Environmental Impacts of Ocean Disposal of CO₂

Final Report - Volume 2
Topical Reports

DOE Grant No. DE-FG22-94PC94227

Period Covered: September 1994 - August 1996

Energy Laboratory
Massachusetts Institute of Technology
77 Massachusetts Avenue
Room E40-455
Cambridge, MA 02139-4307
Telephone: (617) 253-3401
Fax: (617) 253-8013

Edited by: H. J. Herzog and E. E. Adams

RECEIVED
USDOE/PETC
97 JAN 31 AM 8:43
ACQUISITION & ASSISTANCE DIV.

U.S. DOE PATENT CLEARANCE NOT REQUIRED PRIOR
TO PUBLICATION OF THIS REPORT

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

December, 1996

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.

Abstract

One option to reduce atmospheric CO₂ levels is to capture and sequester power plant CO₂. Commercial CO₂ capture technology, though expensive, exists today. However, the ability to dispose of large quantities of CO₂ is highly uncertain. The deep ocean is one of only a few possible CO₂ disposal options (others are depleted oil and gas wells or deep, confined aquifers) and is a prime candidate because the deep ocean is vast and highly unsaturated in CO₂. Technically, the term 'disposal' is really a misnomer because the atmosphere and ocean eventually equilibrate on a time scale of 1000 years regardless of where the CO₂ is originally discharged. However, peak atmospheric CO₂ concentrations expected to occur in the next few centuries could be significantly reduced by ocean disposal. The magnitude of this reduction will depend upon the quantity of CO₂ injected in the ocean, as well as the depth and location of injection.

Ocean disposal of CO₂ will only make sense if the environmental impacts to the ocean are significantly less than the avoided impacts of atmospheric release. In this project, we examined these ocean impacts through a multi-disciplinary effort designed to summarize the current state of knowledge. In the process, we have developed a comprehensive method to assess the impacts of pH changes on passive marine organisms. This final report addresses the following six topics: CO₂ loadings and scenarios, impacts of CO₂ transport, near-field perturbations, far-field perturbations, environmental impacts of CO₂ release, and policy and legal implications of CO₂ release.

While there are several important environmental impacts of ocean disposal of CO₂, the acidification around the release point may be the most important. However, the size and severity of the impacted area varies substantially with the injection scenario. We have quantified the impacts of various injection scenarios relative to each other through mortality measures. Based on available data, it appears possible to inject CO₂ into the deep ocean in such a way as to yield negligible environmental impacts. The key conclusions of this research are:

- The major environmental impact of ocean CO₂ disposal would derive from the lowering of pH caused by the reaction of CO₂ with seawater. Depending on the method of release, pH can be reduced to as low as about 4 very near the injection point from its ambient value of about 8.
- Impacts would be felt primarily by those organisms which reside at depths of 1000 m or greater and are unable to avoid regions of low pH near the point of injection (e.g., zooplankton, bacteria and benthos). In comparison with the size of the world's oceans, the areas of acute impact would be very small for all injection scenarios. Nonetheless, there would be significant differences among scenarios, with the least impact predicted from those methods which disperse the CO₂ as it is being injected and which keep it off the seabed. Based on available data, it appears possible to design a discharge system which effectively eliminates mortality by spreading the CO₂ sufficiently in either the

vertical or horizontal directions, e.g., by releasing it from either an inclined pipe towed by a moving ship or a fixed pipe laid on the sea floor. The precautionary principle suggests that future R&D efforts be focused on such methods.

- At global scales, anthropogenic emissions of CO₂ that are occurring today will cause a gradual decline in average ocean pH of about 0.5 units over the next several centuries. Direct injection of CO₂ to the ocean will perturb the system by less than another 0.1 pH unit. The impacts from the combined pH changes will not cause mortality, but could cause sub-lethal impacts such as shifting population structure, decreased reproduction rates, etc. The regional impacts would be site-specific, as would the effectiveness of sequestration (tendency of the CO₂ to remain in the ocean). In general such chronic impacts will be harder to predict than the more acute impacts expected in the near-field.
- Additional impacts of ocean CO₂ disposal were identified including increased concentrations of trace gases carried with the CO₂, benthic disruption during outfall construction, disturbances to marine organisms caused by injection devices, plumes or hydrated CO₂ particles, and accidents associated with CO₂ transport. While such impacts, and possibly others, would need to be studied on a project-specific basis, they are expected to be minor. We also analyzed the possibility of a Lake Nyos-type of eruption, whereby large quantities of CO₂-enriched seawater (or liquid CO₂ itself) stored in the ocean might accidentally rise to the surface, and result in asphyxiation; it was concluded that such an incident could not occur with ocean CO₂ disposal.
- The viability of ocean CO₂ disposal as a greenhouse gas mitigation option may ultimately hinge on social and political considerations. Although there are no provisions which specifically prohibit ocean CO₂ disposal, international acceptance will require several steps: the public must believe that the threat of global change is real, they must be convinced that there are no other easy mitigation options, and it must be demonstrated that the environmental impacts of ocean CO₂ disposal are significantly less than the impacts of increased build-up of CO₂ in the atmosphere. Such acceptance can only occur if the public is included in the ongoing research and debate on this topic.

The results presented in this report are just one piece of information that is required in doing a comprehensive analysis of the CO₂ ocean disposal option. Other important pieces include: effects of the localized impacts investigated here on larger ocean ecosystems, benefits of reduced atmospheric CO₂ emissions in terms of reduced risk of possible climate and ocean ecosystem change, and the cost of ocean disposal compared to alternate mitigation options. By doing objective and comprehensive studies of these issues, we are building a knowledge base that will allow informed decisions to be made if and when more stringent CO₂ emission controls are required.

Table of Contents

Volume 2

Preface

Acknowledgments

Topical Reports

1. Scope and Basis
2. Environmental Effects of CO₂ Transport Systems
3. Models of Near-Field Perturbations and Probabalistic Organism Exposure
4. Far-Field Environmental Impacts Associated with Ocean Disposal of CO₂
5. Biological Assessment of Environmental Impacts of CO₂ Ocean Disposal
6. Legal and Political Aspects of CO₂ Ocean Disposal

Appendices

1. Near-Field Perturbations Resulting from the Deep Lake Injection Scenario
2. Benthic Impacts Due to the Various Injection Scenarios
3. A Simple Box Model
4. The Possibility of a "Lake Nyos type" Eruption
5. Revisions to the London Dumping Convention

Preface

This report is organized in two volumes. The first volume serves as an executive summary of the entire project and results; the second volume contains more detailed information on each of the topical areas.

Volume 1 describes the objectives and scope of the project (Chapter 1), the background (Chapter 2), previous work (Chapter 3), the project organization (Chapter 4), the approach and results (Chapter 5), and conclusions and recommendations (Chapter 6). References for Volume 1 are included in Chapter 7. Volume 1 has three appendices: Appendix A, Workshop Summary; Appendix B, List of Acronyms; and Appendix C, Color Figures.

Volume 2 contains six, separate topical reports. The first topical report describes the scope and basis of the research. The next five topical reports each focus on key research themes: Transport Systems, Near-Field Perturbations, Far-Field Perturbations, Biological Assessment, and Legal and Policy Aspects. Each of the six topical reports was prepared by the topical team leaders, who are identified as authors at the beginning of each report. Five appendices discuss some additional information not covered in the topical reports.

Acknowledgments

This study was initiated and supported by the U.S. Department of Energy under Grant Number DE-FG22-94PC94227. The information included in this report is based on the collaboration of a large number of participants, including project team members from MIT and selected consultants.

The core project team was made up of:

Eric Adams, Senior Research Engineer (Co-PI), Civil and Environmental Engineering
Howard Herzog, Principal Research Engineer (Project Manager), Energy Laboratory
David Auerbach, Graduate Student, Civil and Environmental Engineering
Jennifer Caulfield, Graduate Student, Civil and Environmental Engineering

We would like to thank the following contributors:

From MIT (Cambridge, MA):

Jefferson Tester, Professor of Chemical Eng., Director Energy Laboratory (Co-PI)
Elisabeth Drake, Associate Director Energy Laboratory
John Edmond, Professor, Marine Chemistry
Mick Follows, Research Scientist, Physical Oceanography
Judith Kildow, Associate Professor, Ocean Policy
John Marshall, Professor, Physical Oceanography
Judith Pederson, Sponsored Research Technical Supervisor, Sea Grant Program
David White, Professor, Electrical Engineering and Computer Science

From Science Applications International Corporation (SAIC) (Bellevue, WA):

Richard Dewey, Sr. Research Scientist, Marine Sciences Operation (currently at Univ. Of Victoria, Canada)
Gilbert Stegen, Manager, Marine Sciences Operation

From Woods Hole Oceanographic Institute (Woods Hole, MA):

John Dacey, Associate Scientist, Biology
Larry Madin, Senior Scientist, Biology

From University of Massachusetts at Lowell (Lowell, MA):

Dan Golomb, Professor, Environmental Sciences
Yulin Shao, Research Assistant

Others:

Robert Bacastow, Scripps Institution of Oceanography (La Jolla, CA)
Roger Bamber, Fawley Aquatic Research Laboratories (Fawley, Southampton, UK)
Bill Eng, U.S. Environmental Protection Agency (Boston, MA)
Yukio Yanagisawa, Harvard School of Public Health (Boston, MA) and RITE (Japan)

A special thanks to Paul Freund and Bill Ormerod of the IEA Greenhouse Gas R&D Programme for their joint sponsorship of the project workshop. We would also like to thank the experts attending that workshop at the invitation of the IEA: Martin Angel (Southampton Oceanography Centre, UK), Richard Haedrich (Memorial University, Newfoundland, Canada), Peter Haugan (University of Bergen, Norway), Takashi Ohsumi (CRIEPI, Japan), Makoto Omori (Tokyo University of Fisheries, Japan), Olaf Pfannkuche (GEOMAR Research Centre at the University of Kiel, Germany), Hans-Otto Pörtner (Alfred-Wegener-Institut für Polar- und Meeresforschung, Germany), and Yoshihisa Shirayama (University of Tokyo, Japan).

We also wish to thank Janice Murphy of the **U.S. Department of Energy**, Pittsburgh Energy Technology Center, the Technical Monitor for this project, for her guidance and assistance. We also appreciated inputs provided by others affiliated with DOE: Perry Bergman, Michael Perlsweig, and Bob Warzinski.

Topical Report 1

Scope and Basis

**Jennifer A. Caulfield
Howard J. Herzog**

**Massachusetts Institute of Technology
Energy Laboratory
77 Massachusetts Avenue
Cambridge, MA 02139-4307**

1. Scope of Study

Driven by the need to develop options that can mitigate potential global warming caused by the increase in atmospheric greenhouse gases, research into the capture and sequestration of CO₂ is underway around the world. The largest potential sink for captured CO₂ is the oceans, but the environmental effects are uncertain. The Energy Laboratory of Massachusetts Institute of Technology (MIT) was awarded a US Department of Energy (DOE) Grant No. DE-FG22-94PC94227 to investigate the environmental impacts of ocean disposal of CO₂.

The project had the following key objectives:

- To review the current "state-of-the-art" relating to ocean disposal of CO₂.
- To generate a report that is a comprehensive reference on the environmental impacts of ocean disposal of CO₂.
- To identify any potential environmental "show-stoppers" involved with ocean disposal of CO₂.
- To compare various scenarios for discharging CO₂ into the ocean and identify the most promising alternatives.
- To propose the next steps in assessing the feasibility of ocean disposal of CO₂, including requirements for environmental monitoring.

The topical reports contained in this volume detail the research effort aimed at addressing the above objectives. Volume I is the executive summary for the report.

2. Standard Power Plant

We defined a "standard power plant" as a 500 MW_e (net) pulverized coal fired power plant capturing 90% of the CO₂ with an energy penalty of 20%. This results in the capture of 130 kg/s of CO₂. Coal was chosen as the fuel because it produces 85% of the CO₂ emissions from power plants in the U.S. [1].

The standard emissions of a 500 MW_e pulverized coal fired power plant with no capture were made consistent with the International Energy Agency (IEA) Greenhouse Gas R & D Programme studies, as follows [2]:

Mass flow (kg/s)	606.25
Pressure (bar)	1.016
Temperature (°C)	93.1
Molecular Weight	29.2

Composition (mole fraction)

N ₂	0.71
CO ₂	0.126
H ₂ O	0.111
O ₂	0.044
Ar	0.008
SO ₂	190 mg/m ³ (STP)
NO _x	666 mg/m ³ (STP)

These emissions have a mass flow of 115 kg/s carbon dioxide. The trace gases of sulfur dioxide and NO₂ are produced at the rate of 0.088 kg/s and 0.31 kg/s respectively. Depending on the capture and disposal technology chosen, the trace gases in these emissions may or may not be disposed of with the carbon dioxide.

Without limiting the capture to any single technology, a capture efficiency of 90% was chosen. Currently, amine scrubbing achieves this level of capture, as do several other technologies, while flue gas recycling effectively captures 100% of carbon dioxide emissions. The amine scrubbing is the only process commercially available today.

Since the carbon dioxide capture process consumes energy, implementation of ocean disposal of carbon dioxide changes overall emission levels. The energy penalty is defined as $100\% \times (a-b)/a$, where a = net power output with no CO₂ controls and b = net power output with CO₂ controls. The energy penalties quoted below include initial CO₂ compression. In many cases, no further energy is required for transportation and disposal.

To choose an appropriate energy penalty, current and predicted energy penalties associated with capture for various energy sources were examined. The energy penalties estimated are as follows [3]:

	TODAY	FUTURE
Conventional Coal	38%	22%
Gas	24%	15%
Advanced Coal	17%	10%

Considering that implementation of ocean disposal with the current energy penalty for a coal plant would be neither environmentally or economically feasible, some level of advanced technology is assumed in order that the study be relevant. If ocean disposal were desired, a large percentage of "future" technologies could be developed rapidly. The 20% energy penalty chosen is a conservative estimate of an achievable level of improvement over today's technology using a mix of conventional and advanced coal combustors.

The effect of ocean disposal for our "standard power plant" is summarized below:

	Net Energy Produced	Release of Carbon Dioxide to Atmosphere	To Ocean
Without Capture	500 MW _e	115 kg/s	0 kg/s
With Capture	500 MW _e	14.4 kg/s	130 kg/s

3. Scenario Matrix

Table 1 summarizes the scenarios that have been investigated.

Table 1: Scenario Matrix			
Analysis	Number of Standard Power Plants		
	One (130 kg/s CO ₂)	Ten (1,300 kg/s CO ₂)	One Hundred (13,000 kg/s CO ₂)
Near Field (<25 km)	Five injection scenarios with generic ambient conditions	Five injection scenarios with generic ambient conditions	---
Mesoscale (25 km - 2500 km)	---	6 specific injection sites with a generic injection scenario	---
Far Field (>300 km)	---	---	One scenario

The emissions loadings that have been studied are multiples of the standard power plant. The impact of the emissions from one power plant was studied in the near field, as was the impact of the emissions from ten power plants. One power plant is essentially the lowest level of disposal anticipated. The emissions from ten power plants represent an upper limit on the amount of emissions that are expected to be disposed of at a single point for reasons of economy of transport. The near field models are injection technique specific and provide information about the distribution of carbon dioxide species in the 100 km square area around the point of injection. These local models assume ocean characteristics to be constant throughout the area modeled.

The injection scenarios considered in the near field models are:

- dry ice injection from the ocean surface,
- liquid CO₂ from a towed pipe,
- a droplet plume injected at 1000 meters,
- a dense CO₂ seawater plume injected below 500 meters, and
- a CO₂ lake on the ocean bottom below 3700 meters.

The mesoscale model uses a grid size of 25 km in which distinctions among injection methods are not resolved. The emissions from ten standard power plants are considered to be injected into a single grid block and basin level mixing phenomena are modeled for several possible injection sites.

The global model is based on a general ocean circulation model. The release point is chosen based on the mesoscale model results. The equivalent of one hundred standard power plants represents a loading of about 1.6% of the world's total anthropogenic CO₂ emissions.

More details on the models, along with the results of our analysis are continued in the topical reports that follow.

References

1. Monthly energy review. Technical Report DOE/EIA-0035(96/03), Energy Information Agency, 1996.
2. Henderson, C. and M.R. Whitfield, *The Characterization of Carbon Dioxide and Other Greenhouse Gas Releases from a Pulverized Coal Fired Power Plan Equipped with Flue Gas Desulfurisation Facilities*, IEA Greenhouse Gas R&D Programme report IEA/91/OE1 (1992).
3. Herzog, Howard J. and Elisabeth M. Drake, *Long-Term Advanced CO₂ Capture Options*, IEA Greenhouse Gas R&D Programme report IEA/92/OE6 (1993).

Topical Report 2

Environmental Effects of CO₂ Transport Systems

**Dan Golomb
Yulin Shao**

**University of Massachusetts Lowell
Lowell, MA 01854**

ENVIRONMENTAL EFFECTS OF CO₂ TRANSPORT SYSTEMS

Dan Golomb and Yulin Shao
University of Massachusetts Lowell
Lowell, MA 01854

1. Introduction

After removal of the CO₂ from power plants flue gas, the CO₂ has to be transported from the power plant to the deep ocean. Because of the vast quantities that need to be transported, this is a formidable task. The transport systems will add to the cost of CO₂ disposal, and additional energy may have to be spent on transporting the CO₂ from the plant to the disposal site. Furthermore, the transport systems may pose an environmental hazard, both during the construction and operational phases.

2. Quantities of CO₂ to be Transported

The quantity of CO₂ emitted by a power plant depends on the characteristics of the fuel (carbon content and heat content), thermal efficiency or heat rate of the plant, and average load capacity of the plant. Taking Illinois No. 6 coal as an example, with carbon content 70.8%, heat content 25.8 MJ/kg, a power plant with rated capacity of 1000 MW that works at 90% of its capacity, will have the emission rates of CO₂ as a function of thermal efficiency listed in Table 1. The average thermal efficiency of US coal fired power plants is in the order of 35%. Such a plant emits 8.2 million metric tonnes per year, or 260 kilograms per second. However, the removal and compression of CO₂ from the flue gas requires additional energy. Golomb et al. (1989) estimated that with CO₂ removal and compression a pulverized coal fired power plant's thermal efficiency will decrease from 35% to 25%. Thus, a 1000 MW plant with CO₂ removal and compression units will emit about 11.5 million metric tonnes CO₂ per year, or 364 kg/s. The transport of such quantities will necessitate enormous transport system capacity, including storage tanks, pipelines and transport vessels.

Table 1. Emission Rates for a 1000 MW Plant

Thermal eff. (%)	25	30	35	40	45
E _{CO2} (10 ⁶ T/y)	11.5	9.6	8.2	7.2	6.4
E _{CO2} (kg/s)	364	304	260	228	203

3. Physical Properties of Transported CO₂

In order to comprehend the technical difficulties and the potential environmental and safety hazards of CO₂ transport, it is useful to review the physical properties of CO₂. Figure 1 presents the phase diagram of CO₂. The triple point of CO₂ is 216.8K (-56.3°C). At the triple point solid, liquid and gaseous CO₂ coexist, and the vapor pressure is 5.11 atm (5.18 bar, 75 psia). Solid CO₂ has a vapor pressure of 1 atm at 194.6K (-78.5°C). At normal ambient temperatures of 20-25°C, liquid CO₂ has a vapor pressure of 54-60 atm (55-61 bar, 795-880 psia). The critical temperature is 304.2K (31.4°C); the critical pressure is 72.8 atm (73.8 bar, 1070 psia). Liquid CO₂ has a density of 914 kg/m³ at 0°C and 34.3 atm; the critical density is 467 kg/m³; and solid CO₂ has a density of 1512 kg/m³ at -56.6°C.

Figure 1. The Phase Diagram of Carbon Dioxide

For transport in pipes it is desirable to have a single phase flow. Thus, for pipe flow of CO₂, the supercritical ("dense") phase is preferred. This means that pipes must withstand very high pressures. In storage tanks and shipping tankers, liquid and gaseous CO₂ can coexist, however, such vessels also need to withstand high pressures. Alternatively, to reduce the pressure, they could be refrigerated. Solid ice could be shipped at atmospheric pressure, but to avoid rapid evaporation the solid ice must be kept at very low temperatures by refrigeration or extensive insulation.

4. Transport Modes of CO₂

CO₂ can be transported as a gas, liquid or solid. CO₂ can be transported in pipes, tankers, cargo vessels, barges, trucks and railroad cars, depending on the phase of the CO₂. For transport of large quantities of CO₂, such as produced by coal fired power plants, the transport systems that appear to be most practical are pipes and tankers, and large cargo vessels for the transport of solid CO₂.

4.1 Pipe Transport

The quantity of CO₂ that can be transported in a pipe depends on the pipe diameter and the state of the CO₂, that is, its density and temperature. In pipes, single phase transport is preferred, that is the supercritical (dense) phase. Thus, the pipes must be able to withstand a pressure of 73.8 bar (1070 psia) or higher. Skovholt (1993) estimated the minimum pipe diameter necessary for transporting CO₂ in onshore and offshore pipes. For the estimates Skovholt used the following conditions:

Phase of CO ₂	dense phase (supercritical)
Pipeline segments between compr. stations	250 km
Onshore temperature	12°C
Offshore (water) temperature	0°C
Max. temperature after compression	30 bar
Max. pressure onshore	110 bar
Max. pressure offshore	300 bar
Min. pressure	90 bar

Table 2 lists Skovholt's estimates of minimum diameters for on- and off-shore pipes for various throughputs. For the emission of 8.2 million metric tons of CO₂ per year (1000 MW plant, 35% thermal efficiency), the minimum diameter is 22 inches (56 cm) for onshore pipes, and 17 inches (43 cm) for offshore pipes.

Table 2. Minimum Pipe Diameters for Transport of CO₂⁽¹⁾

E _{CO2} (10 ⁶ T/y)	11.5	9.6	8.2	7.2	6.4
E _{CO2} (kg/s)	364	304	260	228	203
Pipe dia onshore (in)	24	23	22	20	19
Pipe dia offshore (in)	19	18	17	16	15.5

⁽¹⁾ From Skovholt (1993)

The minimum diameter for *offshore* pipes with various throughputs of a supercritical (dense) phase CO₂ was recalculated using the pipe flow model developed by Uhl et al. (1965) on behalf of the American Gas Association. Also were estimated the repumping pressure, P, the pumping energy, E(MW), and the number of pumping stations, PS, required to transport the CO₂ to the deep ocean over a 100, 200 and 500 km distance, respectively. In the model, the pipe is submerged in water at an average ambient temperature of 10°C. The initial pressure of CO₂ is 140 bar. Repumping is deemed necessary whenever the pressure falls below 80 bar in order to avoid a two-phase flow. Table 3 summarizes the results. For a 1000 MW plant (emission factor 260 kg/s), pipe diameter 24 inches, over a linear distance of 100 to 200 km, the pressure drop is negligible, and no repumping is necessary. Over a distance of 500 km, one repumping station is necessary, requiring an energy of 0.5 MW. However, for the same plant, pipe diameter 16 inches, even over a distance of 100 km, one repumping station would be necessary with an energy requirement of 1.3 MW. For 200 km, three repumping stations would be necessary (E = 2.7 MW), and for 500 km, seven stations (E = 6.6 MW). Clearly, large diameter pipes are necessary if submerged repumping stations are to be avoided. If a pipe is used to discharge the output of ten 500 MW power plants over a linear distance of 100-200 km, a diameter of 40 inches may be necessary.

Table 3. Pipe Diameters, Repumping Stations and Energy Consumption for Offshore Pipes

D (inch)	m (kg/s)	Length of pipeline								
		100 km			200 km			500 km		
		ΔP (bar)	E (MW)	PS	ΔP (bar)	E (MW)	PS	ΔP (bar)	E (MW)	PS
12	130	45	0.9	1	90	1.8	3	245	4.4	7
16	130	0	0	0	2	0.4	1	68	1.3	1
16	260	34	1.3	1	68	2.7	3	170	6.6	7
24	260	0	0	0	0	0	0	13	0.5	1
24	390	0	0	0	70	0.4	1	73	4.3	1
32	650	0	0	0	0	0	0	19	1.9	1
40	1300	0	0	0	0	0	0	46	9	1

4.2 Pipe Laying

Because of the large diameter of the pipe, and the great depth to be reached (minimum 1000 m) for CO₂ disposal, the most likely pipe laying method will be the so-called tow-lay method. In this method long lengths (up to 10 km) of pipe are assembled onshore or in shallow water, towed by a lay barge, and the segments are connected under water (Figure 2).

Figure 2. The Tow-lay Method

4.3 Vertical Pipes

For a vertical pipe mounted to a floating platform with a linear length of 1000 to 3000 m, no repumping will be necessary. However, large diameter free dangling pipes may pose great technical difficulties. Present offshore oil drilling and pumping facilities use pipes that do not exceed 16 inches in diameter, and the pipe is fastened to the sea floor by a template. The Ocean Thermal Energy Conversion (OTEC) facility off the shore of Hawaii uses a sea floor mounted pipe rather than a vertical pipe dangling from a platform, because previous experience showed that dangling pipes are prone to breaking (Nihous, 1995). A free dangling pipe would experience enormous forces, due to gravity, pressure differential inside/outside, thermal expansion and hydrodynamic forces due to water motion. The connection of the pipe to the platform must be flexible to withstand the mutual motions of the pipe and platform of surge, sway, yaw, heave, pitch and roll (Demirbilek, 1989). Srikandarajah and Mahendran (1987) estimated the wall thickness and submerged weight of various diameter pipes as a function of length. For a 36 inch diameter pipe (required for the output of about five 1000 MW power plants) the data is summarized in Table 4. It is seen that for deep reaching pipes the wall thicknesses and weights are very large.

Table 4. Wall Thickness and Submerged Weight of a 36 Inch Diameter Vertical Pipe⁽²⁾

Depth (m)	1000	1500	2000	2500	3000
Wall thickness (mm)	38	46	51	54	57
Submerged weight (tonnes)	200	500	1000	1600	2500

⁽²⁾ From Srikandarajah and Mahendran (1987). Values for depths greater than 1500 m are extrapolated

4.4 Tanker Transport

Transportation of liquid CO₂ in a tanker requires pressurization and refrigeration, or full insulation. An optimal regime would be a temperature of minus 20 to 50°C, at which temperatures the liquid has a vapor pressure of 20 and 5 bars, respectively. Such vessels need to be built with heavily constructed holding tanks. The largest extant pressurized, refrigerated or heavily insulated vessels have a capacity of 4000 - 7500 m³ (McGuire and White, 1986). They are used for the transport of chemicals such as ammonia and LPG. Clearly, such relatively small vessels cannot serve to transport the vast quantities of liquid CO₂ produced by power plants. (One 1000 MW power plant would require about six 4000 m³ tankers *per day* to transport its output of CO₂.) Larger tankers, up to 125,000 m³, for the transport of LNG do exist today, however they are not pressurized. Furthermore, LNG tankers are the most expensive cargo vessels built, in the order of \$250-300 M (Drewry, 1982). Pressurized, large tankers are likely to cost much more. Thus, the capital investment for a tanker would be equal or greater than the investment in the CO₂ removal facility at the power plant (Golomb et al., 1989).

For solid CO₂ transport, special cargo vessels must be used. Solid CO₂ has a vapor pressure of 1 atm at 194.6K (-78.5°C). Therefore, the holds of the vessel need to be refrigerated or well-insulated to prevent evaporation during voyage. Solid CO₂ has a density that is approximately 1.5 times the density of liquid CO₂, but this still requires enormous volumes to transport the output of large power plants. A 1000 MW plant will require one vessel per day with a volume of about 25,000 m³. For rapid sinking and slow dissolution purposes it is desirable to dump the solid CO₂ in large blocks. The loading, storage and unloading on the open seas of large blocks of solid CO₂ onto and from a cargo vessel will be a formidable task. One should mention also the extra energy requirement for producing solid CO₂. After separation from the flue gas, solidifying requires approximately twice the energy for producing liquid CO₂. The thermal efficiency of a power plant that delivers liquid CO₂ is estimated at 25% (Golomb et al., 1989). For delivery of solid CO₂, the efficiency is estimated to decrease to 21%.

It should be noted that research is ongoing in Japan on various disposal schemes of CO₂ in the deep ocean (Nakashiki et al., 1995). These schemes include (a) a vertical pipe from an injection vessel; (b) a pipe from a semi-submersible platform; (c) a pipe from a tension-leg platform; and (d) transfer from a tanker to a spraying vessel. The latter would tow a trailing pipe through which CO₂ is dispersed while the vessel is traveling over a wide loop. This scheme would achieve a dispersed plume instead of a slender plume from a simple point release, thus, avoiding localized low pH

regions. However, in the report of Nakashiki et al. (1995) no assessment is made of the cost and technical difficulties associated with these schemes.

4.5 Floating Platforms

Offshore platforms are usually divided into two general categories, fixed and compliant. Fixed types fully extend to the sea bed and remain in place by a combination of the weight and piles driven into the sea bed. Little or no motion of such structures is experienced. Compliant type platforms are more responsive to external effects. Their movements are controlled by mooring systems which typically consist of chains, cables, ropes and anchors. Alternatively, the compliant platform may be dynamically positioned by means of computer controlled thrusters or propellers, and maintain position within prescribed limits of set location (Mazurkiewicz, 1987; Ranney, 1979). For deep ocean disposal of CO₂, a compliant, semi-submersible platform seems to be most suitable. Usually, the platform is supported by columns connected to large underwater displacement hulls (Figure 3). Because of the large weight of the vertical free dangling pipe attached to the platform (see Table 4), the underwater displacement hulls of a CO₂ disposal platform must be much larger than that of conventional oil exploration platforms. Today's semi-submersible platforms are designed for operation in water depths up to 1000 m. The mooring system usually consists of eight anchors placed in a spread pattern and connected to the hull by chain or wire rope. These platforms are used for oil drilling and pumping from the ocean floor.

Figure 3. Semisubmersible Floating Platform for Oil Exploration

5. Environmental Effects of Transport Systems

5.1 Onshore Pipelines

The major environmental effects for laying an onshore pipeline would occur during the construction phase. After the pipe is buried underground, only an accidental release or rupture of the pipe may cause additional environmental and human hazards. Inland pipelines may cross open water, wetland and upland habitats. New pipeline canals through wetlands are typically 3 m wide, which is necessary for the push-ditch method of pipeline construction. Since 1970, backfilling of newly dredged pipeline canals has been required by permitting agencies (DoI, 1994). In the Gulf of Mexico, offshore and onshore oil explorations typically disturbed 0.7 hectares (1 ha=10,000 m²) of wetlands per km of pipeline (Turner and Cahoun, 1988). Backfilling newly dredged pipeline canals is typically more successful in freshwater wetlands with higher inorganic content in the soils than in salt or brackish wetlands (DoI, 1994). Pipelaying through private lands and urban areas may require complicated right-of-way leases and environmental permits. During the operational phase, pipeline maintenance activities that disturb onshore habitats are not deemed significant and probably will not require further actions or permits.

5.2 Offshore Pipelines

During the laying of submerged pipes, sediment displacement (resuspension of sediments) and coral reef disturbance will be caused by pipeline trenching, which is required by law in water depths less than 61 m (200 ft). Such trenching and burying is required in shallow depths as an engineering precaution in order to reduce movement of the pipe during periods of high currents and storms. It is assumed that 5,000 cubic meters of sediment will be resuspended for each kilometer of pipeline trenched. Pipelaying barges use an array of eight 9,000 kg anchors to both position the barge and to move it forward along the pipeline route. The anchors are continually moved as the pipe-laying operation proceeds. The area actually affected by anchors will depend on water depth, wind, currents, chain length, and the size of the anchor and chain. Service vessel anchoring is assumed not to occur in water depths greater than 150 m. In such water depths the vessels will always tie up to a platform or buoy (DoI, 1994).

Upon completion of the pipelaying operations, underwater trenches will have to be refilled. Probably, it will take several years before the underwater habitat is restored to its previous state. Thereafter, no further disturbances are expected, as maintenance actions of underwater pipelines will be very infrequent.

5.3 Tanker Transport

The environmental impacts of tanker transport include (a) accidental releases from valves and ruptures with possible injury to the crew, and (b) release into the atmosphere of fuel combustion products. Both diesel and steam propelled tankers release into the marine atmosphere copious quantities of particles (flyash and soot), SO_x and NO_x , and of course CO_2 . It has been reported that along the most frequently used shipping channels in the Atlantic and Pacific Oceans, high altitude artificial clouds are formed due to ship emissions (Coakley et al., 1987).

5.4 Floating Platforms and Vertical Pipes

If tanker transport is used for deep sea disposal, floating platforms must be used for unloading the CO_2 from the tanker and pumping it into a vertical pipe extending from the platform. The floating platform and the vertical pipe will cause minimal impact to the marine environment. The operating crew on the platform will be exposed to storms and other environmental hazards, as well as to possible accidental releases of CO_2 during unloading and vessel rupture. The platform may cause a navigational hazard to ships and the vertical pipe to submarines.

5.5 Onshore Facilities

If tankers are used to transport CO_2 from a coastal power plant or a coastal terminal of inland pipelines, a port facility has to be provided for the tankers. The facility will include storage tanks, pumping stations and docks, as well housing for the workers and tanker crew. Constructing the facility will require coastal land acquisition and some disruption of coastal habitat. The facility's presence, along with the associated access routes, alters the natural hydrology and geography of the area over time, resulting in increased runoff from the land. Saltwater intrusion may occur if the facility is built near wetlands. If existing vegetation is modified, greater erosion and land loss around the facility may take place. Increases of nonpoint source pollution due to runoff at support facilities may contribute particulate matter, heavy metals, oil and grease fecal coliform and high nutrient loadings to local streams, estuaries and bays, causing elevation of the contaminants in the surrounding waters, low dissolved oxygen levels, and high turbidity. Supporting onshore infrastructure also contributes to routine and accidental point source discharges to the surrounding bodies of water. Service bases and marine terminals contribute contaminants through their use of anti-fouling marine paints, discharge of domestic waste, and through the release of heavy metals and contaminated sludge. Pipe coating yards, platform construction facilities, repair and maintenance yards contaminate surrounding waters by releasing thermal effluents, anti-fouling paint chemicals, heavy metals and a variety of solid waste such as packaging materials, metal scraps and other debris (DoI, 1994).

6. Dispersion of Accidental Releases of CO_2

An accidental release of pressurized CO_2 in transport systems may arise because of mechanical failures, human error and natural disasters. The released CO_2 will cause a hazard to the surrounding population, workers at the facility and the surrounding fauna. CO_2 is known to be toxic

at concentrations of about 6%, resulting in nausea, vomiting, diarrhea, irritation to mucous membranes, skin lesions and sweating. At about 10% concentrations, CO₂ is fatal due to asphyxiation (Sharp, 1972). The 1986 Lake Nyos, Cameroon, disaster caused death to about 1700 people and 3000 cattle. In that event magmatic CO₂ which accumulated at the lake bottom suddenly was released into the atmosphere. Due to a yet undetermined perturbation the lake rolled over, bringing up the CO₂ from the hypolimnion first to the surface layer and then it was vented into the atmosphere. The resulting cloud of CO₂ inundated the surrounding village with disastrous consequences (Kling et al., 1987). The dispersion of the cloud was modeled by Fay (1987). In the following we use Fay's model. Kruse and Tekiela (1995) used the EPA DEGADIS+ model and obtained similar results.

At ambient temperatures, CO₂ gas is heavier than air and will disperse mainly horizontally. The dispersion rate depends on the CO₂ concentration in the cloud and ambient conditions, such as winds, atmospheric stability and temperature. The principal dilution mechanism is entrainment of air through the top of the cloud. The cylindrical cloud has a radius R, height H and volume V. It is assumed that the concentration of CO₂ is uniform throughout the cloud, and it is isothermal. Furthermore, there is no wind. With these assumptions the set of dispersion equations given by Fay (1987) are as follows:

$$\begin{aligned}
 R^2 &= R_0^2 + 2\alpha t(g'_0 V_0 \pi^{-1})^{0.5} \\
 \chi^{-1} &= k[\pi^{0.5}(R^2 - R_y^2)(2\alpha V_0^{2/3})^{-1} + k^{-1}] && \text{if } R > R_y \\
 &= 1 && \text{if } R < R_y \\
 H &= V_0(\chi \pi R^2)^{-1} \\
 R_y^2 &= R_0^2 + 2\alpha V_0^{2/3}(10 + k^{-1})\pi^{-0.5} \\
 v &= (R_2 - R_1)(\Delta t)^{-1}
 \end{aligned}$$

Here χ is concentration, V_0 is initial volume, R_0 initial radius, g' reduced gravity, g'_0 initial reduced gravity, α constant, and t time. The dispersion velocity $v = (R_2 - R_1)/\Delta t$, where R_2 and R_1 are the radii at times t_2 and t_1 .

We examine two cases, a pipeline rupture and a storage tank rupture. The results are tabulated in Tables 5 and 6, and illustrated in Figures 4 and 5. For the pipeline, a capacity of 390 metric tonnes corresponds to a release of CO₂ from a 1000 m segment of a 40 inch pipeline, 1170 tonnes 3200 m, 2340 tonnes 6400 m, 3510 tonnes 9600 m and 4680 tonnes 13,000 m. The segments have been selected with the assumption that CO₂ can be shut off with check valves at those distances upstream of the rupture point. Taking a midrange, 2340 tonnes, a fatal concentration $\chi = 10\%$ will be reached in 2 minutes at a radius from the rupture point $R = 580$ m (see case P3 in Figure 4). For the storage tank rupture, a capacity of 28,000 tonnes corresponds to an output of a 1000 MW power plant in 3 hours. Each subsequent capacity is a doubling of the number of hours. 224,000 tonnes is

the daily output of the plant. If a daily output is stored in a tank (which is probably necessary, assuming that one tanker will call into port once a day), the rupture of the tank will cause fatalities within a radius of about 3000 m for a time of 4 minutes.

While an accidental release from a pipe or tank rupture is highly unlikely, the risk cannot be dismissed. Leaks from tanker holds, solid CO₂ transport vessels, pumps, loading and unloading pipes may occur more frequently. While their radius and time of impact may be shorter than that of pipelines and storage tanks, such leaks may endanger the operating crew and proper precautions need to be exercised, such as wearing of gas masks and protective clothes.

Table 5. Dispersion From Pipeline Rupture

		Dilution Time (min)							
		0.5	1	1.5	2	3	4	6	10
Capacity (1000 ton)									
0.39	R (m)	187	263	321	370	450	523	640	739
	χ (%)	100	21.9	10.1	6.6	3.9	2.8	1.7	1.3
	v (m/s)	6.3	4.4	3.6	3.1	2.5	2.2	1.8	1.5
1.17	R (m)	245	346	422	487	595	687	842	971
	χ (%)	100	35.7	13.9	8.6	4.9	3.4	2.1	1.6
	v (m/s)	82	5.8	4.7	4.1	3.3	2.9	2.3	2
2.34	R (m)	294	411	502	580	709	818	1001	1155
	χ (%)	100	54.6	17.3	10.3	5.7	3.9	2.4	1.8
	v (m/s)	9.8	6.9	5.6	4.8	3.9	3.4	2.8	2.4
3.51	R (m)	325	456	556	641	784	905	1108	1279
	χ (%)	100	75.9	20	11.5	6.24	4.28	2.6	1.9
	v (m/s)	10.9	7.6	6.2	5.4	4.4	3.8	3.1	2.7
4.68	R (m)	351	491	599	670	843	973	1191	1374
	χ (%)	100	100	22.3	12.5	6.7	4.5	2.8	2
	v (m/s)	11.7	8.2	6.7	5.8	4.7	4.1	3.3	2.9

Table 6. Dispersion From Storage Tank Rupture

		Dilution Time (min)							
		0.5	1	1.5	2	3	4	6	10
Capacity (1000 ton)									
28	R (m)	553	771	939	1082	1322	1524	1865	2405
	χ (%)	100	100	56.9	22.9	10.5	6.7	4	2.2
	v (m/s)	18.4	12.8	10.4	9	7.3	6.4	5.2	4
56	R (m)	660	918	1118	1288	1573	1814	2218	2860
	χ (%)	100	100	100	31	12.7	8	4.6	2.5
	v (m/s)	22	15.3	12.4	10.7	8.7	7.6	6.2	4.8
112	R (m)	787	1094	1332	1533	1872	2158	2639	3402
	χ (%)	100	100	100	45.3	15.8	9.6	5.3	2.8
	v (m/s)	26.2	18.2	14.8	12.8	10.4	9	7.3	5.7
224	R (m)	940	1304	1586	1825	2227	1567	3139	4047
	χ (%)	100	100	100	76.5	20.1	11.5	6.2	3.3
	v (m/s)	31.3	21.7	17.6	15.2	12.4	10.7	8.7	6.7

Figure 4. Dispersion From Pipeline Rupture
P1 is release of 390 T, P2 = 1170 T, P3 = 2340 T,
P4 = 3510 T, P5 = 4680 T

Figure 5. Dispersion From Storage Tank Rupture
S1 is release of 28 kT, S2 = 56 kT, S3 = 112 kT, S4 = 224 kT

7. Conclusions

Transport systems for ocean disposal of CO₂ may include on- and off-shore pipelines, storage tanks, tankers, cargo vessels (for solid CO₂), dock facilities, floating platforms and vertical pipes. Onshore pipelines will cause some environmental disturbances during pipe laying as trenches have to be dug in potentially sensitive habitat, such as coastal wetlands. Environmental laws require that the disturbance be restored to its previous state. During operation of the pipeline, accidental releases may occur from pipe rupture, endangering the surrounding population and fauna. Offshore pipelines may also cause environmental disturbances during the construction phase, as the pipe must be trenched in the sediment in shallow water (to 61 m depth). The lay barges may also disturb the ocean floor because of the anchoring and towing procedure. After construction, the habitat will restore in a matter of a few years. Tankers and cargo vessels emit pollutants into the marine air. Floating platforms and vertical pipes may not pose a significant risk to the environment, but the platform operators may be exposed to harsh weather and storms, and to potential leaks and accidental releases of CO₂ from pipes, valves and storage tanks. Dock facilities may alter the natural hydrology and geography of the area, saltwater intrusion over wetlands, beach erosion, point and nonpoint source pollution of heavy metals, oil, grease, and anti-fouling paint chemicals. Accidental releases of CO₂ from pipes, storage tanks, vessel holds, connecting pipes and valves may endanger the workers and surrounding population. However, the environmental impacts and safety hazards of CO₂ transport systems can be minimized or altogether prevented with prudent management and exercise of precaution.

8. References

Coakley, J. A., R. L. Bernstein and P. H. Durkee (1987) Effect of Ship-Stack Effluents on Cloud Reflectivity, *Science*, **237**, 1020-1022.

Demirbilek, Z. (1989) "Tension Leg Platforms: an Overview of the Concept, Analysis and Design" in Tension Leg Platforms, Z. Demirbilek, ed. Amer. Soc. Civ. Eng. publication, New York, NY.

US Department of Interior (DoI) (1994) Environmental Impact Statement for Central and Western Planning Areas, OCS EIS/EA MMS 94-0019, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA.

Drewry Shipping Consultants Ltd (1982) Market for LPG Carriers in the 1980's. Drewry Shipping Publications, London, UK.

Fay, J. A. (1987) Modeling the Lake Nyos Disaster, *Atmospheric Environment*, **21**, No.3,

Golomb, D., H. Herzog, J. Tester, D. White and S. Zemba (1989) Feasibility Modeling and Economics of Sequestering Power Plant CO₂ Emissions in the Deep Ocean, Energy Laboratory, Massachusetts Institute of Technology, MIT-EL 89-003, Cambridge, MA 02139.

Kling, G. W., M. A. Clark, H. R. Compton, J. D. Devine, W. C. Evans, A. M. Humphrey, E. J. Koenigsberg, J. P. Lockwood, M. L. Tuttle and G. N. Wagner (1987) The 1986 Lake Nyos Gas Disaster in Cameroon, West Africa, *Science*, **236**, 169-175.

Kruse, H. and M. Tekiela (1995) Calculating the Consequences of a CO₂ Pipeline Rupture, Presented at the International Energy Association Greenhouse Gas Mitigation Conference, London, UK, to be published in *Energy Conversion and Mgmt.*

Mazurkiewicz, B. K. (1987) "Offshore Platforms General" in Offshore Platforms and Pipelines, B. K. Mazurkiewicz, ed. Trans Tech Publications, Germany.

McGuire, G. and B. White (1986) Liquefied Gas Handling Principles on Ships and Terminals, Witherby and Co., London, UK.

Nakashiki, N., T. Ohsumi and N. Katano (1995) Technical View on CO₂ Transportation onto the Deep Ocean Floor and Dispersion at Intermediate Depth" in Direct Ocean Disposal of Carbon Dioxide, Terra Scientific Publishing Company, Tokyo.

Nihous, G. C. (1995) Private Communication, Pacific International Center for High Technology Research, Honolulu, HI 96822.

Ranney, M. W. (1979) Offshore Oil Technology, Noyes Data Corporation, Park Ridge, NJ.

Sharp, G. R. (1972) in Aviation Medicine: Physiology and Human Factors, G. Dhenin, ed., pp. 202-203, Tri-med Books, London, UK.

