \]  \hspace{1cm} (1)

The relative proportions of these species are defined by the pH of the solution and by equilibrium relationships. Dissolving additional CO$_2$ increases production of hydrogen ions (decreasing pH), but the change is buffered by conversion of carbonate into bicarbonate. Thus, the principal reactions for CO$_2$ dissolution in seawater are as follows:

\[ \text{CO}_2 + \text{H}_2\text{O} + \text{CO}_3^{2-} \rightarrow 2\text{HCO}_3^- \]  \hspace{1cm} (2)

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HCO}_3^- \]  \hspace{1cm} (3)

Decreased pH is one of the principal environmental impacts threatening marine organisms; the other is the concentration of CO$_2$ itself. Near the injection point, changes in pH and CO$_2$ concentration would be greatest, so injection schemes would have lowest impact if dilution is maximized. Far from the injection point, as CO$_2$ becomes widely distributed in the ocean, its impact would be similar to that of anthropogenic CO$_2$ absorbed from the atmosphere. Adding about 2000 Gt CO$_2$ to the ocean would reduce the average ocean pH by about 0.1 units, similar to the change already observed in the surface ocean. Adding about 5600 Gt CO$_2$ (about 200 years of current emissions) would decrease the average ocean pH by about 0.3 units (IPCC 2005).

The impact of such changes is not well known. However, one can examine spatial and temporal variations in ocean pH to understand how much change might be tolerated. The pH variability within latitudinal bands in each of the three major oceans (Pacific, Atlantic, Indian) during the 1990s was roughly 0.1 unit (IPCC 2005). If a change of 0.1 unit is assumed as a threshold tolerance and if the CO$_2$ is stored in the bottom half of the ocean (to maximize retention), approximately 1000 Gt CO$_2$ could be stored, enough to stabilize atmospheric concentrations at 500 ppm over the next 50 years, assuming energy consumption follows current trends and no other mitigation measures are put into place (Pacala and Socolow 2004). It should be realized that over the long term (millennia), the change in whole-ocean pH would ultimately be the same, whether CO$_2$ is released into the atmosphere or injected into the deep ocean, because thermodynamics drives the system to equilibrium. However, in the shorter term (several centuries), injecting into the deep ocean, below 1000 m depth, would limit pH drop in the near-surface, where marine biota are most plentiful, thus decreasing the adverse impact in the surface ocean.

**INJECTION METHODS**

Injection was first proposed by the Italian physicist Cesare Marchetti, who suggested dissolving CO$_2$ into the outflow from the Mediterranean Sea. Because this water is saltier than average seawater, the higher density would cause the CO$_2$ to sink into the depths of the Atlantic Ocean (Marchetti 1977). As illustrated in Figure 3, a number of options have been considered since then, including introducing the CO$_2$ as a rising or sinking plume, dispersing it from a moving ship, and creating a lake on the deep seafloor.

Before describing these methods in more detail, we first provide some background about the CO$_2$–seawater system. Figure 4 shows a simple phase diagram for CO$_2$ in seawater. At typical ocean pressure and temperature, pure CO$_2$ is in gas form above a depth of 400–500 m and in liquid form below. At a depth of 1000 m, liquid CO$_2$ is about 6% less dense than seawater. Because liquid CO$_2$ is more compressible than seawater, at a depth of 3000 m its density is similar to that of seawater. Thus liquid CO$_2$ would be positively buoyant and rise if it were injected above 3000 m, but it would sink if injected deeper. Below about 400 m depth, if the concentration of dissolved CO$_2$ is high enough, hydrate phases form. CO$_2$ hydrate, whose composition is given by CO$_2$·nH$_2$O (n = 5.75), is a solid in which each CO$_2$ molecule sits in a cage-like structure of water molecules held together by hydrogen bonds. Unlike methane hydrates, which have a similar structure but are positively buoyant (Ruppel 2007), pure CO$_2$ hydrates are about 10% denser than seawater. Unless the surrounding water is saturated with CO$_2$, the hydrate is unstable, but it dissolves more slowly into seawater than does liquid CO$_2$.

