CARBON SEQUESTRATION VIA DIRECT INJECTION

H. Herzog, Massachusetts Institute of Technology, Cambridge, USA
K. Caldeira, Lawrence Livermore National Laboratory, Livermore, USA
E. Adams, Massachusetts Institute of Technology, Cambridge, USA

Copyright © 2001 Dr H. J. Herzog

doi:10.1006/rwos.2001.0041

Introduction

The build-up of carbon dioxide (CO_2) and other greenhouse gases in the Earth's atmosphere has caused concern about possible global climate change. As a result, international negotiations have produced the Framework Convention on Climate Change (FCCC), completed during the 1992 Earth Summit in Rio de Janeiro. The treaty, which the United States has ratified, calls for the 'stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system'.

The primary greenhouse gas is CO_2, which is estimated to contribute to over two-thirds of any climate change. The primary source of CO_2 is the burning of fossil fuels, specifically gas, oil, and coal. Therefore, efforts are being made to reduce our dependence on fossil fuels through improved efficiency and the introduction of nonfossil energy sources, such as solar and nuclear. However, it is becoming clear that although these strategies may slow the build-up of atmospheric CO_2, they will not reduce emissions to the level required by the FCCC. In other words, the fossil fuels, which currently supply over 85% of the world's energy needs, are likely to remain our primary energy source for the foreseeable future. This has led to increased interest in a new strategy termed carbon management and sequestration.

Carbon sequestration is often associated with the planting of trees. As they mature, the trees remove carbon from the atmosphere. As long as the forest remains in place, the carbon is effectively sequestered. Another type of sequestration involves capturing CO_2 from large, stationary sources, such as a power plant or chemical factory, and storing the CO_2 in underground reservoirs or the deep ocean. This article explores the applicability of the deep ocean as a sink for atmospheric carbon.

Why is the ocean of interest as a sink for anthropogenic CO_2? The ocean already contains an estimated 40 000 GtC (billion tonnes of carbon) compared with 750 GtC in the atmosphere and 2200 GtC in the terrestrial biosphere. As a result, the amount of carbon that would cause a doubling of the atmospheric concentration would change the ocean concentration by less than 2%. In addition, discharging CO_2 directly to the ocean would accelerate the ongoing, but slow, natural processes by which over 80% of present-day emissions will ultimately enter the ocean indirectly, thus reducing both peak atmospheric CO_2 concentrations and their rate of increase.

Ocean sequestration of CO_2 by direct injection assumes that a relatively pure CO_2 stream has been generated at a power plant or chemical factory. To better understand the role the ocean can play, we address the capacity of the ocean to sequester CO_2, its effectiveness at reducing atmospheric CO_2 levels, how to inject the CO_2, and possible environmental consequences.

Capacity

How much carbon can the ocean sequester? Based on physical chemistry, a large quantity of CO_2 (far exceeding the estimated available fossil energy resources of 5000–10 000 GtC) may be dissolved in deep ocean waters. However, a more realistic criterion needs to be based on an understanding of ocean biogeochemistry.

After some time, injected carbon would be distributed widely in the oceans and any far-field impact of the injected CO_2 on the oceans would be similar to the impact of anthropogenic CO_2 absorbed from the atmosphere. It is thought that, at the CO_2 concentrations that would be typical of the far field, the primary environmental impacts would be associated with changes in ocean pH and carbonate-ion concentration.

As points of reference, the pH of the surface ocean has been reduced by about 0.1 units since pre-industrial times. Adding 1300 GtC (about 200 years of current emissions) to the ocean would decrease average ocean pH by about 0.3 units.

The impacts of such change are poorly understood. The deep ocean environment has probably been quite stable and it is unknown to what extent changes in ocean pH would affect these organisms or their ecosystems. But it is important to recognize that the far-field changes in ocean pH would ultimately be much the same whether the CO_2 is released into the atmosphere or the deep ocean. Moreover, in the shorter term, releasing the CO_2 in the deep ocean will diminish the pH change in the near-surface ocean, where marine biota are most plentiful. Light is plentiful in the near-surface ocean, so the microscopic plants that form the base of the food chain grow, and support vigorous ecosystems. Thus, direct injection of CO_2 into the deep ocean could actually reduce adverse pH impacts presently occurring in the surface ocean.