Skovholt, O. (1993) CO₂ Transportation System, *Energy Conversion and Mgmt.*, **34**, 1095-1105.

Sriskandarajah, T. and I. K. Mahendran (1987) "Parametric Considerations of Design and Installation of Deepwater Pipelines" in Offshore Oil and Gas Pipeline Technology, IBC Technical Services, Ltd., London, UK.

Turner, R. E. and D. R. Cahoun (1987) Causes of Wetland Loss in the Coastal Central Gulf of Mexico, OCS Study MMS 90-0009, prepared for the US Department of Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA.

Uhl, A.E. (1965) Steady Flow in Gas Pipelines, Report prepared for the American Gas Association, Arlington, VA.

Topical Report 3

Models of Near-Field Perturbations and Probabalistic Organism Exposure

(CHAPTERS 1-5)

**Jennifer A. Caulfield
E. Eric Adams
David I. Auerbach
Howard J. Herzog**

**Massachusetts Institute of Technology
Energy Laboratory
77 Massachusetts Avenue
Cambridge, MA 02139-4307**

Contents

1	Ambient Ocean	3-1
1.1	Chemical Properties	3-1
1.2	Physical Properties	3-4
1.2.1	Ambient Current	3-4
1.2.2	Ambient Turbulence	3-5
1.2.3	Stratification	3-6
1.3	Measures of Impact	3-6
2	Injection Scenarios	3-8
2.1	Dispersion Methods	3-8
2.1.1	Dry Ice	3-8
2.1.2	Spray from Towed Pipe	3-11
2.2	Droplet Plume	3-14
2.2.1	Physical Model	3-14
2.2.2	Relative Importance of Parameters	3-18
2.2.3	Thickness of the Intrusion Layer	3-23
2.2.4	Results	3-27
2.3	CO ₂ -Enriched Seawater Plume	3-27
2.3.1	Physical Model	3-27
2.3.2	Relative Importance of Parameters	3-30
2.3.3	Results	3-33
2.4	Conclusions	3-34
3	Organism Experience	3-38
3.1	Introduction	3-38
3.2	Evaluating mortality due to time varying exposures	3-38
3.3	Relative Diffusion of Organism and Plume	3-39
3.4	Stochastic Simulation	3-43
3.5	Compensation and Intergenerational Effects	3-44
3.6	Organism Experience for Scenarios Analyzed using the Stochastic Approach	3-46
3.6.1	Droplet Plume Organism Experience	3-46
3.6.2	Dense Plume Organism Experience	3-48
3.7	Other Possible Approaches	3-48
3.7.1	"Average Path" Experience	3-48

3.7.2	"Averaged" Experience	3-48
3.7.3	Non-Diffusive Transport	3-50
3.8	Scenario Comparison	3-50
4	Impact Model Sensitivities	3-52
4.1	Sensitivity to pH-Mortality Curves	3-52
4.2	Measures of Plume Severity	3-54
4.3	Another Look at the Base Case Dissolution Scenarios	3-58
4.4	Implication for a droplet plume scenario	3-60
5	Summary, Conclusions, and Recommendations for Future Research	3-63
5.1	Summary	3-63
5.2	Conclusions	3-63
5.3	Recommendations for further research	3-64

List of Figures

1.1	Average northern ocean values measured by GEOSECS expedition.	3-2
1.2	Variation of pKa's of species over depth.	3-3
1.3	Initial ambient pH profile.	3-4
1.4	pH resulting from addition of carbon dioxide.	3-5
1.5	A. Variance versus diffusion time (from Okubo[29]). B. Apparent diffusivity versus scale of diffusion (from Okubo [29]).	3-6
1.6	Density profile of ambient ocean.	3-7
2.1	Flux of CO ₂ to the water column as a function of depth for a single dry ice cube with initial dimensions of 3 meters on a side.	3-9
2.2	Effective diffusivity as a function of distance for 5 cm/s current.	3-10
2.3	Distribution of pH in a horizontal plane at a depth of 1000 meters resulting from ocean CO ₂ disposal in a 5 cm/s current as 3 meter dry ice cubes. Top: Emissions from one standard power plant. Bottom: Emissions from ten standard power plants. Discharge point is at 0,0	3-12
2.4	Liquid CO ₂ sprinkling from the pipe towed by vessel, from Ohsumi [28]. . . .	3-13
2.5	Distribution of pH in a horizontal plane at a depth of 1000 meters resulting from ocean CO ₂ disposal from a towed pipe moving at 5 m/s. Top: Emissions from one standard power plant. Bottom: Emissions from ten standard power plants. Discharge point is at 0,0.	3-15
2.6	Nondimensional half-width with (top) of vertical half-thickness (bottom) of and half-thicknes of the intermediate-field region for the case of linear stratification.	3-17
2.7	Definition sketch for Brooks' model.	3-19
2.8	Sensitivity of diluted flow rate to mass flux from individual release (top) and to initial bubble radius (bottom). All releases occur from a depth of 1000 meters in the ambient ocean. The base case radius is 0.8 cm and the base case release is 13 kg/s per port (10 ports/plant).	3-20
2.9	Ambient density in depth range considered (top). The maximum predicted rise height of the droplets and the trap height of the intrusion layer are shown for releases from 800 to 2000 meters depth with initial radii of 0.8 and 1.0 cm. The base case release is 13 kg/s per port (10 ports/plant) is assumed (bottom).3-21	

2.10	Rise and trap heights resulting from a reduction in mass transfer due to hydrate formation. Mass transfer reduced to one-half of the base case (top), and one tenth of the base case (bottom). The maximum rise height and the and the predicted trap height of the intrusion layer are shown for releases from 800 to 2000 meters depth with initial radii ranging from 0.4 to 1.0 cm. The base case release is 13 kg/s per port (10 ports/plant) is assumed.	3-22
2.11	Relationship between current speed, stratification, and intrusion layer thickness (meters) if transition occurs at $6l_H$	3-24
2.12	Relationship between diluted flow and intrusion layer thickness in different environments with alternate transition assumption. The top figure show the effect of density stratification (in kg/m^4) on intrusion layer thickness with an ambient current of 5 cm/s. The bottom figure shows the effect of current speed on thickness in the base case density gradient of $0.0006 kg/m^4$	3-25
2.13	Relationship between current speed, stratification, and intrusion layer thickness (meters) for a given diluted flow rate. The figure on the left is for a diluted flow rate of $100 m^3/s$; that on the right is for a flow rate of $1000 m^3/s$	3-26
2.14	Distribution of pH in a horizontal plane at a depth of 1000m resulting from the ocean CO_2 disposal in a 5 cm/s current as a droplet plume. Top: Emissions from one standard power plant. Bottom: Emissions from ten standard power plants. Discharge point is at 0,0.	3-28
2.15	Schematic of dense plume geometry.	3-29
2.16	Dependence of Entrainment Coefficient on Richardson Number (from Alavian) [2].	3-31
2.17	Dependence of depth sunk by plume on drag coefficient. Results are for plumes formed from emissions from ten standard power plants with an initial concentration of $12 kg/m^3$, and released at a depth of 750 meters.	3-31
2.18	Distance (m) sunk by a CO_2 seawater solution injected at 780 meter depth, with a velocity of 0.5 m/s, an excess CO_2 concentration of $12 kg/m^3$, mass loading from ten standard power plants, and variable topography.	3-32
2.19	Distance (m) sunk by a CO_2 seawater solution injected at 750 meter depth, with an initial velocity of 0.5 m/s, a C_D of 0.02, base case topography, and variable loadings and initial excess CO_2 concentrations.	3-33
2.20	Dilution versus distance sunk (with $C_D= 0.2$, an injection depth of 780 meters, an initial excess CO_2 concentration of $12 kg/m^3$, and varied topographic conditions).	3-34
2.21	Distribution of pH in the horizontal plane at a depth of 1000 m resulting from the ocean CO_2 disposal in a 5 cm/s current as a dense enriched seawater plume, the x-axis represents the coastline. Top: Emissions from one standard power plant. Bottom: Emissions from ten standard power plants. Discharge point is at 0,0.	3-35
2.22	Centerline dilution over time for the various base case scenarios.	3-37
3.1	Mortality curves for zooplankton exposed to lowered pH (from Auerbach [3]).	3-39
3.2	Effect of additional exposure at different cumulative stress levels.	3-40

3.3	Schematic of scale dependent diffusion (from Richardson [31]).	3-41
3.4	Relative diffusion coordinate system.	3-42
3.5	Detail of grid used for probabilistic simulation of one plant droplet plume scenario.	3-44
3.6	Maximum achievable growth rate, r , as a function of pH.	3-45
3.7	Fractional deficit of zooplankton in a horizontal place at 1000 m depth caused by the base case one plant droplet plume scenario (top). Fractional deficit of zooplankton in a horizontal place at 1000 m depth caused by the base case ten plant droplet plume scenario (bottom). Discharge point is at 0,0.	3-47
3.8	Fractional deficit of zooplankton in a horizontal plane at 1000 m depth caused by the base case one plant dense plume scenario (top). Fractional deficit of zooplankton in a horizontal plane at 1000 m depth caused by the base case ten plant dense plume scenario (bottom). Discharge point is at 0,0.	3-49
4.1	Steps for determining biological impact from injection scenario.	3-54
4.2	Relationship between time to a centerline pH of 7 and total mortality. For each simulation total mortality is the product of the mortality per injection and the number of independent injections needed for the emissions from one standard power plant. The black points come from simulations using the base case diffusivity relationship. The hollow points reflect scenarios with half the base case diffusivity. The gray points reflect a diffusivity of one-third of the base case. Initial concentrations are represented by shapes: triangles represent an initial concentration of 0.07 kg/m^3 , squares of 0.13 kg/m^3 , circles of 0.20 kg/m^3 , and diamonds of 0.30 kg/m^3 . Variation among points with the same diffusivity and initial concentration is due to variation in mass loading.	3-55
4.3	Time to centerline pH of 7 versus mass loading per area for scenarios with various levels of ambient turbulence. The black points come from simulations using the base case diffusivity relationship. The hollow points reflect scenarios with half the base case diffusivity. The gray points reflect a diffusivity of one-third of the base case. Initial concentrations are represented by shapes: triangles represent an initial concentration of 0.07 kg/m^3 , squares of 0.13 kg/m^3 , circles of 0.20 kg/m^3 , and diamonds of 0.30 kg/m^3	3-57
4.4	Mortality flux due to the base case scenarios.	3-58
4.5	Total integrated mortality due to the base case scenarios.	3-59
4.6	Schematic of independent droplet plume injections. The required horizontal spacing is λ_h , and the required vertical spacing is λ_v	3-60

List of Tables

2.1	Summary of results of modeled scenarios. Dry ice distance and pH values are from a depth of 1000 meters.	3-36
3.1	Summary of expected zooplankton mortality for various base case plumes . .	3-51
4.1	Sensitivity of integrated mortality and maximum mortality flux to the determination of the pH-Mortality curves for the base case dissolution scenarios. .	3-53
4.2	Effect of various parameters on injection size and spacing needed to achieve zero mortality. *For the two intrusion case, the depth given is for the lower layer.	3-61

Chapter 1

Ambient Ocean

1.1 Chemical Properties

In order to quantify the effects of different forms of ocean injection of CO_2 it is first necessary to specify the characteristics of the ambient ocean. Because any ocean disposal anticipated in the near future will most likely occur in the northern hemisphere, the standard ocean was defined by the average characteristics of the northern oceans as determined by the GEOSECS expedition [34]. Profiles of temperature, salinity, total inorganic carbon, and total alkalinity are shown in Figure 1.1.

The total inorganic carbon is partitioned among carbonic acid, bicarbonate, and carbonate in the following manner [22]:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

$$[H_2CO_3^*] = C_T / (1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2})$$

$$[HCO_3^-] = C_T / (\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]})$$

$$[CO_3^{2-}] = C_T / (\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1)$$

where $[H_2CO_3^*]$ denotes the sum of the H_2CO_3 and aqueous CO_2 species, and K_1 , K_2 , and K_3 are the equilibrium constants for these reactions.

Similarly, the total alkalinity measured by the GEOSECS expedition was approximated by the sum of carbon, boron, phosphorous, and silicon alkalinities. The carbonate and bicarbonate contribute about 98% of this alkalinity while the boron component ($B(OH)_4^-$) forms the major part of the other 2%. The phosphates and silicates contribute approximately 0.2% of the total alkalinity, and the contribution of the species not considered would be substantially less. The total alkalinity equilibrium is modeled as:

$$TAlk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + [B(OH)_4^-] -$$

Figure 1.1: Average northern ocean values measured by GEOSECS expedition.

Figure 1.2: Variation of pKa's of species over depth.

$$[B(OH)_4^-] = B_T / (1 + \frac{[H^+]}{K_b})$$

$$[HPO_4^{2-}] = P_T / (1 + \frac{[H^+]}{K_{p2}} + \frac{[H^+]^2}{K_{p1}K_{p2}} + \frac{K_{p3}}{[H^+]})$$

$$[PO_4^{3-}] = P_T / (1 + \frac{[H^+]}{K_{p3}} + \frac{[H^+]^2}{K_{p2}K_{p3}} + \frac{[H^+]^3}{K_{p1}K_{p2}K_{p3}})$$

$$[SiO(OH)_3] = Si_T / (1 + \frac{[H^+]}{K_{si}})$$

where the various K 's are the equilibrium constants for the reactions considered.

Based on the ambient conditions of temperature, salinity and pressure, the equilibrium constants of the relevant reactions were determined at different depths[20]. The variations due to the range of temperature and salinity condition were 0.15 pKa units for the first acidity constant and 0.3 pKa units for the second acidity constant for the carbonate species as shown in Figure 1.2.

From these relationships an initial pH profile was calculated. As can be seen in Figure 1.3, for the ocean conditions selected the surface pH is the highest at about 8.1. The pH is lowest at a depth of about 900 meters (7.74) and is about 7.8 in the deep ocean.

The change in pH caused by the addition of carbon dioxide will depend on the ambient ocean conditions. For the ambient ocean conditions chosen, Figure 1.4 shows the response of pH to additional carbon dioxide. The total concentrations of the component species are also shown, and it can be seen that the concentration of HCO_3^- remains essentially constant,

Figure 1.3: Initial ambient pH profile.

while the levels of $H_2CO_3^*$ increase substantially with lowered pH. The difference in pH due to initial conditions and variation with depth of the acidity constants described above is generally less than a tenth of a pH unit. Figure 1.4, which corresponds to the conditions at about 1000 meters, is a good description of the overall relationship between additional carbon dioxide resultant pH.

1.2 Physical Properties

1.2.1 Ambient Current

As will be shown in later analysis, ambient current is the principal environmental determinant of the distribution of excess CO_2 . As such, current will be a principal factor in site selection.

Actual measurements of subsurface current velocities are scarce. One of the few sources of current meter data at the depths of interest comes from the analysis of possible Ocean Thermal Energy Conversion (OTEC) sites in the late 1970's [4, 21, 10]. Although these measurements were limited to potential OTEC sites, these sites are similar to potential CO_2 disposal sites in that they have depths of about 1000 meters and are located fairly close to the coastline.

The velocities generated by global circulation models can also be used to estimate possible current at injection sites. From the mesoscale model used in the far-field analysis (described in Topical Report 4), month-long-averaged current velocities at 1000 meter depth ranged from 1 to 11 cm/s. A base case current of 5 cm/s was chosen for the near-field modeling.

Currents at surface depths are important only for the dry ice scenario. Currents in the deep ocean will also be important for the dry ice scenario. At this time, vertical variation in the current speed is not included, but it is recognized that use of a constant current speed

Figure 1.4: pH resulting from addition of carbon dioxide.

results in an underestimation of surface current speeds and a possible overestimation of deep ocean current speeds.

1.2.2 Ambient Turbulence

After the initial mixing caused by the CO_2 injection itself, ambient ocean turbulence will be responsible for the dilution of the excess CO_2 in the remainder of the “near-field”. Because this study is for a generic site we must rely on general empirical relationships between time and lengths scales and observed horizontal ocean diffusivity. Okubo [29] (See Figure 1.5) has examined the data from a variety of dye studies with length and time scales varying over several orders of magnitude. Because of the nature of the studies, the measured quantity is the horizontal variance for a radially symmetrical distribution, σ_{rc}^2 , which is equivalent to $2\sigma_x^2$, where σ_x^2 is the equivalent one dimensional variance. The apparent diffusivity is obtained by assuming the diffusivity to be constant over the time studied and is defined as $\frac{\sigma_{rc}^2}{4t}$ while the effective diffusivity is defined as $\frac{d}{dt} \frac{\sigma_{rc}^2}{4}$. From these dye study observations, the one-dimensional equivalent effective diffusivity has been determined to be:

$$E_h \cong 0.006t^{1.3} \quad (1.1)$$

where E_h is in (cm^2/s) and t is the time in seconds since the release as a point source. This relationship can also be expressed in terms of a length scale ($3\sqrt{2}\sigma_x$) in which case the equation is:

$$E_h \cong 0.024l^{1.15} \quad (1.2)$$

where E_h is in (cm^2/s) and l is the scale of diffusion in centimeters.

Figure 1.5: A. Variance versus diffusion time (from Okubo[29]). B. Apparent diffusivity versus scale of diffusion (from Okubo [29]).

Although most of the dye studies were done in the surface ocean, a large scale experiment was done with a release depth of 310 meters, using SF_6 as a tracer. Preliminary results indicate that the mixing after a year is of the same order as that predicted using Okubo's relation [16, 38]. Although the depths considered in the following models are about 1000 meters, 310 meters is deep enough that wind-induced mixing can be neglected; consequently, the mixing at both sites should be quite similar. In the absence of site-specific data, these empirical relationships are the best estimate of diffusivity.

1.2.3 Stratification

Because of the importance of buoyancy effects in the mixing and distribution of excess CO_2 in several of the scenarios, it is necessary to determine an ambient density profile. This calculation is straightforward given the temperature and salinity data from the ambient profile chosen (See Figure 1.1). The results of the calculation are shown in Figure 1.6.

1.3 Measures of Impact

The impact of each scenario was quantified using several criteria. As a measure of the overall chemical impact, the pH resulting from the injection of the carbon dioxide emissions was mapped and the water column volume affected was calculated. The dilution over time along the plume centerline was also calculated in order to provide a means to assess impacts from trace contaminants that may be present in the emissions. In Chapter 3 a method to assess the experience of low mobility organisms is outlined and the range of experiences of a

Figure 1.6: Density profile of ambient ocean.

passive organism passing through the affected area was calculated for the various scenarios. Absolute pH was used in order to correlate the experiences with appropriate mortality data. The resulting spatial deficit of zooplankton was mapped and the total volume of water affected was calculated.

Chapter 2

Injection Scenarios

This chapter quantifies the physical impact of CO₂ in the near field. Several different injection methods are considered. These methods are classified as dispersion if emissions are widely distributed during injection, and dissolution if the goal is to dissolve the carbon dioxide and allow ambient ocean mixing processes to provide further dilution.

Isolation strategies (not discussed in this topical report) attempt to isolate all or a portion of CO₂ emissions from the environment. An example of an ocean disposal method which provides an element of isolation is a deep CO₂ lake [26, 24, 27] (See Appendix 1).

2.1 Dispersion Methods

Dispersion methods distribute the carbon dioxide so widely that impact is minimal. This distribution is usually achieved in part by significant distribution over water column depth as natural vertical mixing is negligible. Dry ice cubes and a spray from a towed pipe are both technically feasible, albeit expensive, means to achieve the goal of dispersion.

2.1.1 Dry Ice

One advantage of dry ice disposal is that disposal does not necessarily need to happen at a fixed disposal site and so theoretically the CO₂ emissions could be more evenly distributed over the ocean. However, in order to make the dry ice scenario consistent with the other disposal scenarios, it was decided to model the continuous release of dry ice at a fixed point.

Because disposal in the surface ocean accomplishes little in terms of sequestration, the cubes would need to be made as large as practical to insure that only a small fraction of the dissolution occurs in the upper ocean. A cube with 3 meter sides was chosen as a reasonable size. Since dry ice has a density of 1550 kg/m³ [25], a cube of this size would need to be released every 5.4 minutes to account for the emissions of one standard power plant.

Physical Model

Using data from both laboratory tests and open ocean experimentation, the Japanese Central Research Institute for the Electric Power Industry (CRIEPI) determined the dissolution rate

Figure 2.1: Flux of CO_2 to the water column as a function of depth for a single dry ice cube with initial dimensions of 3 meters on a side.

of solid CO_2 in the ocean [25]. The laboratory rate is given in $g/s - cm^2$ by

$$\text{Mass Loss} = 6.6 * 10^{-5}u + 2.6 * 10^{-3} \quad (2.1)$$

where u is the velocity in cm/s . The dissolution under ambient ocean conditions was compared to the rate experienced in the laboratory and found to be between 2 and 3 times greater.

Taking the dissolution rate as 2.5 times the laboratory value, and using the equations of motion, the mass release of a falling cube to the water column was determined as a function of depth. Figure 2.1 shows the release corresponding to the 3 meter cube studied. This release was then scaled by the number of cubes released per time in each scenario to obtain the mass release per time as a function of depth. Only the release to the water column was modeled. The fraction of dry ice that reached the ocean floor depends on depth. For a depth of 3000 meters, about 46% reaches the ocean bottom; for depths of 4000 and 5000 meters, 33% and 19% of emissions, respectively, reach the ocean floor.

In order to obtain a steady state solution the release was approximated as a continuous line source. However, the turbulence induced by the injection was based on the falling of the 3 meter cube. The line source approximation is a good one since, even with a one power plant scenario and a 10 cm/s current, the distance between the centers of concentration due to each cube would be at most 32 meters. The wake effect due to the cube can be used because the cubes are closely spaced and because the small peaks of concentration that exist close to the source correspond with the centers of induced turbulence.

At each depth, the turbulence induced by the cube was approximated by the turbulence in a wake behind a cube. The mixing length due to the wake can be approximated [35] as

$$l_m \cong K(C_D \text{ Area } x_w)^{1/3} \quad (2.2)$$

Figure 2.2: Effective diffusivity as a function of distance for 5 cm/s current.

where l_m is a measure of the lateral dimension over which wake induced turbulence is felt, K is a constant of proportionality (here about 0.4), C_D is the drag coefficient, $Area$ is the cross sectional area, and the distance from the object x_w is equal to the fall velocity, u_{fall} , multiplied by the time since the fall of the object, t . The contribution from the wake is then

$$E_{wake} \cong \frac{1}{2} \frac{d(l_m^2)}{dt} \quad (2.3)$$

The effect of the introduced turbulence on diffusivity is added to the ambient diffusivity, as described in Section 1.2.2 to yield the total diffusivity, E_t . The sum is then used to determine σ^2 ,

$$\sigma^2 = 2 \int E_t(t) dt + \sigma_o^2 \quad (2.4)$$

The distance x is mapped using time t and the ambient current speed, u_a . Figure 2.2 shows the relative magnitudes of the two sources of diffusivity mapped to a 5 cm/s current. Because the relative contributions are described as a function of time, the distance is proportional to current speed, i.e. for a 2 cm/s current, the corresponding distances would be 2/5 as great.

To obtain an analytical solution for concentration, the net diffusion of the carbon dioxide in the direction of the current was assumed to be negligible. Because both vertical diffusivity and the vertical concentration gradient are small, diffusion in the vertical direction was also neglected. The additional concentration of carbon dioxide is given by,

$$C(x, y) = \frac{\dot{M}/u_a}{\sqrt{2\pi} \sigma} \exp\left(\frac{-y^2}{2\sigma^2}\right) \quad (2.5)$$

where $\dot{M}$ is the mass flux (kg/m-s) at the depth studied, u_a is the current (m/s) modeled, and $\sigma(x)$ is the standard deviation at the distance considered, found using the equations given above.

Relative Importance of Parameters

For the dry ice scenario, the two parameters that can be varied are the size and the shape of the blocks of dry ice. The effect of using larger dry ice blocks would be to lessen the flux of carbon dioxide to the water column since a greater fraction of the dry ice would reach the ocean floor before dissolution. There would of course be a greater impact at the ocean floor; however, only water column impacts are considered in this model. The larger size of the disturbance would also increase the initial mixing due to the wake. The effect of a more streamlined block would be similar to that of a larger block, in that it would allow a greater fraction of the block to reach the ocean floor. Streamlining the block would also reduce initial mixing due to smaller drag. Ambient current is very important in determining the initial water column concentration. Because the effect of current is similar in all scenarios, this sensitivity will be explored in a general sense in Chapter 4.

Results

For the one and ten plant dry ice base case scenarios, the parameters and assumptions are summarized below:

- Ambient current speed: 5 cm/s.
- Length of each cube: 3 m.
- Drag coefficient: 1.07.
- Ambient turbulence as parameterized by Okubo (See Section 1.2.2).

The additional CO₂ concentrations due to the disposal of the dry ice were calculated for both the one plant and the ten plant scenarios. A current of 5 cm/s was assumed. These additional concentrations of CO₂ were added to the ambient concentrations of CO₂ and the new pH values were calculated using the chemical equations described earlier. A map of the resulting pH at a depth of 1000 meters for both the one and ten plant scenarios can be seen in Figure 2.3.

2.1.2 Spray from Towed Pipe

The possibility of disposal of liquid CO₂ as a spray from a towed pipe has been explored recently by Japanese researchers [23, 12]. This method has several advantages over that of dry ice. First, it achieves mobility and significant dispersion levels without requiring the use of the large amount of extra energy needed for solidification. Secondly, it allows for the possibility of more precisely targeting the disposal depth.

Physical Model

The physical model is very similar to that of dry ice (see Section 2.1.1). It differs in that the vertical distribution is considered to be uniform over the depth range chosen, the frame of

Figure 2.3: Distribution of pH in a horizontal plane at a depth of 1000 meters resulting from ocean CO₂ disposal in a 5 cm/s current as 3 meter dry ice cubes. Top: Emissions from one standard power plant. Bottom: Emissions from ten standard power plants. Discharge point is at 0,0.

Figure 2.4: Liquid CO₂ sprinkling from the pipe towed by vessel, from Ohsumi [28].

reference moves with the barge so that the effective current speed is that of the barge, and the wake is based on the drag calculated for a towed pipe.

The base case values for barge speed and pipe diameter are 5 m/s and 1 meter respectively. For the range of values considered, the boundary layer flow around the pipe is expected to be turbulent and the drag coefficient is expected to be about 0.5 [40]. The wake due to the pipe can be considered to be two-dimensional, so that the mixing length is given by [35]

$$l_m \cong 0.252(0.5 C_D d x)^{1/2} \quad (2.6)$$

For these conditions, the wake effect is dominant to ambient turbulence for about 1.4 hours (25 km).

Relative Importance of Parameters

Although the choice of pipe diameter has some effect on initial mixing, the most important parameters are towing speed and the depth over which the carbon dioxide is distributed.

Results

For the one and ten plant dry ice base case scenarios, the parameters and assumptions are summarized below:

- Towing speed: 5 m/s.
- Vertical extent of release: 500 meters.
- Pipe diameter: 1 meter.
- Drag coefficient: 0.5.

- Ambient turbulence as parameterized by Okubo (See Section 1.2.2).

The results for the base case are shown in Figure 2.5, where the distances given are relative to the pipe. The plume formed is very thin, only meters in the case of the one power plant scenario, and tens of meters in the case of the ten plant scenario. Although the plume is very long, it is important to remember that any organisms experiencing these concentrations, will be moving quite rapidly (5 m/s) relative to the reference frame of the ship, and will pass through the plume relatively quickly.

2.2 Droplet Plume

The first dissolution method considered is the formation of a droplet plume. At intermediate depths, liquid CO₂ is less dense than seawater and liquid CO₂ released from a diffuser would tend to form buoyant droplets. The effect of many rising droplets is to entrain and lift ambient water, forming a droplet plume.

2.2.1 Physical Model

Plume Model

The near-field analysis of the droplet plume followed a modification of Liro *et al.* [17]. Individual droplet dynamics of dissolution and slip velocity were coupled with a larger integral plume model in which entrainment was based on centerline velocity, plume width and an empirical entrainment coefficient. Because the source of buoyancy is localized in the droplets, it is possible for some of the water in the plume to detrain allowing the droplets and the plume core to continue to rise. This action is called "peeling". Following Liro *et al.*, the rate of change of momentum was based on the total plume buoyancy, and peeling occurred when the total buoyancy was zero, but the droplets were still locally buoyant. At these points, half of the water in the plume peeled, carrying half of the dissolved mass flux, while the centerline velocity and the centerline density difference remained unchanged. This is a slight change from Liro's original model, where the centerline density difference was halved. The present assumption is more conservative when estimating dilution; Liro's assumption was conservative in estimating rise height. Liro's model was also modified to calculate explicitly the dissolved CO₂ concentrations and to include the effect of dissolution on plume water density using a relationship from Drange and Haugan[9].

As a conservative estimate, all of the flow from the peeling events was assumed to mix and form one intrusion layer. In order to estimate the additional entrainment that occurs as the peeled water sinks to its level of neutral buoyancy, the individual flows were grouped together at the center of mass of the dissolved CO₂ release and were assumed to act as an axisymmetric negatively buoyant plume. This is conservative in the sense that if several smaller plumes resulted, the entrainment would be greater, and the initial concentration lower. If these smaller peels were to trap at different heights, diffusion would occur more rapidly, and the impact would be reduced.

Figure 2.5: Distribution of pH in a horizontal plane at a depth of 1000 meters resulting from ocean CO₂ disposal from a towed pipe moving at 5 m/s. Top: Emissions from one standard power plant. Bottom: Emissions from ten standard power plants. Discharge point is at 0,0.

Intrusion Model

Once the flow and its level of neutral buoyancy have been calculated from the near-field model, the intrusion model used is that of Jirka *et al.* [14]. In this region, mixing due to diffusion is neglected as it causes much less spreading than does buoyancy. Except for the area closest to the source, the velocity in the intrusion layer is equal to that of the ambient current.

Because the depth being modeled is below the pycnocline, the solution developed for linearly stratified ambient conditions is appropriate. Non-dimensional length scales developed for this situation are:

$$l_H = \frac{0.13\bar{S}Q_oN}{2u_a^2} \quad (2.7)$$

$$l_V = \frac{1.2u_a}{N} \quad (2.8)$$

where l_H is the horizontal length scale, determined by $\bar{S}Q_o$, the inflow into the intrusion layer based on mixing due to injection, Q_o in m^3/s times the average dilution $\bar{S}$, u_a , the ambient current in m/s , and the Brunt-Väisälä frequency, N (s^{-1}). The Brunt-Väisälä frequency is a stratification parameter defined by:

$$N = \left(\frac{g}{\rho_a} \frac{\partial \rho_a}{\partial z} \right)^{\frac{1}{2}} \quad (2.9)$$

where g is the acceleration due to gravity, ρ_a is the ambient density, and $\frac{\partial \rho_a}{\partial z}$ is the ambient density stratification.

The vertical length scale, l_V , is determined by the ambient current and stratification. Greater stratification leads to faster spreading. Greater ambient current has the compound effect of reducing the cross sectional area occupied by the flow while at the same time increasing its thickness to width ratio. Since the distance over which change occurs is related to the horizontal length scale, change occurs faster in both time and distance as the current increases.

In the source enclosing region velocities differ from the ambient. The solution presented in Figure 2.6 is a best fit to the governing equations in this region [14, 30]. For values of x/l_H larger than about 3, where the velocity slows to the ambient level, the half-width and half-length are given by:

$$b = l_H \left(9.2 + 6.3 \frac{x}{l_H} \right)^{\frac{1}{2}} \quad (2.10)$$

$$h = \frac{l_V l_H \pi}{b} \quad (2.11)$$

Diffusion Model

Both gravitational spreading and diffusion are occurring from the time that the intrusion layer is formed; however in order to use an analytical solution in the diffusion regime, a transition point must be chosen. A simple approach is to choose a characteristic distance as transition point. The minimum distance of $6l_H$ suggested by Paddock [30] has been chosen

Figure 2.6: Nondimensional horizontal half-width (top) and vertical half-thickness (bottom) of the intermediate-field region for the case of linear stratification.

for this study. This choice is somewhat optimistic in that the intrusion layer thickness predicted is larger than if the transition point were chosen further downstream, allowing for continued vertical collapse.

An alternative way to deal with this transition would be to find the point where diffusion causes spreading comparable to that predicted by Jirka's model and to use that as a starting point for a diffusion based model. The point at which this transition occurs is dependent on the level of ambient ocean mixing. Paddock gave the following formulation based on Jirka's equations for linear stratification [30] :

$$x_t = \left(\frac{u_a^3 l_H}{550 \alpha^3} \right)^{\frac{1}{2}} - 1.46 l_H \quad (2.12)$$

α is the coefficient of the effective diffusivity relationship to length scale, where $E_h = \alpha L^{4/3}$. An appropriate α can be chosen in order to make this relationship consistent with that of Okubo (See Section 1.2.2). The alternative approach is also subject to the requirement that the minimum distance be at least $6l_H$: if x_t is less than $6l_H$, the intrusion model is extended until a distance of $6l_H$ in order to take into account the significant vertical collapse that occurs within that distance. This method does not avoid the optimistic assumption of neglecting collapse after a relatively arbitrary point.

Sensitivity to the choice of a transition point will be explored in Section 2.2.3. The initial concentration of the plume entering the diffusion regime is uniform and is determined by the mixing dynamics close to the point of injection. The initial width and depth are determined by the intrusion model. The plume is moving at the speed of the ambient current and vertical mixing is inhibited by stratification. If we assume that E_z is about $0.15 \text{ cm}^2/\text{s}$ then we find that the time scale for mixing in the vertical direction, h^2/E_z , is much, much longer than the time scale for mixing in the horizontal direction, w^2/E_h , during the time of interest. For this reason, vertical diffusion is neglected and the governing equation becomes:

$$u \frac{\partial c}{\partial x} = E_y \frac{\partial^2 c}{\partial y^2} \quad (2.13)$$

The solution to this problem can be found by generalizing the solution originally given by Brooks [5] and for the case without decay, can be stated:

$$\frac{c}{c_o} = \frac{1}{2} \left(\operatorname{erf} \left[\frac{y + b/2}{2b} \sqrt{\frac{24}{\left(\frac{12(2-n)E_{yo}x}{ub^2} + 1 \right)^{\frac{2}{2-n}} - 1}} \right] - \operatorname{erf} \left[\frac{y - b/2}{2b} \sqrt{\frac{24}{\left(\frac{12(2-n)E_{yo}x}{ub^2} + 1 \right)^{\frac{2}{2-n}} - 1}} \right] \right) \quad (2.14)$$

where erf is the error function. E_{yo} is the value of the lateral eddy diffusion coefficient corresponding to the initial plume width, b , at $x=0$. In this model, L is the plume width defined as $2\sqrt{3}\sigma_y$ so as to be equal to b at $x=0$, and n is the empirical exponent relating the length scale to diffusivity. As explained in Section 1.2.2, n is taken to be 1.15 based on empirical data.

2.2.2 Relative Importance of Parameters

There are many design parameters that can be varied. Sensitivity to most of these parameters has been documented in Liro *et al.* [17]. However, to the extent that this report includes

Figure 2.7: Definition sketch for Brooks' model.

the effect of the dissolved CO₂ and addresses somewhat different issues, it is worth analyzing some of the key design variables in terms of their effect on diluted flow rate.

Number of Ports

Perhaps the easiest variable to control is the number of ports used to release the emissions from one power plant. As seen in Figure 2.8, increasing the number of ports leads to greater total entrainment. The base case chosen was ten ports per plant each with a CO₂ flow rate of 13 kg/s. This seemed to capture most of the benefits of the additional entrainment without adding significant cost. For the analysis of impact due to the one and ten plant releases, the releases from all ports were assumed to combine to form one intrusion layer in order to achieve consistency between scenarios. A large enough port spacing, however, would result in independent intrusion layers. It will be shown in Chapter 4 that the size of these intrusion layers has a significant effect on the biological impact, and that limiting the size of the independent releases may be an important key to mitigating impact.

Initial Droplet Size

Figure 2.8 also shows the effect of larger initial droplet size. Liro *et al.* [17] calculated a maximum stable droplet radius of 1.25 cm for a liquid CO₂ release. The minimum size would most likely depend on release conditions. The base case of 0.8 cm radius was chosen as an achievable size. A larger initial radius would improve overall dilution slightly; however, one of the more important effects (not considered here in the interest of being conservative) might be to spread the peeling events out further, resulting in several intrusion layers at various depths. Dilution could also increase at the other end of the size spectrum. Very small bubbles dissolve rapidly and consequently do not entrain water from higher elevations which would counteract some of the negative buoyancy of the dissolved CO₂. As a result,

Figure 2.8: Sensitivity of diluted flow rate to mass flux from individual release (top) and to initial bubble radius (bottom). All releases occur from a depth of 1000 meters in the ambient ocean. The base case radius is 0.8 cm and the base case release is 13 kg/s per port (10 ports/plant).

Figure 2.9: Ambient density in depth range considered (top). The maximum predicted rise height of the droplets and the trap height of the intrusion layer are shown for releases from 800 to 2000 meters depth with initial radii of 0.8 and 1.0 cm. The base case release is 13 kg/s per port (10 ports/plant) is assumed (bottom).

the plume formed by this more dense peeled water would sink further and entrain more; however, if the diffuser is close to the ocean floor, such small bubbles will result in a plume that reaches the ocean bottom before it reaches its level of neutral buoyancy.

Stratification

Because it delays peeling, weaker stratification can lead to greater entrainment. However, since the difference in density due to water entrained at lower depths is only a fraction of the density difference due to the dissolved CO_2 , the more important effect may occur as the peeled water sinks. If the release occurs close to the ocean bottom, the CO_2 enriched water may fall back to the ocean floor before finding its level of neutral buoyancy. This would result in greater impact than the similar flow in the open ocean that is assumed for the base case. The top graph of Figure 2.9 shows the ambient stratification for the region

Figure 2.10: Rise and trap heights resulting from a reduction in mass transfer due to hydrate formation. Mass transfer reduced to one-half of the base case (top), and one tenth of the base case (bottom). The maximum rise height and the predicted trap height of the intrusion layer are shown for releases from 800 to 2000 meters depth with initial radii ranging from 0.4 to 1.0 cm. The base case release is 13 kg/s per port (10 ports/plant) is assumed.

being considered, while the bottom graph illustrated the maximum rise height and predicted trap height of the intrusion layer formed for the ambient stratification assumed, initial radii of 0.8 and 1.0 cm, and a release of 13 kg/s. Settling out on the ocean floor seems to be a possibility for releases occurring below 1000 meter depths if the initial droplet radius is 0.8 cm. If it is possible to create droplets with radii as big as 1.0 cm, the situation improves slightly; however, releases below 1100 meters are still not recommendable. These results are somewhat sensitive to the assumptions made, and more information on plume peeling and the interaction among the peeled layers is needed.

Clathrate Hydrate Formation

At intermediate depth there is a possibility of clathrate hydrate formation at the droplet-water interface [39, 11]. Clathrate hydrate formed on the outside of the droplets would slow mass transfer and have an effect similar to that of a larger initial droplet size.

One study has shown that under certain conditions the presence of clathrate hydrate can slow mass transfer to as little as 5% of the rate in their absence[39]. This study involved liquid CO₂ at rest, and its application to a droplet plume environment requires some caution. Other studies with flowing water conditions, such as that by Hirai *et al.*[12], find a transfer reduction on the order of 50%. Since the effect of possible clathrate hydrate formation cannot be predicted with precision, sensitivity to this parameter is explored. The base case mass transfer coefficient is that chosen by Liro *et al.* [17] based on studies by Clift *et al.* [6]

$$K = 1.25(g \frac{\rho_w - \rho}{\rho_w})^{1/4} D^{1/2} d^{1/4} \quad (2.15)$$

where K is the mass transfer coefficient, g is the acceleration due to gravity, ρ_w is the density of water, ρ is the droplet density, D is the molecular diffusivity of CO₂, and d is the effective droplet diameter.

Predicted rise and trap heights were found for releases between 800 and 2000 meter depths for mass transfer rates of both one-half and one-tenth of the base case. The results are presented in Figure 2.10. As shown by the top figure, a reduction of one half in the rate of mass transfer increases the range of acceptable discharge depths (i.e. yielding trap levels above the ocean floor). Differences in overall droplet density due to clathrate hydrate would depend on the size of the bubbles and the thickness of the shell formed, and have not been modeled explicitly. The base case droplet size of 0.8 cm radius would be feasible for depths down to about 1300 meters, and the reduced mass transfer, like larger bubble size, would tend to lead to larger travel distances, greater entrainment, and possibly the formation of additional intrusion layers.

If, due to the presence of clathrate hydrate, the mass transfer is only ten percent of that assumed in the base case, there may be problems with effective sequestration. This scenario is shown in the bottom graph of Figure 2.10. Droplets released with an initial radius greater than 0.8 must be released below 1700 meters in order to dissolve completely before reaching 500 meters and flashing into bubbles. For a radius of 0.6 cm, the necessary depth is about 1300 meters.

With more knowledge about the effect of clathrate hydrate on droplet density and mass transfer in the environment of a droplet plume, it would be possible for diffuser design to maximize the environmental benefits of the long travel distances of the droplets without endangering the goal of carbon dioxide sequestration below the thermocline.

2.2.3 Thickness of the Intrusion Layer

Transition to Diffusion Model Occurring at Characteristic Length

In later analysis (See Chapter 4) of the impact of lowered pH on organisms, it will be shown that, for a given loading, the ability of a disposal mechanism to distribute carbon dioxide

Figure 2.11: Relationship between current speed, stratification, and intrusion layer thickness (meters) if transition occurs at $6l_H$.

vertically in the water column is critical to reducing impact. In terms of site selection, the ambient current and stratification can affect the predicted thickness of the intrusion layer as shown in Figure 2.11. Because transition is assumed to occur at a characteristic length, $6l_H$, the diluted flow rate does not affect the thickness predicted for the diffusional regime. The base case conditions of a 5 cm/s current and a density gradient of 0.006 kg/m^3 lead to an intrusion layer thickness of 23 meters. A faster current or weaker stratification would increase the thickness predicted.

Transition to Diffusion Model Dependent on Diffusivity

The alternative model of a transition point occurring where the increase in plume width due to gravitational spreading is equal to that due to ambient diffusivity is sensitive to the ambient diffusivity chosen and the diluted flow rate. Since the diluted flow rate is the only quantity that can be varied by engineering design, these effects are considered quantitatively.

Using the base case parameterization for ambient diffusivity and the alternative transition criteria of equivalent diffusion, the relationship between the diluted flow rate and layer thickness is shown for several different density gradients in the top graph of Figure 2.12. As expected, higher stratification leads to a thinner intrusion layer, with the effect being proportional to the square root of the density gradient. For a given current speed, the range where the diluted flow rate affects the intrusion layer thickness decreases with increasing gradient. For the base case current speed and stratification chosen, this range is only reached for flow rates greater than those anticipated in disposal schemes. The maximum thickness reached is a function of the requirement that transition to a diffusional regime not occur until a distance of at least $6l_H$. In these cases, the flow is so large that there is a period during which horizontal spreading due to ambient diffusion is occurring at a rate comparable

Figure 2.12: Relationship between diluted flow and intrusion layer thickness in different environments with alternate transition assumption. The top figure show the effect of density stratification (in kg/m^4) on intrusion layer thickness with an ambient current of 5 cm/s. The bottom figure shows the effect of current speed on thickness in the base case density gradient of $0.0006 kg/m^4$.

Figure 2.13: Relationship between current speed, stratification, and intrusion layer thickness (meters) for a given diluted flow rate. The figure on the left is for a diluted flow rate of $100 \text{ m}^3/\text{s}$; that on the right is for a flow rate of $1000 \text{ m}^3/\text{s}$.

to that due to gravitational spreading, but the transition point used is that where vertical spreading becomes insignificant.

In the bottom graph of Figure 2.12 the relationship between diluted flow rate and intrusion layer thickness is shown for several different current speeds. Again, the plateau seen for the current speed of 2 cm/s is due to the necessity to use the gravitational spreading model until vertical collapse slows significantly. Larger currents require a smaller cross-sectional area of flow to transport the same volume and the vertical length scale increases with current speed. As a result, the larger the current, the higher the diluted flow rate at which the ultimate intrusion layer thickness is determined by the vertical collapse condition. For flows less than those required to reach the maximum thickness, the ambient current has little effect on the layer thickness at the point of transition to a regime of ambient horizontal diffusion.

Figure 2.13 shows contour plots of the intrusion layer thickness resulting from a given diluted flow rate ($100 \text{ m}^3/\text{s}$ on the left, $1000 \text{ m}^3/\text{s}$ on the right) using the alternative transition assumption under different ambient conditions. The transition point is determined by vertical collapse criteria at currents slower than about 2 cm/s . Less stratification always leads to thicker intrusion layers; however, the impact is more substantial where transition is determined by horizontal spreading criteria.

These results will be helpful in designing a CO_2 injection scheme to reduce environmental impact in any scenario where an intrusion layer is expected to form. The model, however, is only able to take one mechanism (either gravity spreading or ambient diffusion) into account at a time and so the intrusion layer thickness used for the diffusion model is only a best approximation, and differences based only on a slightly different choice of a transition point should not be considered significant.