Methods by which CO$_2$ is dissolved directly into seawater have received the most attention. The easiest scenario is to discharge it as a buoyant liquid, forming a rising droplet plume (Alendal and Drange 2001; Sato and Sato 2002). The required technology is available now to inject CO$_2$ from a manifold lying on the seafloor. Effective sequestration could be achieved by locating the manifold below the natural
thermocline (the depth at which vertical temperature gradients in the ocean are strongest), and adequate dilution could be achieved by making the manifold sufficiently long. Even better dilution could be achieved by releasing CO$_2$ droplets from a ship, where motion provides additional dispersal (Ozaki et al. 2001). Although the delivery methods are different, the resulting plumes would be similar: each would yield a vertical band of CO$_2$-enriched seawater over a predetermined horizontal region.

Another dissolution option is to inject liquid CO$_2$ into a vessel where it can react at a controlled rate with seawater to form hydrates. While 100% reaction efficiency is difficult to achieve, laboratory and field experiments indicate that CO$_2$ sinks with as little as about 15–25% reaction efficiency (Tsouris et al. 2007). Instability leads to dissolution and dispersion during descent. The hydrate reactor could be towed from a moving ship, promoting additional dilution, or attached to a fixed platform, where the large concentration of dense particles and the increased seawater density caused by hydrate dissolution would create a sinking plume (Wannamaker and Adams 2006).

Dissolving high concentrations of CO$_2$ into seawater and then releasing the solution at the seafloor is another option (Haugan and Drange 1992). Enrichment with CO$_2$ causes only a slight density increase, but it is sufficient to promote sinking, especially within a submarine canyon. The environmental impact is higher, because the plume is more concentrated and it would come into direct contact with the seafloor, home to an abundance of relatively immobile fauna, bacteria, and algae. Alternatively, creating a CO$_2$ lake on the seafloor minimizes leakage to the atmosphere and exposure to biota (Ohsumi 1995; Haugan and Alendal 2005). A CO$_2$ lake would exist partly in the form of solid hydrates, which would slow dispersion to the water column, increasing retention time. Producing a lake would require more advanced technology and perhaps cost more than other options, because the lake must be more than 3000 m below the water surface.
Retention could be increased further using the reaction of CO₂ with carbonate minerals. Anthropogenic CO₂ currently transported to the deep ocean will equilibrate with carbonate sediments over a period of about 6000 years (Archer et al. 1998). Technical means could be used to accelerate this reaction, increasing effectiveness and diminishing the environmental impact. Power plant gas could be dissolved in seawater (Eq. 2) and then reacted with crushed limestone, either at the power plant or at the point of release, thus buffering pH change (Caldeira and Rau 2000). Conversely, an emulsion of liquid CO₂ and water could be stabilized by fine particles of pulverized limestone; the emulsion would be sufficiently dense to sink, and pH would be partially buffered by the limestone (Golomb et al. 2007). Drawbacks to these approaches include the cost to mine, crush, and transport large quantities of carbonate rock.

**EFFECTIVENESS**

Since the time when the oceans and atmosphere formed, they have exchanged CO₂ constantly. Now, about 350 Gt are exchanged each year, with a net ocean uptake of about 8 Gt CO₂ (IPCC 2005). Because of this exchange, one can ask how long it would take before injected CO₂ leaks back to the atmosphere. Long-term experiments with directly injected CO₂ have never been carried out, so effectiveness must be estimated from observations of other oceanic tracers, such as radiocarbon (¹⁴C), and from computer models of ocean circulation and chemistry.

As a result of anthropogenic input, the atmosphere and ocean are currently out of equilibrium, so most emitted CO₂ will ultimately end up in the ocean. The percentage of CO₂ permanently sequestered is defined by thermodynamics and depends on the atmospheric concentration (Table 1).

At today’s atmospheric level of ~380 ppm, nearly 80% of CO₂ emitted either to the atmosphere or to the ocean would become permanently stored in the ocean, while at a concentration of 750 ppm, 70% would be stored. Of course, even at equilibrium, CO₂ would continue to be exchanged between the atmosphere and the ocean, so the carbon in the ocean on any given day would not be exactly the same carbon present on the previous day, even though the total would be constant. The predictions in Table 1 include the possibility of increased carbon storage in the terrestrial biosphere, but do not consider natural or engineered dissolution of carbonate minerals. Over thousands of years, retention would increase somewhat as CO₂ reacts with ocean sediments.

Table 1 implies that, for CO₂ injected into the ocean today, the net quantity stored ranges from 100% (now) to about 70–80% as the atmosphere approaches equilibrium with the ocean. One can also define retention as the fraction of injected CO₂ that is retained without ever reaching the surface; this fraction ranges from 100% at the time of injection to zero at equilibrium. The exact time depends on the location and depth of the injection.