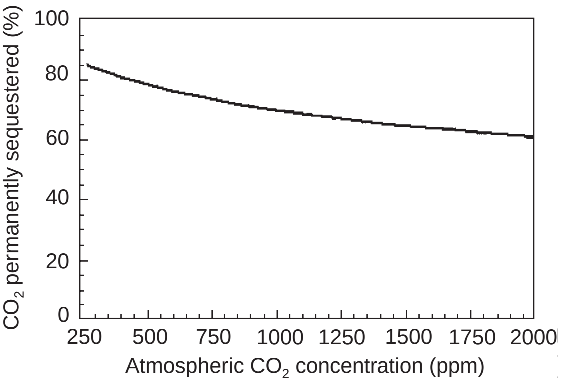

Figure 1 Percentage of injected CO_2 that is permanently sequestered from the atmosphere as a function of the atmospheric concentration of CO_2 calculated from one-dimensional ocean models at Lawrence Livermore National Laboratory. The concentration of CO_2 in the atmosphere today is about 370 ppm; an atmospheric concentration of 550 ppm represents a doubling of pre-industrial levels.

Effectiveness

Carbon dioxide is constantly exchanged between the ocean and atmosphere. Each year the ocean and atmosphere exchange about 90 GtC, with a net ocean uptake currently about 2 GtC. Because of this exchange, questions arise as to how effective ocean sequestration will be at keeping the CO_2 out of the atmosphere. Specifically, is the sequestration permanent and, if not, how fast does the CO_2 leak back to the atmosphere. Because there has been no long-term CO_2 direct-injection experiment in the ocean, the long-term effectiveness of direct CO_2 injection must be predicted based on observations of other oceanic tracers (e.g., radiocarbon) and on computer models of ocean circulation and chemistry. In this section we will show that about 80% of the CO_2 will be sequestered permanently, with the rest taking several hundred years to return to the atmosphere.

The fraction of injected carbon that is permanently sequestered depends on the atmospheric CO_2 concentration, through the effect of atmospheric CO_2 on surface-ocean chemistry (**Figure 1**). The concentration of CO_2 in the atmosphere today is about 370 ppm, meaning that over 80% of any carbon sequestered in the ocean today would be permanent. Even at an atmospheric concentration of 550 ppm (double pre-industrial levels), just under 80% of CO_2 injected into the ocean would be permanently isolated from the atmosphere.

The amount of time over which the remaining 20% of the injected CO_2 would leak depends on the location and depth of the injection. **Figure 2** shows the effect of injection depth on leakage for an ocean site with typical temperature and salinity profiles and no major upwelling or downwelling currents. It can be seen that the deeper the injection, the longer it takes for the 20% of the CO_2 to return to the atmosphere. Also, to make sure the leakage does not significantly exceed the long-term value of 20% in the shorter term, injection depths should be greater than 1000 m. This is because 1000 m is roughly the bottom of the thermocline, which is the layer of the ocean that is stably stratified by large temperature and density gradients, thus inhibiting vertical mixing and slowing the leakage of CO_2. In addition to injecting CO_2 deeper, the amount of leakage could potentially be minimized by injecting the CO_2 in a way that would maximize interaction with carbonate sediments or by purposefully enhancing the dissolution of carbonate minerals.

The time that it would take for carbon to mix from the deep ocean to the atmosphere is roughly equal to the time required for carbon to mix from

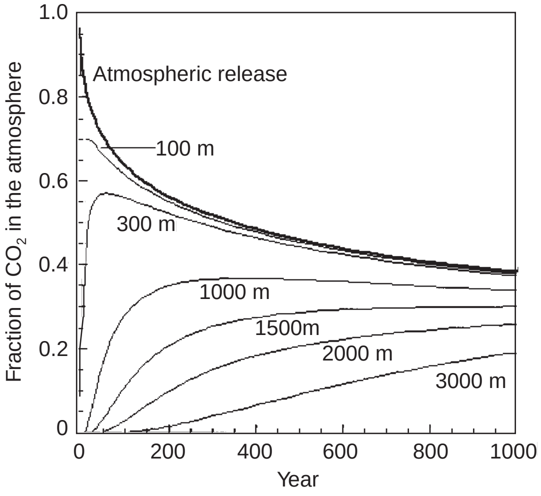

Figure 2 The percentage of injected CO_2 that would leak back to the atmosphere as a function of time. Calculated from one-dimensional ocean models at Lawrence Livermore National Laboratory for an atmospheric concentration of 350 ppm (similar to today's level). The results suggest that injection should be below the thermocline at depths over 1000 m.