2.2.4 Results

For the one and ten plant droplet plume base case scenarios, the parameters and assumptions are:

- Ambient current speed: 5 cm/s.
- Ports per standard power plant: 10.
- Initial Droplet Radius: 0.8 cm.
- Ambient stratification described in Section 1.2.3.
- Release depth 1000 meters, (0.0006 kg/m^4 density gradient).
- One intrusion layer formed, the thickness of which is based on characteristic length scales.
- Ambient turbulence as parameterized by Okubo (See Section 1.2.2).

Since the difference between the one and ten plant scenarios is only the length of the diffuser array, the ten plant scenario entrains ten times the water as the one plant scenario, approximately 10000 and 1000 m^3/s respectively. In a current of 5 cm/s and the density gradient at 1000 meter depth, the plumes enter the diffusion regime with a thickness of 23 meters. For the ten plant plume this occurs after about 23 hours and the resulting width is 8800 meters. The one plant plume reaches its width of 880 meters in less than two hours. The relatively large volume flux involved in this scenario results in a large initial width and relatively rapid diffusion.

The spatial extent of pH change for the base case plume parameters and one and ten power plant emissions are shown in Figure 2.14.

2.3 CO₂-Enriched Seawater Plume

Because dissolution of CO₂ increases the density of seawater, it is possible to form a negatively buoyant plume [9, 8]. However, the negative buoyancy effect is so small that in order to form a plume that will be able to sink significantly, initial concentrations of CO₂ must be a sizable fraction of the saturation concentration. As a result, injection would require some sort of initial mixing device [1]. One advantage of the dense plume scenario is the decreased cost due to savings in pipeline for the distance which the plume can sink by gravity.

2.3.1 Physical Model

Gravity Current Model

Earlier gravity current models [9, 8] had set a fixed height to width aspect ratio and assumed a flat bottom, resulting in turning due to Coriolis force. Calculations based on gravity spreading equations, however, indicate that the height to width ratio will quickly become very

Figure 2.14: Distribution of pH in a horizontal plane at a depth of 1000 m resulting from the ocean CO₂ disposal in a 5 cm/s current as a droplet plume. Top: Emissions from one standard power plant. Bottom: Emissions from ten standard power plants. Discharge point is at 0,0.

Figure 2.15: Schematic of dense plume geometry.

small, so that h reaches a value which is comparable with irregularities in the topography. A better approximation might be to allow the topography to determine the aspect ratio, in which case pressure from the sides of the canyon or valley in which the current flows would counteract the Coriolis force.

Accordingly, this model does not attempt to predict horizontal trajectory as this is considered to be topography dependent. Instead, variation in direction of flow relative to the direction of the steepest overall slope due to topographic irregularities, is taken into account by using a slope that is slightly less than the overall average.

The equations used for the model are essentially the same as those used in models of deep water formation and adopted by Drange and Haugan for use with the density current generated by a concentrated CO_2 -seawater solution [32, 9, 8]. In this model, however, the aspect ratio was considered to be topography dependent and hence Coriolis force was neglected. The equations are as follows:

$$(AU)_\xi = E(Ri_o)WU \quad (2.16)$$

$$(AU^2)_\xi = Ag' \sin \theta - \frac{C_D W}{\cos \phi} U^2 \quad (2.17)$$

$$(AUg')_\xi = -AUN^2 \sin \theta \quad (2.18)$$

$$(X)_\xi = \sin \theta \quad (2.19)$$

where ξ is the along stream direction. C_D is the drag coefficient. X is the depth and U is the velocity. N is the Brunt-Väisälä frequency defined in Equation 2.9. The geometry assumed is shown in Figure 2.15. This simplified geometry also leads to a fixed aspect ratio, and the height and width, W , can be found from the cross-sectional area, A . The downward slope is θ , and the side slope is ϕ . E is the entrainment coefficient, which is a function of Ri_o , the overall Richardson number. This function is described below.

Intrusion Model

In the intrusion layer, fluid was modeled as entering as a point source at the coastline. An image source was used to keep the flow from crossing the boundary of the coast. The analysis of Jirka *et al.* [14], described in Section 2.2.1, was then used to calculate the time spent in the intrusion flow as well as an initial half-width and half-height for the diffusion model.

Diffusion Model

Analysis of the plume in the diffusion-dominated region follows closely the analysis outlined in Section 2.2.1. Because of the presence of the coast, the flow is treated as one-half of the symmetrical flow described by Brooks' model. The turbulence assumed in the calculations, however, is based on the actual width of the plume.

2.3.2 Relative Importance of Parameters

The important parameters in the gravity current model are the entrainment coefficient, the drag coefficient, the topography, stratification, and the initial excess CO₂ concentration and loading. Stratification and current speed affect gravity spreading in the intrusion layer as described in Section 2.2.1. The level of diffusion is the most important factor over long time, but is common to all scenarios.

Entrainment Coefficient

The relationship of entrainment coefficient to Richardson number used was that established by Ellison and Turner [36] and Lofquist[19], which is shown in Figure 2.16. Entrainment decreases as the Richardson number increases, where the overall Richardson number is defined as

$$Ri_o = \frac{\Delta\rho gh\cos\theta}{\rho_a U^2} \quad (2.20)$$

Thus, entrainment increases with increased velocity, and decreases with larger relative density differences.

Drag Coefficient

The drag coefficient affects the flow by affecting plume velocity and hence entrainment. A greater drag coefficient slows the plume and therefore increases the depth reached by the plume. For similar gravity current flows, a C_D of about 0.01-0.03 seems to fit many observed results [32], hence a C_D of 0.02 was chosen for the base case. Sensitivity to this parameter is shown in Figure 2.17. If the plume reaches the bottom of the thermocline with significant negative buoyancy, it will continue to sink to great depths; scenarios run with a C_D above 0.1 sank indefinitely when released from 750 meters depth. If the effective drag coefficient is of this order, there are many options for a highly concentrated plume to sink to great depths when released at or close to the thermocline. If the effective drag coefficient is closer to the 0.02 assumed by the base case, only injection below the thermocline will achieve significant sinking.

Figure 2.16: Dependence of Entrainment Coefficient on Richardson Number (from Alavian) [2].

Figure 2.17: Dependence of depth sunk by plume on drag coefficient. Results are for plumes formed from emissions from ten standard power plants with an initial concentration of 12 kg/m^3 , and released at a depth of 750 meters.

Figure 2.18: Distance (m) sunk by a CO₂ seawater solution injected at 780 meter depth, with a velocity of 0.5 m/s, an excess CO₂ concentration of 12 kg/m³, mass loading from ten standard power plants, and variable topography.

Site Topography

The topography will be determined by site selection. If the plume is to reach a depth of 1000 meters, release will most likely occur on the continental slope. For eastern North America, a large fraction of this slope averages 4 to 6 degrees; however, there are areas of both steeper and more gradual slopes [18]. Because of variation and irregularities of the topography, sensitivity to effective downhill slopes of 1 to 10 degrees was studied. Because of the relatively small scale of the flow, a wide range of side slopes is also possible. Response to side slopes ranging from 1 to 30 degrees was tested. The results of different slope combinations are shown in Figure 2.18. Increased side slope decreases the width of the channel and hence the area open for entrainment, allowing the plume to penetrate deeper. Increased downward slope increases the speed of the plume. Because increased velocity leads to a lower Richardson number, and consequently greater entrainment, increased downward slope generally leads to greater dilution and less penetration. An average downward slope of 2 degrees and an average side slope of 8 degrees were chosen for the base case. This point is marked with an asterisk in Figure 2.18.

Initial Concentration and Loading

Using the base case topography, sensitivity to initial excess CO₂ concentration and loading was examined. In Figure 2.19 it can be seen that without a significant initial concentration, the plume is able to sink very little. After a certain threshold, however, additional excess CO₂ concentration has little effect since the plume adjusts quickly to its topography-determined

Figure 2.19: Distance (m) sunk by a CO_2 seawater solution injected at 750 meter depth, with an initial velocity of 0.5 m/s, a C_D of 0.02, base case topography, and variable loadings and initial excess CO_2 concentrations.

normal Richardson number. The mass loading is also important in achieving greater depths since greater thickness of flow leads to a greater Richardson number, and consequently lower entrainment.

There is a trade-off between depth sunk and plume dilution. Greater depth can only be achieved with more limited dilution. Site selection can be based on the relative importance of these two factors. The general relationship between total entrainment and depth reached is shown in Figure 2.20.

2.3.3 Results

For the one and ten plant dense plume base case scenarios, the parameters and assumptions are summarized below:

- Ambient current speed: 5 cm/s.
- Side slope: 2° , Downward Slope: 8° .
- Ambient stratification described in Section 1.2.3.
- Initial excess CO_2 concentration: 12 kg/m^3 (approximately 20% of saturation).
- Drag coefficient: 0.02.
- Ambient turbulence as parameterized by Okubo (See Section 1.2.2).
- One half of a symmetrical distribution due to effect of coastline.

Figure 2.20: Dilution versus distance sunk (with $C_D = 0.2$, an injection depth of 780 meters, an initial excess CO_2 concentration of 12 kg/m^3 , and varied topographic conditions).

A gravity current resulting from the emissions of ten standard power plants is predicted to intrude at a depth of 1000 meters when released at a depth of 755 meters. After near-field mixing the dense plume is initially more concentrated than the droplet plume, with a flow rate of $3500 \text{ m}^3/\text{s}$, and a pH of 5.5 versus $10000 \text{ m}^3/\text{s}$ and a pH of 6.0. In a current of 5 cm/s and the density gradient at 1000 meter depth, gravitational spreading leads to a thickness of 23 meters and a width 3000 meters as the ten plant plume enters the diffusion regime after a little over 10 hours.

In order for the current generated from the emissions of one power plant to reach the same depth under the same conditions, it must be released at a depth of 855 meters. The resulting intrusion layer is more dilute, with a flow of $600 \text{ m}^3/\text{s}$ and a pH of 5.7. Because of the smaller flow, for the one plant case gravitational spreading dominates for only 2 hours before the transition thickness of 23 meters is reached. The width of the intrusion layer is 520 meters.

In both cases, relatively small initial widths lead to lower rates of effective diffusion and the plume persists over a much longer distance than in the droplet plume scenario. The spatial extent of pH change for the base case plume parameters and one and ten power plant emissions are shown in Figure 2.21.

2.4 Conclusions

Table 2.1 summarizes the base case scenarios with some appropriate physical properties of the resulting pH distributions. Depending on capture technology, levels of trace constituents of

Figure 2.21: Distribution of pH in a horizontal plane at a depth of 1000 m resulting from the ocean CO₂ disposal in a 5 cm/s current as a dense enriched seawater plume, the x-axis represents the coastline. Top: Emissions from one standard power plant. Bottom: Emissions from ten standard power plants. Discharge point is at 0,0.

	Volume of water	Distance to	Minimum pH	Minimum pH
	with pH under 7	pH of 7	(after	(diffusion
	(km ³)	(km)	dissolution)	regime)
Dry Ice				
1 plant	0.001	0.09	6.3	6.1
10 plants	1.1	2.2	5.8	7.4
Towed Pipe				
1 plant	0.00004	0.2	6.5	7.2
10 plants	0.3	14	5.7	6.2
Droplet Plume				
1 plant	1.8	23	5.5	6.0
10 plants	130	60	5.5	6.0
Dense Plume				
1 plant	7.2	94	4.0	5.7
10 plants	510	690	4.0	5.5

Table 2.1: Summary of results of modeled scenarios. Dry ice distance and pH values are from a depth of 1000 meters.

the emissions may be of concern. Figure 2.22 addresses this issue by providing a comparison of dilution along the plume centerline over time for various scenarios. In all scenarios, dilution levels are high after a fairly short initial period.

Dispersion Methods

The impact of ocean disposal using a dispersion method (dry ice or towed pipe for example) on the water column will be minimal due to the dilution over great depths. As with the dissolution methods, impact can be minimized by locating disposal in an area with a medium to large current. The lowest pH experienced for any of the cases examined was still above 5 and the region where pH was below 6 was also quite small (distances of less than 200 meters on the centerline for the most severe scenario).

Droplet Plume

Because the CO₂ -enriched seawater from a droplet plume is confined to an intrusion layer, it is difficult to achieve the same level of dispersion as in the dry ice scenario. The large level of entrainment, however, serves to increase the width of the flow and hence the relative diffusion. The droplet plume scenario also has the advantage of effective design variables: droplet size, number of ports and port spacing; these parameters could be modified to result in greater entrainment as well as possibly greater vertical distribution and consequently less impact.

Figure 2.22: Centerline dilution over time for the various base case scenarios.

Dense Plume

The severity of the impact in the dense plume scenario may be as much related to the limited dilution as the plume enters the diffusion regime as to the very low pH that affects only a small flow. If greater diffusion is an important goal, another drawback to the dense plume scenario is that it is less successful in sinking with smaller loading. If the cost savings of avoided pipeline were not a principal goal, greater initial dilution could be achieved and the results would be slightly closer to those seen for the droplet plume. The biggest obstacle in reducing impact, however, is that the nature of the injection leads to plume formation in a region where diffusion is limited.

Chapter 3

Organism Experience

3.1 Introduction

Although the spatial extent of pH change is one description of impact, a more relevant measure of impact is the mortality suffered by passive organisms passing through the affected area. The effect on an individual organism will depend on the pH experienced by that organism and the duration of the experience (See Topical Report 5). Since organisms will experience a range of pH, their experience must be defined as pH experienced as a function of time.

This chapter provides a brief overview of the method used to evaluate mortality due to time varying pH exposures (Section 3.2), and some general background on relative diffusion (Section 3.3). A method for determining organism experience is proposed in Section 3.4 and a simple population recovery model is presented in Section 3.5. Results using the proposed method for the scenarios proposed are presented in Section 3.6. Simpler alternatives for evaluating organism experience are presented in Section 3.7 and their shortcomings are discussed. Finally, the impacts of the proposed scenarios are compared in Section 3.8.

3.2 Evaluating mortality due to time varying exposures

Most information on mortality effects comes from laboratory studies done at a constant pH. These studies show that mortality due to lowered pH is strongly dependent on exposure time. In order to use the information from laboratory studies to evaluate experiences that include exposures at many different pH levels, a method of adding exposures at different pH needed to be developed. The first step was to plot all the available data on mortality of lowered pH to zooplankton. Isomortality lines of 0%, 50%, and 90% mortality were fit to this data, and in order to take into account possible sublethal effects, the lines were raised by a quarter of a pH unit (see Topical Report 5). The results are shown in Figure 3.1.

In order to evaluate organism experience, the experience must first be discretized into shorter experiences at a constant pH, and then added. Because the stochastic approach uses discrete time steps, the average pH over these time steps are the points chosen to add

Figure 3.1: Mortality curves for zooplankton exposed to lowered pH (from Auerbach [3]).

together. For the other methods, points can be chosen based on similar time steps or on pH ranges. The exposures are added in the order that they occur. The previous exposure is moved to the pH of the new exposure along an interpolated isomortality line. The equivalent times at the same exposure can be added to form a new point. This point would then be moved along its isomortality line to the pH of the next exposure, and the addition would proceed. At any point, the mortality of organisms following the given pathway can be assessed.

Because the pH-mortality curves are nonlinear, the effect of a small additional exposure depends on the cumulative stress to that point. This is illustrated in Figure 3.2 where the stress level is represented by equivalent hours at pH of 6.5.

More information about this method can be found in Topical Report 5.

3.3 Relative Diffusion of Organism and Plume

Because vertical diffusivities are so much smaller than horizontal diffusivities (See Section 2.2.1), passive movement of zooplankton is modeled conservatively as occurring only in a horizontal plane. Also some zooplankton are known to undergo vertical diurnal migration. However, this activity becomes less frequent with depth, and in all cases leads to less severe impacts. For example, if an organism were to migrate over 600 meters, it would spend at most 4% of its time in a 24 meter thick plume. In the worst case, exposures would only last two hours at a time, which individually would not be expected to have any impact (See Figure 3.1). With the exception of special cases where the organism's migration pattern might bring it continually into the most severe area of the plume, or the possibility that organisms sensing the plume might interrupt their migration, the plume is not expected to

Figure 3.2: Effect of additional exposure at different cumulative stress levels.

impact vertically migrating zooplankton. Therefore, the conservative assumption is made that the organisms are moving passively with the current, diffusing in the horizontal plane with ambient turbulence.

Even with these assumptions, the relative position of an organism to the plume centerline concentration will vary with time due to ambient turbulence. Because the turbulence field for the organism is correlated with that of the concentration, relative diffusion is a function of distance between the plume center of mass and the organism. In order to determine the pH-time experience, it is necessary to find how distance between the center of mass of a pollutant and an organism entering the area at a given (non-zero) distance from the source of that pollutant varies with time.

In Section 1.2.2, empirical correlations of the variance (σ_{rc}^2) of mass distribution with time were presented. These were based on observations from point releases of dye. Diffusivity, E , is defined as

$$E \equiv \frac{d}{dt} \frac{\sigma_{rc}^2}{4} \quad (3.1)$$

Based on the data, E can be defined as $E(\sigma)$, $E(t)$, or $E(\sigma, t)$, yielding equivalent (σ_{rc}^2) versus t behavior. In other words, E can be modeled as

$$E = a\sigma^m t^n \quad (3.2)$$

where $m = 0$ and $n = 0$ are special cases. Since the data used to obtain the relationships came from point source diffusion, use of any of the possible formulations gives an equivalent variance when a point source release is modeled. However, in the problem of relative diffusion between two sources with an initial separation distance, the subsequent separation depends on the relationship between the diffusivity and the separation distance (which is proportional to σ .)

Figure 3.3: Schematic of scale dependent diffusion (from Richardson [31]).

The scale dependent nature of natural turbulence was first described by Richardson [31]. Figure 3.3 is that used by Richardson[31] to describe the difference between Fickian diffusion, where E is constant, and the scale dependent diffusion that occurs in the environment. Illustrations 1, 2, and 3, represent a Fickian diffusion process. However in a turbulent environment, once the cluster reaches the size of the smaller eddies in the system it will begin to be sheared and spread by these eddies, so that the actual progression followed is better represented by the progression 1, 2, 4, 5. As it spreads larger, the scale of the eddies affecting the relative distribution increases.

Richardson proposed that the Fickian equation of diffusion be modified to allow the diffusivity to be a function of separation distance between particles, so that

$$\frac{\partial q}{\partial t} = \frac{\partial}{\partial l} (F(l) \frac{\partial q}{\partial l}) \quad (3.3)$$

where q is the density of neighbor particles with a given separation distance, l , and $F(l)$ is the separation distance dependent diffusivity. This formulation allows eddies of scales much larger than the separation distance to affect both particles equally, while smaller scale eddies have the ability to cause relative separation. The larger the separation distance, the larger the range of eddies that are involved in relative diffusion. Based on data related to atmospheric turbulence, Richardson proposed that $F(l)$ was proportional to the separation distance to the four-thirds power. Stommel [33] later provided empirical data suggesting that this four-thirds dependence was also applicable in the ocean, and presented theoretical justification for this dependence based on the Weisaeker-Heisenberg and Kolmogoroff theories.

In spite of the attractiveness of the "four-thirds law", empirical evidence analyzed by Okubo [29] (See Section 1.2.2) suggests that over large temporal and spatial scales the distance dependence is slightly less. As explained earlier, in the analysis of any tracer experiment, the diffusivity can be modeled as dependent solely on separation distance, solely on elapsed time, or some combination of the two factors. Because the mechanism of turbulence

Figure 3.4: Relative diffusion coordinate system.

seems most related to separation distance, Okubo's empirical formulation of length scale dependent diffusivity is used. This is consistent with Richardson's analysis as well as with current numerical modeling practice [13].

Okubo's expression is for an apparent diffusivity, that is, the average diffusivity over the time during which the diffusion has taken place. Because the diffusivity is defined as $\frac{1}{4} \frac{d}{dt} (\sigma_{rc}^2)$, for Okubo's formulation, at any given moment the actual diffusivity is 2.34 times this apparent diffusivity. Richardson proved that the average variance of the separation distance is twice the variance of the distribution. With these substitutions, the expression for diffusivity, Equation 1.2, becomes

$$E = 0.0017l^{1.15} \quad (3.4)$$

where E is actual diffusivity in m/s , and l is the separation distance in m .

In order to make this equation relevant to the problem at hand, the coordinate system must be defined in terms of relative separation and the adjustment must be made for the difference between the separation of two particles and the separation of a particle and a center of mass. If, as in Figure 3.4, one particle is defined as the x-coordinate axis, then the second will be located at a position y , which is identically the separation distance l . This system allows the distance neighbor form of diffusivity to be used in the context of space. The adjustment for separation between the particle and a center of mass can be made by representing the distance as half the distance between a particle and its image, since a particle starting out midway between the two would on the average remain midway between the two, and the center of mass of a concentration represents such an average. In this case, the particle defining the coordinate axis represents not the center of mass, but an image particle on the opposite side of the center of mass (See Figure 3.4).

If we let Richardson's density of particles at a separation distance, q , represent the probability, p , that a particle starting out with an initial separation, y_0 , is at a distance y ,

then Equation 3.3 becomes

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial y} \left(F(y) \frac{\partial p}{\partial y} \right) \quad (3.5)$$

with the initial condition $p(t = 0) = \delta(y - y_0)$ and boundary conditions $p(x = \pm \infty) = 0$. This equation can also be rewritten as

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial y} \left(\frac{\partial F}{\partial y} \right) = \frac{\partial^2}{\partial y^2} (F(y)p) \quad (3.6)$$

where $\frac{\partial F}{\partial y}$ is the apparent or "pseudo" velocity.

3.4 Stochastic Simulation

Although no general analytical solution exists for Equation 3.5, individual organism paths can be simulated using a Monte Carlo approach. In this case, organisms would experience both an appropriate pseudo velocity and a random walk diffusion component that accounts for the variable diffusivity. For each organism path simulated, the concentration experienced at every point in time would then be determined from the spatial distribution of pH. Each experience could then be integrated over time as described in Section 3.2 to find a mortality for that organism, or representative small group of organisms. Because of the random nature of the simulation, a large number of organisms would have to be tracked from each starting point to constitute a complete description of the impact, and the mortality would have to be calculated separately for each experience.

In order to capture the essence of this method with somewhat less computation, the plume area was divided laterally into lanes. The width of the lanes is based on the transverse pH variation, so that the pH at the centerpoint of each lane represents adequately the pH at any point in the lane. Enough lanes are included that any organism entering through the outer boundary can be assumed to have the same (zero) experience as any organism that had gone that far out and come back. A time step was chosen based on the pH variation with time (distance); the shortest time step needed was one day. The grid set up for the one plant droplet plume scenario is superimposed on the pH contours in Figure 3.5. A random walk simulation was performed for a uniform distribution of organisms entering each lane. The time step in the random walk model was determined by the distance between the organism and the center of the plume and was on the order of minutes. From these simulations, the probability that an organism will be in a given lane, j , one time step after it starts from an initial lane, i , was determined for all combinations of i and j .

The experience along all sets of travel paths was calculated, so that the mortality at any given point would be the sum of the mortality along a particular path times the number of organisms expected to have traveled that path. When the number of pathways became too large, the experiences were grouped according to stress level (i.e. equivalent hours at a given pH), and the probabilistic journey of each set of organisms was continued.

This method captures the non-linearity of the effect of pH-experience on mortality because it avoids averaging very different experiences. Furthermore, it provides not only a total

Figure 3.5: Detail of grid used for probabilistic simulation of one plant droplet plume scenario.

mortality from the plume but also a spatial map of the deficit of zooplankton at a point. The magnitude and extent of this deficit may be an important measure of impact.

In cases where vertical diffusion is important, the plume area could be discretized vertically, and the probabilistic simulation could include the vertical component using either a constant or a length-scale dependent diffusivity.

3.5 Compensation and Intergenerational Effects

Mortality due to pH perturbations can be calculated using probabilistic simulation and the method of stress integration described; however, this model includes no compensation mechanism to account for the fact that relatively unstressed organisms will reproduce and that depleted populations, once no longer significantly stressed, will recover. In order to account for recovery, the logistic equation for density limited population growth is used [7]. The simplest form for a single species population is:

$$\frac{dN}{dt} = rN\left(1 - \frac{N}{K}\right) \quad (3.7)$$

where N is the number of organisms, r is the growth rate with unlimited resources, and K is the equilibrium or "carrying capacity" (number) for the species considered. Organism concentrations (densities) can be considered by dividing N or K by a reference volume. $(1-N/K)$ is the fractional deficit that is calculated.

In order to keep the calculations as general as possible, the equation was normalized by

Figure 3.6: Maximum achievable growth rate, r , as a function of pH.

the equilibrium population, so that

$$\frac{d}{dt} \frac{N}{K} = r \frac{N}{K} (\text{deficit}) \quad (3.8)$$

where N/K is the concentration of organisms as a fraction of the equilibrium concentration. No assumption is needed about the magnitude of K . A growth rate, r , is still needed, and that of the copepod was used since it is the most abundant organism at the depths considered. The growth rate used (0.09/day) is taken from laboratory observations of surface organisms; however, Kinne [15] notes that, "in general, within a given group, deep-living species tend to have a slower turnover, produce less offspring, live longer, and so on." Under stress both the growth rate and the equilibrium population would be expected to be depressed, but this effect is difficult to quantify. For simplicity, K has been treated as a constant. Compensation has been modeled as zero while the population is in a relatively stressed environment ($\text{pH} < 7.35$), after which the maximum achievable net growth rate increases linearly to the observed laboratory value at a pH of 7.5, allowing for depressed populations to recover. These simplifications are not expected to produce great uncertainties since, in general, the high potential growth rate of copepods limits the time needed for recovery to only a fraction of the time spent in the plume.

The most severe limitation of the logistic equation is that it deals with a single species in a stable environment, whereas the real situations of interest deal with interacting species in a changing environment. In the event that the plume affects some organisms more severely than others for a substantial period of time, the equilibrium species composition could change. It has been noted that most populations can change behavior or physiology to survive a perturbation with a time scale less than the generation time [37]. For most of the plumes studied the length of the perturbation is expected to be less than the generation time of the majority of organisms, so that long term effects are not expected unless

currents or active migration lead to the same populations of organisms being continuously swept through the same plume. Another limitation is that the equation treats all age classes equally, whereas some are more important to the reproduction, and hence survival, of the species. Also, although reproduction is a process with a finite time scale, no time lags are considered. With the appropriate data, the model could certainly be refined; however, the required data are not available and the model, despite its limitations, provides a reasonable method to quantify the scale of impact.

For surface living copepods the generation time measured in laboratory experiments is about 40 days [15]. The 10 plant plumes tend to maintain stressful pH levels for periods longer than this generation time, although only the duration of 10 plant dense plume is longer than twice this time. Since the organisms live at depth and are under stress, the generation time in situ would be expected to be longer, and many other organisms of interest have longer generation times. The affected area is also rather narrow, so that substantial diffusion in and out of the plume is also expected over a generation time. In the presence of these uncertainties and in the interest of generality, it was decided not to account explicitly for successive generations within the plume. Instead, the mortality calculation was extrapolated over the duration of the plume. This would tend to lead to a slight underestimate of the mortality, the magnitude of which would tend to increase with duration of the plume.

3.6 Organism Experience for Scenarios Analyzed using the Stochastic Approach

Because the exposures due to the dispersion methods (dry ice and towed pipe) are so short, this approach predicts no mortality. For the droplet plume and the dense plume, a finite mortality results that is both scenario and scale dependent.

3.6.1 Droplet Plume Organism Experience

The results of the stochastic method for the base case one plant droplet plume scenario are illustrated by the map of zooplankton deficit in Figure 3.7. One important result is that the maximum deficit is only about 10% of the total population at any point. There is a delay due to the fact there is a threshold exposure below which there is no mortality (Line LC_0 in Figure 3.1). Because in this scenario, this delay is a substantial fraction of the exposure time, the dead organisms are reasonably well spread out.

In the corresponding ten plant droplet plume scenario (see Figure 3.7), the deficit reaches much higher levels, persists for about six times as long, and extends for ten times the width. By any measure, the impact is more severe than ten times the impact of the one plant case. This is largely due to the fact that many of the exposures in the droplet plume case were just under the mortality threshold, while the additional exposure due to greater loading in the ten plant case brings a large number of organisms into stress levels where additional exposure time leads to relatively high mortality. (See Figure 3.2)

Figure 3.7: Fractional deficit of zooplankton in a horizontal place at 1000 m depth caused by the base case one plant droplet plume scenario (top). Fractional deficit of zooplankton in a horizontal place at 1000 m depth caused by the base case ten plant droplet plume scenario (bottom). Discharge point is at 0,0.

3.6.2 Dense Plume Organism Experience

Because the base case one plant dense plume has higher initial concentrations and a longer duration than the one plant droplet plume, the majority of organism experiences do fall above the mortality threshold. As a result the level of mortality and the corresponding deficit are much higher. Figure 3.8 (top) illustrates the resulting zooplankton deficit using the stochastic method to evaluate the one plant base case dense plume scenario. One important result is that an area of the plume exists with greater than 40% mortality. The area with greater than 5% mortality is also very large. Comparing the results with that of the one plant droplet plume demonstrates the importance of injection method for releases of this size.

The results of the ten plant base case scenario are shown in Figure 3.8 (bottom). The impact of this release is very severe in the region around the release— the spatial zooplankton deficit reaches 95%. Such high spatial deficits are only possible in scenarios where there is a significant area with relatively low pH. Reexamining the pH-mortality curves (Figure 3.1) or Figure 3.2 illustrates how, even at long times, a pH of less than about 6.3 is needed to cause such high mortality. This plume is more persistent and much wider than either the one plant dense plume or the ten plant droplet plume.

3.7 Other Possible Approaches

3.7.1 "Average Path" Experience

Because the stochastic method— even with discretized lanes— is computationally intensive, different formulations of an "average" experience were attempted. These methods attempted to take into account the fact that on the average, organisms would tend to move away from the plume centerline, but did not attempt to distinguish between paths taken by different organisms entering the plume area at the same distance from the plume centerline.

One approach was to simply use the pH experience at the average particle position to represent the experience for all organisms passing through the plane of injection at a given distance, y_o , from the plume centerline. This average position was determined by integrating the pseudo velocity described earlier.

3.7.2 "Averaged" Experience

A variation of this method was to use the probability distribution of the separation distance. When this information is combined with the spatial distribution of pH, the experience can be integrated spatially to obtain a representative pH at every point in time for a given entrance position. The plane perpendicular to the current at the point of injection is discretized into "lanes" with the average experience of the flux through the area being characterized by the experience of an organism entering at the center of the area (y_o, z_o). In this description, the x coordinate is a representation of time, since $x = ut$ where u is the current velocity and t is time. Vertical diffusion is neglected compared with horizontal diffusion, and the result is one-dimensional diffusion in the y -direction. For the entrance position and point of time

Figure 3.8: Fractional deficit of zooplankton in a horizontal plane at 1000 m depth caused by the base case one plant dense plume scenario (top). Fractional deficit of zooplankton in a horizontal plane at 1000 m depth caused by the base case ten plant dense plume scenario (bottom). Discharge point is at 0,0.

chosen, the average concentration can be expressed as,

$$\bar{c}(y_o, z_o, t) = \int c(y, z_o, x/u)p(y, z_o, x/u)dy \quad (3.9)$$

This average experience can then be integrated with respect to time (see Section 3.2) to give an "average" mortality for organisms that enter at a given distance from the plume centerline.

Unfortunately, because mortality is a non-linear function of pH exposure (Figure 3.1), this method and the "average path" method suffer from the problem that the result depends on the designation of the initial plane. This can be shown by redefining the initial plane further back from the plume release point. The distributions at every point within the plume would become wider, which would result in higher average pH. One could imagine a case where the initial plane was defined far enough back that all distributions would include enough low concentrations that all exposures would fall below the mortality threshold. Another way of looking at it is that this probability average ignores spatial correlation. An organism that is closer to the plume centerline at one moment is more likely to be closer to the plume centerline at the next. Again, since the effect of pH is non-linear, averaging this experience with another that is further away from the plume centerline during the same time period would underestimate the effect on the population.

3.7.3 Non-Diffusive Transport

The above procedures not only introduce inaccuracies in the calculations, but also do so differentially for the various scenarios. For example, because the duration of the ten plant dense plume scenario is much longer than the other scenarios, the inaccuracy due to large spatial organism distributions is larger than in the other scenarios. For this reason, a less partial and relatively conservative method for estimating mortality was also explored. This estimate can be obtained by taking the experience of an organism maintaining constant separation distance as it travels through the plume. It is impartial in that all plumes are sampled equally; however, for plumes of low duration its mortality predictions tend to be high, while for very persistent plumes the predictions are low. This is simply due to the shape of the pH-mortality curves; the effect of an additional exposure at a given pH depends on past experience. For shorter plumes the additional exposure to a smaller group of organisms may lead to significantly increased mortality relative to the actual case of a more widely sampled plume where more organisms may be stressed but many will not reach the mortality threshold. In the longer plumes the additional exposure to the small group of organisms assumed would cause less mortality than the same exposure to additional organisms that had migrated into the plume and are still at stress levels where a small additional exposure causes significant increase in mortality.

3.8 Scenario Comparison

If the criteria of zooplankton deficit is to be used, it remains to be determined what deficit levels and volumes are critical. The results of the various scenarios as seen through this filter

	Integrated Total	Maximum Mortality	Highest Spatial
	Mortality (km^3)	Flux (m^3/s)	Deficit (percent)
Dry Ice			
1 plant	0	0	0
10 plants	0	0	0
Towed Pipe			
1 plant	0	0	0
10 plants	0	0	0
Droplet Plume			
1 plant	0.45	307	11
10 plants	162	27500	69
Dense Plume			
1 plant	11	1980	50
10 plants	800	46900	95

Table 3.1: Summary of expected zooplankton mortality for various base case plumes

are shown in Table 3.1. Mortality flux and integrated total mortality represent mortality as equivalent flow rates and volumes, respectively, for which all contained organisms would be lost. Integrated total mortality comes from integrating the deficit over the volume affected, while mortality flux represents the integration of the deficit of the flow passing through a given vertical plane. The maximum mortality flux occurs just before compensation begins, while the total integrated mortality continues to grow until the population recovers completely. For ecosystem level effects the maximum spatial deficit may be an important measure.

As mentioned previously, all experiences in the dispersion scenarios (dry ice and a towed pipe) are short enough to come under the mortality threshold. For the one plant droplet plume, many pathways led to experiences that were also below the mortality threshold, but those organisms that experienced much of the center of the plume suffered significant mortality.

Using the total integrated mortality as a measure of impact, the one plant dense plume case is much more severe than the one plant droplet plume case (about 20 times the total mortality); the relative difference between the ten plant cases is much less, although still significant (5 times). Within a scenario, the effect of a ten plant case is more than that of ten one plant cases; however, the relative difference between the droplet plume cases is much more severe than that between the dense plume cases. This is largely due to the fact that exposures for the one plant droplet plume are near the mortality threshold.

Comparing the physical descriptions of the plumes from Table 2.1, with the biological impacts assessed in Table 3.1, it can be seen that although there is clearly a relationship between the size of the plume and the resulting mortality, the exact nature of this relationship is not at all obvious. For this reason, the relationship between plume size and resulting mortality is explored in Chapter 4, with particular attention paid to the area around the mortality threshold.

Chapter 4

Impact Model Sensitivities

Although scenario-specific sensitivities related to the physical dimensions of the plumes were explored in Chapter 2, this chapter analyzes more general sensitivities in terms of biological impact. The sensitivity of predicted mortality to the pH-Mortality curves chosen is explored in Section 4.1. Section 4.2 illustrates the factors that correlate most strongly with impact, in Section 4.3 the differences among the base cases are explained in terms of these parameters, and in Section 4.4 ways of eliminating the near-field impact of the droplet plume are explored.

4.1 Sensitivity to pH-Mortality Curves

Since all the physical information is being passed through a biological filter, it is necessary to determine how sensitive the results are to changes in the pH-time-mortality relationships. One quarter of a pH unit is the safety factor that was built into the curves to account for sublethal effects not measured in the studies on which the curves were based. Although it is possible that the actual shape of the curves may be slightly different than that modeled, the simplest test of sensitivity comes from moving the curves by a quarter of a pH unit in either direction. Even with an additional quarter of a unit of pH, the organism experience with either the dry ice or towed pipe scenarios are both too short to have an impact. The results for the dissolution scenarios are shown in Table 4.1.

As expected, lowering the pH curves by a quarter of a unit (raising them on the graph in Figure 3.1), decreases the mortality for all scenarios. This is the level of impact that would have resulted if possible sublethal effects had been neglected in drawing the curves. As might be expected from Figure 3.2, the results are most sensitive for the smaller plumes with more exposures around the zero-mortality threshold than for the longer plumes. With these optimistic curves, the integrated total mortality for the one plant droplet plume is only 7% of the base case value, for the one plant dense plume it is about one-third of the base case, while for the ten plant plumes, the mortality is about a half of that in the base case.

When the pH values of the mortality curves are increased by a quarter of a pH unit, greater total mortality results. Again, the largest relative change occurs for the one plant droplet plume scenario (over four times the mortality) followed by the other plumes in order of severity, 1.6, 1.5, 1.4 times the base case scenarios for the one plant dense, ten plant droplet, and ten plant dense plume respectively.

	Integrated Total	Maximum Mortality	Highest Spatial
	Mortality (km^3)	Flux (m^3/s)	Deficit (percent)
	<i>Base Case</i>		
Droplet Plume			
1 plant	0.45	307.00	11
10 plants	162.00	27500.00	69
Dense Plume			
1 plant	10.60	1980.00	50
10 plants	800.00	46900.00	95
	<i>with .25 decrease in pH curves</i>		
Droplet Plume			
1 plant	0.03	19.00	0.86
10 plants	72.80	12650.00	50
Dense Plume			
1 plant	3.40	730.00	32
10 plants	387.00	23070.00	79
	<i>with .25 increase in pH curves</i>		
Droplet Plume			
1 plant	2.06	1221.00	30
10 plants	248.00	47890.00	87
Dense Plume			
1 plant	17.00	3985.00	69
10 plants	1113.00	77210.00	99

Table 4.1: Sensitivity of integrated mortality and maximum mortality flux to the determination of the pH-Mortality curves for the base case dissolution scenarios.

Figure 4.1: Steps for determining biological impact from injection scenario.

For the larger plumes, it is unlikely that the results are off by more than a factor of two due to inaccuracies in the pH-curves used. The smaller plumes are more sensitive because of the importance of the threshold.

4.2 Measures of Plume Severity

Due to the large number of environmental conditions, model parameters, and engineering design factors, and because the amount of computation involved in the biological assessment is substantial, it is impractical to model all possible scenarios. One approach is to try to summarize the extent of the plume with a few physical dimensions, and to determine how these dimensions affect the biological impact.

Figure 4.1 illustrates the various steps taken to predict the biological impact from a given injection scenario. Various environmental and design parameters, including the size of the independent injection, are used to determine the near field dilution and the thickness of the intrusion layer. At this point the scenario can be summarized in terms of a mass loading

Figure 4.2: Relationship between time to a centerline pH of 7 and total mortality. For each simulation total mortality is the product of the mortality per injection and the number of independent injections needed for the emissions from one standard power plant. The black points come from simulations using the base case diffusivity relationship. The hollow points reflect scenarios with half the base case diffusivity. The gray points reflect a diffusivity of one-third of the base case. Initial concentrations are represented by shapes: triangles represent an initial concentration of 0.07 kg/m^3 , squares of 0.13 kg/m^3 , circles of 0.20 kg/m^3 , and diamonds of 0.30 kg/m^3 . Variation among points with the same diffusivity and initial concentration is due to variation in mass loading.

per area, where the mass loading per area is defined as the mass rate of CO_2 divided by the product of the vertical thickness and current speed. If the discharge consists of more than one independent injection (e.g. the discharge is through several groups of ports with large spatial separation between groups), then the loading per injection is used. Mean loading is an important value, since for a given turbulence level, it will determine the width at which the plume has no impact.

The next step in the process is to apply the far field model and the chemical equations to determine the physical and chemical dimensions of the plume. As demonstrated below, these can be fairly well summarized by a centerline time to pH 7. The impact model is then used to determine the probability and mortality associated with the possible organism pathways. The overall impact is the sum of the impact assessed for each pathway. It is this biological evaluation that requires extensive calculation.

In order to demonstrate the correlation between the centerline time to pH 7 and the total integrated mortality predicted for each power plant's worth of emissions, these two values are plotted in Figure 4.2 for simulations involving a range of initial concentrations, independent

mass loadings, and parameterizations for ambient diffusivity.

The most important result is that the correlation of mortality with time to centerline pH of 7 is quite strong. The primary factors that contribute to this time are mass loading and ambient diffusivity. For a diffusivity,

$$K = \frac{d \sigma^2}{dt} = a \sigma^n \quad (4.1)$$

where σ is the standard deviation, a is a constant, and n is the exponent that reflects the time dependence of the diffusivity, then

$$t = \frac{\sigma_f^{2-n}}{a(2-n)} - \frac{\sigma_o^{2-n}}{a(2-n)} \quad (4.2)$$

where σ_f is the final σ , and σ_o is the initial σ . If a σ_7 is defined as the width at which the centerline pH reaches 7, and C_7 is the concentration associated with a pH of 7, then

$$\sigma_7 \cong \frac{\dot{m}}{u h C_7} = \frac{\text{Mass Loading}}{C_7} \quad (4.3)$$

where the mass loading is $\frac{\dot{m}}{u h}$.

Since C_7 is fixed, t rises steeply with increasing mass loading for a given parameterization of diffusivity. This dependence is illustrated in Figure 4.3, which plots the time to pH 7 versus the mass loading for scenarios with different diffusivity parameterization. Increasing turbulence (a or n) leads to a decrease in t for the same mass loading. Scenarios with different initial concentrations are included; however this effect is secondary because the initial concentration only contributes to the σ_o , which is dwarfed by the σ_7 in most scenarios that lead to mortality.

Looking at Figure 4.2 again, some of the variation in the mortality resulting from the same time to pH 7 can be explained. Near the zero-mortality threshold, scenarios with higher ambient diffusivity but the same time to a centerline pH of 7 have more severe impact since their experience would have included some experience at lower pH. For more severe scenarios, the duration of the average organism experience becomes more important, and this is influenced by both the width and the duration of the plume. Plumes with higher ambient diffusivity but the same time to a centerline pH of 7 tend to be thinner, so that organisms are more likely to diffuse out of the plume and have a shorter average experience in spite of the longer duration of the plume. Whether more impact results from more organisms having a shorter experience, or less organisms having a longer one, depends on the levels of stress that are involved.

For scenarios with the same turbulence parameterization and the same time to pH 7, the cases with lower initial concentrations tend to lead to higher mortality. This reflects the fact that for a lower initial concentration to take the same time to reach a centerline pH of 7 in a similar environment, the mass loading, and hence the final width, must be greater. This leads to organisms spending longer times in the plume, and in the area near the zero-mortality threshold, this leads to higher overall mortality.

Since the ambient turbulence and current speed are determined by site, the point at which engineering design can have the most impact is in lowering the mass loading. Working

Figure 4.3: Time to centerline pH of 7 versus mass loading per area for scenarios with various levels of ambient turbulence. The black points come from simulations using the base case diffusivity relationship. The hollow points reflect scenarios with half the base case diffusivity. The gray points reflect a diffusivity of one-third of the base case. Initial concentrations are represented by shapes: triangles represent an initial concentration of 0.07 kg/m^3 , squares of 0.13 kg/m^3 , circles of 0.20 kg/m^3 , and diamonds of 0.30 kg/m^3 .

Figure 4.4: Mortality flux due to the base case scenarios.

with a mass loading also facilitates comparison between plumes in different current speeds. The effect of current speed is only important in determining the initial loading; thereafter diffusion occurs in the lateral direction and consequently is not affected by current speed. If we consider the development of plume concentrations in the moving frame of the current (as they are seen by an organism moving through) there is no difference between two plumes with the same initial distribution but different current speeds.

In a given environment, impact can only be reduced by decreasing mass loading. This can be done by having smaller independent injections, increasing the thickness of the intrusion layer or increasing the number of intrusion layers. Of these three options, the simplest one is increasing the number of independent injections. Section 2.2.3 discusses the uncertainties around the ultimate thickness of the intrusion layer formed, and possible leverage points. Section 2.2.2 discussed some of the factors that might influence the number of intrusion layers that form; however these are only hypotheses at this point, and experimental data are needed.

4.3 Another Look at the Base Case Dissolution Scenarios

The base cases of the one and ten plant droplet and dense plumes have been plotted against the maximum mortality flux in Figure 4.4. It can be seen that the dense plume cases are more serious than the corresponding droplet plume cases. Although the initial concentrations are

Figure 4.5: Total integrated mortality due to the base case scenarios.

higher, this affects only a small number of organisms and is not the most important factor. The major difference stems from the different environment in which the dense plume is modeled. Because it will intrude along the slope over which it descends, it is modeled as one half of a symmetrical distribution, and so the effective independent mass loading is twice that of a similar droplet plume. This effect, however, does not completely explain the difference, since it has been taken into consideration in the plot in Figure 4.4 and the different injection methods still do not lie on the same curve. In addition to increasing effective mass loading, diffusion along a slope decreases effective diffusivity, diffusion along a slope decreases effective diffusivity, since diffusivity is based on the actual width of the plume. The droplet plume, on the other hand, is modeled as diffusing in the open ocean. If the droplet plume were sited or designed in such a way that its diffusion were similarly limited, i.e. along a steep slope or with diffuser conditions that led to the intrusion layer forming very close to the bottom, the results would be similar to those of the dense plume.