Several computer-modeling studies have investigated CO₂ retention time in the world’s oceans. The most comprehensive summary is the Global Ocean Storage of Anthropogenic Carbon (GOSAC) intercomparison study of several ocean general circulation models (OGCM). Ten models simulated the fate over 500 years of CO₂ injected at seven locations and three depths (Orr 2004). **Figure 5** shows the fraction of CO₂ retained as a function of time, averaged over the seven sites. Although there is substantial variability, all models indicate increased retention with injection depth, and most predict over 70% retention after 500 years for injection at 3000 m. Note that these calculations assume CO₂ is dispersed in the water column at the injection depth. Formation of a CO₂ lake or reaction with marine sediments could increase retention time.

The time required for injected carbon from the deep ocean to enter the atmosphere is roughly equal to the time required for carbon from the atmosphere to reach the deep ocean. This can be estimated from observations of ¹³C. Correcting for mixing with waters from various sources (polar ice, rivers, other oceans), the age of North Pacific deep water is estimated to be between 700 and 1000 years, while other basins, such as the North Atlantic, have turnover times of 300 years or more. These estimates are consistent with OGCM output and collectively suggest retention times of 300 to 1000 years. It is important to stress that CO₂ leakage to the atmosphere would take place gradually, over large areas of the ocean surface. Thus, unlike sequestration in porous rock, it would not be possible to produce a sudden release that could lead to harmful CO₂ concentrations at the ocean or land surface.

**LOCAL ENVIRONMENTAL IMPACT AND PUBLIC PERCEPTION**

Environmental impact may be the most significant factor determining the acceptability of ocean storage, because the strategy is grounded on the notion that impact on the deep ocean would be significantly less than the impacts avoided by limiting emission to the atmosphere. Above, we discussed environmental impacts from the global perspective. Here, we focus on the injection point.

A number of studies have summarized the potential impact on a variety of organisms, including adult and developing fish, zooplankton, and benthic fauna (Kikkkawa et al. 2003; Ishimatsu et al. 2004; Pörtner et al. 2004; Watanabe et al. 2006). Earlier studies focused on the lethal impact on coastal fauna exposed to strong acids such as HCl (Auerbach et al. 1997), but recent work has examined the impact on deepwater organisms when exposed to CO₂, including sublethal effects (Kurihara et al. 2004). Organisms experience respiratory stress (decreased pH limits oxygen binding and transport of respiratory proteins), acidosis (low pH disrupts acid/base balance), and metabolic depression (elevated CO₂ causes some animals to reach a state of torpor). Data show a number of trends: (1) H₂CO₃ generally causes greater stress on an organism than an equivalent change in pH produced by another acid; (2) there are large differences in tolerance among different species and among different life stages of the same species; and (3) the duration of stress, as well as the level of stress, are important. While some studies suggest that deep organisms would be less tolerant than surface organisms, other studies have shown the opposite. Likewise, some animals are able to avoid regions of high CO₂ concentration (Vetter and Smith 2005), while others are less able (Tamburri et al. 2000). Results generally imply

<table>
<thead>
<tr>
<th>Atmospheric CO₂ concentration (ppm)</th>
<th>CO₂ permanently sequestered (%)</th>
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<tbody>
<tr>
<td>350</td>
<td>80</td>
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<tr>
<td>450</td>
<td>77</td>
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<td>550</td>
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Based on data in IPCC (2005) and references therein.
that lethal effects can be avoided by achieving high near-field dilution. However, more research is needed, especially at the community level (e.g. studies of reduced lifespan, reproduction effects, and tolerance to other stresses).

The viability of ocean storage as a greenhouse gas mitigation option hinges on social, political, and regulatory considerations. In view of public precaution toward the ocean, which is a common, global resource, the strategy will require that all parties (private, public, non-governmental organizations) be included in ongoing research and debate. But the difficulty in this approach is highlighted by the recent experience of an international research team whose aim was to assess ocean carbon sequestration, as encouraged by the United Nations Framework Convention on Climate Change. A major part of their activity would have been a field test with 5 tons of CO₂ released off the coast of Norway. The plan was to monitor the physical, chemical, and biological effects of the injected CO₂ over a period of about a week. However, lobbying from environmental groups caused the Norwegian minister of the environment to rescind the group’s permit (Giles 2002). Such actions unfortunately prevent collection of data that are critical for policy makers to evaluate the prudence of full-scale implementation.