the atmosphere to the deep ocean. This can be estimated through observations of radiocarbon (carbon-14) in the oceans. Radiocarbon is an isotope of carbon with a half-life of 5730 years, produced in the stratosphere by the bombardment of nitrogen by cosmic rays. Radiocarbon mixes through the atmosphere, is absorbed by the oceans, and is transported to the deep sea, undergoing radioactive decay as it ages. About 24% of the original radiocarbon has decayed in the mid-depth waters of the North Pacific, indicating that these are the oldest waters in today's ocean. Taken at face value, this would indicate isolation from the atmosphere for over 2200 years. However, this is an overestimate because the source of this water is from Southern Ocean waters which have not equilibrated isotopically with the atmosphere. Considering this, the age of North Pacific deep water is in the range 700–1000 years. Other basins, such as the North Atlantic, have characteristic overturning times of 300 years or more. Collectively, these data suggest that outgassing of the 20% of injected carbon would occur on a time-scale of 300–1000 years.

The issue of how much carbon will be permanently sequestered away from the atmosphere and how long it will take the remaining fraction to return to the atmosphere has been explored in several modeling studies. The first studies used relatively simple one-dimensional models. These models are valuable tools for exploring problems that do not depend on geographical particulars. Later, three-dimensional studies have used ocean general circulation models (OGCMs) from the Max Planck Institut für Meteorologie in Hamburg (MPI), the Institut Pierre Simon Laplace (IPSL), and elsewhere. Results of a simulation made at Lawrence Livermore National Laboratory are shown in **Figure 3**. These modeling studies generally confirm inferences based on considerations of ocean chemistry and radiocarbon decay rates. However, the three-dimensional models yield information that is not directly accessible from other sources. For example, model results indicate that for injection at 1500 m depth, the time scale of the partial CO_2 degassing is very sensitive to the location of the injection, but results at 3000 m are relatively insensitive to injection

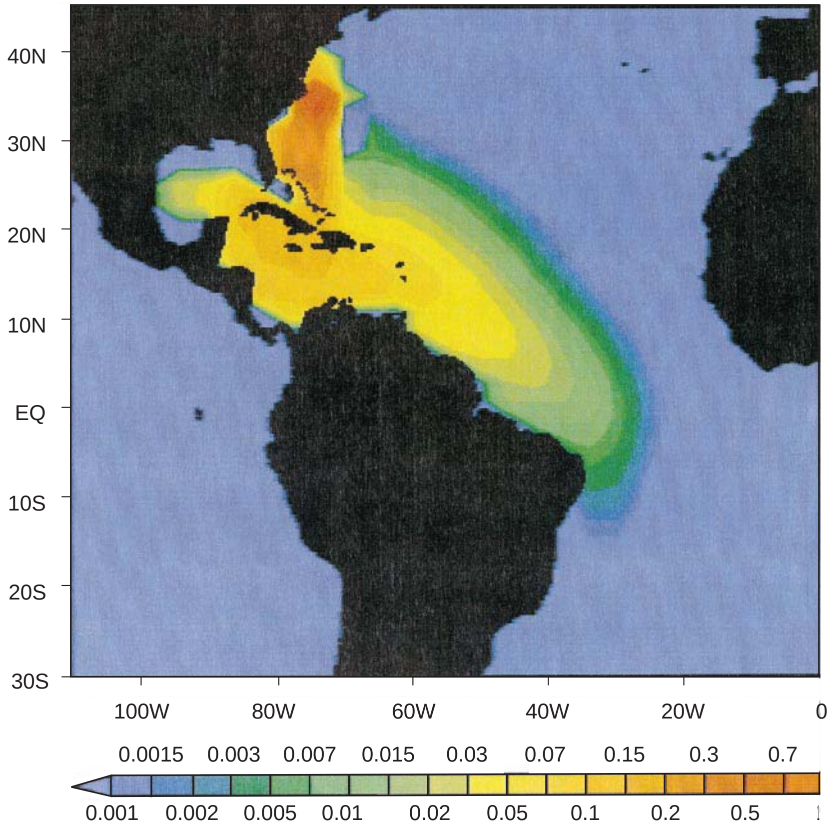

Figure 3 Simulated CO_2 injection at 1750 m depth off the east coast of the United States using a three-dimensional Lawrence Livermore National Laboratory ocean model. The contours represent the concentration of the injected carbon relative to the concentration in the grid cell containing the injection point. Results are for 20 years after the start of injection and at the injection depth, showing the CO_2 is advected southward with the countercurrent running beneath the Gulf Stream.