Another way to compare plume impact is through total integrated mortality per plant, as in Figure 4.5. Even though longer exposure times begin to show diminishing returns in terms of mortality flux for the more severe scenarios (See Figure 4.4), the other dimension of impact is spatial persistence. Comparisons between total integrated mortality take this into account, since compensation only begins to occur as pH reaches ambient levels, and the deficit is integrated over the distance for which the plume persists.

The trend with almost any measure of impact is that increasing the size of each independent release increases the impact even when normalized to the size of a standard plant.

Figure 4.6: Schematic of independent droplet plume injections. The required horizontal spacing is λ_h , and the required vertical spacing is λ_v .

Greater initial dilution lessens impact, but the most important design factor is the mass loading per area. Current speed and ambient turbulence are site specific environmental factors that are critical in determining impact.

4.4 Implication for a droplet plume scenario

If the most important measure of impact is zooplankton mortality, this research suggests that it is possible to eliminate near field impact of ocean disposal of CO_2 using a dispersion method, or a dissolution method in which emissions are distributed in independent releases of less than one power plant's worth of emissions.

Because of the nature of the dense plume, such small releases would not be effective in achieving sinking; however, there are possible solutions using the droplet plume method. Independent releases can be achieved through vertical and/or horizontal separation of ports or groups of ports. Vertical separation is preferable since it is independent of current direction. Figure 4.4 demonstrates possible spacing for independent injections. The required horizontal spacing is λ_h , and the required vertical spacing is λ_v . Either would be sufficient for the injection to be considered independent.

The characteristics of the site are critical, with high ambient turbulence and current speed preferable. If the base case parameters of this study apply, i.e. a 5 cm/s current and turbulence similar to that parameterized by Okubo, then slightly more than two independent releases per power plant would eliminate mortality. This could be accomplished by 23 meters of vertical separation between releases, and/or 8.6 kilometers of horizontal separation. If the slope is greater than about 3%, vertical separation is easier to achieve. Table 4.2 show the

	Height of	Number of	Horizontal	Vertical
	layer	Plants	spacing	spacing
	(m)		(km)	(m)
Base case	5	0.47	8.6	23
Diameter of 0.6	-15	0.48	8.8	23
Diameter of 1.0	25	0.46	8.2	23
Injection at 800 m	14	0.40	8.2	23
Current of 2 cm/s	5	0.08	8.6	9.2
Current of 10 cm/s	5	1.8	8.6	45
Transition model	5	0.21	5.3	10.5
Two intrusions*	5	0.94	8.6	23
1/3 Diffusivity	5	0.08	1.5	23
Mass transfer*0.5	54	0.57	10.5	23
Mass transfer*0.1	139	0.58	10.7	23

Table 4.2: Effect of various parameters on injection size and spacing needed to achieve zero mortality. *For the two intrusion case, the depth given is for the lower layer.

different separation distance and injection rates necessary to achieve the same result with different environmental conditions, design factors and parameterizations.

The base case involves injection of 0.8 cm droplets at a depth of 1000 meters. No reduction in mass transfer due to hydrates is assumed. An increase in initial radius to 1.0 cm improves dilution; however, the most important effect is to insure that the intrusion layer is trapped a sufficient distance above the ocean floor. Smaller diameters are infeasible. Injection from 800 meters would help to maintain the intrusion layer above the ocean floor, but would possibly jeopardize the sequestration potential of the scenario.

A faster current would allow larger injections, while a smaller one would require smaller injections. The horizontal separation distance required does not change as it is based only on mass loading per area, which remains the same. The vertical thickness assumed increases with current; however, this effect may be exaggerated by the choice of the transition point. Using the alternative criteria for transition, where gravitational collapse is allowed to continue until the horizontal spreading due to diffusion is equal to that due to gravitational spreading, demonstrates the importance of this choice. Compared with the base case, the resulting thickness would be reduced by a factor of two and the injection rate would need to be reduced proportionally. Formation of more than one intrusion layer has the opposite effect.

A lower ambient diffusivity than that assumed would have serious implications for the injection scheme. If diffusivity were one-third of that assumed in the base case, the number of independent injections per plant would need to be increased by a factor of six.

When the mass transfer coefficient was reduced by a factor of two, the resulting intrusion layer is more dilute and traps significantly higher. Because of the low initial concentration, the maximum mass loading was increased slightly, leading to a slight decrease in the number of independent injections needed per plant. For the case where the mass transfer coefficient was assumed to be only one-tenth of that of the base case, the injection depth chosen was

1200 meters and the initial droplet size was chosen to be 0.4 cm to lead to an intrusion layer at a similar depth to the base case.

Chapter 5

Summary, Conclusions, and Recommendations for Future Research

5.1 Summary

The purpose of this study was to evaluate the environmental impact of ocean disposal of carbon dioxide and to determine which factors most influence its severity. In order to achieve this goal, several possible injection scenarios and mass loadings were modeled. These included dispersion scenarios such as dry ice cubes and a towed pipe, as well as the dissolution options of both droplet and dense plume scenarios. The resulting spatial maps of pH were generated for all of the base cases studied. The effect of variation of different design parameters on the distribution was explored.

The plume volume was then discretized into lanes and time steps, and a random walk model accounting for the scale-dependent nature of relative diffusion was used to simulate the paths of the organisms over one time step. From these simulations, the probability that an organism will be in a given lane, j , one time step after it starts from an initial lane, i , was determined for all combinations of i and j . These probabilities were used to find the number of organisms following each of the possible pathways, and the mortality to the organisms in the group due to their time varying exposure to low pH was determined by using a toxicity model (As described in T.R. 5). This method allows the impact of the plume to be described in terms of total organism mortality as well as spatial deficit of organisms.

Sensitivity to the plume and toxicity models, environmental conditions, and the scale of the release was also explored, and key environmental and design parameters were identified. Recommendations for reducing impact are summarized below.

5.2 Conclusions

Because pH is a stress with a threshold effect, it is possible to design injection scenarios that result in zero mortality. The biological impact assessment performed predicts no impact for

the dispersion methods considered, even with the most pessimistic assumptions about the disposal environment. The dissolution methods studied all yield impacts for the base case scenarios. The results are non-linear with the impact per plant increasing with the size of the effective CO₂ injection; e.g. the impact from disposing of the CO₂ emissions from ten plants is more than ten times the impact from a single plant.

Because the dissolution methods are not as energy and maintenance intensive as the dispersion methods, they may be preferable if they can achieve a similar level of impact. This can be achieved by increasing either the number of independent injections per plant or the thickness of the resulting intrusion layer. Several sets of conditions lead to experiences that fall below the mortality threshold. For example, a flow rate of about one half of the standard 500 MW_e coal-fired power plant emissions injected as a droplet plume under the base case conditions is predicted to have no impact if it is separated from a similar injection by at least 23 meters of vertical distance or 8.6 kilometers of horizontal distance. As long as each injection is independent (See Section 4.4), near field effects can be avoided.

For a given injection, the two most important environmental factors are ambient turbulence and current speed. To minimize impact, the disposal site should be chosen so that both are as large as possible.

5.3 Recommendations for further research

In analyzing the impact due to the various scenarios, many assumptions had to be made. For most, the sensitivity, the uncertainty or both is small; however, there are several that warrant further study before any plans for ocean disposal of CO₂ go forward.

Environmental parameters Because ambient turbulence is so critical in determining impact, it is important to have more information on the level and scales of ambient turbulence at the depths under consideration. The same is true of current speeds at depths greater than 1000 meters, preferably at possible injection sites.

Droplet Plume More research into the dynamics of peeling plumes is necessary. In particular, at what elevations in the plume do peeling events occur, what fraction of the flow and the buoyant flux peel during each event, and how much mixing occurs as the peeled water sinks to its level of neutral buoyancy. To minimize impact, the intrusion layer must form above the ocean floor. To optimize design, it is necessary to know how the waters that peel off at different elevations interact, and how many intrusion layers are expected to form.

The presence of clathrate hydrate could have a significant effect on the mass transfer from the droplets, and consequently the height to which the plume rises, and traps, and the level of dilution which occurs. Further research on clathrate hydrate formation in conditions similar to those expected in the droplet plume is necessary before the number and trap height of the intrusion layers can be predicted with confidence.

Dense Plume In terms of the expected sinking of the dense plume, the most important uncertainty concerns the magnitude of the drag coefficient and its relationship to entrain-

ment for high Richardson number flows. Before such a method could be implemented the topographic conditions of the possible site would also have to be determined.

Bibliography

- [1] E. E. Adams, D. Golomb, X. Y. Zhang, and H. J. Herzog. Confined release of CO_2 into shallow seawater. In N. Handa and T. Ohsumi, editors, *Direct Ocean Disposal of Carbon Dioxide*, pages 153–164. Terra Scientific Publishing Company, Tokyo, Japan, 1995.
- [2] V. Alavian. Behavior of density currents on an incline. *Journal of Hydraulic Engineering*, 112:27–42, 1986.
- [3] David I. Auerbach. Global warming mitigation via ocean disposal of power-plant-generated CO_2 : An environmental and political analysis. Master's thesis, MIT, Department of Civil and Environmental Engineering, June 1996.
- [4] Charles L. Bretschneider. Hurricane design winds and waves and current criteria for potential OTEC sites. Technical report, James K. K. Look Laboratory of Oceanographic Engineering, University of Hawaii, Honolulu, Hawaii, 1980.
- [5] N.H. Brooks. Diffuser of sewage effluent in an ocean current. In *Proc. 1st International Conference on Waste Disposal in the Marine Environment*, pages 246–267. Pergamon Press, 1960.
- [6] R. Clift, J. R. Grace, and M. E. Weber. *Bubbles, Drops, and Particles*. Academic Press, New York, 1978.
- [7] Paul Colinvaux. *Ecology*. Wiley and Sons, New York, second edition, 1986.
- [8] H. Drange, G. Alendal, and P. M. Haugan. A bottom gravity current model for CO_2 -enriched seawater. *Energy Conversion and Management*, 34:1065–1072, 1993.
- [9] H. Drange and P. M. Haugan. Carbon dioxide sequestration in the ocean: the possibility of injection in shallow water. *Energy Conversion and Management*, 33:697–704, 1992.
- [10] Daniel Frye, Allan Davison, and Karen Leavitt. Physical oceanographic data from the OTEC Punta Tuna, Puerto Rico site, September 1979 - June 1980. Technical Report LBL-12327 UC-64, Lawrence Berkeley Laboratory, University of California, Berkeley, 1981.
- [11] S. Hirai, K. Okazaki, N. Araki, H. Yazawa, H. Ito, and K. Hijikata. Transport phenomena of liquid CO_2 in pressurized water flow with clathrate-hydrate at the interface. IEA Greenhouse Gas Programme, 1995.

- [12] Shuichiro Hirai, Ken Okazaki, Yutaka Tabe, Kunio Hijikata, and Yasuo Mori. Dissolution rate of liquid CO₂ in pressurized water flow and effect of clathrate film. Submitted 1996.
- [13] A. D. Jenkins. Simulation of turbulent diffusion using a simple random model of the flow field. *Applied Mathematical Modelling*, 9:239–245, 1985.
- [14] Gerhard H. Jirka, Janet M. Jones, and Frank E. Sargent. Theoretical and experimental study of the intermediate field dynamics of ocean thermal energy conversion plants (progress report 1978-1979). Technical report, Cornell University, Ithica, N.Y., 1980.
- [15] Otto Kinne. *Marine Ecology: A Comprehensive, Integrated Treatise on Life in Oceans and Coastal Waters V.4*. Wiley-Interscience, New York, 1978.
- [16] J. R. Ledwell and A. J. Watson. Evidence for slow mixing across the pycnocline from an open-ocean tracer-release experiment. *Nature*, 364:701–703, 1993.
- [17] C. R. Liro, E. E. Adams, and H. J. Herzog. Modelling the release of CO₂ in the deep ocean. Technical Report MIT-EL 91-002, Energy Laboratory, M.I.T., 1991.
- [18] V. M. Litvin. *The Morphostructure of the Atlantic Ocean Floor*. D. Reidel Publishing Company, Boston, MA, 1984.
- [19] K. Lofquist. Flow and stress near an interface between stratified liquids. *Physics of Fluids*, 3:72–182, 1960.
- [20] Frank J. Millero. Thermodynamics of the carbon dioxide system in the oceans. *Geochimica et Cosmochimica Acta*, 1994.
- [21] Robert L. Molinari, Dennis Mayer, and Frank Chew. Physical oceanographic conditions at a potential OTEC site in the Gulf of Mexico; 88°W, 29°N. Technical Report ERL AOML-41, National Oceanic and Atmospheric Administration, Miami, Florida, 1979.
- [22] Francois M. M. Morel and Janet G. Hering. *Principle and Applications of Aquatic Chemistry*. John Wiley & Sons, New York, NY, 1993.
- [23] N. Nakashiki, T. Ohsumi, and N. Katano. Technical view on CO₂ transportation onto the deep ocean floor and dispersion at intermediate depths. In N. Handa and T. Ohsumi, editors, *Direct Ocean Disposal of Carbon Dioxide*, chapter 21. Terra Scientific Publishing Company, Tokyo, Japan, 1995.
- [24] Norikazu Nakashiki and Takashi Ohsumi. Simulation of the near-field behavior of CO–2 from a source on the deep-sea floor. In *Proc. of The Int. Symp. on CO₂ Fixation & Efficient Utilization of Energy*, pages 331–336. 1993.
- [25] Norikazu Nakashiki, Takashi Ohsumi, and Kiminori Shitashima. Sequestering of CO₂ in a deep-ocean. Technical report, Central Research Institute of Electric Power Industry, 1646 Abiko, Abiko-City, Chiba 270-11, JAPAN, 1994.

- [26] T. Ohsumi, N. Nakashiki, K. Shitashima, and K. Hiramama. Density change of water due to dissolution of carbon dioxide and near-field behavior of CO₂ from a source on a deep sea floor. In *Proc. of The Int. Symp. on CO₂ Fixation & Efficient Utilization of Energy*, pages 331–336. 1993.
- [27] Takashi Ohsumi. Prediction of solute carbon dioxide behavior around a liquid carbon dioxide pool on deep ocean basins. *Energy Conversion and Management*, 34:1059–1064, 1993.
- [28] Takashi Ohsumi. CO₂ disposal options in the deep sea. *Marine Technology Society Journal*, 29(3):58–66, 1995.
- [29] Akira Okubo. Oceanic diffusion diagrams. *Deep-Sea Research*, 18:789–802, 1971.
- [30] R. A. Paddock and J. D. Ditmars. Initial screening of license applications for ocean thermal energy conversion OTEC plants with regard to their interaction with the environment. Technical Report ANL/OTEC-EV-2, Argonne National Laboratory, 1983.
- [31] Lewis F. Richardson. Atmospheric diffusion shown on a distance neighbour graph. *Royal Society of London Proceedings*, 110:709–737, 1926.
- [32] P. C. Smith. A streamtube model for bottom boundary currents in the ocean. *Deep-Sea Research*, 22:853–873, 1975.
- [33] Henry Stommel. Horizontal diffusion due to oceanic turbulence. *Journal of Marine Research*, VIII:199–225, 1949.
- [34] T. Takahashi, W. S. Broecker, and A. E. Bainbridge. Supplement to the alkalinity and total carbon dioxide concentration in the world oceans. In Bert Bolin, editor, *Carbon Cycle Modelling*, volume 16 of *Scope*. John Wiley & Sons, New York, 1981.
- [35] H. Tennekes and J. L. Lumley. *A First Course in Turbulence*. MIT Press, Cambridge, MA, 1972.
- [36] J. S. Turner. *Buoyancy Effects in Fluids*. Cambridge University Press, London, U.K., 1973.
- [37] Ivan Valiela. *Marine Ecological Processes*. Springer-Verlag, New York, NY, 1984.
- [38] Kim A. Van Scoy. Tracer release experiments: Applications in ocean physics and chemistry experiments. In B. Omerond, editor, *Ocean Storage of Carbon Dioxide, 1: Ocean Circulation*, Cheltenham, U.K., January 1996. IEA Greenhouse Gas R & D Programme.
- [39] Robert P. Warzinski and Anthony V. Cugini. Observations of CO₂ clathrate hydrate formation and dissolution under deep-ocean disposal conditions. In J. A. PAJARES and J. M. D. Tascón, editors, *Proceedings of the 8th International Conference on Coal Science*. Elsevier Science, 1995.
- [40] Frank M. White. *Fluid Mechanics*. McGraw-Hill, New York, NY, second edition, 1987.

Table of Contents

1	Introduction	4-1
2	Review of Previous Far-Field Impact Assessments	4-2
3	Meso-Scale Dispersion Modelling	4-8
3.1	Meso-Scale Dispersion Model Formulation	4-8
3.2	Mesoscale Ocean Dispersion Results and Discussion	4-13
3.2.1	Dispersion Simulations	4-16
3.2.2	Discussion of Mesoscale CO ₂ Distributions	4-20
3.3	Conclusions on Mesoscale Environmental Impacts	4-22
4	Far-Field Global Carbon Cycle Modelling	4-23
4.1	GCCM Description	4-23
4.2	Model Simulations	4-27
4.3	Conclusions: Far-Field Global Carbon Cycle Modelling	4-31
5	References	4-33
	Figures	4-36
	Appendix	4-60

1 Introduction

In this topical report, previous studies that predict the far-field and long-term environmental impacts associated with ocean disposal of CO_2 were reviewed and two detailed ocean circulation models were employed to further evaluate oceanic and atmospheric impacts at meso- and global scales. Oceanic disposal of CO_2 may be a viable alternative for reducing the transient peak in atmospheric levels of CO_2 if the far-field environmental impacts associated with its application can be demonstrated to be minimal and the sequestration characteristics of the disposed CO_2 are long-term (e.g. centuries). For the following discussion, efficient sequestration will be evaluated by monitoring the short- (e.g. decades) and long-term (e.g. centuries) response in the atmospheric concentration of CO_2 for various disposal scenarios, and by monitoring the peak oceanic concentrations of dissolved CO_2 . During the next several centuries it is believed that anthropogenic production of CO_2 will both peak and decline resulting from continued economic development and the consumption of known fossil fuel reserves. The transient atmospheric peak in CO_2 concentrations during this period may exceed 1500 ppm, nearly four times the present concentration. After the known fossil fuel reserves are exhausted (i.e. possibly between years 2100 and 2200, Hidy and Spencer (1994)), the inevitable relaxation of the global ecosystem towards a new equilibrium will result in a gradual decline in the atmospheric CO_2 concentration. However, our concerns are the environmental impacts, both terrestrial and oceanic, during the next several centuries and whether ocean disposal of CO_2 is a viable option in alleviating excessive atmospheric build-up during the next two hundred years.

The modelling analyses presented here will attempt to predict changes in the local concentration of CO_2 in the ocean and the global concentration in the atmosphere, including contributions from other chemical compounds important to the carbon cycle, from which ecosystem and climate analyses may be inferred. In particular, the concentration of CO_2 in both the ocean and atmosphere will be evaluated for various ocean disposal scenarios, from which first order assessments of the long-term and far-field efficiency of ocean disposal of CO_2 can be made. The impact assessments presented here do not include detailed analyses of the impacts to local biological ecosystems and specific carbon cycle elements, neither in the ocean or terrestrial environments. Nor do any of the ocean

sequestration studies make climate alteration predictions, although several coupled atmosphere/ocean models do predict a climatic response to increasing atmospheric CO₂ levels and these will be discussed in the context of ocean disposal of CO₂.

The following discussion on far-field impacts associated with ocean disposal of CO₂ is separated into three sub-sections. First is a general review of the existing literature related to far-field environmental impact assessments. Second is the application of a Mesoscale Ocean Dispersion Model (MODM) to evaluate CO₂ concentrations and oceanic diffusion up to scales of 1000's of km over several years. Finally, there is an application of a Global Carbon Cycle Model (GCCM) with a 3-dimensional circulating ocean, a well mixed atmosphere, and key carbon cycle elements, where injection from two sites (New York and Tokyo) will be evaluated.

2 Review of Previous Far-Field Impact Assessments

Previous studies directed towards evaluating the far-field environmental impacts associated with ocean disposal of CO₂ can generally be grouped into two categories: 1) Box Diffusion Models and 2) 3-Dimensional Circulation Models. In general these two approaches give consistent results and predictions of the far-field environmental impacts. However, the more complex circulation models are capable of distinguishing important differences between injection locations and potential impacts to the climate. In summary, it can be stated that the studies to date have found that: 1) ocean disposal of CO₂ becomes more efficient the deeper the injection and the larger the fraction of anthropogenic CO₂ which is injected, 2) significant differences exist between different injection locations, and 3) potential climate alterations due to increasing atmospheric CO₂ concentrations may dramatically alter the ocean/atmospheric circulations. Although these findings are helpful and indicate that ocean disposal may be an effective mitigation strategy, details associated with the engineering, application, economics, and selection of injection sites are non-trivial, and much study still remains to further refine the possible disposal techniques and implementation.

Before proceeding to review specific studies, it will be useful to describe the scope of environmental impacts which are anticipated with oceanic disposal of anthropogenic CO₂. There are three primary

regions and/or ecosystems which can be identified that could be affected by anthropogenic disposal of CO₂: 1) the atmosphere, 2) the terrestrial biosphere, and 3) the ocean. The complex terrestrial biosphere has not yet been fully integrated into the global carbon cycle models employed to predict the long-term impacts associated with oceanic disposal of CO₂. Ocean sequestration models have typically estimated both the oceanic and atmospheric impacts, and assumed that the terrestrial biosphere will not represent a significant sink for anthropogenic CO₂. This assumption is based on the evidence that the amount of CO₂ extracted from the atmosphere by terrestrial biota (1.4 GtC/year, IPCC 1991) is mostly offset by the release of CO₂ due to land clearing. However, the response and role of the terrestrial biosphere in the global carbon cycle is likely to become more important as land clearing slows and the atmospheric CO₂ concentration over the next two centuries increases. Also, it is fairly well accepted that in the extremely long-term (millennia), the ocean/atmosphere/terrestrial system will equilibrate towards a steady state, where carbon distributions and concentrations in the atmosphere, ocean and terrestrial biosphere are nearly constant. The predictions considered here will therefore concentrate on impacts during the next few centuries by monitoring only ocean and atmospheric CO₂ inventories.

To measure how efficient ocean disposal of CO₂ is in comparison to other mitigation or reduction strategies, far-field impact models typically generate estimates of the time frame and quantity of CO₂ which returns to the atmosphere from the ocean disposal site. Disposal scenarios which predict a long time between disposal and return to the atmosphere are considered better than those which predict a more rapid exchange with the atmosphere. The "control" scenario is the discharge of an equivalent quantity of CO₂ directly into the atmosphere (no ocean sequestration). Also, disposal scenarios that significantly impact local environments and specific ecosystems are to be compared against those which introduce less significant impacts over larger regions.

The idea of capturing anthropogenic CO₂ and sequestering it in the ocean was first put forward by Marchetti (1977, 1979). Marchetti suggests, correctly, that for ocean sequestration to be effective, the CO₂ must reach significant depths, away from the surface layers of the ocean which interact directly with the atmosphere. He proposes that the CO₂ be discharged in regions of natural subduction, such as the deep out-flow from the Mediterranean. He notes that an injection near the Straits of Gibraltar need only be at 400 m depth, while the effective depth of sequestration, once the dense out-flow has penetrated the mid-Atlantic will be closer to 1500 m. He makes no estimation

of the long term efficiency of this technique, but acknowledges that the alternatives are no less attractive. Marchetti even suggests that the global anthropogenic production at that time (10^{10} tons/year) could be sequestered at this single site (based on volume flux). Drange and Haugan (1992) also consider the natural sinking capabilities of "gravity currents", where CO_2 enriched sea water is responsible for the increased density. Marchetti also references (personal communications) W.D. Nordhaus as suggesting that the CO_2 could be injected through a long pipe to depths where the dissolved CO_2 sea water mixture would have higher densities than ambient sea water and sink to the bottom, forming a deep CO_2 "lake". Marchetti notes that such a "lake" might have a half life of several centuries, effectively removing the CO_2 from the atmosphere for the near future. This preliminary work by Marchetti contains the two central elements important to ocean sequestration as we understand it today: 1) get the CO_2 as deep as possible, and 2) find regions of the ocean which inhibit early interaction with the atmosphere. Most of the subsequent research into ocean disposal of CO_2 merely refine and quantify these two issues.

A number of studies have analyzed the removal, recovery, transport and disposal of CO_2 from electric power plants (Baas et al. 1980; Albanese and Steinberg 1980; and Steinberg and Chang 1985 and 1987; Kheshgi et al. 1994). These studies include descriptions of the various elements and estimates of the processes and efficiencies associated with the entire procedure of CO_2 capture and disposal. Ocean disposal is consistently referred to as a viable option for the subsequent disposal, quoting the ocean's huge capacity to accommodate additional CO_2 without significantly (on a global scale) altering the natural sea water state (i.e. pH levels). The most recent of these comprehensive studies is work presented by Herzog et al. (1991) and the subsequent study for the U.S. Department of Energy (DOE, 1993), which includes estimates of the economic cost, engineering requirements, legal implications and energy efficiencies of various systems. The disposal from either land-based pipelines or sea-going platforms are discussed, and the injection of gaseous, liquid, and/or solid (clathrate) forms of CO_2 are presented. Return of CO_2 to the atmosphere is estimated through use of vertical upwelling/diffusion calculations which assume a uniform ocean structure. More effective sequestration is obtained for disposal below 1000m. Environmental impacts are estimated to be limited to local regions around the injection site, although no quantitative long-term environmental impacts are made.

Stegen et al. (1991) and Bacastow et al. (1991 and 1994) provide some first estimates on the

efficiency of ocean disposal of CO_2 from various sites and depths around the world. They adapt a 3-dimensional global ocean circulation model developed for climate studies (Mairer-Reimer et al 1982) and include an annual oceanic carbon cycle, within which the injected CO_2 participates. The model includes a well-mixed atmosphere which exchanges CO_2 with the surface ocean, except in regions buffered by sea-ice. Injection sites can be varied both horizontally and vertically within the gridded ($72 \times 72 \times 10$ layer) ocean, and subsequent ocean and atmospheric CO_2 levels can be monitored for many centuries. The present version of this model (see chapter 4) includes 15 vertical levels, which enhances the resolution of the thermohaline circulation and high latitude convection. These early simulations used a pre-industrial atmosphere/ocean system and the injection from a single 1 GWe electric power plant (3.27×10^{12} gC/yr) in order to emphasize the processes and impacts associated with ocean disposal, without post-industrial ocean and atmospheric changes. Injection sites in the Pacific and Atlantic Oceans were investigated and disposal depths ranging from near surface (0-112.5m) to near-bottom (3500-4500m) regions were simulated. It was found that both the Pacific and Atlantic Oceans have regions of upwelling that can reduce the long-term efficiency. However, the Atlantic injections also permit CO_2 to reach the deep-water convection regions of the north Atlantic, forcing a fraction of the injected CO_2 into the deep Atlantic where it is effectively sequestered for many centuries. They also note that, for the north Pacific injection sites, the transient peak in the atmospheric CO_2 concentration can be reduced by 25%, 40%, 60% and 95% for injection depths increasing from 275m, 712.5m, 2000m, to 4000m, respectively. These results have been supplemented by additional carbon cycle, ocean circulation simulations (Bacastow et al., 1994 and Stegen et al., 1994) which reveal characteristics of additional injection sites and the influence on CaCO_3 dissolution at the sediment interface. For a Revelle (buffer) factor between the surface ocean and atmosphere of 9.4, the very long-term CO_2 equilibrium between the ocean and the atmosphere results in an atmospheric retention of 12% of the anthropogenic CO_2 regardless of injection location or depth. This model and more recent simulations are presented in detail below.

The multi-box carbon cycle modelling work of Wilson (1992) also includes estimates of the pH change in the ocean and the potential gain in sequestration efficiency when calcium carbonate (CaCO_3) dissolution is allowed to occur when the injected CO_2 is adjacent to the bottom. This carbon cycle model includes an atmospheric box, a mid- and low-latitude ocean surface box, a high-latitude ocean surface-to-intermediate depth box, and a global intermediate-to-deep ocean box. Injection is considered for $\frac{1}{2}$ of the anthropogenic CO_2 generated by Great Britain (0.1 GtC/yr). He

notes only a small (-0.005) change in the pH (globally), and that including CaCO_3 chemistry at the bottom could increase the ocean's capacity to assimilate anthropogenic CO_2 by as much as 50%. These findings are consistent with the studies by Cole et al. (1993), who used a similar box diffusion model and a global CaCO_3 data base. Cole et al. note however, that the injected CO_2 must come in contact with the sediments, or be at depths where the water is undersaturated with calcite, which may take centuries from injection sites at mid- (1500m) to upper- ($< 1000\text{m}$) ocean depths. The vertical diffusion model of Liro et al. (1992) suggests a simple relation between depth and lag for return of CO_2 to the atmosphere [$\text{lag} = (z_{\text{injection}} - z_{\text{mld}})^2 / K_z$], where z_{mld} is the ocean mixed layer depth ($\approx 100\text{ m}$) and K_z is a global average vertical diffusivity ($\approx 1\text{ cm}^2/\text{s}$). These models provide qualitatively the right answers, but over simplify the advective and diffusive properties of the real ocean. The upwelling/diffusion model of Kheshgi et al. (1994) improves upon this slightly by including a globally averaged upwelling velocity (4 m/yr). However, the real ocean is typically less diffusive and more advective than these models predict (see section 3.2 below).

Finally, the long-term environmental impacts of ocean sequestration have been considered when the form of CO_2 deposited in the ocean is not allowed to enter directly into the advective/diffusive sea-water. In particular, the disposal of clathrate CO_2 (solid hydrates) was investigated by Golomb et al. (1992), who note that the laboratory studies of Sakai et al. (1990) predict a high ratio of clathrate formation for deep ($< 500\text{ m}$) injection. Clathrate formation is likely to be highly dependent on both ambient conditions and diffuser design. However, if a significant fraction of the injected CO_2 is "locked" into clathrate shells, which are denser than the ambient sea-water, then the CO_2 may sink to the ocean bottom and be sequestered for many centuries. (Accurate rates of clathrate dissolution are unknown, so the half life of deep clathrate deposits is unclear.) Similarly, if anthropogenic CO_2 can be piped directly to deep ocean depressions (Ohsumi et al., 1992), and allowed to form large pools of liquid CO_2 , then the slow dissolution and mixing from such pools is predicted to sequester the CO_2 from the atmosphere of many centuries, and possibly millennia. For both of these injection scenarios, the injected CO_2 is concentrated into local regions, where impacts may be high, but where the sequestration efficiency may be excellent.

Related to investigations into the long-term impacts associated with ocean sequestration of CO_2 are simulations into climatic changes as a result of global warming and other phenomena. Studies into potential climatic changes that might occur during the coming centuries as a result of the continued

build up of atmospheric CO₂ levels are presented by Manabe et al (1991, 1992), Segal et al (1994), and Murphy (1995). Although these studies do not consider ocean sequestration specifically, they are related to the present study in that they predict climatic changes to the ocean/atmosphere system as CO₂ levels increase. Each of these studies suggests a gradual warming of the atmosphere and surface ocean in response to increasing CO₂ levels in the atmosphere. Of particular interest is the study of Manabe and Stouffer (1994) who use a coupled ocean-atmosphere model and show that increasing the atmospheric CO₂ concentration by factors of 2 and 4 over the next 70 and 140 years, respectively, may have dramatic impacts to ocean circulation, and therefore the natural buffering mechanisms for CO₂. Their numerical experiments suggest that if the atmospheric CO₂ is doubled, main elements of the ocean circulation (i.e. the thermohaline circulation) are significantly weakened during the first 150 years. After CO₂ emissions abate due to the exhaustion of fossil fuel reserves, the ocean and atmospheric circulations gradually recover. However, if the CO₂ concentrations are allowed to quadruple through the next 140 years, the thermohaline circulation is all but eliminated during the first 250 years, and does not return even after CO₂ emission cease and atmospheric concentrations are stable. These preliminary results have direct bearing on the entire issue of CO₂ abatement and the potential mitigation strategies such as ocean sequestration which, at least in their present form, assume that the atmosphere and ocean circulations continue with present patterns and diffusivities.

The efforts described above indicate that improved predictions of the far-field environmental impacts associated with ocean sequestration of CO₂ can be made by utilizing advanced 3-dimensional models which include the necessary physics and chemistry. In the following chapters, two models are presented to predict the far-field impacts over time scales of months to years, and decades to centuries, respectively. The Global Carbon Cycle Model (GCCM), which includes carbon cycle elements and interaction with a diffusive atmosphere, resolves the oceanic circulations important at longer (decades) time scales. Eddy fields and meanders in the main ocean currents are not resolved by the GCCM. The Mesoscale Ocean Dispersion Model (MODM) does include circulation patterns with structures on the order 100 km (i.e. eddies and meanders), but assumes that over time scales of several years, the assimilation of the sequestered CO₂ into the oceanic carbon cycle is less important than the local advection and dilution due to the time-varying, sheared ocean currents.

3 Meso-Scale Dispersion Modelling

A wide range of oceanographic and hydrodynamic processes influence the advection and dispersion of material discharged into the stratified ocean. The temporal and spatial scales associated with oceanic dispersion vary from seconds to decades, and from centimeters to thousands of kilometers, respectively. To first order, the problem can be broken down into two dominant processes: advection by the unbounded mean flow and diffusion by turbulence and eddies (non-mean flow components). The development of a global, or even regional ocean model which attempts to include a numerical solution to both the large and small scale processes affecting the dispersion of material is a difficult problem to both formulate and execute computationally. A natural approach to modelling oceanic dispersion is to separate these two components. However, the task of simulating a real 3-dimensional ocean influenced by spatially varying winds, tides, boundaries, buoyancy flux, and internal density variations still remains non-trivial. Superimposing a realistic turbulent field on top of this flow could easily make the computations intractable. Our approach is rather more simple. Utilize an existing 3-dimensional ocean velocity field from the advanced Parallel Ocean Circulation Model (POCM) of the Naval Postgraduate School (Monterey CA) and NCAR, and combine this "mean flow field" with a stochastically driven turbulent velocity field. Within this turbulent, 3-dimensional, time-varying ocean we track neutrally buoyant particles representing clouds of dissolved CO₂. Injection sites throughout the global ocean can be investigated, and the resulting CO₂ plume(s) can be monitored and evaluated.

3.1 Meso-Scale Dispersion Model Formulation

The mesoscale dispersion model applied here is a stochastic particle model driven by an externally calculated, time-dependent 3-D velocity field. It is ideally suited for determining the intermediate environmental impacts associated with ocean sequestration of CO₂ at time scales of days to years and spatial scales between 10 and 1000 km (meso-scales). The "particles" or "clouds" of CO₂ are continuously released at user specified injection site(s) and tracked as they are advected by a seasonally varying ocean, which is composed of local mean currents and stochastic turbulent fluctuations. The distribution and concentration of CO₂ clouds can be calculated and plotted. At present the concentrations are plotted at a resolution of $\frac{1}{4}^{\circ} \times \frac{1}{4}^{\circ}$ latitude and longitude, within depth layers specified by the POCM model grid (20 vertical layers).

At scales greater than several kilometers, the dominant process in ocean dispersion is the straining influence of the complex ocean currents. These currents are driven by boundary (wind, bottom friction, buoyancy flux) and internal (geostrophic) dynamics. Within the interior ocean, these currents are virtually unbounded and have very large Reynolds numbers (10^8). The monthly mean global current fields generated by the POCM are utilized in this model. The POCM data has a $\frac{1}{2}^\circ \times \frac{1}{2}^\circ$ horizontal resolution in longitude and latitude, and 20 vertical layers, more closely spaced near the ocean surface. At mid and low latitudes, the POCM global circulation model resolves most of the ocean's complex, 3-dimensional, time varying eddy and mean circulation structures (Semtner and Chervin, 1992). At higher latitudes (i.e. $>50^\circ$), where the Rossby deformation radius introduced by the earth's rotation reduces the natural scale of ocean eddies, the model does not fully resolve the eddy activity. However, many known oceanic features are reproduced, indicating that the model physics are reasonably faithful. We integrate these POCM velocity fields with locally scaled stochastic turbulent velocities (u', v', w'). The resulting 3-dimensional turbulent velocity vectors advect particles in a geophysically and statistically correct manner.

The "mean" ocean current (U, V and W) represents the mesoscale ocean velocity and is interpolated for any time and location in the ocean from the monthly POCM velocity fields. The "turbulent" components of the velocity field (u', v', w') are locally "pseudo-random" (obeying turbulent velocity statistics) components scaled by the local kinetic energy of the mean velocity field. The turbulence is therefore inhomogeneous and more energetic in regions of strong mean flow. The neutrally buoyant particles (clouds of dissolved CO_2) are tracked as they are advected by the velocity interpolated to the exact location of each particle,

$$[u, v, w] = [(U(x, y, z, t) + u'(x, y, z, t)) , (V(x, y, z, t) + v'(x, y, z, t)) , (W(x, y, z, t) + w'(x, y, z, t))], \quad (1)$$

where $[U, V, W]$ are the spatially and temporally interpolated velocities at each particle location derived from the monthly POCM velocity data, and $[u', v', w']$ are the locally estimated stochastic turbulent velocities. Although the "mean" velocity field is gridded at the resolution set by the POCM model, the velocity of each particle is spatially interpolated to an exact position, so particles are free to move anywhere in the ocean. The POCM data has global coverage and any injection site in the world's ocean may be investigated. However, a limited dispersion model domain ($25^\circ \times 25^\circ$ or approximately 2500km x 2500km) is established around each injection site for computational purposes. The temporal dependence in the mean velocity field is interpolated from the monthly

POCM data. These data were generated by a seasonally forced run of the POCM (Semtner and Chervin, 1992).

The turbulent components of the velocity represent the influence of sub-grid scale processes not resolved by the POCM. In stochastic models where the turbulence is weak in comparison to the mean flow, the fluctuating components can be modeled as a first order Markov process (Sawford, 1984; Bennett, 1987) using the Langevin equation, from which we obtain,

$$u'(x,y,z,t+\Delta t) = \left(1 - \frac{\Delta t}{T_L(y)}\right) u'(x,y,z,t) + \sigma_u(x,y,z,t) \left(\frac{2\Delta t}{T_L(y)}\right)^{1/2} \xi, \quad (2)$$

where Δt is the dispersion model time step (4 to 24 hours), T_L is the local Lagrangian integral time scale of the turbulence, σ_u^2 is the variance of the local turbulent velocities, and ξ is a random number drawn independently from a Gaussian distribution with zero mean and unit variance. A similar equation provides the fluctuating horizontal velocity component v' . The Langevin equation, as formulated (2), can result in the "false" accumulation of particles and material in regions of the flow where both the mean and turbulent velocities are very weak, trapping the particles indefinitely. To alleviate this, a small horizontal "drift" velocity is added to the turbulent components in regions of very weak mean flow (< 1 cm/s). The drift velocity is determined from the local gradient in the spatial distribution of turbulent kinetic energy,

$$(u'_{drift}, v'_{drift}) = \Delta t \nabla \sigma_u^2(x,y,z,t) \quad (3)$$

and is directed towards the region of increasing kinetic energy (stronger mean flow). Although small, the drift velocity prevents the long-term accumulation of CO_2 in stagnation regions of the model ocean.

The variance of the local turbulent velocities [$\sigma_u^2(x,y,z)$] is parameterized to be a fraction (i.e. 0.05) of the local variance in the mean velocity field. In other words, the local turbulent kinetic energy (TKE) is scaled to 5% of the local mean kinetic energy (MKE). The value of 5% (0.05) is consistent with *in situ* observations of oceanic turbulence (Dewey *et al.*, 1991). The dispersion characteristics and plume structures are only weakly dependant on the magnitude of this scalar (0.05). Plume structures are dominated by the temporal and divergent characteristics of the "mean" advecting velocity field. The stochastic components only act to slowly migrate particles across streamlines in

the mean flow. The inherent divergence and time variability in the mean velocity field governs and dominates the fate of the injected CO₂ "clouds". Model particles are reflected from the POCM boundaries (i.e. the ocean surface and bottom), and "lost" once they leave the limited (25°x25°) domain of the dispersion model.

The Lagrangian time scale for the horizontal turbulence is set equal to ½ the local inertial period,

$$T_L(y) = \frac{\pi}{2\Omega \sin(\phi(y))} \quad (4)$$

where Ω is the rotation rate of the Earth ($=7.292 \times 10^{-5} \text{ s}^{-1}$) and $\phi(y)$ is the local latitude. Flow components with integral time scales longer than one-half the inertial period are strongly influenced by the Earth's rotation, are not considered "turbulence" by this formulation, and must obey more complex geophysical dynamics, as contained within the under-lying POCM model. However, if the local Lagrangian integral time scale is shorter than the model time step, then the ratio ($\Delta t/T_L$) is set equal to one (no memory) and the stochastic formulation becomes a simple random walk (Bennett, 1987).

The vertical component of the stochastic velocity field (w') is derived separately by scaling the square root of the horizontal turbulent variance by the local Richardson number (Ri),

$$w'(x,y,z,t) = \sigma_h(x,y,z,t) \left(\frac{1}{4Ri(x,y,z,t)} \right) \xi \quad (5)$$

where $Ri(x,y,z,t)$ is calculated from the local density and current fields extracted from the time dependant POCM data,

$$Ri(x,y,z,t) = \frac{-\frac{g}{\rho_0} \frac{\partial \rho}{\partial z}}{\left(\frac{\partial U}{\partial z} \right)^2 + \left(\frac{\partial V}{\partial z} \right)^2} \quad (6)$$

This formulation realistically allows for more vigorous vertical mixing in regions of strong vertical shear and weak stratification, while simultaneously suppressing the vertical turbulent components in strongly stratified regions or where the mean velocity shear is weak. We also note that w' does not contain any "memory" as do u' and v' , since the Lagrangian integral time scale for the vertical

motions are typically much shorter than the model time step. As a result, the vertical components of the turbulence given by (5) are random walk elements scaled by both the local turbulent kinetic energy and the local Ri .

A primary feature of the CO_2 plumes generated using the particle tracking technique is the apparent confinement of the material within specific regions of the flow. Unlike finite difference gradient diffusion models, where material is forced to diffuse uniformly in all directions, the Lagrangian formulation constrains the effective dispersion to path-lines in the flow. The small amount of stochastic dispersion, in good agreement with observed oceanic dispersion (Ledwell, *et al.* 1993), acts only to migrate material across path-lines (time varying streamlines), which may subsequently diverge or converge. The dominant path-lines of the flow act to limit the dispersion to specific regions and patterns, much as ocean drifter experiments have found that Lagrangian advection tends to preferentially sample convergent regions of the ocean (Davis, 1991).

Various model validation tests have been performed which indicate the model is well behaved statistically and reproduces realistic oceanic plumes. There is no analytic solution for an unbounded turbulent ocean such as that represented in this model. There are in fact only two methods available to validate the simulated dispersion: further numerical simulation or comparisons against empirical measurements. Three distinct tests were performed on the material distributions generated by this dispersion model. First was a check on the temporal variability of the concentration variance associated with particle separations (Sawford, 1984). Second was an estimation of the effective diffusivities predicted by the model, which can be evaluated against numerical and theoretical results. And finally a comparison of the dispersion characteristics was made against the available empirical data. When the Lagrangian time scale is set equal to the model time step, the model obeys random walk statistics. Under these conditions, the variance of particle displacement variances increase linearly, as expected (Bennett, 1987). When forced with a uniform flow, for which analytic solutions do exist, the model was in excellent agreement with the classical Gaussian plume solution. Finally, when compared against oceanic drifter and dye studies for specific regions of the ocean, the model is in good qualitative and quantitative (effective horizontal diffusivities in the range $10^3 - 10^5 \text{ m}^2 \text{ s}^{-1}$) agreement with the *in situ* observations (McWilliams *et al.*, 1983; Okubo, 1971; Ledwell, *et al.* 1993).

3.2 Mesoscale Ocean Dispersion Results and Discussion

The Mesoscale Ocean Dispersion Model (MODM) is ideal for evaluating the intermediate dispersion characteristics for various injection sites throughout the global ocean. The present study involves the injection of CO₂ at sites primarily concentrated along the United States east coast. It is assumed that the CO₂ has dissolved into solution with the ambient seawater, and that the resulting solution has reached a depth of neutral buoyancy (i.e. the clouds of CO₂ enriched water have the same density as the ambient seawater). The injection rate at each site is 1.119×10^{-2} GtC/year, or 1.26 m³/s of pure CO₂ liquid, although some disposal sites (pipelines) will be configured with numerous nozzles and this quantity will be distributed between multiple sources. This amount of CO₂ represents the CO₂ from ten 500 MWe power plants configured to capture CO₂. These power plants generate 144.4 kgCO₂/s each, of which 130 kgCO₂/s is captured for sequestration and 14.4 kgCO₂/s is assumed to be released directly into the atmosphere. Specific details of the ocean diffuser characteristics are not considered here. The speed of the ambient currents in the vicinity of the injection site determines the model time step, where slower currents permit a longer time step. The amount of CO₂ represented by each particle (cloud) in m³ of CO₂ is then the injection rate multiplied by the time step (in seconds).