COSTS AND COMPARISON WITH OTHER STORAGE METHODS

The storage media most comparable to the ocean, in terms of size and cost, are depleted or partially depleted hydrocarbon reservoirs and saline aquifers (Friedmann 2007; Benson and Cole 2008). Ocean storage and use of these geological media both require that CO₂ be captured and then compressed and transported to an injection site. Summarizing a number of studies, IPCC (2005) estimates the cost (2002 basis) of capture and compression for a coal- or gas-fired power plant at US$20–95 per ton CO₂ net captured and the cost of transportation at US$1–10 per ton CO₂ transported. The cost of geological storage is estimated at US$0.5–10 per ton CO₂ net injected, while the cost of ocean storage is estimated at US$5–30 per ton CO₂, making ocean storage somewhat more expensive (more details in Rubin 2008 this issue).

The aim of geological sequestration is to permanently trap the CO₂ within well-defined regions, so that it cannot interact with terrestrial or oceanic ecosystems. Sometimes CO₂ can be used to enhance oil recovery or coalbed methane production. For these reasons, geological storage has been favored. In contrast, most ocean disposal schemes aim to minimize impact by diluting the CO₂ in the vastness of the ocean, and while it may be isolated from the atmosphere for centuries, approximately 20–30% of it will eventually leak back. The ocean storage option that promises the most permanence is mineral carbonation, but this is more expensive—IPCC (2005) estimates the cost at US$50–100 per ton CO₂. On the other hand, compared with deep underground storage, CO₂ dispersed in the ocean is relatively easy to monitor, and because it is dispersed, the CO₂ that eventually reaches the atmosphere will escape slowly.

In a method that is hybrid between ocean and geologic storage, CO₂ would be injected into marine sediments, deep offshore (House et al. 2006). Because of the relatively high pressure and low temperature in this environment, the CO₂ would be negatively buoyant, perhaps forming solid hydrates, thus minimizing leakage through the sediment–water interface. And any CO₂ that was eventually released to the ocean would be dispersed and diluted.

Another form of ocean sequestration is enhanced production of biomass. Fertilizing portions of the world’s oceans with iron would stimulate phytoplankton growth. The phytoplankton would increase the rate of biological uptake of CO₂ from the surface water and the atmosphere, and a portion would be transported to the ocean depths when the plankton dies. Iron fertilization is relatively inexpensive, and the organisms do most of the capture and transport, making this process an attractive solution. However, the technique is considered risky because it relies on deliberate manipulation of an ecosystem, with uncertain effects. At least ten international field experiments have been conducted to examine the short-term effects of iron fertilization (Coale et al. 2004). Although these experiments have demonstrated a clear response over the short term, the long-term effectiveness and the potential for detrimental changes to marine ecosystems are uncertain.
CONCLUSIONS
Ocean storage is one method to help mitigate global climate change. Compared to business as usual, ocean storage would reduce the peak CO₂ concentration and slow its rate of increase in both the atmosphere and ocean surface water. A number of injection schemes show promise for effective sequestration for several centuries, while diluting the concentration of CO₂ below levels of environmental concern. While such strategies appear promising, they require field verification. Reliable data are necessary before responsible decisions can be made about the safety of ocean storage. Because the ocean is common to all, public participation is essential. The ocean is vast but none the less finite, meaning ocean storage should be viewed as a potential interim solution, to be used while society prepares for its transition to more sustainable energy sources.

REFERENCES
Caldeira K, Wickett ME (2003) Accelerating ocean storage is one method to help mitigate global climate change. Compared to business as usual, ocean storage would reduce the peak CO₂ concentration and slow its rate of increase in both the atmosphere and ocean surface water. A number of injection schemes show promise for effective sequestration for several centuries, while diluting the concentration of CO₂ below levels of environmental concern. While such strategies appear promising, they require field verification. Reliable data are necessary before responsible decisions can be made about the safety of ocean storage. Because the ocean is common to all, public participation is essential. The ocean is vast but none the less finite, meaning ocean storage should be viewed as a potential interim solution, to be used while society prepares for its transition to more sustainable energy sources.


Elements 324 October 2008