location. Furthermore, present-day models disagree about the degassing time scale for particular locations. For example, the IPSL model predicts that Tokyo would be a better injection site than New York, whereas the MPI model predicts the opposite. Clearly, three-dimensional models must be improved and carefully evaluated if they are to be useful in siting direct injection facilities.

Injection Methods

Most methods suggested for injecting CO_2 into the ocean involve the production of relatively pure CO_2 at its source and transporting it to the injection point. Several specific injection strategies have been suggested (see **Figure 4**).

1. Droplet plume: liquid CO_2 injected below 1000 m from a manifold lying on the ocean bottom and forming a rising droplet plume.
2. Dense plume: a dense CO_2–sea water mixture created at a depth of between 500 and 1000 m forming a sinking bottom gravity current.
3. Dry ice: dry ice released at the ocean surface from a ship.
4. Towed pipe: liquid CO_2 injected below 1000 m from a pipe towed by a moving ship and forming a rising droplet plume.
5. CO_2 lake: liquid CO_2 introduced to a seafloor depression forming a stable 'deep lake' at a depth of about 4000 m.

To better understand these methods, some background information is required on the CO_2–sea water system. 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. In seawater, the liquid would be positively buoyant (i.e., it will rise) down to about 3000 m, but negatively buoyant (i.e., it will sink) below that depth. At about 3700 m, the liquid becomes negatively buoyant compared to sea water saturated with CO_2. In sea water–CO_2 systems, CO_2 hydrate ($CO_2 \cdot nH_2O$, $6 < n < 8$) can form below about 500 m depth depending on the relative compositions of CO_2 and H_2O. CO_2 hydrate is a solid with a density about 10% greater than that of sea water.

The droplet plume and towed pipe methods are probably the most viable in the short term. Both methods rely on commercially available technology and inject the CO_2 below the thermocline for effective sequestration. In addition, the resulting plumes can be made to have high dilution to minimize any local environmental impacts due to increased CO_2 concentration or reduced pH. Researchers in the US are looking more closely at pipe transport, whereas Japanese researchers are examining ship transport more closely. Although the means of delivery are different, the plumes resulting from these two options would be quite similar.

Figure 5 shows a sketch of two droplet plumes that would result from discharging CO_2 from adjacent ports of a bottom-mounted manifold. Proper design would call for separating the ports so as to minimize interaction between adjacent plumes, illustrated here for conditions with little or no ambient current. Each plume consists of a core of buoyant

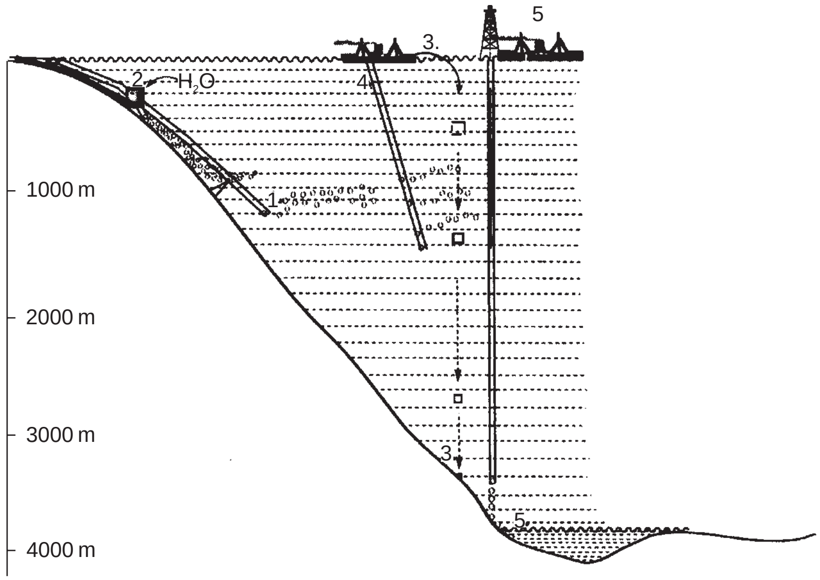

Figure 4 Five suggested methods to inject CO_2 into the deep ocean. Goals are to minimize costs, leakage, and environmental impacts. Dissolution: 1, droplet plume; 2, dense plume. Dispersion: 3, dry ice; 4, towed pipe. Isolation: 5, CO_2 lake.