Twenty five (25) distinct model simulations were conducted as part of this study. These simulations represent CO₂ injection at nine (9) geographic locations on the east coast and one on the west coast of the U.S., with two (approximately 1000 and 1500 m) or three (1000, 1500, and 2000 m) distinct depths at each location. Two model runs were made with simultaneous injection at two east coast locations, and one model run was made with multiple (3) injections from a single site. Finally, four model simulations were made with injection sites in the Pacific, for comparison to both the east coast simulations and the global carbon cycle simulations discussed in section 4, below.

The injection locations will be referred to by the following names, labeled by the nearest major city or geographic feature: New York (NY1 and NY2), Washington DC (DC1 and DC2), Cape Hatteras (CH1, CH2, and CH3), Miami (MI1 and MI2), San Francisco (SF) and Japan (JP). For each site, at least two depths of injection were tested, nominally at 1000 and 1500 m, water depths permitting. For each of the geographic locations NY, DC, and CH locations, two injection sites were selected, the first in water depths of approximately 1750 m, the second further off-shore in water

approximately 3700 m deep. For CH, a shallow (CH1 in 1750 m deep water) and a deep (CH2 in 3700 m of water) site were simulated, in addition to a bottom-lying multiple (CH3: 1500, 1700 and 2000m) injection scenario. For the MI sites, where adjacent water depths are limited by the shallow Straits of Florida, one of the injection sites (MI1) was placed near the center of the Strait (water depths of 350 m) and one (MI2) much further off-shore, in deep (3700 m) water northeast of Nassau. A single injection site west of SF was tested with injections at 1000 and 1500 m and a single injection site south of Japan at 1000 m. Most of the sites were selected to correspond to populated areas (NY, DC, MI, SF and JP), while one location (CH) represents a logical geographic site for injection due to the local bathymetry (i.e. the continental slope is closest to shore at Cape Hatteras and this site therefore represents the most logical location in terms of accessibility for a pipeline to reach significant depths). It should be noted that the densely populated eastern sea-board of the United States lies on a western ocean boundary, a region dominated by the Gulf Stream and known for vigorous advection and eddy activity. It turns out these properties may not be those best suited for long-term ocean sequestration of CO₂.

Simulations were typically run for three calendar years (1095 days). Although not yet at steady state (which may take tens of simulated years depending on the local current structure and variability), the resulting plumes reveal the more significant dispersion and plume characteristics for each site. Due to the relatively low currents off of San Francisco, in addition to the three year simulations, a six year simulation was performed there. Finally, a near bottom simulation was conducted for the near shore DC site, where the injection was placed 25 m above the bottom (1750 m). Table 1 shows the pertinent run parameters for each of the 25 simulations.

During model execution, the exact position of each individual CO₂ cloud is tracked. Depending on the time step and injection rate, a fixed number of clouds, each representing a fixed quantity of CO₂, is injected into the flow at each time step. As the model progresses, the number of CO₂ clouds within the model domain and being tracked by the model increases. Therefore, the computational requirements increase linearly with time, and the model gradually becomes slower and slower. None-the-less, three year simulations with 5 clouds injected per day (5475 total clouds) were executed in approximately 30 minutes on a 486/33 MHz PC.

The evolving distributions of CO₂ in the model ocean (i.e. the CO₂ plume), represented by the

Table 1 Meso-Scale Dispersion Model Run Parameters and Injection Site Locations

#	Locations	Injection Depth (m)	CO ₂ Injection Rate (m ³ /s)	Latitude	Longitude	Water Depth (m)
1	DC1	1000	1.26	36.75°N	74°W	1750
2	DC1	1500	1.26	36.75°N	74°W	1750
3	NY1	1000	1.26	39°N	72°W	1335
4	NY1	1200	1.26	39°N	72°W	1335
5	DC2	1000	1.26	35.35°N	73°W	3850
6	DC2	1500	1.26	35.35°N	73°W	3850
7	DC2	2000	1.26	35.35°N	73°W	3850
8	NY2	1000	1.26	37.5°N	70.54°W	3300
9	NY2	1500	1.26	37.5°N	70.54°W	3300
10	NY2	2000	1.26	37.5°N	70.54°W	3300
11	MI1	300	1.26	26.36°N	79.5°W	360
12	MI2	1000	1.26	26.68°N	76.2°W	2750
13	MI2	1500	1.26	26.68°N	76.2°W	2750
14	DC1 and NY1	1000 +1000	1.26 +1.26	36.75°N 39°N	74°W 72°W	1750 1335
15	DC1 and NY1	1500 +1200	1.26 +1.26	36.75°N 39°N	74°W 72°W	1750 1335
16	DC1	1725	1.26	36.75°N	74°W	1750
17	CH1	1000	1.26	34.7°N	75°W	1750
18	CH1	1500	1.26	34.7°N	75°W	1750
19	CH2	1000	1.26	33.95°N	74.19°W	3850
20	CH2	1500	1.26	33.95°N	74.19°W	3850
21	CH3	1500 1700 2000	0.42 0.42 0.42	34.7°N 34.5°N 34.3°N	75°W 74.8°W 74.6°W	1750 1750 2200
22	SF/3yrs	1000	1.26	36.5°N	122.7°W	2200
23	SF	1500	1.26	36.5°N	122.7°W	2200
24	SF/6yrs	1000	1.26	36.5°N	122.7°W	2200
25	JP	1000	1.26	32°N	134°E	2750

individual CO₂ clouds, are contoured and plotted in terms of the local CO₂ concentration in $\mu\text{mole/kg}$. In order to convert the local concentration of model particles (each representing a fixed quantity of dissolved CO₂) into a meaningful concentration, the data were gridded into cells $\frac{1}{4}^\circ \times \frac{1}{4}^\circ$ in the horizontal and separated vertically by the ocean layers represented in the POCM. The POCM layer interfaces are located at (m): 0, 25, 50, 75, 100, 135, 185, 260, 360, 510, 710, 985, 1335, 1750, 2200, 2750, 3300, 3850, 4400, 4800, and 5200. Therefore, shallow layers are as thin as 25 m, while the deeper layers are 400 m thick. The bathymetry represented in the dispersion model is limited to the resolution provided by these interfaces. The CO₂ concentrations represented in this $\frac{1}{4}^\circ \times \frac{1}{4}^\circ \times 20$ variable thickness grid are displayed as a 2-dimensional horizontal map during model execution. The user may select to display the vertically averaged CO₂ concentration, or the CO₂ concentration from a particular depth (i.e. within one of the predetermined layers). Concentrations are displayed in units of $\mu\text{mole CO}_2/\text{kg seawater}$ [$\mu\text{mole/kg}$]. For reference, natural levels of CO₂ typically range between 1900 and 2400 $\mu\text{mole/kg}$ in the ocean. Environmental impacts will be evaluated by comparing the plume concentration of CO₂ relative to the natural background concentration. Although not calculated here, the local change in pH for the northwest Atlantic is approximately -1.0 for an increase in CO₂ of 250 $\mu\text{mole/kg}$ (Stegen et al. 1994).

3.2.1 Dispersion Simulations

Presented below are the mesoscale dispersion simulations for the various injection sites and depths, grouped by similarities in the resulting dispersion characteristics. Most of the injection sites are located along the east coast of the United States and are limited to depths between 1000 and 2000m. Although the ocean used in these simulations is time dependant and 3-dimensional, its structure within the northwest Atlantic is reasonably stable and many of the simulations reveal plumes similar in appearance. Due to the similarity among many of the different simulation, example plots will be presented here, while a complete set of plume figures is included in Appendix A.

New York and Washington DC

Four injection locations were tested off the northeast coast of the United States; two sites off-shore (east) from New York (NY1 and NY2) and two east of Washington DC (DC1 and DC2). The sites NY1 and DC1 were located in water 1335 and 1750 m deep, respectively, while NY2 and DC2

where further off-shore in water depths between 3300 and 3850 m, respectively. CO₂ was injected separately at 1000 and 1200 m for NY1, 1000 and 1500 m for DC1, and at depths 1000, 1500, and 2000 for each of NY2 and DC2. Finally, two simulations were conducted with simultaneous injections at each of NY1 and DC1 at depths of 1000 and 1000 m, and then 1200 and 1500 m, respectively. The injection rate at each site was 1.26 m³/s of (liquid) CO₂.

Except for the relatively deeper simulations (at 1200 for NY1 and 2000 m for NY2 and DC2), these four sites exhibited similar dispersion characteristics (e.g. Figures 1 and 2). The injected CO₂ was advected by several dominant ocean circulations in the region, and the resulting plumes share many characteristics. The most significant oceanic feature near these injection sites which influenced the resulting CO₂ plumes were the local regions of strong upwelling. The 1000 m injected CO₂ plumes from both the near-shore sites (NY1 and DC1) would circulate and slowly enter into regions of local upwelling and rise towards the upper layers of the ocean. Examination of the model Gulf Stream structure in this region reveals that the isopycnals (surfaces of constant density) are tilted significantly upwards towards the northwest. Vertical velocities in the model (represented by mean flow along tilted isopycnal surfaces) in this Gulf Stream region may be significant, with magnitudes as large as 2.5 m/day (2.8×10^{-3} cm/s). Consequently, portions of the CO₂ plumes at both NY1 and DC1 rise sharply from the injection depth of 1000m. Such large vertical velocities are common in many regions affected by the Gulf Stream (Stommel, 1965), and estimates by Hall (1986) indicate persistent vertical velocities can be as large as 50 m/day at depths down to 1200 m. Vertical displacements of the injected CO₂ were as large as 650 m during the first year, bringing some CO₂ up to depths of 350 m from the injection depth of 1000 m.

Horizontal dispersion during the first year (Figure 3) was limited to regions within several hundred kilometers of the injection sites. However, once portions of the CO₂ plume had reached shallower depths (i.e. 600 m), they would enter more advective regions of the Gulf Stream, with larger horizontal velocities (20 - 60 cm/s). Consequently, after the first year, the plume would begin to spread horizontally, branching both towards the southeast and northwest (i.e. Figure 1). By examining different vertical layers it is revealed that there was virtually no CO₂ below 1000 m (effectively no down-welling), regionally confined CO₂ between 710 - 985m (Figure 4), and CO₂ advecting away from the injection region between 510 - 710m (Figure 5). Only small traces of injected CO₂ were found above 510m (Figure 6), within the northern branches of the Gulf Stream

meanders. These vertical characteristics were persistent for all injections above 2000m at the NY and DC injection sites except for the 1200 m injection at NY1. The CO₂ plume extensions within the depth layer 510 - 710m (i.e. Figure 5) are characteristic of the circulation within the main thermocline. CO₂ injected for many of the east coast sites found its way into this dominant circulation, resulting in similar horizontal CO₂ distributions. Due to the relative shallow water depth at NY1 (1350 m), the second injection at this location was at 1200 m, only 150m above the bottom. Currents at this depth were weak (<1cm/s), and the CO₂ plume advected very slowly to the northeast. Examination of the historical observations of the Gulf Stream (i.e. Stommel, 1965) indicate that its position and structure near the eastern continental rise are stable and persistent, with meanders and variability confined primarily to the Gulf Stream extension further to the northeast (longitudes < 60° W). This suggests that the Gulf Stream may act as a significant barrier to CO₂ injected from coastal sites along the east coast, especially for those located north of Cape Hatteras (see below).

For deeper injections (i.e. 2000m) at NY2 and DC2 (see for example Figure 2) only a small portion of the CO₂ would enter into the upwelling regions, the majority would enter the southward undercurrent and vent out of the southern wall of the model domain. A characteristic of this steady (3 cm/s) southward stream was the confinement of the CO₂ to a narrow filament, only a few tens of kilometers wide but over 2000 kilometers long. Despite the "turbulent" dispersion apparent in the more divergent upper circulation, this deep steady flow exhibits very little dispersion due to the non-divergent character of the streamlines. Similar non-dispersive regions of the ocean are more plentiful at depth (i.e. > 2000m) away from boundaries and convective circulations. Several CO₂ dispersion simulations were made with simultaneous injection at NY1 and DC1, both at 1000 and 1500m. The "combined" plumes are visually indistinguishable from the individual site injections, except for the net increase in concentrations due to the doubling of CO₂ entering the ocean (Figure 7).

Miami

Two injection sites were studied east of Miami. Due to the relatively shallow bathymetry within the Straits of Florida (500m), where MI1 was located, MI2 was chosen in the deeper (2750m) water east of the Bahamas. With an injection depth of 300m at MI1, the CO₂ was injected in the heart and

southern most origin of the Gulf Stream (Figure 8). The CO₂ initially follows the swift (80cm/s) Gulf Stream currents up the eastern coast, past Cape Hatteras. From there the CO₂ branches and disperses in various directions, spreading into a broad and diffuse eastward plume, extending 1000 km in latitude. The breadth of this dispersion is significantly enhanced by the time varying nature of the 3D model currents. From MI2, just east of the Bahamas, the CO₂ injected at 1000m splits vertically into a weak northward filament and a more dense southward plume (Figure 9). From MI2 at 1500m the CO₂ is completely trapped within the narrow southward undercurrent, and advects towards the equatorial regions near South America (Figure 10).

Cape Hatteras

The CO₂ dispersion simulations described so far reveal some significant characteristics of the northwest Atlantic. Shallower (i.e. < 1500m) injection depths allow portions of the CO₂ to enter the vigorous Gulf Stream system, dispersing the CO₂ both horizontally and vertically. Deeper injections (> 1500m) may more effectively sequester the CO₂ from the upper layers of the ocean, and therefore from the atmosphere. In an attempt to evaluate east coast disposal sites, the bathymetry of the northwest Atlantic was examined and the location where the continental slope is closest to shore and therefore where "deep" ocean regions can be reached most directly is found east of Cape Hatteras. Several simulations were conducted with injections sites in this region: two nearer shore (1000 and 1500m) at CH1 in water 1750m deep, two (1000 and 1500m) at CH2 in water 3850m deep, and one simulation considering a multiple (three) diffuser configuration extending in a line east of Cape Hatteras (depths of 1500, 1700 and 2000m) at CH3.

The CO₂ plumes from both CH1 and CH2 exhibit many of the features already discussed for the sites associated with New York, Washington, and Miami. Generally, deeper injections allowed some CO₂ to enter the southward undercurrent, while a majority of the CO₂ recirculated in the main thermocline and the eastern extensions of the Gulf Stream. These characteristics are also represented in the multiple injection simulation CH3 (Figure 11). For this simulation, the total injection rate of 1.26 m³CO₂/s was divided into three and allowed to diffuse from progressively deeper sites in a line east of Cape Hatteras. After three years, both eastward and southward plume extensions are evident (Figure 11), with an approximate partition of 1/3 of the CO₂ heading upwards to the northeast, 1/3 towards the south (within the under current) and 1/3 remaining trapped within the "slowly"

dispersion eddy fields associated with meanders in the Gulf Stream. Shown in Figure 12 is the $\log_{10}$ histogram of CO_2 concentrations from simulation #21 (CH3). Over 1000 of the model cells ($\frac{1}{4}^\circ \times \frac{1}{4}^\circ \times \Delta z$) have concentrations less than $100 \mu\text{mole/kg}$. The distribution drops off quickly, with less than 200 model cells in the range $100 < \text{CO}_2 < 200 \mu\text{mole/kg}$, less than 50 in the range $200 < \text{CO}_2 < 300 \mu\text{mole/kg}$ and only 30 cells (2%) with CO_2 concentrations greater than $500 \mu\text{mole/kg}$.

Pacific Ocean Injection Sites

For comparison to the simulations with CO_2 injection in the northeast Atlantic, two disposal sites were selected in the north Pacific. The first was west of San Francisco, in water 2200 m deep, the second south of Japan, near the Kuroshio current, in water 2750 m deep. Due to the relatively weak subsurface (> 1000 m) currents west of San Francisco, the subsequent CO_2 plume advects and diffuses very slowly (Figure 13). For this reason, the simulation was allowed to proceed for 6 years instead of 3 years, as was the case for all other simulations. The San Francisco plume is advected both towards the north (winter) and south (summer) in the seasonally driven California Current, resulting in a net dispersion covering only 600 km (net advection rate is a few mm/s). South of Japan, within the strong Kuroshio current (analogous to the Gulf Stream in the Atlantic), the injected CO_2 is advected and recirculates within a complex, time-varying flow (Figure 14). Plume separations during the seasonal shifts in the Kuroshio result in isolated patches and detached filaments of CO_2 . Here, portions of the CO_2 are advected eastward within the main Kuroshio extension, while significant amounts of CO_2 recirculate on an annual time scale back towards the initial injection longitude and latitude. For this injection site and depth (1000 m) vertical transport was both upwards and downwards, with minimum and maximum plume depths of 518 and 1620 m, respectively.

3.2.2 Discussion of Mesoscale CO_2 Distributions

A sub-grid scale dispersion model has been used to simulate the CO_2 plumes which might result from injection at various sites in the Atlantic and Pacific oceans. The underlying currents in the model are the 3-dimensional monthly POCM fields described by Semtner and Chervin (1992). The

resulting plumes reveal various characteristics of the potential dispersion patterns for the northwest atlantic, and give preliminary estimates of the resulting CO₂ concentrations during the first few years after injection. It should be noted that specific characteristics and concentration levels generated by the model are not intended to reflect exact distributions which might be realized if CO₂ were injected into the deep ocean, but rather are intended to give the general dispersion characteristics and patterns which are likely. For example, the specific filaments of CO₂ simulated here may not exist if CO₂ were injected at the same locations. However, the general influence of the Gulf Stream, the vertical advection along tilted isopycnals, the transport of CO₂ into the north Atlantic by the Gulf Stream extension, the trapping and recirculating influence of meanders and eddies, and the southward advection by the Gulf Stream undercurrent are all likely to play an important role in the dispersion and advection of CO₂ injected along the east coast of North America. Concentrations are likely to be in the same order of magnitude, with histogram distributions much like that shown in Figure 12.

For the simulations of CO₂ injection along the east coast of the United States, several important features are revealed by the mesoscale dispersion simulations. First, not unexpectedly, is the dominant role played by the hydrographic and current structures associated with the Gulf Stream. The Gulf Stream represents a dominant oceanographic feature which acts to advect material towards both the central north (upper) and equatorial (deeper) Atlantic. The Gulf Stream system consists of steep dynamic topography (tilted isopycnals) and complex vertical and eddy like motions. Many regions near the Gulf Stream transported the injected CO₂ upwards along these tilted isopycnals, bringing the injected CO₂ from depths greater than 1000 m, up into the main thermocline (≈ 500 m). This "upwelling" may be avoided if the injection depth is greater than 2000m, below which the currents are weak and the isopycnals less tilted.

Within the complex CO₂ plumes generated by the mesoscale dispersion model, the CO₂ concentration levels are larger than those predicted by larger scale finite difference schemes (i.e. the GCCM), or by simple box-diffusion models. This is a simple consequence of the later allowing unrealistically broad dispersion, while the Lagrangian formulation tends to rely more heavily on the relative dispersion characteristics of the divergent streamlines in an eddy resolved ocean. Although typical CO₂ concentration increases after three years of ocean disposal were predicted by the MODM to be between 50 and 200 $\mu\text{mole/kg}$, peak CO₂ concentration increases within limited

regions were as large as 1500 to 2000 $\mu\text{mole/kg}$. This level of CO_2 represents an almost doubling of the ambient concentration of natural CO_2 . Such large concentrations of injected CO_2 were limited to one or two small (25×25 km by 200m) regions. These high concentrations occurred either near the injection site (source), or in regions where the model circulation exhibited persistent convergence. Although the location of such regions in the real ocean may not coincide with those in our model ocean, it is likely that similar convergent regions do exist and will have a similar affect on locally injected CO_2 . For the northwest Atlantic, CO_2 increases of 50 to 200 $\mu\text{mole/kg}$ would result in pH changes of less than -1.0, while CO_2 increases of 1000 $\mu\text{mole/kg}$ could result in pH decreases on the order of -2.0. It should be noted that this model does not include biological assimilation or chemical adjustment processes which would alter the effective CO_2 concentration and therefore the local pH levels.

3.3 Conclusions on Mesoscale Environmental Impacts

The model simulations presented here identify several key aspects of ocean disposal of CO_2 along the east coast of the United States. Within 300 to 500 km of the coast, the dispersion of CO_2 is dominated by the vertical and northwest advection of the Gulf Stream. Regions of strong upwelling may cause CO_2 to rise from depths of 1500 m to 500 m within periods of months, while strong horizontal currents associated with the main thermocline act the quickly advect the CO_2 into the central north Atlantic. A steady southward undercurrent was identified along the western boundary of the Atlantic, which transported deep (2000 m) CO_2 into the equatorial Atlantic. CO_2 concentrations were higher than those predicted by advection/diffusion or box diffusion models, with isolated peak concentrations of injected CO_2 in the range 1000 to 2000 $\mu\text{mole/kg}$.

4 Far-Field Global Carbon Cycle Modelling

A Global Carbon Cycle Model (GCCM), with a realistic circulation ocean, a well mixed atmosphere, and various oceanic carbon cycle elements has been applied to evaluate the far-field environmental impacts associated with ocean disposal of CO_2 on time scales out to 500 years. The GCCM is based on the non-biological ocean circulation model of Mairer-Rierner and Hasselmann (1987). The addition of annual biological carbon cycle components is described by Bacastow and Mairer-Rierner (1990). The model consists of two primary components; the ocean circulation model driven by seasonal climatology (wind, temperature, salinity) and thermohaline dynamics, and the oceanic carbon cycle components which integrate the sequestered CO_2 as dissolved inorganic carbon. The global distribution of CO_2 is most influenced by the natural ability of the oceans to advect, convect, and mix carbon and nutrients, and to establish fertile biological regions for primary productivity.

4.1 GCCM Description

The ocean general circulation component of the model and the simulated ocean currents are described by Maier-Reimer (1993). The model consists of a 72×72 grid covering the entire globe, divided into 15 vertical layers. Average grid spacing is $2.5^\circ \times 5^\circ$ in latitude and longitude, and vertical bins range between 100 and 1000m in depth, with thinner layers near the surface of the ocean. The circulation model satisfies all necessary numerical stability criterion (i.e. cfl). The circulation generated by the model is well representative of the real ocean, given the model's resolution. The model does not resolve eddies or Gulf Stream meanders. However, for a long-term prediction model, with carbon cycle elements, such features are not likely to be important. These features are important at meso (100-1000km) time and space scales, and these impacts are addressed in the preceding chapter. Realistic "net" ocean transport and important convection ocean processes (i.e. deep water formation) are resolved. Long-term CO_2 predictions are then based on simulations over many carbon cycle years.

The basic carbon cycle is divided into 7 main elements:

- 1) Anthropogenic CO_2 emitted into the atmosphere and ocean (during sequestration).
- 2) Air/sea exchange of CO_2 based on local partial pressures, location and ice cover.
- 3) Biological assimilation (photosynthesis) of carbon and nutrients and the generation of local concentrations of dissolved organic carbon (DOC), particulate organic carbon (POC) and calcium carbonate CaCO_3 .
- 4) Particulate (POC and CaCO_3) sinking from the upper oceanic layers.
- 5) Ocean advection and convection of all dissolved components (including nutrients/upwelling).
- 6) Remineralization of organic carbon (DOC and POC) below the surface layers.
- 7) CaCO_3 dissolution at depths of undersaturation.

For each of the carbon cycle components, a variety of preconditions and environmental influences determine the rate and location of carbon cycling. For example, the advection, convection and mixing of carbon by ocean currents depends on the magnitude, direction and structure of the 3-dimensional current field which, in turn, is driven by atmospheric and thermohaline forcing. Similarly, biological assimilation of carbon occurs primarily in the near surface euphotic layer, and is a function of light intensity and nutrient availability. Light intensity is a function of latitude and season, while nutrient availability depends on previous biological uptake (Redfield ratios), remineralization, and oceanic transport of carbon and nutrients. Experience with the model indicates that much of the structure and variability in the global carbon cycle system can be reproduced (Bacastow and Maier-Reimer, 1990; Maier-Reimer, 1993; Stegen *et al.* 1993)

The absorption and release of CO_2 from the ocean to the atmosphere is a function of the local partial pressures of CO_2 in both the ocean surface layer and the over-lying atmosphere, as well as geographic location and extent of ice cover. In the surface layer of the ocean, regional biological productivity represents a significant sink for dissolved inorganic carbon (DIC). As an essential element to photosynthesis, CO_2 is assimilated into a complex food chain where it is eventually excreted as soft (POC) and hard (CaCO_3) biological tissue debris, or as dissolved organic carbon (DOC). The rate and occurrence of biological assimilation therefore directly impacts the local ocean concentration of CO_2 and the partial pressure which determines whether the ocean is a source or sink for atmospheric CO_2 . A known limitation of the present model formulation is the omission of dissolution of CaCO_3 rich sediments, although dissolution of in situ CaCO_3 during photosynthesis

is included. Cole et al. (1993) suggest that at time scales over which the sequestered CO₂ comes in contact with deep CaCO₃ rich sediments, water once undersaturated with respect to calcite would cause the sediments to dissolve, consequently raising the local pH and alkalinity. This would allow additional CO₂ buffering in the deep ocean, and improve the sequestration efficiency. This limitation becomes important at longer time scales (i.e. 100 years), and would be more important in the Atlantic than the Pacific due to the deep convection in the Atlantic which brings CO₂ in contact with the CaCO₃ rich Atlantic sediments.

The simulations described here have two primary components. First is the global anthropogenic CO₂ production, most of which is assumed to be discharged directly into the atmosphere, and second, the CO₂ associated with the sequestration process. The global production curve $q(t)$ of anthropogenic CO₂ is matched to the observed CO₂ production up to 1990 and also to the rate of production during 1990 (IPCC, 1991), and is modelled as a logistics function,

$$q_i = q_{i-1} + \frac{dq_i}{dt}$$

$$\frac{dq_i}{dt} = 0.03 q_{i-1} \left(1 - \frac{q_{i-1}}{q_t} \right)$$

$$q(1990)=214.61, q_t=4240, \frac{dq}{dt}(1990)=6.01$$

where the units for q and q_t are Gigatons Carbon (GtC = 10¹⁵ g carbon)), and dt is assumed to be 1 year. This accurately represents observations up to the present and predicts a peak production near 2090 (Figure 15). Relative to the predictions of Hidy and Spencer (1994), the curve is less peaked and smoother, and the maximum production comes ten years earlier. The total anthropogenic CO₂ production (area under curve in Figure 15) has been set to 4240 GtC, which is larger than the optimistic IPCC predictions, but consistent with a symmetric production curve as hypothesized by Hidy and Spencer (1994). For purposes of consistency with earlier modelling efforts, we have employed a sequestration schedule starting in the year 2000, and running 99 years. Therefore, the global production of anthropogenic CO₂ continues (in decline) even after ocean sequestration is terminated in 2100. This formulation represents a more realistic post-industrial atmosphere, not represented in previous simulations.

The global carbon cycle model was initiated from a pre-industrial state, taken to be the year 1740,

up to the year 2000. This model state is taken as the "spin-up" condition, from which various disposal and sequestration scenarios are simulated. Ocean sequestration is assumed to begin in the year 2000 at a constant rate. For the following simulations, the CO₂ captured from multiple (50) coal burning 500 MWe electric power plants is assumed to be the source for the sequestered CO₂, with an ocean injection rate of 5.597×10^{-2} GtC/year (2.051×10^{11} kg CO₂/year) at two separate oceanic locations (off of New York and Tokyo). The total CO₂ sequestered in the ocean is then 1.1194×10^{-1} GtC/year (4.102×10^{11} kg CO₂/year). For comparison, the estimated 1990 global production of CO₂ was 6.01 GtC/year (2.2×10^{13} kg CO₂/year). The sequestered amount of CO₂ represents less than 2% (1.86%) of the global production in 1990, and by the year 2090 when global production is predicted to reach levels of ~ 32 GtC/year (1.17×10^{14} kg CO₂/year), this sequestration level represents only 0.34% of the global CO₂ production. Therefore, it should be noted that the present simulations sequester a very small fraction of the global CO₂ emissions, and that any real sequestration program would likely inject an increasing amount, or a more constant fraction (%) of the anthropogenic CO₂ than the scenarios considered here.

There are important computational consequences with regard to sequestering a small amount of CO₂ in relation to the total amount of CO₂ discharged into the atmosphere. First is the fact that in order to determine the atmospheric concentration of sequestered CO₂, two relatively large numbers are subtracted (i.e. atmospheric concentration without sequestration minus atmospheric concentration with sequestration). Small errors or fluctuations in these large numbers may result in increased uncertainty in the difference. These small errors may be due to small fluctuations in the model solutions, or even computational resolution of the larger quantities (numerical roundoff). In addition, by stressing the global carbon cycle with CO₂ levels that are 4 to 5 times the present concentrations, it is not clear that the existing formulations for the various ocean/atmosphere components (i.e. the ocean circulation and air/sea exchange) correctly parameterize the associated process, or are appropriate for the higher concentrations predicted during the next 100 years. For example, the model, as applied here, does not include remineralization of CaCO₃ within the sediments, a process which has been predicted to be important over periods of centuries and when increased levels of CO₂ comes in contact with deep sediments (Cole *et al.* 1993). Also, it is assumed that the ocean circulation, climate dynamics, and important processes such as high latitude convection, continue in a manner similar to that observed today.

Three model simulations were conducted: 1) No ocean sequestration, all anthropogenic CO₂ is discharged into the atmosphere; 2) Ocean sequestration off New York; and 3) Ocean sequestration off Tokyo. Due to the relatively small amount of CO₂ sequestered, a combined ocean sequestration is obtained by summing the New York and Tokyo results. The depth of ocean sequestration was set at 1000m, which represents a GCCM model layer with interfaces at 900 and 1500 m. (An injection depth anywhere in this layer would have produced similar results.) Due to the energy expended capturing and transporting the CO₂ to the sequestration sites, the "no ocean sequestration" simulation generates less CO₂ per MWe, and therefore actually discharges less CO₂ into the ocean/atmosphere system. For the "no ocean sequestration" simulation, the amount of CO₂ generated by each 500 MWe power plant is 115 kgCO₂/s, which is assumed to be discharged directly into the atmosphere. For the "ocean sequestration" cases, 144.4 kgCO₂/s is produced by each 500 MWe power plant, of which 130 kgCO₂/s is captured for sequestration and 14.4 kgCO₂/s is discharged into the atmosphere. Consequently, the "no ocean sequestration" simulation tracks 26% less "sequestration" CO₂ than do the "ocean sequestration" simulations.

Various model parameters and quantities were saved during execution in order to evaluate the environmental perturbations associated with ocean disposal of CO₂. First is the amount of "sequestered" CO₂ in the atmosphere, either discharged directly, or vented through the air/sea interface. Second is the amount of sequestered CO₂ in the ocean, either injected directly, or exchanged from the atmosphere. Finally, the spatial and temporal distribution of sequestered CO₂ in the ocean was monitored periodically throughout the 500 year simulations. For these simulations, the sequestered CO₂ represents only a small fraction (<2%) of the anthropogenic carbon in the ocean and atmosphere system and has been tracked separately. Recall that the atmosphere is a "well-mixed" box, and all atmospheric carbon is uniformly distributed over the globe. Sequestered CO₂ may vent into the atmosphere at specific "upwelling" locations and after one year that CO₂ is globally distributed within the atmosphere and re-enters the global ocean surface layer.

4.2 Model Simulations

Three simulations using the GCCM were conducted. A control run with CO₂ discharged directly into the atmosphere, and two simulations with ocean disposal; one with injection off New York, a second with injection off Tokyo. The ocean sequestration simulations were done separately in order to better

track the characteristics of the individual injection site. Due to the relatively small amount of CO_2 considered in the sequestration, a combined (New York plus Tokyo) result can be obtained by adding the individual concentrations. For all three simulations, the increase in atmospheric CO_2 is dominated by the global production of CO_2 (Figure 15), which results in a significant increase in the atmospheric concentration of CO_2 over the simulation period (Figure 16). As noted earlier, a quadrupling of the atmospheric CO_2 levels may cause significant alterations in the atmosphere/ocean circulation dynamics, which is not considered in this version of the GCCM.

Shown in Figure 17 are the time histories of the amount of sequestered CO_2 returned to the atmosphere in units of ppm (parts per million) for the control (no sequestration) and ocean sequestration simulations. The control shows a linear increase in atmospheric concentration of the captured CO_2 during the sequestration interval (2000 - 2100), with a net increase of approximately 4.15 ppm. Once the sequestration has stopped, a steady decline in the control case reveals the natural up-take of atmospheric CO_2 by the ocean. The ocean sequestration curve shows a much more gradual increase during the first 100 years, due partly to the small fraction of CO_2 discharged directly into the atmosphere plus CO_2 exchanged from the ocean surface. After year 2100, when sequestration has ceased, the ocean sequestration curve increases more slowly, revealing the sequestration efficiency of the deep ocean. However, CO_2 continues to escape from the ocean into the atmosphere, and after 500 years, the two curves are only 0.6 ppm apart. At even longer time scales, when the ocean/atmosphere system has reached equilibrium (12% atmosphere/ 88% ocean), the curves will have crossed and the ocean sequestration case will result in more net CO_2 reaching the atmosphere. This is because the ocean sequestration procedure produces 26% more CO_2 per MWe. The processes affecting the efficiency of the ocean sequestration between years 2000 and 2500 are not evident from the single ocean sequestration curve shown in Figure 17.

Differences between New York and Tokyo become more apparent when the amount of CO_2 returned to the atmosphere from each site is examined independently (Figure 18). For reference, $\frac{1}{2}$ of the control (no sequestration) CO_2 is also plotted in Figure 18. Although similar during the first 100 years, the period of actual ocean injection, the curves representing the amount of CO_2 returned to the atmosphere for the ocean sequestration cases for New York and Tokyo depart significantly after year 2100 (when ocean sequestration ceases). The diverging curves reveal differences between the local circulation and effective buffering capabilities of the north Atlantic and north Pacific. These

curves clearly indicate that New York (north Atlantic) is a more efficient sequestration site than Tokyo (north Pacific) at time scales out to 500 years. However, it should be noted that after 200 years (year 2200) both injection sites buffer at least 55 % of the CO_2 from returning the atmosphere, and in the case of New York, the return is less than 35 %. In these simulations, the global production of CO_2 has nearly ceased by the year 2200. It is therefore more important to evaluate the buffering capabilities during this early period, when global CO_2 production is most vigorous.

The CO_2 injected at 1000 m off of New York enters into the Gulf Stream system, which advects most of the CO_2 into the central north Atlantic. Once the CO_2 reaches the high latitude regions of the Atlantic, a portion of the sequestered CO_2 is transported to great depths by deep water convection, a process resulting from surface cooling of high saline water. The nature of vertical convection (mixing) acts to simultaneously transport CO_2 both towards the surface and to the bottom of the ocean. CO_2 that reaches the ocean surface is allowed to exchange with the atmosphere, and after a year, is globally distributed and may return to the ocean through local air/sea exchange. The deep water convection transports a significant amount of CO_2 down to the bottom layers of the ocean, where it is advected by the deep (3000 m), southward thermohaline circulation. Shown in Figure 19 are four horizontal sections of CO_2 concentration ($\log_{10}[\text{moles/kg}]$) at different depths after 10 years, revealing the transport of CO_2 into the central north Atlantic at the depth of injection (1000m), partial leakage of CO_2 to the global ocean surface (after recirculating in the atmosphere) and deep advection along the western Atlantic towards the south. The CO_2 which enters the deep (3000 m) thermohaline circulation is efficiently buffered from the atmosphere, and is the primary reason for the lower amount of CO_2 returned to the atmosphere for New York than Tokyo (Figure 18). This deep pool of CO_2 is also evident in the same distribution plots after 60 and 300 years (Figures 20 and 21). We should note also that had CaCO_3 rich sediment dissolution been formulated in the model, the buffering capacity for the Atlantic would be further enhanced.

The CO_2 that is injected off of Tokyo enters a similar western boundary current, the Kuroshio. The Kuroshio advects and diffuses the CO_2 into the central north Pacific (Figure 22), much in the same way that the Gulf Stream transports "New York" CO_2 into the central north Atlantic. However, the Pacific does not extend as far north as does the Atlantic, nor is it open to cool, high saline water exiting the Arctic ocean, and there are no regions of deep water formation and convection. In addition, the Pacific represents the "end" of the deep thermohaline conveyor belt (which initiates

in the north Atlantic), and the general trend in the north Pacific is a gradual diffusion upwards. After 60 years (Figure 23) the upper layers (< 1000 m) of the north Pacific contain most of the injected CO_2 . Very little of the CO_2 is penetrating into deep regions of the ocean, except for small traces in the high latitude convective regions in the north and south Atlantic. After 300 years (Figure 24), 200 years after injection has stopped, the upper layers of the entire global ocean contain Tokyo sequestered CO_2 . The CO_2 concentrations are lowest in the deep (3000m) Pacific, further indicating the presence of persistent upwelling and vertical diffusion in the Pacific. This vertical transport gradually advects the injected CO_2 towards the surface waters of the Pacific, where it vents into the atmosphere and causes a more rapid increase in atmospheric CO_2 concentrations. Ultimately, after 500 years the amount of CO_2 reaching the atmosphere from the Tokyo injection site exceeds that for an equivalent electric power generation without sequestration due to the energy penalty introduced by the capture and sequestration processes which consume energy. Despite this long term trend, the buffering capacity of the north Pacific after 200 years (year 2200) is still 45 % better than the case of no sequestration, thereby alleviating some of the short-term impacts associated with pure atmospheric discharge of anthropogenic CO_2 .

The CO_2 injection rates considered in the GCCM are 10 times that simulated in the Mesoscale Ocean Dispersion Model (MODM). The peak oceanic CO_2 concentrations however, are typically much smaller, since the GCCM has a coarser horizontal and vertical resolution. The largest CO_2 concentrations observed in the GCCM were of the order $10 \mu\text{mole/kg}$ (near the injection sites), up to two orders of magnitude less than peak concentrations predicted by the MODM. Over time scales of 2 to 3 years, the general spreading of CO_2 is consistent between the two models (i.e. 1000 to 1500 km). Over much longer time scales (10 to 100 years) the GCCM disperses the CO_2 over vast regions of the globe, including efficient transport by the "well-mixed" atmosphere. After 60 years, CO_2 injected off New York has resulted in a global ocean surface layer increase of $0.01 \mu\text{mole/kg}$ (Figure 20). At depth, large horizontal gradients in CO_2 still exist, with maximum concentrations remaining near the injection site. After 300 years (Figure 21), global ocean surface layer concentrations have increased to $0.5 \mu\text{mole/kg}$, while concentrations in the deep Atlantic are on the order $1.0 \mu\text{mole/kg}$. Virtually no sequestered CO_2 reaches the deep (3000m) Pacific, where concentrations remain below $0.001 \mu\text{mole/kg}$ even after 300 years. For the injection simulation off of Tokyo (Figure 24), marginally higher surface layer concentrations persist after 300 years (0.6 to $0.9 \mu\text{mole/kg}$), while deep Pacific concentrations are still low ($0.001 \mu\text{mole/kg}$). Convection in

the north Atlantic has transported "Tokyo" CO_2 into the deep thermohaline circulation there, resulting in deep Atlantic concentrations of "Tokyo" CO_2 of the order $0.5 \mu\text{mole/kg}$. Changes in the pH due to these concentration increases are predicted to be small (-0.1) even near the source where concentrations increase by $10 \mu\text{mole/kg}$.

The participation of the injected CO_2 in the model's carbon cycle enhances the buffering predictions over non-carbon cycling models (i.e. MODM). Biological assimilation of the CO_2 through photosynthesis in the ocean surface layers is the single most important component of the carbon cycle in reducing atmospheric concentrations. Ocean biological production is governed by the availability of nutrients, which are replenished from below by diffusion and upwelling. Both dissolved and particulate organic carbon (DOC and POC) are formed and are advected away. In the case of POC, the material is allowed to sink below the surface layer, where it is remineralized. Approximately $\frac{1}{3}$ of the flux is associated with sinking POC, while $\frac{2}{3}$ is advected and diffused away as DOC. One important chemical change to sea water in response to elevated CO_2 levels is the loss of saturation conditions with respect to biogenic calcite (calcium carbonate: CaCO_3). When sea water becomes undersaturated with respect to calcite, local calcite-rich sediments can dissolve, raising the local pH and alkalinity, and subsequently altering the capacity of the sea water to absorb additional CO_2 . In order to add this process to the present GCCM, the global distribution of calcite in the deep-ocean sediments would need to be integrated. Although this enhanced buffering capacity only affects CO_2 coming in contact with deep calcite-rich sediments, it would further distinguish injection site characteristics, such as those revealed between Tokyo and New York.

4.3 Conclusions: Far-Field Global Carbon Cycle Modelling

Three simulations were conducted with a Global Carbon Cycle Model (GCCM) in order to evaluate far-field environmental impacts associated with ocean disposal of CO_2 . A control simulation was conducted with a fully activated ocean circulation, an oceanic carbon cycle, and a well-mixed atmosphere. For this simulation 0.1 GtC/year ($3.63 \times 10^{11} \text{ kgCO}_2/\text{year}$) was discharged directly into the atmosphere (representing one hundred 500 MWe power plants). This CO_2 was monitored separately from the global production of CO_2 , which in 1990 was 6.01 GtC/year ($2.2 \times 10^{13} \text{ kgCO}_2/\text{year}$) and was allowed to increase following a logistics type curve, peaking in the year 2090.

Two ocean sequestration simulations were conducted (injection off of New York and Tokyo). For these simulations, 1.24×10^{-2} GtC/year (4.55×10^{10} kgCO₂/year) was discharged directly into the atmosphere and 1.119×10^{-1} GtC/year (4.1×10^{11} kgCO₂/year) was injected into the ocean, split between two injection sites. For each simulation, the "sequestration" process was activated between years 2000 and 2100.

Both ocean injection simulations indicate that a significant ($\approx 50\%$) reduction in the atmospheric CO₂ concentration is realized over the first two centuries (2000 - 2200). Between years 2200 and 2500, CO₂ returned to the atmosphere increases from 50% to 80%, illustrating the long-term trend towards an equilibrium between the ocean and atmosphere. Different sequestration efficiencies between the two ocean injection sites reveals important differences in the ocean circulation and processes between the north Atlantic and north Pacific. CO₂ sequestered in the north Atlantic (i.e. off New York) results in considerable CO₂ entering the deep convective currents of the north Atlantic. CO₂ sequestered in the north Pacific is gradually diffused upwards, towards the surface of the ocean. These ocean characteristics result in different return rates of sequestered CO₂ to the atmosphere. The north Atlantic is revealed to be a better location for long-term (500 year) sequestration than the north Pacific. CO₂ concentrations increase only slightly ($10 \mu\text{mole/kg}$) in the vicinity (< 1000 km) of the injection locations, while on a global and basin scale, CO₂ levels increase by only 0.01 to $1.0 \mu\text{mole/kg}$. Changes in the pH (and alkalinity) over periods of 100 years due to these small increases in sequestered CO₂ will be small (on the order -0.1 pH).