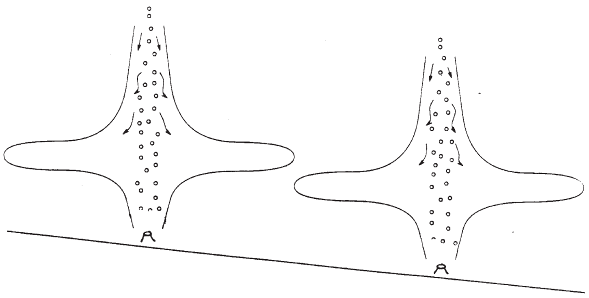

Figure 5 Schematic of buoyant droplet plumes from adjacent ports of a manifold lying on a sloping seafloor.

CO_2 droplets that dissolve as they rise. As the droplets rise, they entrain sea water into the plume. The dissolved CO_2, combined with ambient density stratification, increases the density of the plume water, until it ultimately peels away from the droplets, sinks, and then intrudes into the ambient at a level of neutral buoyancy. The maximum height of rise, the level of intrusion and the concentrations of dissolved CO_2 depend strongly on the flow rate of CO_2 per port, the initial droplet size, and the extent to which hydrates, formed on the droplet–sea water interface, impede mass transfer. The dynamics of hydrate formation are not completely understood, and represent an area of intense current study.

The concept of a CO_2 lake is based on a desire to minimize leakage to the atmosphere and exposure to biota. This would require more advanced technology and perhaps higher costs. Led in part by the oil industry, great strides have been made in undersea offshore technology. It is becoming routine to work in depths approaching 2000 m. However, there are still technical challenges in going deeper. The depth of the lake must be at least 3000 m, the depth at which CO_2 becomes negatively buoyant (i.e., sinks) in sea water. The CO_2 in the lake would be mostly in the form of solid hydrates. This would slow the dissolution of CO_2 into the water column, further slowing leakage to the atmosphere from that shown in **Figure 2**, which assumes the CO_2 is injected into the water column.

The two other methods that have been discussed for injecting CO_2 are dry ice released at the ocean surface from a ship and a dense CO_2–sea water mixture created at a depth of between 500 and 1000 m forming a sinking bottom gravity current. The former is probably too expensive due to the production and handling of dry ice, and the latter has many questions concerning environmental impact due to the highly concentrated nature of the plume.

As discussed earlier, the deep-ocean equilibrates with the surface-ocean on the scale of 300–1000 years, and by injecting anthropogenic CO_2 into the deep ocean, the surface-to-deep mixing time-scale is effectively bypassed. Anthropogenic CO_2 also equilibrates with carbonate sediments, but over a much longer time, about 6000 years. It has been suggested that technical means could also be used to bypass this time-scale, thereby increasing the effectiveness and diminishing environmental impacts of intentional storage of CO_2 in the ocean.

CO_2 reacts with carbonate sediments to form bicarbonate ions (HCO_3^-) in solution. Sea water could be brought into contact with flue gases in a reactor vessel at a power plant, and that CO_2-rich water could be brought into contact with crushed carbonate minerals, which would then dissolve and form bicarbonate ions. Drawbacks of this approach are the cost due to the need for large amounts of water and carbonate minerals. The principle of carbonate-dissolution could be utilized in conjunction with direct CO_2 injection. 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 the water column upstream from the CO_2-rich plume emanating from a direct CO_2 injection site. The suspended carbonate minerals could then be advected with the ambient seawater into the plume, where the minerals could dissolve, increasing the effectiveness of ocean CO_2 storage and diminishing the pH impacts of direct injection.

Local Environmental Impacts

Environmental impacts may be the most significant factor determining the acceptability of ocean storage, since the strategy is predicated on the notion that impacts to the ocean will be significantly less than the avoided impacts of continued emission to the atmosphere. In the Capacity section above, environmental impacts were discussed from the global viewpoint. Here, we examine the environmental impacts near the injection point.

Several reviews have identified potential impacts, with the most significant deriving from lowered pH resulting from the reaction of CO_2 with sea water. Impacts would occur principally to nonswimming marine organisms (e.g., zooplankton, bacteria and benthos) residing at depths of about 1000 m or greater and their magnitude will depend on both the level of pH change and the duration of exposure. **Figure 6** summarizes data showing that organisms can tolerate small pH excursions for many days, but must limit exposure to larger excursions to a matter of hours. The data shown in **Figure 6** involve organisms found in the surface waters. There is a need for similar data on deep-water organisms to see if the same pattern holds and whether the deep-water organisms are more or less sensitive to pH than those in the surface water.

The pH of sea water which is saturated with CO_2 is less than 4, but an injection system designed to promote efficient mixing would produce minimum pH values of about 7 near the discharge, gradually returning to an ambient value of about 8 away from the injection point. Available data suggest that acute impacts associated with pH change can be completely avoided if the injection is properly designed to disperse the CO_2 as it dissolves.

The viability of ocean storage as a greenhouse gas mitigation option will also hinge on social and political considerations. In view of public precaution toward the ocean, the strategy will require that all parties (private, public, nongovernmental organizations) be included in ongoing research and debate.

Research Activities

In order for ocean sequestration of CO_2 to become a viable option, much research must be done in the areas of ocean modeling, environmental assessment, engineering analysis, and public outreach. Several significant efforts are underway, but we are just at the beginning of the journey. Several ongoing research efforts into ocean sequestration of CO_2 are described below.

DOE Center for Research on OceanCarbon Sequestration (DOCS)

DOCS has been established as a center to conduct, focus, and advance the research necessary to evaluate and improve the feasibility, effectiveness, and environmental acceptability of ocean carbon sequestration. The Center addresses fertilization and direct injection, and other ocean carbon sequestration strategies. It advances our understanding of the biological, chemical, and physical processes that are critical to the ocean carbon cycle to help us understand the effects of proposed sequestration strategies on this system. The Center is directed by the Lawrence Berkeley and Lawrence Livermore National Laboratories. Participants include the Massachusetts Institute of Technology, Moss Landing Marine Labs, the Pacific International Center for High Technology Research, Rutgers University, the Scripps Institution of Oceanography and the Monterey Bay Aquarium Research Institute.

International Field Experiment

Many of the important physical, chemical, and biological processes related to ocean sequestration of CO_2 cannot be scaled, which means that more experimental research must eventually be conducted in the field. To this end, Japan, Norway, and the United States signed a Project Agreement for International Collaboration on CO_2 Ocean Sequestration in December 1997; since that time, Canada, Australia, and Switzerland have joined the project. The objective of the project is to investigate the technical feasibility of, and improve understanding of the environmental impacts from, CO_2 ocean sequestration in order to minimize the impacts associated with the eventual use of this technique to reduce greenhouse gas concentrations in the atmosphere. The project will continue to 31 March 2002, and a field experiment will take place in the latter half of 2001 off the Kona Coast of Hawaii. The implementing

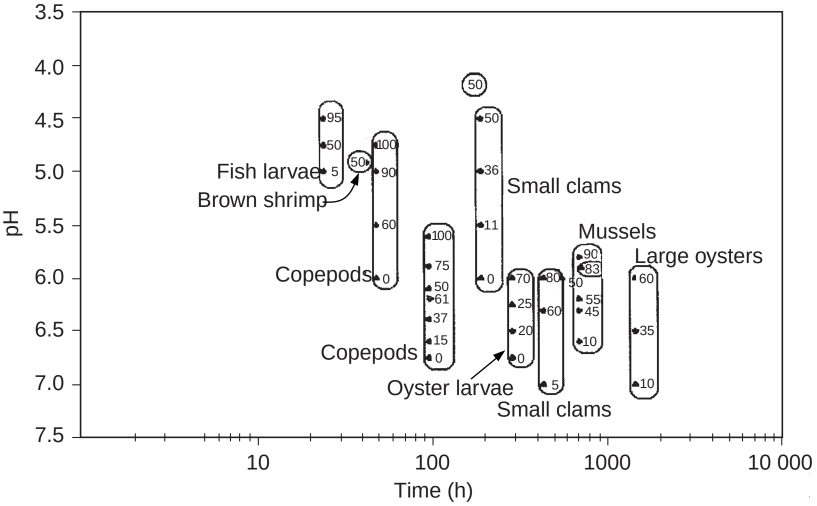

Figure 6 Mortality rates for various marine organisms plotted as a function of pH and time of exposure. The plot shows that impacts will depend on both the level of pH change and the duration of exposure.