5 References

- Albanese, A.S. and M.Steinberg, 1980; Environmental control technology for atmospheric carbon dioxide., DOE/EV-0079, Brookhaven National Lab., Upton, NY.
- Bacastow, R. and E.Mairer-Reimer, 1990; Ocean-circulation model of the carbon cycle., *Climate Dyn.*, 4, 95-125.
- Bacastow, R., and G.R.Stegen, 1991; Estimating the potential for CO₂ sequestration in the ocean using a carbon cycle model., *Proceedings Oceans '91*, Oct 1-3, 1991, Honolulu, Hawaii.
- Bacastow, R., K.H.Cole, R.K.Dewey, and G.R.Stegen, 1994; Effectiveness of CO₂ sequestration in the oceans considering location and depth, 2nd International Conf. on Carbon Dioxide Removal (ICCDR-2) Oct 24-27, 1994, Kyoto, Japan.
- Baes, C.F.Jr., S.E.Beall, and D.W.Lee, 1980; The collection, disposal and storage of carbon dioxide., In: *Interactions of Energy and Climate*, ed. W.Bach, D.Reidel Pub., 495-519.
- Bennett, A. F., 1987; A Lagrangian analysis of turbulent diffusion, *Reviews of Geophys.*, Vol 24(4), 799-822.
- Cole, K.H. and G.Stegen, 1993; The capacity of the deep oceans to absorb CO₂, *Energy Covers. Mgmt.*, 34(9-11), 991-998.
- Davis, R.E., 1991; Lagrangian ocean studies, *Annu. Rev. Fluid Mech.*, 23, 43-64.
- Department of energy, 1993: A research needs assessment for the capture, utilization and disposal of carbon dioxide from fossil fuel-fired power plants, Vols 1 and 2, DOE/ER-30194.
- Dewey, R.K., J. N. Moum, C. A. Paulson, D. R. Caldwell, and S. D. Pierce, 1991; Structure and dynamics of a coastal filament, *J. Geophys. Res.*, Vol 96(C4) 14,885-14,907.
- Drange, H. and P.M.Haugan, 1992; Carbon dioxide sequestration in the ocean: The possibility of injection in shallow water., *Energy Covers. Mgmt.*, 33(5-8) 697-704.
- Golomb, D.S., S.G.Zemba, J.W.H.Dacey, and A.F.Michaels, 1992; The fate of CO₂ sequestered in the deep ocean, *Energy Convers. Mgmt.*, 33(4-8), 675-683.
- Hall, M.M., 1986: Horizontal and vertical structure of the Gulf Stream velocity field at 68° W., *J. Phys. Oceano.*, 16, 1814-1828.
- Herzog, H., D.Golomb, and S.Zemba, 1991; Feasibility, modeling and economics of sequestering power plant CO₂ emission in the deep ocean., *Envir. Progress.*, 10(1), 64-74.
- Hidy, G.M. and D.F.Spencer, 1994; Climate alteration: A global issue for the electric power

- industry in the 21st century., *Energy Policy*, 22(12), 1005-1027.
- Intergovernmental Panel on Climate Change, 1991; *Climate Change: The IPCC response strategies*, Island Press, Washington DC, Chapter 2.
- Kheshgi, H.S., B.P.Flannery, M.I.Hoffert, and A.G.Lapenis, 1994; The effectiveness of marine CO₂ disposal, *Energy*, 19(9), 967-974.
- Ledwell, J.R., A.J.Watson, and C.S.Law, 1993; Evidence of slow mixing across the pycnocline from an open-ocean tracer-release experiment., *Nature*, 364, 701-703.
- Liro, C.R., E.E.Adams, and H.J.herzog, 1992; Modeling the release of CO₂ in the deep ocean., *Energy Covers. Mgmt.*, 33(5-8), 667-674.
- McWilliams, et al., 1983; The local dynamics of eddies in the western North Atlantic, In *Eddies in Marine Science.*, Edited by A.R.Robinson, pp 92-113, Springer-Verlag, New York.
- Mairer-Reimer, E., K. Hasselmann, D. Olbers and J.Willibrand, 1982; An ocean circulation model for climate variability studies, Technical Report, Max-Plank Institut fuer Meteorologie, Hamberg, Germany.
- Mairer-Reimer, E. and K.Hasselmann, 1987; Transport and storage of CO₂ in the ocean - An inorganic ocean-circulation carbon cycle model, *Climate Dyn.*, 2, 63-90.
- Manabe, S., R.J.Stouffer, M.J.Spelman and K.Bryan, 1991; Transient responses of a coupled ocean-atmosphere model to gradual changes of atmospheric CO₂. Part I: Annual mean response., *J. of climate*, 4, 785-817.
- Manabe, S., M.J.Spelman, and R.J.Stouffer, 1992; Transient response of a coupled ocean-atmosphere model to gradual changes of the atmospheric CO₂. Part II: Seasonal response., *J. of Climate*, 5, 105-126.
- Manabe, S., and r.J.stouffer, 1994; Multiple-century response of a coupled ocean-atmosphere model to an increase of atmospheric carbon dioxide., *J. of Climate*, 7, 5-23.
- Marchetti, C., 1977; On geoengineering and the CO₂ problem., *Climate Change*, 1, 59-68.
- Marchetti, C., 1979; Constructive solutions to the CO₂ problem, In: *Man's Impact on Climate*, ed. W.Bach, J.Pankrath, and W.Kellogg, Elsevier Scientific Publ., 299-311.
- Murphy, J.M., 1995; Transient response of the Hadley Centre Coupled Ocean-Atmosphere Model to increasing carbon dioxide. Part I: Control climate and flux adjustment (36-56) and Part II: Spatial and temporal structure of response (57-80), *J. of Climate*, 8(1), 36-80.
- Ohsumi, T., N.Nakashiki, K.Shitashima, and K.Hirama, 1992; Density change of water due to dissolution of carbon dioxide and near-field behavior of CO₂ from a source on the deep-sea

- floor., Energy Covers. Mgmt., 33(5-8), 685-690.
- Okubo, A., 1971; Oceanic diffusion diagrams, Deep Sea Research, Vol 18, 789-802.
- Sakai, H., T.Gamo, E.S.Kim, M.Tsutsumi, T.Tanaka, J.Ishibashi, H.Wakita, M.Yamano, and T.Oomori, 1990; Venting of carbon dioxide-rich fluid and hydrate formation in mid-Okinawa Trough Backarc Basin, Science, 248, 1093-1096.
- Sawford, B.L., 1984; The basis for, and some limitations of, the Langevin equation in atmospheric relative dispersion modelling, Atmospheric Environ., Vol 18(11), 2405-2411.
- Segal, M., M.J.Mitchell, and r.W.Artritt, 1994; Some sensitivity evaluations of potential $2\times\text{CO}_2$ climate impact on deep convection over water bodies., J. of Climate., 7, 1014-1018.
- Semtner, A. J., and R. M. Chervin, 1992; Ocean general circulation from a global eddy-resolving model., J. Geophys. Res., Vol 97(C4), 5493-5550.
- Stegen, G.R., K.H.Cole, and R.Bacastow, 1991; Sequestering CO_2 in the ocean., IEA Conference on Technology Responses to Global Challenges, Nov 6-8, 1991, Kyoto, Japan.
- Stegen, G.R., K.H.Cole, and R.Bacastow, 1993; The influence of discharge depth and location on the sequestration of carbon dioxide., energy Covers. Mgmt., 34(9-11) 857-864.
- Stegen, G.R., K.H.Cole, and R.Bacastow, 1994; Biogeochemical impacts of CO_2 storage in the ocean., 2nd International Conference on Carbon dioxide Removal (ICCDR-2), Oct 24-27, Kyoto, Japan.
- Steinberg, M. and H.C.Cheng, 1985; A systems study for the removal, recovery, and disposal of carbon dioxide from fossil fuel power plants in the U.S., Brookhaven National Lab., report BNL-36428.
- Steinberg, M. and H.C.Cheng, 1987; Advanced technologies for reduced CO_2 emissions, Brookhaven National Lab, Report BNL-40730.
- Stommel, H., 1965; *The Gulf Stream: A physical and dynamics description.*, 2nd Edition, Uni.of California Press, Berkeley.
- Wilson, T.R.S., 1992; The deep ocean disposal of carbon dioxide., Energy Convers. Mgmt, 33(5-8), 627-633.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 39.01(d) Long= 288.51(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1459.6 Min: 325.7
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 8194.9 Minimum: 19.7

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure 1: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=39°N, longitude=72°W (NY1), at 1000 m using the MODM. Minimum and maximum plume depths are 235 and 1459 m, respectively.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 35.35(d) Long= 287.01(d) Injection Depth=2000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 2232.1 Min: 193.8
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 2759.2 Minimum: 13.3

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure 2: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=35.35°N, longitude=73°W (DC2), at 2000 m using the MODM. Minimum and maximum plume depths are 194 and 2232 m, respectively.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 35.35(d) Long= 287.01(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1069.7 Min: 457.2
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 365.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 2086.7 Minimum: 23.2

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure 3: One year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=35.35°N, longitude=73°W (DC2), at 1000 m using the MODM. Minimum and maximum plume depths are 447 and 1070 m, respectively.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 36.75(d) Long= 286.01(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1090.8 Min: 354.5
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 13430.5 Minimum: 22.7

Figure 4: Three year horizontal distribution of CO₂ (μmole/kg) within model layer 710-985 m for an injection of 1.26 m³/s of liquid CO₂ at latitude=36.75°N, longitude=74°W (DC1), at 1000 m using the MODM.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 36.75(d) Long= 286.01(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1090.8 Min: 354.5
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 13430.5 Minimum: 22.7

Figure 5: Three year horizontal distribution of CO_2 ($\mu\text{mole/kg}$) within model layer 510-710 m for an injection of $1.26 \text{ m}^3/\text{s}$ of liquid CO_2 at latitude= 36.75°N , longitude= 74°W (DC1), at 1000 m using the MODM.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 36.75(d) Long= 286.01(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1090.8 Min: 354.5
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 13430.5 Minimum: 22.7

Figure 6: Three year horizontal distribution of CO₂ (μmole/kg) within model layer 360-510 m for an injection of 1.26 m³/s of liquid CO₂ at latitude=36.75°N, longitude=74°W (DC1), at 1000 m using the MODM.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 39.01(d) Long= 288.01(d) Injection Depth=1200.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1597.2 Min: 376.2
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 31338.8 Minimum: 17.2

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure 7: Three year horizontal distribution of CO_2 ($\mu\text{mole/kg}$) for a combined injection of 1.26 m^3/s of liquid CO_2 at each of latitude= 36.75°N , longitude= 74°W (DC1) and latitude 39°N , longitude= 72°W (NY1), at 1500 and 1200 m, respectively.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 26.36(d) Long= 280.51(d) Injection Depth= 300.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 550.4 Min: 1.9
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 7257.6
 Model Run Duration: 1095.0 (Days) Time Step: 8.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 874.3 Minimum: 12.8

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure 8: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=26.36°N, longitude=79.5°W (MI1), at 300 m using the MODM. Minimum and maximum plume depths are 2 and 550 m, respectively.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 26.68(d) Long= 283.80(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1202.1 Min: 192.0
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 3111.0 Minimum: 20.0

Figure 9: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=26.68°N, longitude=76.2°W (MI2), at 1000 m using the MODM. Minimum and maximum plume depths are 192 and 1202 m, respectively.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 26.68(d) Long= 283.80(d) Injection Depth=1500.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1567.2 Min: 162.9
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 1922.6 Minimum: 16.0

C=Concentration

V=Vector

O=Overlay

D=Drifter Track

#=Graph Update

+--=Vector Size

Figure 10: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=26.68°N, longitude=76.2°W (MI2), at 2000 m using the MODM. Minimum and maximum plume depths are 162 and 1567 m, respectively.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 34.70(d) Long= 285.01(d) Injection Depth=1500.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 2259.6 Min: 165.1
 Injection Rate: .42 (m**3/Sec) Volume/particle (m**3): 12096.0
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 2550.4 Minimum: 8.7

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure 11: Three year horizontal distribution of CO₂ (μmole/kg) for a total injection of 1.26 m³/s of liquid CO₂ distributed between three sites east of Cape Hatteras (CH3). Minimum and maximum CO₂ concentrations are 8.7 μmole/kg and 2550 μmole/kg, respectively.

14:47 10/30/95

Figure 12: Histogram of $\log_{10}$ CO₂ concentrations in $\mu\text{mole/kg}$ for the plume shown in Figure 11.
The value 10^0 represents a single observation, values less than 10^0 are zero.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 36.51(d) Long= 237.30(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1161.4 Min: 915.6
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 54432.0
 Model Run Duration: 2190.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 19098.4 Minimum: 57.3

Figure 13: Six year horizontal distribution of CO₂ (μ mole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=36.5°N, longitude=122.7°W (SF), at 1000 m using the MODM. Minimum and maximum plume depths are 915 and 1161 m, respectively.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 32.01(d) Long= 134.01(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1620.6 Min: 518.8
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 2075.9 Minimum: 17.8

Figure 14: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=32°N, longitude=134°E (JP), at 1000 m using the MODM. Minimum and maximum plume depths are 518 and 1620 m, respectively.

15:39 10/30/95

Figure 15: Global CO₂ production curve (logistics function) in GtC/year used in Global Carbon Cycle Model. Function was fit to known levels in 1990 and projected to peak near the year 2100 with a total carbon production of 4240 GtC (Hidy and Spencer, 1994).

22:36 2/11/96

Figure 16: Total atmospheric CO₂ concentration in ppm predicted by the GCCM when considering the global production curve shown in Figure 15. Long-term equilibrium content of the atmosphere is 509 GtC, or approximately 900 ppm.

22:33 2/11/96

Figure 17: Amount of CO₂ returned to the atmosphere for the sequestration simulations. The upper curve is the "control" case (100 power plants generating 115 kgCO₂/s), the lower curve is the combined return from New York and Tokyo for 100 power plants generating 144.4 kgCO₂/s.

2231 2/11/96

Figure 18: Amount of CO₂ returned to the atmosphere for ½ of the control case (50 power plants generating 115 kgCO₂/s) and 50 power plants generating 144.4 kgCO₂/s with ocean sequestration off of both New York and Tokyo.

New York Injection at 1000m after 10 years (2.05×10^{11} kg CO₂/yr)

Figure 19: Horizontal distributions of sequestered CO₂ in log₁₀ mole/kg for an injection site at 1000 m east of New York as predicted by the GCCM after 10 years. Peak and surface concentrations are 10 and 10^{-4} μ mole/kg, respectively.

22:47 2/11/96

New York Injection at 1000m after 60 years (2.05×10^{11} kg CO₂/yr)

Figure 20: Horizontal distributions of sequestered CO₂ in log₁₀ mole/kg for an injection site at 1000 m east of New York after 60 years. Peak concentrations in the north Atlantic (1000 m) are $10 \mu\text{mole/kg}$, while surface concentrations are $10^{-2} \mu\text{mole/kg}$.

22.55 2/11/96

New York Injection at 1000m after 300 years (2.05×10^{11} kg CO₂/yr)

Figure 21: Horizontal distributions of sequestered CO₂ in log₁₀ mole/kg for an injection site at 1000 m east of New York after 300 years. Peak concentrations in the north Atlantic (1000 m) are 1 μ mole/kg, while surface concentrations are 0.5 μ mole/kg.

22:58 2/11/96

Tokyo Injection at 1000m after 10 years (2.05×10^{11} kg CO₂/yr)

Figure 22: Horizontal distributions of sequestered CO₂ in log₁₀ mole/kg for an injection site at 1000 m southeast of Tokyo after 10 years. Peak and surface concentrations are 10 and 10⁻³ μmole/kg, respectively.

23.02 23.02

Tokyo Injection at 1000m after 60 years (2.05×10^{11} kg CO₂/yr)

Figure 23: Horizontal distributions of sequestered CO₂ in log₁₀ mole/kg for an injection site at 1000 m southeast of Tokyo after 60 years. Peak concentrations in the northwest Pacific (1000 m) are 10 μ mole/kg, while surface concentrations are 10⁻¹ μ mole/kg.

23/04 2/11/96

Tokyo Injection at 1000m after 300 years (2.05×10^{11} kg CO₂/yr)

Figure 24: Horizontal distributions of sequestered CO₂ in log₁₀ mole/kg for an injection site at 1000 m southeast of Tokyo after 300 years. Peak concentrations in the northwest pacific (1000 m) are 5 μ mole/kg, while surface concentrations are 1.0 μ mole/kg.

23/07 2 11/96

Topical Report 4

Appendix A

Model Run	Description (See Table 1)	Page
1	DC1, 1000 m	4-61
2	DC1, 1500 m	4-62
3	NY1, 1000 m	4-63
4	NY1, 1200 m	4-64
5	DC2, 1000 m	4-65
6	DC2, 1500 m	4-66
7	DC2, 2000 m	4-67
8	NY2, 1000 m	4-68
9	NY2, 1500 m	4-69
10	NY2, 2000 m	4-70
11	MI1, 300 m	4-71
12	MI2, 1000 m	4-72
13	MI2, 1500 m	4-73
14	DC1 1000 m + NY1 1000 m	4-74
15	DC1 1500 m + NY1 1200 m	4-75
16	DC1, 1725 m	4-76
17	CH1, 1000 m	4-77
18	CH1, 1500 m	4-78
19	CH2, 1000 m	4-79
20	CH2, 1500 m	4-80
21	CH3, 1500, 1700, and 2000 m	4-81
22	SF, 1000 m, 3 years	4-82
23	SF, 1500 m	4-83
24	SF, 1000 m, 6 years	4-84
25	JP, 1000 m	4-85

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 36.75(d) Long= 286.01(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1090.8 Min: 354.5
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 13430.5 Minimum: 22.7

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure A-1 DC1: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=36.75°N, longitude=74°W, at 1000 m using the MODM. Water depth at this site is 1750 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 36.75(d) Long= 286.01(d) Injection Depth=1500.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1553.5 Min: 346.2
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 14189.3 Minimum: 17.3

Figure A-2 DC1: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=36.75°N, longitude=74°W, at 1500 m using the MODM. Water depth at this site is 1750 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 39.01(d) Long= 288.51(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1459.6 Min: 325.7
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 8194.9 Minimum: 19.7

Figure A-3 NY1: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=39°N, longitude=72°W, at 1000 m using the MODM. Water depth at this site is 1350 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 39.01(d) Long= 288.01(d) Injection Depth=1200.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1617.8 Min: 200.6
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 29738.4 Minimum: 19.6

Figure A-4 NY1: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=39°N, longitude=72°W, at 1200 m using the MODM. Water depth at this site is 1350 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 35.35(d) Long= 287.01(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1102.4 Min: 305.9
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 12102.6 Minimum: 23.2

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure A-5 DC2: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=35.35°N, longitude=73°W, at 1000 m using the MODM. Water depth at this site is 3850 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 35.35(d) Long= 287.01(d) Injection Depth=1500.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1841.9 Min: 144.1
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 3532.7 Minimum: 16.1

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure A-6 DC2: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=35.35°N, longitude=73°W, at 1500 m using the MODM. Water depth at this site is 3850 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 35.35(d) Long= 287.01(d) Injection Depth=2000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 2232.1 Min: 193.8
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 2759.2 Minimum: 13.3

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure A-7 DC2: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=35.35°N, longitude=73°W, at 2000 m using the MODM. Water depth at this site is 3850 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 37.51(d) Long= 289.46(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1412.9 Min: 316.2
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 13354.6 Minimum: 18.5

Figure A-8 NY2: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=37.5°N, longitude=70.54°W, at 1000 m using the MODM. Water depth at this site is 3300 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 37.51(d) Long= 289.46(d) Injection Depth=1500.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1987.9 Min: 189.8
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 3572.4 Minimum: 16.1

Figure A-9 NY2: Three year horizontal distribution of CO₂ (μ mole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=37.5°N, longitude=70.54°W, at 1500 m using the MODM. Water depth at this site is 3300 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 37.51(d) Long= 289.46(d) Injection Depth=2000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 2259.7 Min: 576.4
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 3461.6 Minimum: 14.6

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure A-10 NY2: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=37.5°N, longitude=70.54°W, at 2000 m using the MODM. Water depth at this site is 1750 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 26.36(d) Long= 280.51(d) Injection Depth= 300.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 550.4 Min: 1.9
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 7257.6
 Model Run Duration: 1095.0 (Days) Time Step: 8.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 874.3 Minimum: 12.8

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure A-11 M11: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=26.36°N, longitude=79.5°W, at 300 m using the MODM. Water depth at this site is 360 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 26.68(d) Long= 283.80(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1202.1 Min: 192.0
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 3111.0 Minimum: 20.0

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure A-12 MI2: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=26.68°N, longitude=76.2°W, at 1000 m using the MODM. Water depth at this site is 2750 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 26.68(d) Long= 283.80(d) Injection Depth=1500.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1567.2 Min: 162.9
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 1922.6 Minimum: 16.0

Figure A-13 MI2: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=26.68°N, longitude=76.2°W, at 1500 m using the MODM. Water depth at this site is 1750 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 39.01(d) Long= 288.51(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1433.6 Min: 382.0
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 18742.0 Minimum: 19.5

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure A-14 DC1+NY1: Three year horizontal distribution of CO_2 ($\mu\text{mole/kg}$) for injection of $1.26 \text{ m}^3/\text{s}$ of liquid CO_2 at both latitudes= $36.75^\circ + 39^\circ\text{N}$, longitudes= $74^\circ + 72^\circ\text{W}$, at 1000 m using the MODM. Water depths at these sites are 1750 and 1350 m, respectively.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 39.01(d) Long= 288.01(d) Injection Depth=1200.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1597.2 Min: 376.2
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 31338.8 Minimum: 17.2

Figure A-15 DC1+NY1: Three year horizontal distribution of CO₂ (μmole/kg) for injection of 1.26 m³/s of liquid CO₂ at both latitude=36.75°+39° N, longitude=74°+72° W, at 1500 and 1200 m using the MODM. Water depths at these sites are 1750 and 1350 m, respectively.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 36.75(d) Long= 286.01(d) Injection Depth=1725.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1748.1 Min: 348.1
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 13847.8 Minimum: 27.1

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure A-16 DC1: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=36.75°N, longitude=74°W, at 1725 m (bottom) using the MODM. Water depth at this site is 1750 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 34.70(d) Long= 285.01(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1495.7 Min: 269.7
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 23661.0 Minimum: 17.0

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

CONCENTRATION Depth Average

Figure A-17 CH1: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=34.7°N, longitude=75°W, at 1000 m using the MODM. Water depth at this site is 1750 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 34.70(d) Long= 285.01(d) Injection Depth=1500.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1831.3 Min: 171.0
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 5064.7 Minimum: 16.3

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure A-18 CH1: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=34.7°N, longitude=75°W, at 1500 m using the MODM. Water depth at this site is 1750 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 33.95(d) Long= 285.81(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1734.3 Min: 297.5
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 16429.7 Minimum: 18.3

Figure A-19 CH2: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=33.95°N, longitude=74.19°W, at 1000 m using the MODM. Water depth at this site is 3850 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 33.95(d) Long= 285.81(d) Injection Depth=1500.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1854.1 Min: 214.0
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 2583.7 Minimum: 16.1

Figure A-20 CH2: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=33.95°N, longitude=74.19°W, at 1500 m using the MODM. Water depth at this site is 3850 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 34.70(d) Long= 285.01(d) Injection Depth=1500.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 2259.6 Min: 165.1
 Injection Rate: .42 (m**3/Sec) Volume/particle (m**3): 12096.0
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 2550.4 Minimum: 8.7

Figure A-21 CH3: Three year horizontal distribution of CO₂ (μmole/kg) for injection of 0.42 m³/s of liquid CO₂ at latitudes = 34.7° + 34.5° + 34.3° N, longitudes = 75° + 74.8° + 74.6° W, at 1500, 1700 and 2000 m, respectively, using the MODM. Water depths at these sites are 1750, 1750 and 2200 m, respectively.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 36.51(d) Long= 237.30(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1138.4 Min: 916.4
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 13674.0 Minimum: 23.3

C=Concentration
 V=Vector
 O=Overlay
 D=Drifter Track
 #=Graph Update
 +=Vector Size

Figure A-22 SF1/3yrs: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=36.5°N, longitude=122.7°W, at 1000 m using the MODM. Water depth at this site is 2200 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 36.51(d) Long= 237.30(d) Injection Depth=1500.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1659.0 Min: 1342.2
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 11869.1 Minimum: 19.6

Figure A-23 SF1: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=36.5°N, longitude=122.7°W, at 1500 m using the MODM. Water depth at this site is 2200 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 36.51(d) Long= 237.30(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1161.4 Min: 915.6
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 54432.0
 Model Run Duration: 2190.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 19098.4 Minimum: 57.3

Figure A-24 SF1/6yrs: Three year horizontal distribution of CO₂ (μmole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=36.5°N, longitude=122.7°W, at 1000 m using the MODM. Water depth at this site is 2200 m.

LAGRANGIAN SUB-GRID SCALE DISPERSION MODEL

Injection Site: Lat= 32.01(d) Long= 134.01(d) Injection Depth=1000.0 m
 Turbulence Level (TKE/MKE): .050 Plume Depth Max: 1620.6 Min: 518.8
 Injection Rate: 1.26 (m**3/Sec) Volume/particle (m**3): 21772.8
 Model Run Duration: 1095.0 (Days) Time Step: 24.(hrs) Day:
 Concentrations in (umol/kg) Maximum: 2075.9 Minimum: 17.8

Figure A-25 JP1: Three year horizontal distribution of CO₂ (μ mole/kg) for an injection of 1.26 m³/s of liquid CO₂ at latitude=32°N, longitude=134°E, at 1000 m using the MODM. Water depth at this site is 2750 m.

Topical Report 5

Biological Assessment of Environmental Impacts of CO₂ Ocean Disposal

(Chapters 1-3 and Appendices)

**David I. Auerbach
Howard J. Herzog
E. Eric Adams
Jennifer A. Caulfield**

**Massachusetts Institute of Technology
Energy Laboratory
77 Massachusetts Avenue
Cambridge, MA 02139-4307**

Table of contents

Page

Chapter 1. Background and Motivation	5-5
1.1 Introduction	5-5
1.2 Climate change mitigation	5-6
1.3 CO ₂ capture and disposal	5-7
1.4 Environmental impacts of CO ₂ ocean disposal	5-9
Chapter 2. Toxicological Assessment and Model Development	5-11
2.1 Introduction	5-11
2.2 CO ₂ ocean disposal scenarios	5-11
2.3 Physiochemical impact of CO ₂ on the marine environment	5-13
2.4 Current knowledge of effects of low pH on marine zooplankton and benthos	5-14
2.4.1 <i>Zooplankton groups and abundance</i>	
2.4.2 <i>The importance of exposure time</i>	
2.4.3 <i>Literature studies of effects of reduced pH on marine zooplankton and bacteria</i>	
2.5 Derivation of a toxicity model	5-19
2.6 Integration of literature studies with simulated pH exposures	5-20
2.6.1 <i>Methodology for adding exposures</i>	
2.6.2 <i>Isomortality approximation method</i>	
2.6.3 <i>Justification for exposure addition</i>	
2.6.4 <i>Mechanisms of pH toxicity</i>	
Chapter 3. Model integration and results	5-28
3.1 Introduction	5-28
3.2 Scenario development	5-28
3.3 Plume modeling	5-29
3.4 Exposure assessment	5-31
3.5 Primary measures of impact	5-33
3.5.1 <i>Spatial deficit</i>	
3.5.2 <i>Mortality flux</i>	
3.5.3 <i>Integrated mortality</i>	
3.6 Resulting quantitative impact of CO ₂ disposal	5-35
3.6.1 <i>Ecological measures of impact</i>	
3.6.2 <i>Discussion of results</i>	
3.7 Sensitivity analysis	5-38
3.8 Other considerations and potential impacts	5-40
3.8.1 <i>Benthic Impacts</i>	
3.8.2 <i>Dissolution of Calcium Carbonate</i>	
3.8.3 <i>Effects on bacteria</i>	
3.8.4 <i>Effects of trace gases</i>	
3.9 Background effects - no action scenario	5-43
3.9.1 <i>Effects on phytoplankton of slightly reduced pH</i>	
3.9.2 <i>Effect on metal toxicity</i>	
3.10 Ecosystem level impact of CO ₂ disposal	5-47
3.11 Conclusions and summary of impacts	5-48
Appendices	5-49
A. Alternative measures for adding exposures	5-49

B. Compensation and intergenerational effects	5-55
References	5-57

List of Figures

	Page
Figure 1.1 Net CO ₂ entering atmosphere over time	5-9
Figure 2.1 Schematic illustration of CO ₂ ocean disposal scenarios	5-12
Figure 2.2 Percent mortality of various marine zooplankton and benthos as a function of pH and time exposed to that pH	5-18
Figure 2.3 LC ₀ , LC ₅₀ and LC ₉₀ curves which represent 'isomortality' lines	5-19
Figure 2.4 Hypothetical organism experience curve	5-22
Figure 2.5 Illustration of method of adding discretized point exposures	5-24
Figure 3.1 pH contours resulting from release of CO ₂ in the one-plant droplet plume scenario	5-30
Figure 3.2 Grid showing 'lanes' used for Monte-Carlo simulation	5-32
Figure 3.3 One plant spatial deficits for droplet plume and dense plume	5-35
Figure 3.4 Ten plant spatial deficits for droplet plume and dense plume	5-36
Figure 3.5 Marine impacts of CO ₂ with and without ocean disposal	5-44
Figure A.1 Illustration of Schubel's method of adding exposures	5-50
Figure A.2 Illustration of Mattice and Zittel's method for adding exposures	5-52
Figure B.1 Function used for variation in growth rate with pH	5-56

List of Tables

	Page
Table 2.1 Mortality expressed as a percentage of organisms dying from exposure to reagent grade hydrochloric acid	5-17
Table 3.1 Summary of physiochemical results of plume modeling for four scenarios	5-31
Table 3.2 Summary of primary results of impact assessment analysis	5-36
Table 3.3 Additional results of environmental impact assessment of CO ₂ discharge	5-37
Table 3.4 Sensitivity of results to isomortality curves in toxicity model	5-40
Table 3.5 Average metal concentrations in seawater	5-45
Table A.1 Illustration of hazard function exposure addition method in comparison with two other methods	5-51

Chapter 1. Background and Motivation

"Human beings are now carrying out a large-scale geophysical experiment of a kind that could not have happened in the past nor be repeated in the future. Within a few centuries we are returning to the atmosphere and oceans the concentrated organic carbon stored in the sedimentary rocks over hundreds of millions of years. This experiment, if adequately documented, may yield a far-reaching insight into the processes determining weather and climate."

-Revelle and Suess (1957)

1.1 Introduction

We are indeed involved in a geological experiment of massive proportions. The readily available organic hydrocarbons that have built up over millennia in geological sediments have fueled the industrial revolution, providing cheap sources of energy in their combustion to the lower energy products of H_2O and CO_2 . Yet the optimism of Revelle and Suess as to the potential insights gained from the experiment has been replaced over the nearly four decades since their statement with increasing dread and alarm. Concern has recently prompted the Vice President of the United States, Al Gore, to call global climate change as attributed to increased concentrations of greenhouse gases as "the most important environmental issue affecting the world today" (USDOE, 1994). This shift in attitudes reflects the realization that our global experiment may have catastrophic consequences for the future of human life on the planet.

CO_2 in the atmosphere is essentially transparent to solar radiation, but impedes the outward flow of heat back from the earth. The result is a net warming of the earth, (commonly known as the greenhouse effect) and a change in the global climate. While other gases such as man-made CFCs and methane contribute significantly to global climate change as well, CO_2 emissions account for over half of the effect, and emission rates of CO_2 are increasing more quickly than those for other greenhouse gases (NAS, 1992, p.8). The release of fossil carbon to the atmosphere as CO_2 has increased exponentially since 1860 causing atmospheric concentrations of CO_2 to rise from 280 ppm (.028%) to near 360 ppm in 1996 (Baes, 1977; DeBaar, 1992). Levels could reach as high as nearly 750 ppm by the year 2100 if serious mitigation measures are not taken (IPCC, 1995).

The effects of this increase are difficult to state with certainty. For example, it is fairly well established that global mean temperatures have increased about 0.3 to 0.6 °C over the last 100 years, although natural variation can not be ruled out as a possible cause at this time (NAS, 1992). Yet as time marches on, we are likely to see more and more evidence of significant climate change. A further increase of 1 to 4°C has been predicted by the year 2100 by the IPCC, a trend which is projected to result in many potentially disastrous climatic effects. Direct effects of the temperature increase would be a rise in the global mean sea level by .1 to .8 m, and changes in regional rainfall and temporal patterns, resulting in increased incidence of floods and droughts.

These climate modifications would have serious repercussions for human economic activity and production, especially in island or coastal nations. Other suggested indirect impacts of a climate change of this magnitude are changes in forest ecosystems resulting from a poleward shift in isotherms, increased desertification in dry zones, increased glacial retreat affecting rivers and snow cover, disruptions of oceanic circulations which could further feedback into climatic modification, and increases in vector-borne diseases and changes in life-cycle patterns of many parasites (IPCC, 1995). In economic terms the costs of a doubling of preindustrial CO₂ levels have been estimated by several authors to fall between 1 and 2% of total world output (Nordhaus, 1994). These numbers are of course highly uncertain. Yet while we are uncertain about the effects and costs of future climate change, it is a fact that atmospheric CO₂ concentrations are rising exponentially (at about 0.4% per year) and that taking early action to mitigate this increase may have significant payoffs in the future.

1.2 Climate change mitigation

In the most significant landmark step to combat climate change to date, developed nations present at the UN Conference on Environment and Development in June, 1992, agreed under the Framework Convention on Climate Change (FCCC) to adopt policies and measures to reduce anthropogenic emissions of CO₂ and other greenhouse gases to their 1990 levels by the year 2000. By 1995, 160 countries had agreed to ratify the FCCC which called for states to develop action plans to achieve this reduction. In the course of researching mitigation options, the most commonly suggested measures fall into five general categories: 1) greater conversion efficiency and fuel switching within the fossil fuel sector, 2) greater reliance on non-fossil fuel energy sources, 3) greater energy conservation and end-use efficiency, 4) geo-engineering options to reflect solar radiation or increase CO₂ uptake by phytoplankton or forests, and 5) methods to capture, and utilize, convert or store CO₂ before emission to the atmosphere can take place.

The most favored options generally discussed are the energy efficiency and conservation options, as they often are estimated to provide the greatest emission reduction for the lowest cost (or even at a net savings) (NAS, 1992). Yet as populations in the world increase steadily and energy demand increases also (world energy use is projected to increase roughly 48% between 1990 and 2010 with an even larger increase expected in the use of coal), efficiency measures would likely have little impact on overall CO₂ emissions - especially if they result in a decrease in energy prices (USDOE, 1994). The other strategies are generally accepted to have great potential for counteracting climate change but would be quite expensive to implement in the near future.

In a move to increase efforts to pursue these options, 30 nations including the European Community endorsed a statement known as the Climate Technology Initiative (CTI) at the 1995 Annual Conference of the Parties which was an outgrowth of the FCCC attended by the signatories to the Convention. The statement includes eight initiatives to accelerate mitigation activities, the last of which includes measures to "assess the feasibility of developing longer-term technologies to capture, remove or dispose of greenhouse gases and strengthen relevant basic and applied research." As shall be seen, removal and disposal of greenhouse gases could be a powerful and effective mitigation strategy. Yet the feasibility is largely uncertain today. In 1991, in a study of mitigation options and their costs, Naill *et al.* expressed this sentiment as well.

The potentially high cost of limiting carbon emissions suggests that policies for removing carbon from the power plant emissions should be considered. Technologies exist to scrub carbon dioxide from the effluent stream of power plants, but costs are extremely high and disposal poses a substantial problem (Naill *et al.*, 1991).

Naill begins and ends his mention of CO₂ disposal as a possible strategy with this sentence. Yet recent studies and activities including the 1995 IPCC report suggest that CO₂ disposal might be more feasible than was thought even five years ago.

1.3 CO₂ capture and disposal

The concept of CO₂ capture and subsequent storage, or utilization is not a radical or groundbreaking concept. Most developed countries currently use these strategies of capture and storage or utilization of flue gases to reduce emissions of SO₂ and NO_x and particulates from fossil fuel burning power plants. Technologically, CO₂ capture is already a proven concept and has been used in limited capacity where the CO₂ is then used in Enhanced Oil Recovery (EOR) and other industrial processes. The potential for mitigation of climate change

via this strategy is also quite large as approximately one third of anthropogenic CO₂ emissions are derived from fossil fuel electric power plants (USDOE, 1994).

Although the technology exists to capture the CO₂ emitted from power plants, storage or disposal is another issue. Storage in depleted oil and gas wells would likely be the cheapest and easiest solution, as these wells are often located near the power plants. However, capacity is limited, and the integrity of storage (i.e. containment) in the long term is under question. Exhausted gas and oil wells together are estimated to have the capacity for storage of about 150 Gt C which is large relative to current emissions (7-8 Gt/yr), but not all of this storage potential is accessible (IPCC, 1995).

The ocean, however, presents abundant opportunities for CO₂ storage. The upper 100-200 m of the ocean are well-mixed and saturated in CO₂ with respect to atmospheric CO₂ concentrations; if CO₂ were injected in this layer, it would quickly be released to the atmosphere. But below the well-mixed surface layer down to approximately 1000 m, an increasing density profile exists due to decreasing temperatures (the thermocline), making the unsaturated waters stably stratified. It is the deeper layers of the ocean, below the thermocline, that are a leading candidate to serve as a sequestering medium for anthropogenic CO₂ emissions.

These deep layers already store much more CO₂ than surface layers, and apparently have the potential for even greater storage with little impact. The total dissolved inorganic carbon content of the ocean has been estimated at 38,000 Gt C, compared to 750 Gt C in the atmosphere (IPCC, 1990). If all of the current annual worldwide anthropogenic carbon emissions of about 7 Gt C were disposed in the ocean, the yearly increase would be only 0.016%. Such storage is possible because the deeper layers are highly unsaturated in CO₂ compared to the solubility of CO₂ at the temperature and pressure (>100 atm) prevailing in those layers. In fact, Spencer (1993) has estimated that the ocean could hold at least 1,200 additional Gt with little impact to its overall chemistry (a pH change of less than .2 units) (IPCC, 1995).

Still, sequestration would not be permanent. The atmosphere and ocean surface continually exchange carbon dioxide, as does the well-mixed surface layer with the rest of the ocean. However, the rate at which the entire system comes to equilibrium with respect to CO₂ concentrations is slow compared to the rate of anthropogenic CO₂ generation. In the long-term (i.e. on the order of 1000 years), the atmosphere/ocean system will come to the same equilibrium regardless of whether the CO₂ is initially emitted to the atmosphere or to the ocean. Nevertheless, the *peak* of atmospheric CO₂ concentrations, expected to occur in the next couple of centuries, could be significantly reduced if CO₂ were released into the ocean rather than into the atmosphere.

Figure 1.1 shows estimated amounts of CO₂ entering the atmosphere from 100 typical (500 MW_e) coal fired power plants under conditions of no action vs. ocean disposal as modeled by Science Applications International Corporation (SAIC) (Topical Report 4). Reductions of cumulative atmospheric concentrations would be quite significant (over 3 ppm maximum reduction) for this limited disposal from 100 plants. This 'peak shaving' would reduce the chance of possible severe climate change consequences that might be associated with a maximum atmospheric CO₂ concentration. The two curves approach each other as the long-term ocean/atmosphere system eventually achieves equilibrium.

Figure 1.1 Net CO₂ entering atmosphere over time under no sequestration scenario and scenario involving ocean disposal of CO₂ from 100 power plants for 100 years divided between two sites in the Atlantic and Pacific Oceans injected at depths between 900 m and 1500 m (from Topical Report 4).

1.4 Environmental impacts of CO₂ ocean disposal

Since the conception of CO₂ ocean disposal as a potential mitigation strategy to global warming in 1977 (Marchetti), most studies of the concept have focused on technical feasibility and effectiveness of this strategy (DeBaar, 1992; Khesghi *et al.*, 1994; Oshumi, 1995; Ormerod *et al.*, 1993; Herzog *et al.*, 1995). By now, it has been fairly well established that injection of CO₂ effluents at depths of below 1000 m would indeed be effective in reducing atmospheric concentrations of CO₂ and that the reductions shown in Figure 1.1 are technically achievable. The science and technology of capture, condensation, transport, and assimilation

and sequestration in the ocean carbonate system are quite sound. A minor technical barrier is the feasibility of constructing a pipeline to reach such great depths, as the deepest pipelines in use today extend to no more than 1,000 m (Herzog *et al.*, 1995). Yet, assuming this barrier could be overcome in the near future if CO₂ ocean disposal were a priority to society, it is time to confront what is potentially a more formidable barrier to the eventual implementation of this strategy - the direct environmental impact on marine life near the discharge point.

In the IPCC Second Assessment Report published in 1995, these concerns are noted in the section on CO₂ ocean disposal (Ch.19, section 2.3), "Concern over potential environmental impacts, the practical limitations on pipeline depth, and the assurance of adequate retention time suggest that injection at 1000 m at carefully selected sites could be a realistic option...Little is known about the ecological impact on marine life of CO₂ disposal. This aspect needs further research." While significant research efforts are currently underway to study CO₂ ocean disposal in Japan, Norway, England, and the US, a comprehensive assessment of the potential environmental impact of this strategy has not yet been attempted.

Several brief reviews on the subject have suggested qualitatively potential impacts that should be considered and have served as useful backgrounds to this work (Magnezen, 1993, IEA, 1994). Yet there are enormous uncertainties and unknowns with respect to these impacts which ultimately must be understood before such a project would ever be deemed feasible. The scale of the proposal - ocean disposal of a typical 500 MW_e power plant's emissions amounts to about four million tons of CO₂ per year - would undoubtedly invite very strict scrutiny from national and international communities. While the potential for climate change mitigation is great, most policy makers would be loath to undertake a costly strategy which may present an entirely new Pandora's box of environmental nightmares.

The primary focus of this work, then, is toward a comprehensive, toxicological assessment of the environmental impacts of CO₂ ocean disposal as implemented through several predefined scenarios. The methodology of the impact assessment will roughly follow the structure typical of such assessments - hazard definition, toxicological assessment, exposure assessment, and risk characterization and evaluation (Cockerham and Shane, 1994). Chapter 2 will discuss the effects of excess CO₂ on marine life and the derivation of the toxicity model which will be used to evaluate the impacts of the predicted exposures to the CO₂ plume. Chapter 3 will discuss briefly the derivation of the plume models used to predict the exposures themselves and will present and place in context the results of the integrated environmental assessment performed using the plume modeling and the toxicity model. The national and international regulatory framework will be laid out and discussed in Topical Report 6, in light of the impact results found in Topical Report 5, and some overall conclusions will be made about the strategy at the end of the report.

Chapter 2. Toxicological Assessment and Model Development

2.1 Introduction

Toward the end of assessing the potential regional impact of CO₂ ocean disposal on the marine environment, this chapter describes the derivation of the model developed to assess toxicity of the CO₂ plume to entrained organisms. The assessment is performed for several defined disposal scenarios which are quite different in character. The methodology of integration of this model with the plume modeling is discussed in detail in Chapter 3.

2.2 CO₂ Ocean Disposal Scenarios

There are three general strategy types under discussion for transporting captured CO₂ to depths of greater than 1000 m with the objectives of minimum cost, maximum sequestration effectiveness and minimum environmental impact as considerations (Herzog *et al.*, 1995). Perhaps the most feasible methods today in terms of cost and available technology are *dissolution* methods. These would most likely involve direct injection via pipelines of liquid or supercritical CO₂ at depths near 1000 m. The CO₂, a positively buoyant liquid at these depths, would form a bubble plume and dissolve fairly quickly. Alternatively, it has been suggested that if CO₂ can be premixed with seawater in a confined vessel and the resulting dense solution released at about 500 m depth, the solution will sink along the seafloor to depths near 1000 m before the solution stratifies horizontally below the thermocline (Adams *et al.*, 1995; Drange and Haugan, 1992). This latter technique would save on pipeline cost. The above two concepts are quantitatively modeled and termed the droplet plume (#1 in Figure 2.1), and dense plume (#2).

Dispersion methods distribute the CO₂ over a wide range of depth, creating small local impacts. One proposed method of dispersion involves solidifying the CO₂ to dry ice blocks which are about 50% more dense than seawater and hence, could be discharged at the surface and expected to distribute CO₂ as they dissolved along the entire depth of the ocean. A more recent dispersion concept is to discharge CO₂ from a dangling pipe towed by a moving tanker with diffuser ports along the length of the pipe between 1000 and 1500 m. The CO₂ would

form small bubbles and dissolve with a small plume rise. These scenarios are modeled quantitatively, and are illustrated as #3 and #4 in Figure 2.1.

Probably most effective in terms of sequestration would be the *isolation* methods, including the often discussed strategy of formation of a 'CO₂ lake' at the bottom of a marine abyss or trench. If the CO₂ could be transported in any phase to depths of about 3700 m or more, it would have a density greater than that of CO₂-saturated seawater and hence, it would sink and collect on the ocean floor (Oshumi, 1995). The CO₂ lake method, shown in Figure 2.1 as scenario #5, is not modeled quantitatively but possible impacts are discussed in Chapter 3.

Figure 2.1 Schematic illustration of CO₂ ocean disposal scenarios

Though there may be slight differences in sequestration effectiveness among the scenarios, it will be assumed that each scenario will achieve necessary sequestration to mitigate greenhouse warming as in Figure 1.1. More extensive descriptions of how the above scenarios were developed and modeled physically are given in Sections 3.2 and 3.3. Essentially, all scenarios will result in plumes with which marine organisms will come into contact. The potential for harm due to this contact will be explored in general in the remainder of this chapter, and in specific in Chapter 3 with respect to the modeled scenarios.

2.3 Physiochemical impact of CO₂ on the marine environment

The main impact of increased concentrations of CO₂ on marine life takes place via its pH-lowering effect which is a result of the stability of the HCO₃⁻ ion derived from the reaction of CO₂ with water and subsequent loss of a proton from the H₂CO₃ species. At equilibrium, the relative proportions of the carbonate species in the ocean would be approximately 0.5% CO₂, 88% HCO₃⁻ and 11% CO₃²⁻, i.e. the equilibrium lies strongly toward the HCO₃⁻ species and H⁺ is released rather readily (Sarmiento, 1993).

The actual resulting acidity of the water due to the increased H⁺ concentration is not as drastic as shown by the above reactions because the ocean has an abundance of stored carbonates, many in the form of CaCO₃, which act as a buffer as in the below reaction.