research organizations are the Research Institute of Innovative Technology for the Earth (Japan), the Norwegian Institute for Water Research (Norway), and the Massachusetts Institute of Technology (USA). The general contractor for the project will be the Pacific International Center for High Technology Research in Hawaii. Based on the results of this effort, a phase II may be initiated to investigate longer-term acute and chronic biological impacts.

The CO_2 Ocean Sequestration Project in Japan

In April 1997, a five-year national program looking at ocean sequestration of CO_2 began in Japan. Annual funding is in excess of 10 million US$ per year. The lead research institutes for this program are the Research Institute of Innovative Technology for the Earth and the Kansai Environmental Engineering Center. The R&D agenda includes studying the behavior of liquid CO_2 released in the ocean, developing an engineering system for CO_2 injection, assessing the impacts of CO_2 on marine organisms, developing a near-field environmental impact assessment model, predicting the long-term fate of the sequestered CO_2, and participation in the international field experiment.

Comparison of Ocean Carbon Cycle Models

The International Geosphere-Biosphere Programme initiated the Ocean Carbon–cycle Model Intercomparison Project (OCMIP) in 1995 through the Global Analysis, Interpretation, and Modeling task force. OCMIP is an international project devoted to improving marine carbon cycle models by comparing them with each other and by evaluating them using observational data sets. The European research program on Global Ocean Storage and Anthropogenic Carbon participates in OCMIP and will also look at global scientific aspects of the deep–ocean CO_2 sequestration issue. Specifically, the researchers will compare models of dispersion of CO_2 from seven hypothetical point sources in order to get a better understanding of sequestration efficiency.

Experiments at the Monterey Bay Aquarium Research Institute (MBARI)

Researchers at MBARI have conducted several small-scale field experiments to observe the reaction of CO_2 with sea water at various depths. For example, in April 1998, they carried out a controlled experiment with a 9 liter liquid CO_2 release at a depth of 3650 m (*in situ* temperature about 1.6°C) from their Remotely Operated Vehicle (ROV) *Tiburon*. For several hours they observed the transformation of liquid CO_2 into solid hydrate. Future plans call for a series of biological response experiments.

Acknowledgments

All three authors participate in the DOE Center for Research on Ocean Carbon Sequestration (DOCS), with Ken Caldeira being a co-director. We would like to acknowledge the support for this center from the Office of Biological and Environmental Research, U.S. Department of Energy.

See also

Abrupt Climate Change. Carbon Cycle. Carbon Dioxide (CO_2) Cycle. Data Assimilation in Models. Deep-sea Drilling Methodology. Dispersion and Diffusion in the Deep Ocean. Iron Fertilization. Law of the Sea. Ocean Circulation. Ocean Carbon System, Modelling of. Open Ocean Convection. Remotely Operated Vehicles (ROVs).

Further Reading

Auerbach DI, Caulfield JA, Adams EE and Herzog HJ (1997) Impacts of ocean CO_2 disposal on marine life: a toxicological assessment integrating constant-concentration laboratory assay data with variable-concentration field exposure. *Environmental Modeling and Assessment* 2: 333–343.

Caulfield JA, Adams EE, Auerbach DI and Herzog HJ (1997) Impacts of ocean CO_2 disposal on marine life: probabilistic plume exposure model used with a time-varying dose-response analysis. *Environmental Modeling and Assessment* 2: 345–353.

Herzog H, Drake E and Adams EE (1997) *CO_2 Capture, Reuse and Storage Technologies for Mitigating Global Climate Change, A White Paper*. Prepared for US Department of Energy by the MIT Energy Laboratory [web.mit.edu/energylab/www/].

Herzog H, Eliasson B and Kaarstad O (2000) Capturing Greenhouse Gases. *Scientific American* (February).

Hoffert MI, Caldeira K, Jain AK *et al.* (1998) Energy implications of future stabilization of atmospheric CO_2 content. *Nature* 395: 881–884.

CASCADES

See **OVERFLOWS AND CASCADES**