Still, the amount of available carbonate for buffering, while abundant in the ocean sediments (though only the upper few centimeter's worth would be available to react) and shallow regions, may be limited in many other regions (Cole *et al.*, 1993). Further, the ocean's stock of carbonate would certainly not be able to offset local increases in acidity due to CO₂ releases on the order of hundreds of kilograms per second - as would be expected from several power plants. The local increase in acidity is actually determined to be quite significant (regions of pH as low as 4 may be created very close to the release point), and thus, we must make a comprehensive assessment of the direct effect of lowered pH on marine life, and we must consider any secondary effects of the pH perturbation as well.

For CO₂ discharges, pH change is used as the relevant perturbation in the marine environment instead of the change in CO₂ concentration itself. This is primarily because for the overwhelming majority of laboratory and field studies that have been performed to assess affects of acidification on marine life, pH is the independent variable and not CO₂ concentration. In these studies, strong acids were generally used to lower pH instead of CO₂. Yet seawater reduced to a given pH (in the range which we would observe with CO₂ ocean disposal) via strong acids and seawater reduced to the same pH with CO₂ are virtually indistinguishable.

The CO₂-reduced seawater may have slightly higher concentrations of CO₂, but the additional impact would be negligible. In the few available studies where authors set out to measure effects of CO₂ alone on organism behavior and survival, it was found that, while CO₂ can reduce O₂ carrying capacity in blood and thus induce a narcotic effect, these effects did not begin to be noticeable until CO₂ concentrations were such that the pH itself was below 6.5 (Nikolsky, 1963). At this pH, as will become clear later, the effect of H⁺ itself would likely dominate any adverse effect of CO₂. Omori suggests that there may be respiratory effects resulting from elevated pCO₂ levels at the pressures found at 1000 m, but there is no research or evidence to confirm such an effect (Omori *et al.*, 1996). Further, if there were CO₂ effects acting on the organisms in the pH laboratory studies, these would have been accounted for in the empirical mortality figures. Thus, we may confidently assess impacts of CO₂ ocean disposal as impacts of the resulting pH from the discharge.

2.4 Current knowledge of effects of low pH on marine zooplankton and benthos

Because of the phenomena of acid rain and the many studies of its impact on aquatic life (Morris *et al.*, 1989, Hoffman *et al.*, 1995), a great deal more is known about the effects of pH on freshwater species than on marine species. This body of work is useful in pointing out the types of effects to look for, and in illuminating the mechanisms of how pH impacts aquatic life - in the absence of good mechanistic studies on marine organisms. But for quantitative assessment of the impact of low pH exposure on marine organisms, we rely only on marine studies in the field and the laboratory, since the salinity and alkalinity differences between seawater and freshwater make the studies not directly comparable. These differences are especially relevant since the major mechanism of pH toxicity as borne out in freshwater studies (see Section 2.6.4) appear to be related to disruptions in the flux of ions such as sodium across cellular membranes. The vast difference in sodium concentrations in seawater versus freshwater would make the freshwater data difficult to translate to a marine assessment. Further, the deep ocean experiences lower natural variability in pH than shallow freshwater, a factor that would likely cause freshwater species to exhibit greater tolerance to pH change than their marine counterparts.

In fact, the deep ocean exhibits less natural variability in pH and other chemical parameters than the shallow *ocean* as well, which is somewhat problematic in the below analysis. It turns out that because of problems involved with testing deep water species (they often can not survive at surface pressures), most marine studies that will be relied upon were performed on relatively shallow-living species. This fact may tend to make deep ocean

organisms slightly more sensitive to pH changes than shallow organisms, a factor which will be acknowledged later in the analysis.

Therefore, the literature was surveyed for studies of pH effects on marine organisms, with the following limitations to the scope of the survey. Since most CO₂ disposal scenarios necessarily introduce the CO₂ at depths greater than 500 m, we are not concerned with direct effects on phytoplankton which do not reside at these depths. Second, since animals with significant swimming ability (nekton) such as adult fish and shrimp have been shown to actively avoid water with pH levels less toxic than those that would cause the animals harm (Davies, 1991; Portmann, 1970), they will be exempt from this study also. Thus, our pH hazard assessment focuses on zooplankton, bacteria, and benthos, although, it may be noted that data are available on the pH effects on phytoplankton and nekton, and the below methods may be applied to these groups if one wished.

2.4.1 Zooplankton groups and abundance

Grouped in the zooplankton is the range of organisms from protozoans and bacteria to larger crustaceans and ostracods (measuring up to 5 cm in length), all sharing the defining trait of limited locomotion abilities (Sumich, 1992). Zooplankton living near 1000 m, far below the region where phytoplankton can survive, are forced to feed on falling organic materials from the surface waters or on each other, and their abundance (biomass) generally drops with depth (Menzies, 1977). However, several studies have indicated a rise in zooplankton biomass (after a steep drop from the surface to 200 m) as depth decreases between 500 and 1000 m, and even a biomass maximum in this range in some instances (Angel and Baker, 1982; Grice and Hulsemann, 1965). Below 1000 m, biomass is nearly always found to decline steadily.

Although recent studies using new techniques in surveying oceanic abundances seem to indicate that gelatinous organisms such as ctenophores exist in larger numbers and species than previously thought (Barnes *et al.*, 1992), according to most surveys, the most abundant group of zooplankton at 1000 m in terms of biomass are the crustaceans, and of these, the copepods. In traditional surveys, copepods typically account for about 70% of the biomass in pelagic waters below about 500 m, and are represented by large numbers of species (Friedrich, 1969). Feeding on the smaller zooplankton and the raining detritus, the crustaceans themselves are main sources of food for fish and other larger pelagic species. Other main groups of zooplankton besides crustaceans and microscopic organisms are the gelatinous ctenophores and tunicates, wormlike, carnivorous chaetognaths, and calcareous mollusks. These are present in smaller relative numbers than the crustaceans and microscopic

zooplankton, but are quite diverse in species. Finally, there are large numbers of larvae of zooplankton and of nekton that are characterized as zooplankton in their early stages. These made up about 10% of zooplankton biomass in samplings in the Pacific Ocean, and are especially vital to the survival of pelagic ecosystems.

2.4.2 The importance of exposure time

In analyzing the available studies on pH effects on marine life, and accounting for what we know about pH buffering in the ocean, it becomes clear that pH effects cannot be dealt with in the same way that one often deals with the effects of highly toxic, rare, and non-dissipatory toxins such as heavy metals or toxic organic chemicals. For these, an experimental LC_{50} value (the concentration at which 50% of organisms would die during the experimental exposure time) usually suffices to describe the toxicity of the chemical to the organisms of concern. The time an organism would be exposed to an LC_{50} concentration is usually assumed to be either 24, 48, or 96 hours, though these exposure times are generally not of great concern to those assessing impacts of a certain toxin or to those conducting the toxicity studies. Many of these chemicals exhibit threshold effects, and thus, organisms exposed to concentrations of the chemicals exceeding certain levels are often at the same risk of death regardless of exposure time (within limits). For example, in a study of benzene toxicity to several species of fish, LC_{50} values were reported for 24, 48, and 96 hours. For all species, there was almost no difference (7% at most) in the LC_{50} concentrations at 24 hours and at 96 hours, showing that exposure time was almost irrelevant in this range (NAS, 1975).

Exposure times are also often of little consequence to exposure assessors because many pollution exposure situations are concerned with chronic exposures. Where a certain toxin concentration exists in a confined water body such as a lake, then the exposed organisms will generally be exposed to relatively constant concentrations over lifetimes.

In assessing the impacts of CO_2 disposal, however, the time of exposure to the acid hazard experienced by the organism is of critical importance, almost as important as the H^+ concentration itself. Because of the nature of the dispersion and dissolution scenarios, organisms would experience widely differing H^+ concentrations, and over widely varying exposure times, often less than the lifetime of the organism. Further, because of the nature of H^+ toxicity (discussed below), our LC_{50} values vary by more than a factor of 10 when exposure time is varied between 24 and 96 hours. Thus, it would be extremely inaccurate if we were to assess mortality using a standard toxicological approach (Cockerham *et al.*, 1994) which is to simply divide the estimated environmental concentration of the pollutant by the 96

hour LC₅₀, and to estimate mortality based on this ratio (greater than 1 indicates more than 50% mortality). The actual exposure time of the organism to changing environmental concentrations is of critical importance and this exposure time must be worked into our analysis as a fundamental component.

2.4.3 Literature studies of effects of reduced pH on marine zooplankton and benthos

Most studies of pH effects on the survival of aquatic organisms were designed to measure effect of changing pH at a constant exposure time. For example, in a typical experiment such as that of Rose *et al.*, (1977) equal numbers of marine zooplankton captured near the Florida coast were placed in several tanks of bioassay seawater acidified with reagent grade hydrochloric acid (HCl) for 96 hours, and after a certain period of time, the mortality rate (above the control rate) was assessed. Their results were as follows:

pH of bioassay seawater	6.78	6.60	6.38	6.22	6.10	5.88	5.64
Corrected 96 hr. mortality	0%	16%	37%	61%	51%	75%	100%

Table 2.1 Mortality expressed as a percentage of organisms dying from exposure to reagent grade hydrochloric acid. Corrected mortality is obtained by subtraction of control mortality from observed mortality of test organisms (Rose *et al.*, 1977).

A study such as this is useful for predicting effects of pH exposure for 96 hours, but it tells us little of effects of exposures for different time periods - which are expected to be different based on a cursory examination of the literature studies. In attempting to express this relationship between exposure time, exposure concentration and mortality, with results such as the above, several examples analogous situations have proven helpful.

In attempting to assess the potential for harm to exposed organisms exposed to thermal stresses associated with cooling systems in coastal power plants, Schubel *et al.* (1978) also found simple LC₅₀ data from experiments involving exposure of organisms to constant temperature stress for a given time to be inadequate for his purpose. Exposure time there was also of critical importance, and thus, he used the available data to generate a curve expressing the LC₅₀ as a function of exposure time. He also suggests the use of LC₁₀ and LC₉₀ curves if the data were available.

Similarly, in a paper assessing the impacts of exposures to chlorine compounds released from coastal power plants, Mattice *et al.* (1976) found it necessary to include exposure time in his assessment also. He plotted data from chlorine toxicity studies at constant times and concentrations on a graph of chlorine concentration vs. log time, and sketched a curve through the data representing 0% mortality or the threshold level of effect. The data

Thus, following the general methodology of toxicity assessment (Reichle *et al.*, 1989; Cockerham *et al.*, 1994; Hoffman *et al.*, 1995), and incorporating the examples of the two studies mentioned above (which will be discussed later in greater detail), the available marine pH effect studies expressing mortality as a function of pH and time have been combined in Figure 2.2. In some cases, a large number of similar species were tested in a given study for their pH sensitivity. In the attempt to maintain a balanced, diverse set of species, one representative species was often picked from the set. Uncertainty in the data is limited through the use of many different species, use of data covering as many orders of magnitude as possible in concentration and time, and incorporation of chronic and sublethal effects where available (e.g. if only 10 percent of a given species succumbed to a certain pH exposure, but they produced on average, only 50 percent as many young as the controls, then a 50 percent mortality is assumed).

2.5 Derivation of a toxicity model

The next step is to use the data in Figure 2.2 to derive a curve to describe the LC_{50} concentrations as a function of time exposed. (Organisms are treated as a homogeneous group in the interest of a general curve for all species). The above data can also be used to derive LC_0 and LC_{90} curves since mortality figures for the range between 0 and 100% mortality are available (the LC_0 can also be thought of as what is often termed an LC_1 curve or the concentration at the threshold of any observable affect). These curves are derived using a computerized best fit regression curve in the form of a quadratic in log exposure time. To achieve this, each study is converted by interpolation to 0, 50, and 90% mortality points at the given exposure time. The points and the fitted curves are shown in Figure 2.3. Note that times are now represented as logs which was necessary for the curve fit.

Figure 2.3 LC_0 , LC_{50} and LC_{90} curves which represent 'isomortality' lines, i.e. percent mortality for the indicated exposure is equal for all points on that curve. Curves extend asymptotically to 100,000 hours where limiting pH values are 7.5, 6.8, and 6.3 for LC_0 , LC_{50} and LC_{90} respectively.

The choice of a quadratic expression is based on the fact that the fits were the best (r^2 was between 0.7 and 0.8 for the three curves) and that the shape of the curve makes intuitive

sense. However, the curves only made sense in the downward sloping part - clearly a U-shaped curve would be nonsensical. Therefore, at the point where the fitted curves reached their minima, which was generally on the order of 1000 hrs, the curves are manually extended to endpoints which are reasonable estimates of chronic mortality as suggested by the studies.

In addition, to account further for reproductive and sublethal effects, and the fact that deep-water organisms are likely to be more sensitive to pH change than shallow organisms, the curves are depressed by .25 pH units. This type of correction is not uncommon in toxicological analyses of this sort. Charles and Christie in modeling pH effects in freshwater lakes "considered an offset of up to 0.5 pH units between apparent thresholds for effects from bioassays and field surveys to be reasonable" (Baker and Christensen, 1987).

The above curves are similar to those arrived at by Mattice and Zittel, (1976) in their study of the toxicity of chlorine on aquatic organisms. However, where they only indicated a 0% or no effect level curve (and Schubel derived a 50% mortality curve only), in this study 0%, 50% and 90% mortality curves are approximated based on the data. It is these curves, and not the individual data points which will be used to predict mortality from the predicted low-pH exposures derived from the modeling studies of the CO₂ releases (see Chapter 3).

2.6 Integration of literature studies with simulated pH exposures

Once the mortality curves are approximated, the next step is to use these curves to predict the harm to organisms experiencing reduced pH as a result of the CO₂ discharge plume as modeled for the scenarios mentioned above. This would be a simple task if the organisms were exposed to an unchanging pH for a fixed time; one would simply locate the exposure on the graph, interpolating between the curves if appropriate, and estimate the % mortality. The actual situation is much more complex, however, as organisms passively drifting through a low-pH section of water, or entrained into the CO₂ plume will experience a pH that gradually varies with time, depending on the experience.

To evaluate the impact of a typical realistic experience in the framework of the isomortality curves in Figure 2.3, several considerations and manipulations must be made. A hypothetical experience pathway is shown in Figure 2.4, overlaid onto the isomortality curves derived from Figure 2.3. This curve indicates the changing pH over time experienced by the organism as it travels with the plume away from the discharge point and experiences pH that gradually returns to ambient levels. In this example, the organism suddenly becomes entrained into a region of pH 5.5. After 10 hours, it is in a region of pH approximately 5.7, and after 100 hours, it is experiencing a pH of about 6.4. This typical experience is very different from those in the studies used to create the isomortality curves. In the studies, an

organism is exposed to a constant pH for a given time period, and thus, the curves in Figure 2.3 are only directly useful in interpreting the expected mortality given a constant pH experience for a given time.

This is a general problem that has been recognized by the EPA and others working in exposure assessment fields. Currently, the EPA designs its regulations based on a maximum allowable concentration or in some cases a maximum allowable averaged concentration that an organism might experience over a set time period such as an hour, a day or four days (USEPA, 1985). The agency realizes that this is not a very accurate representation of real experience, and is currently investigating "the best way that the statement of a criterion can bridge the gap between the nearly constant concentration used in most toxicity and bioconcentration tests and the fluctuating concentrations that usually exist in the real world" (Eng, 1996). Several methods for 'bridging this gap' are proposed below, and what is probably the superior method will be utilized in this assessment.

A two step manipulation is involved in interpreting gradual experiences in terms of constant experience data. The first step, required in almost any approach to this problem, is similar to the current EPA approach in that the gradual experience is approximated by average experiences over a period of time. Yet instead of averaging an entire experience or only selecting a maximum average exposure for a given time period, the entire experience pathway can be broken down into many averaged segments or 'discretized'. This process is somewhat analogous to approximating the area under a curve by rectangulation. This process is illustrated in Figure 2.4, in which the hypothetical curve shown is discretized and may be approximated as similar to the set of the four points labeled a, b, c, and d. The method used makes the assumption that if the organism spent a ten hour period starting at pH 6.0 and ending at pH 6.5, that experience may be approximated as a ten hour experience at the constant pH of 6.25. The use of 0.5 pH units as discretization steps is arbitrary here and is used only for illustration purposes. To do the discretization, we perform the following:

$$\text{time spent at pH } X_1 \approx \text{time to arrive at pH } (X_1 + 0.25) - \text{time to arrive at pH } (X_1 - 0.25)$$

So, in Figure 2.4, if our first point of interest is time spent at pH 5.75, we find that the organism reaches pH 5.5 after approximately 3 hours, and pH 6.0 after 45 hours, and thus, we plot point *a* as the constant exposure of 42 (45-3) hours at pH 5.75. This discretization method is used in all representative experience paths, though in the actual analysis, the curves are discretized by time units of days, not by pH. That is, successive points are plotted at 24 or 72 hour intervals, each point representing the time-averaged pH experienced for that day.

Figure 2.4 Hypothetical organism experience curve (thick line) discretized into the points a-d. Curve is overlaid on isomortality curves from Figure 2.3.

Once discretized in this manner, the individual point exposures may be associated with a specific mortality based on the graph. Interpolation is performed vertically by pH because the studies were performed by varying the pH, not the exposure time, and because pH is more strongly correlated with mortality than exposure time, especially for exposures greater than 96 hours. Thus, for a point (vertically) between the 50% mortality line and the 90% mortality line, the approximate mortality for an organism experiencing that point exposure would be 70%. Or for an organism experiencing the exposure marked by point *a* in figure 2.4 above, its probability of suffering mortality would be approximately 30%.

2.6.1 Methodology for adding exposures

The second manipulation step required to interpret the gradual experiences in the context of a toxicological map for interpreting constant pH experiences (Figure 2.2) is more complex and less well established. Now that we are able to express the actual organism's continuous experience as a series of discretized points, we must assess the mortality potential of the entire experience of the organism from its first contact with reduced pH to its eventual return to ambient pH. Realizing that the journey through the plume is now represented by the series of discretized point exposures that would be experienced by the same organism in succession, we must find a method to *add* an exposure of X hours at pH Y, followed by Z

hours at pH (Y+5), etc. That is, the organism will experience these exposures one after the other in series, and we must account for this in a way that is not readily obvious from the mortality data. Fortunately, there are several methods for performing such an addition; a method derived in our group and based on Figure 2.3 will be used in this assessment, but methods based on simply summing concentration time products as well as methods developed by Schubel *et al.* (1978), Mattice and Zittel (1976), and Evans (1990) for slightly different applications were considered. These alternative methods are illustrated and discussed in detail in Appendix A.

2.6.2 *Isomortality approximation method*

Our method rests on the fundamental assumption that two exposures that result in the same effects - as measured by the resulting mortality they cause - may be approximated as equivalent. For example, if an exposure of 40 hours at a pH of 5.5 results in the same mortality (approximately 50%) as an exposure of 70 hours at pH 6.0, we assume that the two exposures are roughly interchangeable.

This approximation is then used to convert exposures at different pH to exposures at the same pH such that total exposure times for the experiences may simply be added at that pH. For example, let us assume the entire exposure experience of an organism were represented by the two exposure points shown in Figure 2.5 as point *a* (42 hours at pH 5.75) and point *b* (80 hours at pH 6.25). First it is noted that point *a* would have an individual mortality of about 30%. The next step is to travel along the hypothetical 30% isomortality curve until the pH of point *b* is reached. This point is denoted *a'* and hypothetically would represent an equivalent exposure to point *a*. Now instead of experiencing point *a* followed by point *b*, the organism is said to experience point *a'* followed by point *b*, which would be in this case an experience of 84 hours at pH 6.25 followed by an experience of 116 hours at pH 6.25. This experience is equivalent to an experience of 200 hours at pH 6.25, or point *x*, the mortality potential of which can easily be read off of the graph as approximately 70%

Figure 2.5 Illustration of method of adding discretized point exposures to arrive at cumulative exposure. Points *a* and *b* are hypothetical exposures, and point *x* represents their cumulative experience or sum.

Note that the effective mortality of this cumulative experience becomes approximately 70%, upon 'adding' two exposures that would result in about 80% mortality if simply combined (30% and 50%). This non-linear effect is derived directly from the data itself and shows the diminished importance of increased exposure time at this range of pH. Note that in the regions of the graph of higher pH (6.5-7.5), increased exposure time has a much smaller effect and that the naive approach of simply adding the percentages of individual point exposures to determine total mortality would result in an overestimate of the actual mortality, while such addition at low pH, below 6.0, would result in an underestimate of actual mortality.

Thus, all of the discrete points for a given exposure may be converted to the metric of hours at a given pH, and the resulting cumulative exposure at that pH may be evaluated. Even points for which the individual mortality would be at the 0% threshold or below may be accounted for by assuming the slope of the isomortality curves remains the same below the threshold and that we may extrapolate below the curves, following the assumed slopes to find the equivalent number of hours at the target pH for any experience. It makes sense that such experiences be counted in our mortality assessment because an organism experiencing several 'exposures' in succession that are just below the no effect threshold, would presumably start

to suffer some harm (this is perhaps not universally true as it would depend on the nature of the toxic effect, but in this case it is fairly certain there is an additive effect - this will be discussed in the next section).

The final determination to be made, then, is the 'target' pH, or the pH to which exposures are converted, e.g., do we move point *a* to the pH of point *b* or vice-versa? We have found that there is some sensitivity in the final mortality assessment to which pH is chosen, this sensitivity increasing as the pH difference between actual point and converted point increases. One approach might be to choose a pH value that is roughly between the lowest pH experienced and the highest pH for which there is an effect. Another approach is to successively move points in the order in which they would be experienced in the plume, i.e. considering the exposures *a*, *b*, *c*, and *d* in Figure 2.4, to move point *a* to the pH of point *b*, add them to arrive at a point *x*, then move this point *x* to the pH of point *c*, and so on. The latter approach will be used in this assessment as it more consistent with the physical situation. Thus, the point representing the average pH experienced by the organism on day 1 will be moved to the pH of the day 2 experience, the experiences will be summed, the sum will be moved to the pH of the day 3 experience, and so on until the organism has returned to pH conditions such that additional exposures have negligible effect on overall mortality.

2.6.3 Justification for exposure addition

An implicit assumption involved in all of the methods of exposure addition, which ultimately attempt to approximate the combined harm or effect of a series of exposures experienced in succession, is being made about the nature of the toxic effect of the hazard, low pH in our case. First, it is assumed that individual exposures, before being summed to arrive at a final survival probability, do not exhibit a clear threshold. Every exposure will have an additive effect to the total harm, though many minor exposures will be essentially deemed negligible if they do not add significantly to the final exposure. The final summed exposure, on the other hand, *will* be a probability of survival from 0 to 100% where the LC_0 curve, effectively defines a threshold of effect.

Further, if the toxic effect of exposure to low pH were an irreversible or biocumulative type effect as opposed to a reversible effect, then the above methods for adding exposures and assessing mortality might be more valid or less valid depending on the situation. For example, if the toxic effect were irreversible, then one might have to keep track of organism's experience in the plume once out of the plume and account for loss of reproductive abilities or other adverse effects over the course of the organism lifetime. On the other hand, if the effect were completely reversible, and the organism traveled along an exposure path that decreased

in severity (concentration) and then increased again, it might not be valid to add the exposures of the first period to later exposures if the organism were able to re-equilibrate to its normal state during the milder period in the middle of the experience. Thus, it is important that we do understand the nature of the effect that we are modeling.

The available evidence supports the view that the effects are indeed reversible - that they are similar in character to the effects of increased temperature (Schubel *et al.*, 1978) which were confirmed by others to indeed be additive. While the hazard stresses the systems of the organism, the organism has built-in compensating forces as the stress is not completely 'unnatural'. Temperature gradients and H^+ ion concentration gradients are natural occurrences in the ocean, unlike large concentrations of mercury or large amounts of radiation. Additionally, temperature and high H^+ concentrations dissipate naturally with time, so we might expect the internal systems of organisms stressed due to the exposure to return to equilibrium when the stress dissipates. In empirical tests of pH effects such as those of Grice and Wiebe (1973), it was observed that organisms recovered completely after initial sublethal exposure to a pH of 3. Similar observations were made by Havas and Hutchinson in studies of low pH on freshwater crustaceans (Havas *et al.*, 1982).

Further, although the effects may indeed be non-linear and irregular, the graph in Figure 2.2 itself takes into account non-linearities in pH effects. For example, doubling the exposure time usually does not double the mortality, nor does doubling the H^+ ion concentration. These effects are accounted for in the isomortality method of exposure addition, which merely assumes that effects resulting in the same mortality are similar.

2.6.4 Mechanisms of pH toxicity

What is the nature of these effects, then, that we might justify adding them? Although Bamber claims that the main cause of death or decreased growth of mollusks under acidic conditions is the dissolution of their calcareous shells (calcium carbonate is believed to dissolve at pH 6-6.3 - Knutzen, 1981), none of the above referenced studies on marine pH effects seriously investigate the mechanisms of the effects, and thus we are left to draw on the body of knowledge from freshwater studies, which is abundant (Wellburn, 1988, Morris *et al.*, 1989). According to several authors, the major cause of death or stress in fish from low pH exposure is disruption of the natural balance of salts in the organism bodies. Because protons easily permeate the animal membranes, the body is either left with an excess of charge that must be balanced by dissolving internal sources of carbonate (primarily calcium), or ejecting other necessary ions such as sodium or potassium, or the body must cope with that proton excess, which can disrupt body chemistry and cellular reactions and fluxes. If ionic

imbalances are kept far from the optimal level for too long, the organism may die. But if the stress is lessened or relieved, the salt balance will return toward normal. Also, adaptation to permanent conditions of lowered pH has been shown to be possible through storage of calcium ions which can prevent H^+ ions from entering and sodium ions from leaving. That we may use information from freshwater studies at all is supported by Brownell who notes that, "The data show that marine fish are about as tolerant of low pH as freshwater species, at least in the short term" (Brownell, 1980, p. 289).

If the pH effects on the marine organisms are truly of the general nature as described above, we may be fairly confident that a real experience of exposure to gradually changing pH may be approximated by discretizing the experience, summing the discrete points by the methods above, and comparing the final point-experience to empirically discovered pH effects on a graph like Figure 2.3. In essence this approach assumes that when organisms are placed under stress in low pH conditions, and as the stress remains or increases in severity, the chances of survival decrease. The degree to which the chance of survival decreases is determined by adding stresses.

Implicit also in the assumption of additive, reversible effects is that the organism does not experience a stressful exposure followed by a period of low or no stress, followed by a period of high stress again. The addition exposure method would overestimate mortality in this case if the effects of pH stress were reversible on a small timescale relative to the different time periods of the experience. However, this is not a great worry, since the plume modeling shows that this high-low-high stress experience would be a rare event given the physical situation resulting from a CO_2 discharge. In addition, it is also assumed that once out of dangerous conditions, the organisms will gradually recover to normal, an assumption which will have implications in a later section on population modeling (see section 3.4).

Thus, now that the general methodology has been laid out for assessing impact of passive marine organisms experiencing periods of pH stress on their ultimate survival, the next chapter will apply this methodology to simulated organism experiences and present the results of the assessment.

Chapter 3. Model integration and results

3.1 Introduction

The derivation of the plume models for each of the scenarios will first be discussed briefly followed by a discussion of the methodology used to arrive at the predicted organism exposure pathways. The toxicology model derived in Chapter 2 will then be integrated with the exposure assessment methodology to arrive at a set of results for each scenario. The results will be interpreted in several contexts, and a wider discussion of other potential impacts will close the chapter.

3.2 Scenario development

In order to model the perturbation to the marine environment due to CO₂ disposal, it is necessary to first define a base power plant and the resulting emissions to estimate the volume of CO₂ discharged to the ocean per unit time. The chosen base plant is a pulverized coal fired power plant of 500 MW_e (net after CO₂ capture) with a 90% CO₂ capture efficiency resulting in a total discharge of 130 kg/s of CO₂ to the ocean. Small amounts of SO₂ and NO_x may also be discharged, though the amounts would depend on the capture technology used. The potential additional environmental impact of these gases is discussed later in this chapter. The capture technology used in the emissions calculation is a technology currently in use which involves passing the CO₂ effluent through methylethanolamine (MEA), which will selectively bind the CO₂ at low temperature, and release it upon heating whereby the CO₂ can be collected and condensed (Topical Report 1).

Three different discharge scenarios, the dry ice, the dense plume, and the droplet plume, as have been discussed previously, were chosen to be modeled quantitatively. For each scenario, a single plant and a ten plant case (given the same release location and mechanism) were modeled as it has been suggested that ten plants might be bundled and combined in a single discharge system to take advantage of economies of scale. Some calculations were also performed on the towed pipe scenario, which was modeled using

features of the other three models. The following is a brief discussion of some of the main components of the models, though for more extensive information, see Topical Report 3.

It is important to stress that for each of the three scenarios, the spatial pH impacts are considered to be steady state perturbations of pH, not changing over time. This assumption is plausible because there is a finite current providing a constant influx of previously unaffected water and because the ocean has such enormous buffering capacity. Possible far-field impacts have been studied to answer the question - would there be an increasing effect over time such as a gradual degradation of the marine environment if this strategy were carried out on a large scale? The results from a study of this question by SAIC (Topical Report 4) suggest that the global oceanic pH change in the long term resulting from 100 power plants worth of CO₂ discharge per year would be less than 0.1 pH unit. Therefore, we may justifiably focus on only near-field (in the region of the discharge) impacts of the CO₂ release. These regional impacts could have far-field secondary effects or implications, but primary, direct physical impacts will be assumed to be regional only.

3.3 Plume modeling

Many assumptions have been made in the construction of the models of the three scenarios designed to determine pH variations caused in the ocean. (The assumption that pH is the critical parameter of measure as opposed to carbonate or CO₂ concentration is justified in Chapter 2). Each model contains empirical data on ocean temperature, salinity, carbonate/bicarbonate amounts, and pH conditions as a function of depth as obtained mainly from the GEOSECS expedition (Takahashi *et al.*, 1981). Modeled CO₂ concentrations are converted to pH values based on the carbonate equilibrium equations and the empirically determined concentrations of species contributing to total alkalinity in the ocean as a function of depth. Assumptions are also made based on past studies about ambient currents, turbulence, and stratification, all of which would also affect plume behavior. These assumptions are central to each discharge scenario modeled and more detailed information about these can again be found in Topical Report 3.

The three scenarios are then modeled specifically with the goal being an output of the pH variation with space produced in the ocean. The dry ice model uses empirical information about mass loss from the cube combined with equations for diffusion of the CO₂ which depend on current, turbulence, cube size and other parameters. The resulting pH change from the cube disposal is expressed as a steady state perturbation. Although the cubes are dropped periodically, their effect on the ocean pH can be thought of as resulting from a continuous

release from a vertically distributed source extending from the surface to the bottom in which main loadings of CO₂ per depth decline with depth.

To model the droplet plume scenario, a previous model of Liro (1991) was used as a basis and modified to include larger scale ocean diffusion dynamics. Lateral spreading due to plume intrusion in the stratified ambient ocean was then calculated based on models of Jirka *et al.* (1980) and Paddock and Ditmars (1983). In Figure 3.1 is plotted a horizontal slice of the pH change induced by one plant's worth of discharge in the form of a droplet plume. To model the dense plume scenario, which has the additional elements of a plume traveling along a shelf or bottom, the mixing and ultimate depth reached by the plume are governed by the release depth, the initial CO₂ concentration, the bottom slope, the ambient stratification, and the entrainment and drag coefficients (Adams, 1995; Drange and Haugan, 1992).

Figure 3.1 pH contours resulting from release of CO₂ in the one-plant droplet plume scenario. Discharge point is at 0,0, and Y axis represents horizontal distance from discharge point normal to direction of the current flow. From Caulfield, 1996.

Some results of the plume modeling are summarized in Table 3.1. These figures are interesting for comparisons among scenarios and as to the absolute magnitudes of the perturbations involved (ambient ocean pH is approximately 7.8 at 1000 m). These numbers may also be useful from a regulatory standpoint as will be seen in Topical Report 6. Yet it is the specific pH perturbations in space (i.e. the contours as in Figure 3.1, but in three dimensions) that will be used in combination with the toxicology modeling to perform the impact analysis.

	Volume of Water with pH under 7 (km ³)	Distance to pH of 7 (km)	Minimum pH (after dissolution)	Minimum pH (diffusion regime)
Dry Ice				
1 plant	0.001	0.09 ^a	6.3 ^a	7.4 ^a
10 plants	1.1	2.2 ^a	5.8 ^a	6.1 ^a
Towed Pipe				
1 plant	0.00004	0.2	6.5	7.2
10 plants	0.3	14	5.7	6.2
Droplet Plume				
1 plant	1.8	23	5.5	6.0
10 plants	130	60	5.5	6.0
Dense Plume				
1 plant	7.2	94	4.0	5.7
10 plants	510	690	4.0	5.5

^aat 1000 m only

Table 3.1 Summary of physiochemical results of plume modeling for four scenarios

3.4 Exposure assessment

Given the pH perturbations resulting from the CO₂ discharge, the next step is to approximate the experience pathways of organisms passing through the plume (as in Figure 2.3). Clearly, it is impossible to model the exposure pathway of every organism and several methods for averaging or grouping organisms have been considered (Topical Report 3). What was arrived upon as the most accurate method for representing the experience of each organism within the constraints of reasonable computational abilities was a Monte-Carlo-like method to simulate random walk pathways.

As is shown in Figure 3.2, the pH contour map resulting from the plume modeling is divided into a grid with horizontal lines representing 'lanes' and vertical lines representing the distance traveled in a given time period. The x axis represents distance downstream from the plume origin and the y axis is horizontal distance perpendicular to the current flow (current flows left to right in Figure 3.2). This map can be thought of as the surface of a table resting at 1000 m in the ocean with a small thickness (23 m) representing the thickness of the plume. The perturbation in pH is approximated as uniform all through the table thickness with ambient conditions existing above and below the table. Organisms enter the plume from any point along the upstream (left) edge of Figure 3.2 and travel from left to right with the current. As they travel through the plume, they are allowed to stay in the lane they were in previously, or to move to any other lane with probabilities determined through simulation and calculation

(Caulfield, 1996). Every organism in a given lane is assumed to be equivalent, and the resolution of the approach is limited by lane size.

Figure 3.2: Grid showing 'lanes' used for Monte-Carlo simulation superimposed onto pH contours from one plant droplet plume model. (From Caulfield, 1996)

This simulation results in many experience pathways that are easily discretized and analyzed in the format presented in Ch. 2. The downstream spacings on the above grid are placed at intervals of approximately one day's travel time (for the 10-plant plumes, the intervals are three 3 days), so for a given pathway, the average pH experienced on the first day is plotted on the mortality map as the first point. The average pH experienced for the second day is plotted as the second point, and the first point is 'moved' to the pH of the second point as was described previously. The experience times for the two points are added to arrive at a new point. The new point is then moved to the pH of the point from the third day experience, etc. In this way, the mortality for any pathway is calculated.

A final element that must be considered in the impact modeling involves the regeneration abilities of the affected organisms. If organisms did not recover and reproduce, a single source of net mortality in the ocean would eventually result in the death of all organisms since the ocean circulation system will eventually bring all seawater through the mortality source. This is clearly not the case. Organisms have finite lifetimes, and are able to produce offspring when unstressed.

The difficult question is when to 'turn on' regeneration in a mortality model such as the above. As organisms travel through the plume it is necessary to choose a point, whether by absolute pH or by cumulative experience of the organism thus far, at which the organism

may start reproducing and the population will begin to recover from the plume effect. Because it is too complex at this stage to allow each organism pathway to begin recovery based on its cumulative experience, absolute pH values in the plume will be used to derive a regeneration/recovery function. Basically, recovery will be allowed to begin gradually at pH 7.35 and fully by pH 7.5, where 7.35 is approximately the lowest observed pH effect level and 7.5 is the extrapolated chronic lowest observed effect level. More information on how recovery is modeled can be found in Caulfield (1996) and is summarized in Appendix B.

One additional complication that arises when working with actual exposure data is that the total exposure time for some of the experience paths is longer than the natural organism lifetimes. It is questionable whether to continue adding experiences and adding mortalities after the organism's natural lifetime, since the organism would already be dead from natural causes. Intergenerational effects and their handling are also discussed in Appendix B.

3.5 Primary measures of impact

With the integration of exposure assessment with the toxicity modeling of the previous chapter, there now arise many ways expressing impact on organism survival. Several primary measures and results will be presented followed by some additional derived measures which are more ecological in context.

3.5.1 Spatial deficit

A key measure from which most others will be derived is termed the spatial deficit. A spatial deficit refers to the net percentage loss of organisms in a given volume or area against a static background. To obtain a spatial deficit, one would pick any square in the grid in Figure 3.2, e.g. the square along the centerline at three days downstream from the origin. Organisms arrive at this square from any number of pathways starting from the left edge of the graph at time (distance) = zero with some pathways being more probable than others. The probability of a given pathway is multiplied by the percentage mortality that the pathway would result in, and the summation would be expressed as the deficit in that quadrant. At the square chosen in this example, mortality would be quite high since the pathways involving straight line travel from the plume's origin are more probable than pathways involving diffusion from the side which would result in lower mortality estimates. Some further approximations are made to arrive at the spatial deficits far downstream since after many timesteps, the number of possible pathways that must be considered rises exponentially. Results from the spatial deficits from the one and ten plant dense and droplet plume scenarios are shown in Figures 3.3 and 3.4.

This spatial deficit represents the net loss of organisms in the region as background populations are assumed to be in steady state. The maximum spatial deficits for each scenario are reported in Table 3.2.

3.5.2 Mortality flux

Another useful representation of impact is the number of organisms lost per unit time. If instead of choosing single 'boxes' in space at which to evaluate the steady state impact, we choose an entire vertical slice such as the 2-day line parallel to the y-axis in Figure 3.2, we can find the flux of dead organisms crossing this line by integrating the spatial deficit laterally over the plume. Such a measure would require knowledge of ambient organism density (number per volume). However, if we assume that ambient organism density is spatially uniform, we can express this flux in terms of the 'volume of dead water.' The flux of dead water per time can be expressed as the following equation:

$$\text{mortality flux} = u h \int \text{mortality}(y) dy$$

where u is the current speed, h is the thickness of the plume, and mortality (y) is the spatial measure of mortality (expressed as a fraction) along the y axis as a function of distance from the centerline ($y=0$) for a given x . Since the mortality flux will vary with the point chosen along the x direction, the maximum mortality flux is reported in Table 3.2.

3.5.3 Integrated Mortality

Still, with reporting the maximum mortality flux, the distinction between a very intense, short-lived plume and a very long, gradual, diffused plume, would be lost. If two such plumes had the same maximum mortality flux, the diffused plume would certainly have larger overall impact. Therefore, it will also prove useful to integrate this mortality deficit in the x direction. The resulting summation will be in units of volume only and will be called the integrated mortality.

$$\text{integrated mortality} = h \iint \text{mortality} dx dy$$

The integrated mortality can be thought of as the equivalent volume of water with 100% mortality.

3.6 Resulting quantitative impact of CO₂ disposal

As mentioned previously, the main impact would be on organisms with no avoidance ability that are found below 700 m or so, which would include zooplankton, bacteria and microorganisms and benthos (though we are focusing this study on pelagic impacts of the CO₂ disposal). Some zooplankton do indeed have varying degrees of movement ability, and thus, our mortality assessment would be a conservative estimate in this respect. A further assumption is that the organisms in the regions of water affected by the low pH have similar sensitivity to pH. Thus, the affected seawater will be thought of as a container for a given density of passive organisms, different in species and order, but homogenous in terms of pH sensitivity. This is not a necessary assumption to the analysis - it would be possible to break down the organisms into groups and evaluate separate mortality approximations for each. But in the interest of simplicity, homogeneity is assumed.

Figures 3.3 and 3.4 are the spatial deficits for one plant droplet and dense plumes followed by deficits for the ten plant droplet and dense plumes. The dispersion scenarios do not result in significant spatial deficits. Table 3.2 summarizes the results of the assessment in terms of the primary measures of impact.

Figure 3.3. One plant spatial deficits for droplet plume (left) and dense plume (right). From Caulfield, 1996.

Figure 3.4. Ten plant spatial deficits for droplet plume (left) and dense plume (right). From Caulfield, 1996.

	Integrated Total Mortality (km ³)	Maximum Mortality Flux (m ³ /s)	Highest Spatial Deficit (percent)
Dry Ice			
1 plant	0	0	0
10 plants	0	0	0
Towed Pipe			
1 plant	0	0	0
10 plants	0	0	0
Droplet Plume			
1 plant	0.45	310	11
10 plants	160	28000	69
Dense Plume			
1 plant	11	2000	50
10 plants	800	47000	95

Table 3.2. Summary of primary results of impact assessment analysis. The three impact measures are described in the text above.

3.6.1 Ecological measures of impact

Given these primary measures of impact there are several other measures or statistics that may be useful in analyzing impact from the scenarios. For example, one might wish to attempt to assess the impact using some of the more common ecological endpoints such as species richness and diversity, abundance, or biomass loss. Drawing on estimates (Sullivan *et al.*, 1981) of the average biomass of zooplankton at these depths (approximately .3 mg/m³), and the approximate numbers of fish larvae (.01/m³), it is possible to calculate the maximum biomass or larvae loss per second from the mortality flux (Table 3.3). Loss of species diversity is a much more difficult impact to estimate. Little is known of the species richness at

such depths and locations. Some recent work has illuminated the fact that the benthic plains, once thought to be sparse in terms of diversity because of their relatively monotonous features and limited food sources, are actually extremely species rich and dissimilar from area to area (Broad, 1995; Oceanus, 1995).

Another measure that could prove to be enlightening and is a type of result often reported in impact statements is to define a reference volume and describe the impact as a percentage loss of organisms in that volume. Although the spatial mortality maps define a sort of volume for which at least a given percentage of organisms would be lost, it would still be useful to have a broader measure of impact. This could be accomplished in this case using the integrated mortality figure, which represents the total volume of organisms containing water for which all life would be lost, and dividing this volume by a suitable reference volume.

In situations of a discharge into an estuary or bay, a suitable, well defined reference volume is often fairly easy to arrive at. Yet for release far offshore into the deep ocean, there are few clear geographical boundaries which may define a reference volume. As an extreme upper bound we may use the entire Northern Atlantic Ocean as a reference volume. Mortality percentages using such a reference volume are presented for the various scenarios in Table 3.3. For a release at 1000 m, the reference depth used is the 200 m slice between 900 and 1100 m which are upper bounds for the range of expected mortality. Alternatively, instead of defining a volume and finding the percentage loss within that volume, we might ask what the volume would be within which a given percentage loss or deficit would be at least a certain value. This volume has been calculated for deficits of 10% or greater and 50% or greater and is presented in Table 3.3 below.

	Zooplankton maximum biomass loss (g/s wet weight)	% of N. Atlantic zooplankton lost betw. 900-1000 m	Volume of seawater with deficit 10% or greater (km ³)	Volume of seawater with deficit 50% or greater (km ³)
Dry Ice				
1 plant	0	0%	0	0
10 plants	0	0	0	0
Towed Pipe				
1 plant	0	0	0	0
10 plants	0	0	0	0
Droplet Plume				
1 plant	.093	.0000067	.12	0
10 plants	8.4	.0024	550	70
Dense Plume				
1 plant	.60	.00017	26	0
10 plants	14	.012	5000	1000

Table 3.3 Additional results of environmental impact assessment of CO₂ discharge in three different scenarios. Impacts on water column only are presented.

3.6.2 Discussion of results

Some very interesting and unexpected results are revealed in the above tables. Of primary interest is the relative impacts of each scenario, as the absolute numbers are subject to large uncertainty (see sensitivity analysis below). The dry ice plume is essentially harmless, while the impacts of the dense plume generally exceed those of the droplet plume by an order of magnitude. These greater impacts are a result of the higher concentrations of CO₂ required in the dense plume concept to achieve sinking of the plume. Also interesting is the fact that the 10-plant impacts are significantly more than 10 times the impact of single plant scenarios. This is not an intuitive result and is related to the empirical non-linearities in the exposure and toxicity models. This fact led us to conclude that if the single plant releases could again be broken down into several individual releases, the overall impacts can be reduced further, as is illustrated by the towed pipe scenario which embodies this concept.

As to the absolute magnitude of these impacts, they are generally below any meaningful value if the Northern Atlantic Ocean is used as a reference volume. Within smaller volumes, however, there does appear to be potential for significant damage to local zooplankton populations, though this is very scenario dependent. The spatial map for the 10 plant droplet plume scenario indicates a possible 10% or greater zooplankton loss over an area near the size of Lake Erie (centered between 900 and 1100 m depth in the ocean), though the one plant droplet plume scenario would have a 10% loss over only two square miles.

But what can be said about the absolute damage potential of impacts such as these, and of the significance of the damage? These questions will be considered further after a discussion of the uncertainty of the results and of other potential impacts of the disposal scenarios that were not modeled quantitatively, and possible impacts of no-action scenarios which might be ameliorated with ocean disposal.

3.7 Sensitivity analysis

It should be noted that the results reported in Tables 3.3 and 3.4 have a high degree of uncertainty. Many assumptions have been made in the analyses leading to these numbers, and these assumptions, along with the direction toward which they would likely bias the results are listed briefly below.

Factors, assumptions tending to cause our analysis to be conservative (overestimating mortality):

- Organisms have no movement or avoidance ability

Some copepods can move at a rate of between 15 and 50 m/hr (Sumich, 1992).

Most copepods are also known to migrate vertically over great distances to avoid predators during daylight hours. These migrations are less significant at depths near 1000 m, but to the extent that they do occur, they would tend to decrease time spent in the plume of migrating organisms.

- Organisms cannot compensate for or adapt to increased acidity

Some adaptation to permanently lower pH is possible (Morris *et al.*, 1989).

- Sensitive species used in testing

At least two authors used the most sensitive species available in their studies (Rose *et al.*, 1977; Portmann, 1971).

- Possible decreased predatory activity due to avoidance of plume by predators
- Exposure hours added after natural lifetime of organism has expired

Factors, assumptions causing our analysis to underestimate mortality:

- Additional pH or CO₂ effects that have not been accounted for or observed in the available studies

Other factors and assumptions adding to uncertainty of results:

- Use of shallow ocean experiments to extrapolate to deep sea organisms

Deep sea species may be much less tolerant than shallow species from which data are derived (by more than the 0.25 pH unit correction factor applied). On the other hand, it has been observed in at least one example that a species living in a shallow, variable environment (in pH) was more sensitive to pH changes than one living in a more stable environment (Bamber, 1996).

- Inaccuracy of exposure addition methods (in approximating single point mortality)
- Approximation that all organisms in water column are similar
- Hydrodynamic assumptions made in plume and exposure modeling (Caulfield, 1996)
- Assumption that all life stages of affected organisms are present in their natural distributions at plume depth. It is possible that certain zooplankton go through their various life stages at different depths, e.g., certain species might spawn at 1000 m but reside primarily at 500 m. If different life stages have different sensitivity to pH, our analysis might be biased in either direction.

Quantitative sensitivity to isomortality curves of Figures 2.3 and 2.4

• The isomortality curves, which are a fundamental element to the mortality assessment have been uniformly moved up (less sensitive than estimated in Figure 2.3) and down by 0.25 pH units, and the resulting effect on the final results has been calculated below. This analysis suggests that even within a total range of 0.5 pH units in the isomortality curves, which is very substantial, the range of mortality estimates is within a factor of 5 except for the 1 plant droplet plume figures. The exposure times in this scenario are close to the threshold of no effect as shall be seen later, and thus with a decrease in pH sensitivity from the current isomortality curves, the impact approaches zero mortality fairly quickly.

	Isomortality curves <i>depressed</i> by 0.25 pH units	Base Case	Isomortality curves <i>augmented</i> by 0.25 pH units
Integrated Mortality (km³)			
Droplet Plume			
1 plant	0.03	0.45	2.06
10 plants	72.8	162	248
Dense Plume			
1 plant	3.4	10.6	17
10 plants	387	800	1100
Highest Spatial Deficit (%)			
Droplet Plume			
1 plant	0.86	11	30
10 plants	50	69	87
Dense Plume			
1 plant	32	50	69
10 plants	79	95	99

Table 3.4. Sensitivity of results to isomortality curves in toxicity model (Ch.2).

3.8 Other considerations and potential impacts

Outside of the scope of the quantitative impact assessment presented above, there are other potential impacts of CO₂ ocean disposal among the various scenarios that must be considered. Little is known about the potential significance of the below impacts.

3.8.1 Benthic impacts

Though biomass and species richness generally decrease gradually with depth, there is a sudden increase near the bottom, as the ocean floor offers a unique environment for many varieties of species (Friedrich, 1969). This environment is rich physically, offering habitats from rocky crevasses to soft and muddy plains, and is rich in nutrients as well. The falling

detritus and large carcasses collect on the seafloor, offering a steady source of food. Some 'deposit feeders' collect food through filtering the bottom sediments while other suspension feeders collect the material before they reach the bottom. Others live within the bottom sediments while larger scavengers feed directly on the other benthic organisms. Echinoderms (including sea cucumbers) are one of the most abundant benthic classes, and also abundant are polychaete worms, nematodes, crustaceans and bivalves.

Mainly as a result of more recent work (Oceanus, 1995), the benthic regions of the world are believed to be quite rich in biodiversity which in these areas has been acclaimed as 'as high as any other region on earth' (Broad, 1995). Thus, it is important to attempt to assess the impact of CO₂ disposal on these species, most of which would be quite unable to avoid a CO₂ lake or significant coverage by an acidic plume. Although these impacts have not been modeled and will not be explored in the same quantitative fashion as the pelagic effects, there is much we can say concerning the environmental impacts of the scenarios which involve significant coverage of the benthic regions by high concentrations of CO₂.

The bivalves would be perhaps the most in danger of acidification, as they have extremely limited movement abilities and their shells are quite susceptible to dissolution. As noted in Figure 2.2, Bamber has found dissolution to occur at pHs as high as 7.5, and suggests that the long term survival of a community would be threatened if the chronic pH level were below 7.0. Most other benthic species for which pH effects have been studied (Magnesen *et al.*, 1993) have shown at least threshold effects at pH 6.5 or above, and significant adverse effects at pH 6 or higher. Since the CO₂ lake scenario is expected to create a CO₂ pool in constant contact with the bottom and surrounding regions of pH 5 or lower, one would expect that the benthic community under such a lake would be devastated (though a few, highly tolerant species may thrive). Not only is this above the concentration at which most organisms suffer complete mortality in the benthic studies, but organisms in a CO₂ lake would experience this pH over their whole lifetimes, where the organisms in most of the benthic studies experienced the assay pH for a limited period of time. Further, it is suggested that a hydrate crust might form over such a lake which may prevent detritus of other decomposing materials from reaching the bottom and the organism-rich sediments below (Oshumi, 1995).

Still, the overall impact on the benthic region might be said to be not as great as a pelagic impact because this impact would likely be confined or isolated to a small area. If one were filling up a trench on the ocean bottom with CO₂, the area covered by the lake would only increase gradually with huge increases in volume of CO₂ disposed. For example, if a deep sea trench were modeled as an inverted square pyramid shape, then 10 power plants worth of CO₂ released for 100 years would fill up a pyramid of height 400 m and base 4.4

km, covering a bottom area of just over 21 km². The impacts on the pelagic region above the bottom would also be devastating, though the volume involved is relatively small compared to the pelagic impacts of the dissolution scenarios.

The question has been raised as to the possibility of a catastrophic sudden upwelling of the isolated CO₂ to the surface, possibly stimulated by a sudden temperature rise at the seafloor or seismic activity (Harrison *et al.*, 1995). If such an event were to occur, and large amounts of gaseous CO₂ were to come into contact with populated areas, the results could be disastrous as they were near Lake Nyos in 1986. However, to date, no plausible mechanism has been proposed where gaseous CO₂ would have to travel through several kilometers of ocean depth.

3.8.2 Dissolution of Calcium Carbonate

A potentially important effect, mentioned briefly above, of decreased pH in the ocean is the potential dissolution of calcium carbonate, a vital compound to many organisms and features of the marine environment. This compound, a basic component of the shells and bodies of many marine organisms is in equilibrium with dissolved calcium at ambient pH, and its dissolution rate is known to gradually increase as pH is decreased. Sea mussels have been shown to dissolve their internal CaCO₃ to produce carbonate ions to react with the incoming H⁺ in acidic conditions, a strategy that is not feasible under long term or severe stress (Booth, 1984). If loss of calcium carbonate saturation were to occur in widespread areas, some animals may have trouble producing shells and other calcium carbonate based skeletal structures. Effects on existing shallow calcium carbonate based structures such as coral reefs could also be significant.

Cole *et al.* (1993) has shown that loss of calcium carbonate saturation would occur more readily in the Pacific Ocean than in the Atlantic for a given quantity of added CO₂. In both regions, undersaturation would begin to occur when the pH is reduced below 7.0, a condition which could occur over large volumes in many of the scenarios (see Table 3.1).

3.8.3 Effects on bacteria

Though not mentioned explicitly on the graph in Figure 2.2, there have been studies performed on effects of reduced pH on marine bacteria. Zobell showed aerobic bacteria to be only 50% as effective at breaking down material at pH 6.5, (Zobell, 1941) while methane bacteria were shown to be still 50% effective at pH 5.0 (Hutton *et al.*, 1949). In looking further at the study of Zobell, we see that the aerobic bacteria are approximately 75% as

effective at pH 7.0 as they are at ambient conditions, 50% at pH 6.5, 25% at pH 6.0, and about 10% at pH 5.5. These reductions in effectiveness are roughly similar to the survival rates of zooplankton at the chronic exposure times in Figure 2.2 (the chronic region of the graph being more relevant because the bacteria assays were performed using exposure times greater than the lifetime of the bacteria, i.e. chronic exposures). Thus, for a rough approximation of the reduction in effectiveness of bacteria in their vital function of breaking down organic matter into basic nutrients, it may be a fair approximation to use the spatial mortality maps for the zooplankton shown above. With this approximation, the losses of bacterial function could certainly be significant to regional ecosystems as fewer nutrients would be recirculated to surface waters and phytoplankton productivity may be affected.

3.8.4 Effects of Trace Gases

As noted previously, under some capture scenarios, there may be significant amounts of SO₂ and NO_x released to the marine environment along with the predominant CO₂. For a standard pulverized coal plant, the amounts of these gases released under standard conditions might be 0.088 kg/s of SO₂ and .31 kg/s of NO₂ (Topical Report 1). These amounts are probably an upper bound because certain capture technologies could essentially reduce these amounts to zero. Still, the pH reduction potential of these gases in the amounts given would be most likely less than one percent of that of the CO₂. Because no other adverse affects of these compounds in their combination with seawater are expected, the effects of trace gases can be ignored.

3.9 Background effects - no action scenario

In assessing the magnitude of the impacts discussed up to this point, it is important to remember that these impacts would be taking place against a background of impact due to existing and future atmospheric CO₂. The oceans currently serve as a sink for up to 50% of the CO₂ emitted to the atmosphere (De Baar, 1992). This CO₂, unless taken up directly by phytoplankton in photosynthesis, is absorbed by the ocean at the surface through the same process by which CO₂ dissolves in water (Ch. 2) and eventually is carried to the deep ocean via biological or physical mechanisms.

If the flux of CO₂ into the ocean is unnaturally increased such that it is greater than the natural rate out outflow (as has been the case in the industrialized era), there is a net influx and hence a very gradual pH decrease in the ocean. It has been estimated that over the next few

hundred years, the ocean pH may decrease by as much as 0.5 pH units in some regions, with the largest effect felt at the surface (Topical Report 1).

Deep ocean disposal of CO₂ would essentially bypass the slow equilibration of the atmospheric CO₂ with the deep ocean in one quick step. While significant local impacts would result (Table 3.2), the gradual pH decrease in the surface waters would be certainly delayed. This pH decrease may, in fact, be permanently lessened, as potential atmospheric CO₂ that would have been absorbed at the surface is directly transported to the ocean depths where it dissolves, or reacts with abundant sediment carbonates. DeBaar states, "It might be argued that pumping CO₂ down will be beneficial for avoiding of changes in the upper-ocean ecosystem" (DeBaar, 1992).

In addition to a potential mitigation of the surface pH decrease, ocean disposal may, in mitigating climate change in general, lessen climate change impacts on surface marine life as well. Several recent papers have reported a significant decline in zooplankton populations off of the California coast due to a small rise in oceanic temperatures (attributed to the greenhouse effect) (Barry *et al.*, 1995, Roemmich *et al.*, 1995). Perhaps disposing of CO₂ in the deep ocean would amount to a tradeoff in some respects of deep water zooplankton (through direct mortality) for surface zooplankton (less oceanic warming). These tradeoffs and background effects are illustrated in Figure 3.5.

Figure 3.5 Schematic diagram of impacts of CO₂ emissions on marine environment with and without ocean disposal.

While it is very difficult to quantify the potential impacts of (and potential mitigation of, through CO₂ disposal) the inevitable surface pH decrease and temperature increase, it is important that we do understand these effects in the overall impact assessment. This

understanding is also important in light of the fact that the dry ice scenario and perhaps others may involve some contact of captured CO₂ with the surface ocean.

3.9.1 Effects on phytoplankton of slightly reduced pH

Many species seem to exist in a fragile equilibrium with surface seawater chemistry that if perturbed even slightly, could have significant impacts. Although there is a good deal of variation of effect among species, the overall effect of a pH reduction from the current average of about 7.8 to a value near 7.3 would likely be slightly reduced growth, production, and calcification. The green alga, *halimeda tuna* showed a general downward trend of calcification and photosynthesis with decreasing pH (Borowitzka *et al.*, 1976), and in a separate study, a red algae showed a decline in calcification to about 80% of its maximum level when pH is reduced to 7.3 (Smith and Roth, 1979). Further, H. Albert Barker found several species of diatoms to exhibit a strong decrease in their cell division rate (by about 30%) as pH is reduced from about 7.8 to 7.3 (Barker, 1935). Although some phytoplankton species exhibit maximum growth and effectiveness at pH below 7, the majority appear to be maximally effective at a pH of 8 or above (Knutzen, 1981) suggesting that any decrease below ambient levels would be generally anti-productive. A shift in species composition also would seem inevitable, the effects of which are difficult to estimate.

3.9.2 Effect on metal toxicity

Also mentioned by several authors (Knutzen, 1991, Magnesen, 1993) as a potential harmful effect of reduced marine pH is the change in the speciation of certain metals which could possibly results in a more toxic form of the metal becoming more predominant. It appears that copper is the only metal that undergoes a radical change in speciation in the range of pH 8 to 7 (Zirino *et al.*, 1972), and which is also present in concentrations that may approach their toxic level to some marine organisms (see Table 3.5 below). Specifically, the species, Cu⁺⁺ accounts for about 2% of all copper in seawater at pH 8, while at pH 7, Cu⁺⁺ accounts for approximately 30% of total copper species.

	Copper	cadmium	lead	zinc	mercury
Metal natural conc. in seawater (nM)	15.7	0.2	0.1	29.9	0.5
Minimum toxic concentration (nM)	234.4	537.0	195.0	1514	44.7

Table 3.5 Average metal concentrations in seawater (Reed, 1975) shown with minimum concentration found to be toxic to *Ditylum brightwellii* over a range of chelator (EDTA) concentrations (Borgmann, 1984).

While the table indicates that none of the above metals are near their toxic levels for the given species (*Ditylum brightwellii*), there are species in existence that are much more sensitive to copper than this one, some experiencing growth inhibition in the presence of natural levels of copper or lower (Gavis, 1981).

It is generally agreed that it is the Cu^{++} species that is toxic to phytoplankton (Borgmann, 1984), although the concentration of this copper species is difficult to estimate in natural seawater, given varying pH and concentration of other organic substances which can act as chelators. Assuming no organic chelation, Sunda and Guillard have estimated a pCu (analogous to pH) in natural seawater off of the Oregon coast to be approximately 9.6, where the pH was 8.2 (Sunda *et al.*, 1976). They then estimate that a pH reduction to 7.7 would reduce the pCu to about 9.2. If we assume that the gradual oceanic acidification reduces ambient pH to 7.5, and that the resulting pCu would be reduced further to around 9.0, we can estimate the effect of this on 11 species of marine phytoplankton for which Gavis has tabulated effects of pCu on growth. At the ambient (off of the coast of Oregon) pCu of 9.6, 3 of 11 species actually suffer 50% growth inhibition and 6 experience more minor effects. If pCu were reduced to 9.0, 6 species would suffer at least 50% growth inhibition and 10 of 11 experience a negative effect on growth. It should be noted that the species studied may be a more sensitive set than the natural distribution of species, as Borgmann notes that several species of phytoplankton are not inhibited by copper in concentrations as high as the metal's solubility limit in water.

There are other considerations that cast some doubt on the significance of the increase in copper toxicity with decreased pH. First, it is noted that the pCu values used in the above studies were all obtained by using chelators to control the Cu^{++} concentration, and one author believed that the chelator itself was at least partially responsible for the toxicity (Anderson *et al.*, 1978). Borgmann is also somewhat skeptical of the results and the estimations of pCu, which were calculated, not measured. Third, Gavis explains that many species in his study that may have been exposed to high copper concentrations showed excellent tolerance, indicating a potential for adaptation to gradually changing levels. Finally, Campbell and Stokes (1985) in a review of metal toxicity in freshwater species note that the effect of decreased pH actually appears to be toward lessening toxicity. In 12 studies of copper toxicity to phytoplankton and zooplankton mentioned in their review, 11 actually showed *decreased* toxicity with decreased pH, and similarly, in 10 studies of zinc toxicity, 7 showed decreased toxicity with decreased pH.

3.10 Ecosystem level impact of CO₂ disposal

Now that the potential impacts have been considered in a fairly comprehensive manner, we again return to the larger questions of the meaning of the results presented above. Relatively little is known about the food webs and life forms in the deep ocean as compared to the shallower, coastal waters. We know that most forms of life that feed directly on the surface phytoplankton do not migrate as low as 1000 m, so the zooplankton at these depths must subsist on falling organic materials (detritus) from surface waters Sumich, 1992. (Many zooplankton that feed on surface phytoplankton do migrate vertically over enormous depth ranges daily, but these migrations usually do not carry them to depths as low as 1000 m.) Organic material is digested, and transformed through the food chain or directly by bacteria into the rich nutrients that eventually make their way back to surface waters. The zooplankton loss in some of the more harmful scenarios could certainly translate into less material being digested, but since the impact should be confined vertically to a relatively small slice of ocean, the repercussions of this might not be so great. If the discharge were close to the sea floor, it is possible that there would be some buildup of undigested material on the floor.

As for upper tropic levels, would there be effects on fish or animals that feed on the zooplankton? It is often taken as a general rule that some 10% of energy of a trophic level is transferred up to the next level (Chisholm, 1996). But whether a loss of 10% of zooplankton over a given volume would translate ultimately to a 10% loss of the fish and other predators that feed on these zooplankton is difficult to say. It is certainly true that large numbers of ichthyoplankton would be lost along with the zooplankton, so if the impact on fish is small through loss of food, there would be some losses due to lack of development of young. Knowledge as to what kinds of fish lay eggs in the pelagic ocean at 1000 m, and of what percentage do eventually develop is limited, however. (Marshall, 1979). These mesopelagic fish sometimes serve as prey to larger, deep diving animals that can live near the surface, but are generally not a main part of the diet (Sumich, 1992).

Angel speculates on the potential ecosystem or surface ocean impact of a large lifeless region directly below.

There is the possibility that a volume of the ocean would become almost lifeless [due to CO₂ ocean disposal]. Such virtually lifeless waters are to be found naturally in the Eastern Tropical Pacific and the Northwest Indian Ocean as a result of very low oxygen concentrations. These are both high productivity regions, where the functioning of the surface water ecosystem continues unabated in the absence of the mesopelagic and bathypelagic components present in other oceanic regions (IEA, 1993).

These links between deep ocean and surface ocean are not well understood at this time, but the above quote suggests that even were there significant loss of life at 1000 m, the impact may be negligible on surface ecosystems.

3.11 Conclusions and summary of impacts

The major impact of CO₂ ocean disposal is expected to be loss of regional non-swimming organisms near the discharge point as a result of acidification of the seawater. The extent of these impacts would vary greatly with disposal scenario. In comparison of impacts on zooplankton and bacteria in the water column, the dry ice and towed pipe scenarios are predicted to have essentially no impact. The droplet plume would have what might be termed minor impact and the dense plume is projected to have an impact approximately an order of magnitude larger than the droplet plume.

Surface impacts of reduced pH are likely to be more significant than impacts at 1000 m implying that: 1) there may be minor impacts resulting from the dry ice release and 2) that any avoidance of an ongoing surface pH decrease, as might occur to a small extent through deep ocean disposal of CO₂, might be beneficial to phytoplankton. The benthic impacts of the CO₂ lake scenario and the dense plume where contact with the bottom is indicated would be devastating, but confined to a relatively small area.

Comparisons between the dense plume and the more dispersed droplet plume, and between the one and ten plant cases within scenarios reveal greatly decreased environmental impact through increased plume dispersion. These non-linear effects are taken advantage of with the towed pipe scenario to achieve zero impact. This same zero impact result could be achieved with the droplet plume release if individual releases are kept to below a third of a plant's worth of CO₂.

In determining the best injection scenario for a given situation, ideally one would like to do a cost benefit analysis and minimize cost. How to value this environmental impact would be extremely difficult, however, as the ecosystem level significance of the impacts from the dissolution scenarios is open to question.

In addition, there are other factors aside from cost that would play a large part in eventual decisions among scenarios or even decisions to allow implementation of the concept at all. Topical Report 6 explores some of these other factors.

Appendix A. Alternative methods for adding exposures

A.1 - Summing Concentration Time

Perhaps the simplest and most intuitive method for adding successive exposures is simply to convert all exposures to the unit of concentration-time. In what appears to be the standard for exposure assessments in air pollution (NAS, 1991), the total exposure for a given organism can be expressed as the sum:

$$\text{total exposure} = E_{ij} = \sum_{i=1}^I C_{ij} \Delta t_j$$

where C is the concentration experienced for time t to the i^{th} chemical in the j^{th} microenvironment. In our situation, the equation would have to be modified to express concentration as excess concentration of H^+ minus ambient concentration because there should be no impact when concentrations are at their normal background level.

Before attempting to sum discretized exposures j to arrive at total exposure for a given experience, we naturally check to see if there is indeed a clear relationship between total exposure (as calculated above) and empirical mortality. When the data from Figure 2.2 are used to test this relationship, (using $i=1$, $j=1$, and plotting excess concentration of H^+ * exposure time vs. observed % mortality) there is barely a discernible trend ($r^2=.25$). Thus, while it may be easy to evaluate the discretized exposures as sums of concentration * time, this would be fruitless as there would be little correlation with expected mortality. No more will be said about this method as it is clearly inappropriate for our purposes.

A.2 - Summing fractions of time to 50% mortality

A second alternative method for adding exposures is described by J. R. Schubel (1978) in his paper about the thermal effects on zooplankton and phytoplankton entrained in power plant cooling systems. These organisms would experience a time history of elevated temperatures as they pass through the cooling system, all of which contribute to the organism's mortality. A curve is derived from experimental data indicating 50% mortality of organisms for a range of temperatures (' LT_{50} ') vs. time (analogous to our 50% isomortality curve except that temperature is the stress instead of decreased pH). With this curve, he assesses the mortality-causing potential of individual experiences by finding the quotient of the

number of hours at the given temperature of that point divided by the number of hours at which an organism would experience 50% mortality at that same temperature. For a point directly on the 50% mortality line, for example, this quotient would be equal to one.

To add a series of point exposures, one would simply add the individual quotients for each point, and evaluate the sum. Since Schubel was simply interested in a coarse assessment of either 'mortality' or 'no mortality', he was only interested in whether the sum was greater than or less than 1. But we may apply this method toward more specific mortality assessments by assuming that a sum of 1 is equivalent to 50% mortality and therefore, that any sum, may be multiplied by 50% to obtain the estimated mortality, i.e.:

$$\text{Mortality \%} = 50\% * \sum_i (X_i \text{ hours at pH } Y_i / Z_i \text{ \# of hours required for 50\% mortality at pH } Y_i)$$

This method is illustrated with Figure A.1 below. (The isomortality curves used in Appendix A are for illustration purposes only, but the same concepts that apply to the curves derived in Ch. 2 apply here).

Figure A.1. Illustration of Schubel's method of adding exposures. X_a and X_c are the exposure times for exposures represented by points a and c respectively. Z_a and Z_c are the times at 50% mortality for points a and c (see above equation).

Using the sample exposures above represented by points a and c, we find the fraction to 50% mortality for exposure a is 43 hours (the number of hours of exposure to pH 5.5, the pH for point a) divided by 61 hours (61 hours results in 50% mortality at pH 5.5, the pH of exposure a), or .705. For exposure c, this fraction is 200/1100 or .182. The sum is .867, which corresponds to approximately 43% mortality.

A.3 Adding hazard functions

This method could be described as a modification of or more sophisticated variation of the above method. Developed to measure effects of cumulative radiation doses that can occur at intermittent time periods, the method defines risk in terms of the cumulative hazard, and hazard in terms of the ratio of the experienced dose to the LD₅₀ dose. Specifically,

$$r = 1 - e^{-H}, \quad \text{Where } H = 0.693 [d/D_{50}]^v \text{ for } d > T$$

Where r is the probability that the organism will exhibit the effect, T is the threshold dose, D_{50} is the dose level required to cause the effect in question in 50% of the population, d is the experienced dose, and v is a shape parameter. To add experiences, one would sum d/D_{50} fractions for each point to calculate a cumulative hazard (H). The final r value would be the total % mortality for the population.

Yet unclear from this method in application to our situation is first, whether *time* or *concentration* should be used as the 'dose' since both are relevant, and second, how to arrive at a suitable value for v . Below, using the sample exposures from Figure 2.4, this method was used once with time as the dose and once with pH, in comparison to our method and Schubel's method.

pH as dose

point	pH at point	pH at LC50	d/D50	V	H	r
a	5.82	5.50	0.48	1.20	0.29	0.25
b	6.32	6.25	0.85	1.20	0.57	0.44
c	6.80	6.60	0.63	1.20	0.40	0.33
d	7.25	6.70	0.28	1.20	0.00	0.00

Time as dose (hr)

point	time at point	time at LC50	d/D50	V	H	r
a	40.74	52.48	0.78	1.20	0.51	0.40
b	97.72	112.20	0.87	1.20	0.59	0.44
c	257.04	1.00E+06	0.00	1.20	0.00	0.00
d	2511.89	infinite	0.00	1.20	0.00	0.00

	H (tot)	Tot mort.
Total mortality with pH as dose	1.26	71.5 %
Total mortality with time as dose	1.10	66.6 %
Total mortality using Schubel's method		112.1 %
Total mortality using our method		64.0 %

Table A.1. Illustration of hazard function exposure addition method in comparison with two other methods.

Because of the functional form of the risk equation, these methods appear more reasonable than Schubel's method as discussed above. Within the hazard function method, using pH as the dose unit instead of exposure time makes more physical sense because of a problem also experienced with the Schubel method - the LC_{50} time, which would appear in the denominator for individual experiences, does not exist for higher pH. Perhaps ideal would be to somehow use a combination of the pH - time factors as a dose, but it would be beyond the scope of this work to undertake such an analysis.

A.4 Successive weighted averages

Finally, we turn to a method developed by Mattice and Zittel (1976) to account for exposure to toxic chlorine discharges in the marine environment. Similarly to our endeavor, they attempt to evaluate mortality due to exposure to varying concentrations of chlorine compounds as the organism passes through and out of a discharge plume. They first discretize the experience as we do, and take successive weighted averages of the discretized points, plot these new weighted average points, and connect them with a line. If the line falls above where their threshold line of 0% (no effect) falls on their graph (analogous to the 0% curve in Figure 2.3), they claim mortality as opposed to no mortality. This method is illustrated in Figure A.2 and explained in detail below.

Figure A.2 Illustration of Mattice and Zittel's method for adding exposures. a,b,c, and d represent sample exposures. Point e is the weighed average time and concentration of a and b. Point f is the weighted average of a, b, and c (or simply e and c), and point g is the weighted average of f and d.

For example in Figure A.2, we have a sample discretized exposure represented by the points **a**, **b**, **c**, and **d**. We first would find a point **e** which would represent the sum or cumulative exposure of point **a** + point **b**. This sum is approximated as the weighted average of points **a** and **b** and is arrived at as follows:

If we let X_a = the exposure time for point **a** and X_b = exposure time for point **b**, etc., and $y_a = H^+$ concentration experienced at point **a**, etc., then to find X_e, y_e ,

$$X_e = X_a + X_b, \text{ and } y_e = (X_a y_a + X_b y_b) / (X_a + X_b)$$

Point **f** may be found by simply taking the weighted average in the same manner as above of points **a**, **b**, and **c**, or equivalently, of points **e** and **c**.

In Figure A.2, the line e-g connecting the weighted average points **e**, **f**, **g**, and **h** would be the output of Mattice's assessment. If this line, when compared to similar lines derived from literature studies, were over the threshold level of effect, he would claim that mortality would be experienced by the organism. Attempts to further quantify the mortality based on such a method, however, would be difficult to justify. Thus, this method is not very appropriate in the interest at a more quantitative mortality assessment.

A.5 Discussion and critique of alternative methods

In applying the methods for adding exposures, it becomes apparent that Mattice's method is not very applicable for the type of data we have above. If the new weighted average points form a line when connected that is not parallel to the isomortality curves, it is difficult to estimate percentage mortality for the experience. Indeed, when the method is applied to the above data, one obtains downward sloping curves because each successive point represents a milder experience at a higher pH, causing the weighted average experience to drop monotonically in severity. In our situation, it is not appropriate to weight experiences by time when the longer-time experiences will always be closer to ambient pH.

Second, neither Schubel's method nor the hazard function method is very accurate for exposures near ambient pH because for pH 7, for example, there is no time for which 50% of the organisms would die. Thus, the denominator would be infinite for exposures at pH 7, and they would not contribute to overall mortality. Yet, experiments have shown definite deleterious effects to some species at pH 7. There is a second problem if we have an exposure that is far below the no effect level. Even if the exposure should reasonably not contribute to overall mortality, the exposure would still give a mortality percentage of greater than 0 because

there will be a finite number of hours in the numerator and in the denominator (assuming the hours to 50% mortality is defined). Third, these methods only utilize the 50% mortality curve in estimating fractional mortalities and not the other curves and thus, some important information from laboratory or field experiments may be under-utilized.

Finally, Schubel's method and one version of the hazard function method use time as the critical factor in determining how severe one exposure is relative to another. In fact the method assumes the effect is linear in time, i.e., an experience of X hours at pH Y is assumed to cause half as much mortality as 2X hours spent at pH Y. While exposure time is certainly an important factor, the data show that pH is more important, especially at higher pH, and thus, our method is a more accurate representation for finding an approximate cumulative exposure point as a sum of individual exposures. Using pH as the dose factor in the hazard function method (this could also be possible in Schubel's method) would correct this problem somewhat, but it would still remain true that twice the dose would be counted as twice the mortality, which is usually untrue given the non-linear isomortality curves.

Thus, the isomortality approximation method will be used exclusively to calculate mortality from the discretized exposures. The other methods are useful and illuminating in this area and may be more useful for other applications. They are general, not responsive to extremely specific mortality data as in Figure 2.3, and probably best used in applications for which the authors had intended them, that is, to justify zero impact, or to design a system with zero impact on an ecosystem where parameters of discharge volume, concentration, etc. are highly controllable.

Appendix B. Compensation and Intergenerational Effects

Mortality due to pH perturbations can be calculated using probabilistic simulation and the method of stress integration described; however, this model includes no mechanism to account for the fact that relatively unstressed organisms will reproduce and that depleted populations, once no longer significantly stressed, will recover. In order to account for this recovery, the logistic equation for density limited population growth will be used (Colinvaux, 1986). The simplest form for a single species population is:

$$dN/dT = rN (1-N/K)$$

where N is the number of organisms, r is the growth rate with unlimited resources, and K is the 'carrying capacity' (number) for the species considered. Organism concentrations (densities) can be considered by dividing N or K by a reference volume. $(1-N/K)$ is the fractional deficit that is calculated.

In order to keep the calculations as general as possible, the equation was normalized by the equilibrium population, so that:

$$d/dt (N/K) = r N/K (\text{deficit})$$

where N/K is the concentration of organisms as a fraction of the equilibrium concentration. No assumption is needed about the magnitude of K. A growth rate, r, is still needed, and a value typical of copepods is used since they are the most abundant organisms at the depths considered. The growth rate used (0.09/day) is taken from laboratory observations of surface organisms; however, Kinne (1978) notes that, "in general, within a given group, deep-living species tend to have a slower turnover, produce less offspring, live longer, and so on." Under stress, both the growth rate and the equilibrium population would be expected to be depressed, but this effect is difficult to quantify. For simplicity, compensation has been modeled as taking place only when the population reaches an unstressed environment (in this case, a pH of 7.5 or above) and r and K can be treated as constants (Figure B.1). These simplifications are not expected to produce large errors since, in general, the high potential growth rate of copepods means that the recovery time is comparable with or less than the time spent in the plume.

Figure B.1 Function used for variation in growth rate with pH

The most severe limitation of the logistic equation is that it deals with a single species in a stable environment, whereas the real situations of interest deal with interacting species in a changing environment. In the event that the plume affects some organisms more severely than others for a substantial period of time, the equilibrium species composition could change. It has been noted that most populations can change behavior or physiology to survive a perturbation with a time scale less than the generation time (Valiela, 1984). For most of the plumes studied the length of the perturbation is expected to be less than the generation time of the majority of organisms, so that long term effects are not expected unless currents or active migration lead to the same populations of organisms being continuously swept through the same plume. Another limitation is that the equation treats all age classes equally, whereas some are more important to the reproduction, and hence survival, of the species. Also, although reproduction is a process with a finite time scale, no time lags are considered. With the appropriate data, the model could certainly be refined; however, the required data are not available and the model, despite its limitations, provides a reasonable method to quantify the scale of impact.

For surface living copepods a typical generation time measured in laboratory experiments is about 40 days (Kinne, 1978). The 10 plant plumes tend to maintain stressful pH levels for periods longer than this generation time, although only the 10 plant dense plume has a duration longer than twice this time. Since the organisms live at depth and are under stress, the generation time in situ would be expected to be longer, and many other organisms of interest have longer generation times. In the presence of these uncertainties and in the interest of generality, it was decided not to account explicitly for successive generations within the plume. Instead, the mortality calculation was extrapolated over the duration of the plume. This would tend to lead to a slight underestimate of the mortality, the magnitude of which would tend to increase with duration of the plume.

Brownell, C.L. (1980), "Water Quality Requirements for First-feeding in Marine Fish Larvae. II. pH, Oxygen, and Carbon Dioxide" *Journal of Experimental Marine Biology and Ecology*, 44, pp. 285-298.

Calabrese, A., David, H.C. (1966), "The pH Tolerance of Embryos and Larvae of *Mercenaria Mercenaria* and *Crassostrea Virginica*," *Biological Bulletin*, 131, pp. 427-436.

Campbell, P.G.C., Stokes, P.M. (1985), "Acidification and Toxicity of Metals to Aquatic Biota," *Canadian Journal of Fisheries and Aquatic Sciences*, 42, 12, pp.2034-2049.

Caulfield, Jennifer (1996), "The Environmental Impacts of CO₂ Ocean Disposal: Plume modeling and Exposure assessment," Master's Thesis, Massachusetts Institute of Technology, Cambridge, MA, USA.

Chisholm, Sally (1996), Personal communication.

Cockerham, L.G., and Shane, B.S. (1994), Basic Environmental Toxicology, CRC Press.

Cole, K., Stegen, G.R., Spencer, D. (1993), "The Capacity of the Deep Oceans to Absorb Carbon Dioxide," *Energy Conversion Management*, v.34, 9-11, pp.991-998.

Colinvaux, P. (1986), Ecology, Wiley and Sons, New York, 1986.

Davies, J.K. (1991), "Reactions of Sand Smelt to Low pH Sea-water," *Marine Pollution Bulletin*, 22, No.2, pp74-77.

De Baar, H.J.W. (1992), "Confining and Abating CO₂ From Fossil Fuel Burning - a Feasible Option?," in TNO Environmental and Energy Research, TNO Institute of Environmental and Energy Technology, The Netherlands.

Drange, H., Haugan, P.M. (1992), "Carbon Dioxide Sequestration in the Ocean: The Possibility of Injection in Shallow Water," *Energy Conversion Management*, 33, pp. 697-704.

Eng, William (1996), USEPA Region I, Personal Communication.

Evans, J.S. (1990), "Health Effects Models for Nuclear Power Plant Accident Consequence Analysis," Sandia National Laboratories, prepared for Nuclear Regulatory Commission, NUREG/CR-4214 SAND85-7185 Rev.1, Part 1, Sandia, NM.

Friedrich, Hermann (1969), Marine Biology. University of Washington Press.

Fry, F.E.J., Hart, J.S., Walker K.F. (1946), "Lethal Temperature Relations for a Sample of Young Speckled Trout (*Salvelinus fontinalis*)," Univ. of Toronto Stud., Biol. Ser., No. 54. Pub. Ont. Fish. Res. Lab, 66, pp. 5-35.

Gavis, J., Guillard, R.R.L., and Woodward, B.L. (1981), "Cupric Ion Activity and the Growth of Phytoplankton Clones Isolated From Different Marine Environments," *Journal of Marine Research*, 39, pp. 315-333.

Grice, G. D., Hoagland, E., Wiebe, P.H. (1973), "Acid-Iron Waste as a Factor Affecting the Distribution and Abundance of Zooplankton in the New York Bight," *Estuarine and Coastal Marine Science*, 1, pp. 45-50.

References

- Adams, E.E., Golomb, D., Zhang, X.Y., Herzog, H.J. (1995), "Confined Release of CO₂ Into Shallow Seawater," In Ocean Disposal of Carbon Dioxide, Eds. Handa, N., Oshumi T., Terrapub, Tokyo, pp. 153-161.
- Anderson, D.M., Morel, F.M.M. (1978), "Copper Sensitivity of *Gonyaulax tamarens*," *Limnology and Oceanography*, 23, pp. 283-295.
- Angel, M.V., Baker, A. de C. (1982), "Vertical Standing Crop of Plankton and Micronekton at Three Stations in the Northeast Atlantic," *Biological Oceanography*, 2, pp.1-30.
- Baes, C.F. Jr., Goeller, H.E., Olson, J.S., Rotty, R.M. (1977), "Carbon Dioxide and Climate: The Uncontrolled Experiment," *American Scientist*, 65, pp. 310-320.
- Baker, J.P., Christensen, S.W., (1987) "Effects of Acidification on Biological Communities in Aquatic Ecosystems," Chapter 4 in Acidic Deposition and Aquatic Ecosystems, Charles, D.F., Christie, S. eds., Springer Verlag, NY.
- Bamber, R.N. (1987), "The Effects of Acidic Seawater on Young Carpet-shell Clams *Venerupis decussata* (L.) (Mollusca : Veneracea)," *Journal of Experimental Marine Biology and Ecology*, 108, pp. 241-260.
- Bamber, R.N. (1990), "The Effects of Acidic Seawater on Three Species of Lamellibranch Mollusc," *Journal of Experimental Marine Biology and Ecology*, 143, pp. 181-191.
- Bamber, R.N. (1996), Personal communication.
- Barker, H.A. (1935), "Photosynthesis in Diatoms," *Archives fur Mikrobiologie*, 6, pp.157-181.
- Barnes, R.S.K., Mann, K.H. eds. (1992), Fundamentals of Aquatic Ecology, Blackwell Scientific Publications, Oxford, England.
- Barry, J.P., Baxter, C.H., Sagarin, R.D., Gilman, S.E. (1995), "Climate-related Long-term Faunal Changes in a California Rocky Intertidal Community," *Science*, 267, pp. 672-675.
- Booth, C.E., McDonald, G., Walsh, P.J. (1984), "Acid-Base Balance in the Sea Mussel, *Mytilus Edulis*. I. Effects of Hypoxia and Air-exposure on Hemolymph Acid-base Status," *Marine Biology Letters*, 5, pp. 347-358.
- Borgmann, U. (1984), "Metal Speciation and Toxicity of Free Metal Ions," Ch.2 in *Environmental Toxicology*.
- Borowitzka, M., and Larkum, A.W.D. (1976), "Calcification in the Green Alga *Halimeda*," *Journal of Experimental Botany*, 27, 100, pp. 879-893.
- Broad, W.J. (1995), "The World's Deep, Cold Sea Floors Harbor a Riotous Diversity of Life," NY Times, Oct.17, Section C, p.1.

- Grice, G.D., Hulsemann, K. (1965), "Abundance, Vertical Distribution and Taxonomy of Calanoid Copepods at Selected Stations in the Northeast Atlantic," *Journal of Zoology*, 146, pp. 213-262.
- Handa, N., Oshumi, T. (1995), eds. Direct Ocean Disposal of Carbon Dioxide, Terra Scientific Publishing Company, Tokyo, Japan.
- Havas, M., Hutchinson, T.C. (1982), "Aquatic Invertebrates from the Smoking Hills, N.W.T.: Effect of pH and Metals on Mortality," *Can. J. Fish. Aquat. Sci.* **39**: 890-903.
- Harrison, W.J., Sloan, E.D., Wendlandt, R.F. (1995), "Geochemical Interactions Resulting from Carbon Dioxide Disposal on the Sea Floor," *Applied Geochemistry*, 10,4, pp. 461-486.
- Herzog, H., Drake, E., Tester, J., Rosenthal, R. (1993), "A Research Needs Assessment for the Capture, Utilization, and Disposal of Carbon Dioxide from Fossil Fuel-Fired Power Plants," U.S. Department of Energy Report DOE/ER-30194.
- Herzog, H.J., Adams, E.E., Auerbach, D., Caulfield, J. (1995), "Technology Assessment of CO₂ Ocean Disposal," Massachusetts Institute of Technology (MIT) Energy Laboratory, MIT-EL 95-001, Cambridge, MA, USA.
- Hoffman, D.J., Rattner, B.A., Burton, G.A. jr., Cairns, J. jr. (1995), Handbook of Ecotoxicology, Lewis Publishers, pp.310-329.
- Hutton, W.E., Zobell, C.E. (1949), "The Occurrence and Characteristics of Methane-Oxidizing Bacteria in Marine Sediments," *Journal of Bacteriology*, 5, pp.463-473.
- Intergovernmental Panel on Climate Change (IPCC) (1990), "Climate Change - The IPCC Scientific Assessment," Houghton, J.T., Jenkins, G.T., Ephraums, J.J., Eds., Cambridge University Press, Cambridge, England.
- Intergovernmental Panel on Climate Change (IPCC), Working Group II, Second Assessment Report, (1995), "Summary for Policy makers - Impacts, Adaptation, and Mitigation," Office of the US Global Change Research Program, <http://www.unep.ch/ipcc95.html>.
- International Energy Agency (IEA), The Greenhouse Gas R&D Programme (1994), "The Disposal of Carbon Dioxide from Fossil Fuel Fired Power Stations," IEAGHG/SR3.
- Jirka, G.H., Jones, J.M., and Sargent, F.E. (1980), "Theoretical and Experimental Study of the Intermediate Field Dynamics of Ocean Thermal Energy Conversion Plants," (Progress report for 1978-1979), Cornell University, Ithaca, NY.
- Khesghi, H.S., Flannery, B.P., Hoffert, M.I., Lapenis, A.G. (1994), "The Effectiveness of Marine CO₂ disposal," *Energy* 19, 9, pp. 967-74.
- Kinne, O. (ed.) (1978), Marine Ecology: A Comprehensive, Integrated Treatise on Life in Oceans and Coastal Waters v.4, Wiley-Interscience, New York.
- Knutzen, J. (1981), "Effects of Decreased pH on Marine Organisms," *Marine Pollution Bulletin*, 12, pp. 25-29.
- Liro, C.R., Adams, E.E., Herzog, H.J. (1991), "Modeling the Release of CO₂ in the Deep Ocean," Technical Report MIT-EL 91-002, Energy Laboratory, M.I.T., 1991.

- Marchetti, C. (1977), "On Geoengineering the CO₂ Problem," *Climatic Change*, 1, pp. 59-68.
- Marshall, N.B. (1979), Developments in Deep Sea Biology. Blanford Press.
- Magnesen, T., Wahl, T. (1993), "Biological Impact of Deep Sea Disposal of Carbon Dioxide," The Nansen Environmental and Remote Sensing Center (NERSC) Technical Report No. 77A.
- Mattice, J.S., Zittel, H.E. (1976), "Site Specific Evaluation of Power Plant Chlorination," *Journal of the Water Pollution Control Federation*, 48, 10, pp. 2284-2307.
- Menzies, R.J., George, R.Y., Rowe, G.T. (1977), Abyssal Environment and Ecology of the World Oceans, Wiley and Sons, New York.
- Morris, R., Taylor, E.W., Brown, D.J.A., and Brown, J.A. (1989), Acid Toxicity and Aquatic Animals, Society for Experimental Biology Seminar Series #34, Cambridge University Press.
- Naill, R.F., Belanger, S., Klinger, A., Petersen, E. (1992), "An Analysis of the Cost Effectiveness of U.S. Energy Policies to Mitigate Global Warming," *System Dynamics Review*, 8,2, pp. 111-128.
- National Academy of Sciences (NAS) (1975), Assessing Potential Ocean Pollutants, Chapter 4, "Synthetic Organic Chemicals," A Report of the Study Panel on Assessing Potential Ocean Pollutants, Washington, DC.
- National Academy of Sciences (NAS) (1991), Human Exposure Assessment for Airborne Pollutants, National Research Council, Washington, DC.
- National Academy of Sciences (NAS), National Academy of Engineering, Institute of Medicine (1992), "Policy Implications of Greenhouse Warming: Mitigation, Adaptation, and the Science Base," National Academy Press.
- Nikolsky, G.V. (1963), The Ecology of Fishes, Academic Press London & New York.
- Nordhaus, William D. (1994), Managing the Global Commons: The Economics of Climate Change, MIT Press, Cambridge, MA, USA.
- Oceanus* (1995) Fall, Winter ed., v. 38, 2. Many authors and articles.
- Omori, M., Norman, C.P., Maeda, M., Kimura, B., and Takahashi, M. (1996), "Some Considerations on the Environmental Impact of Oceanic Disposal of CO₂ With Special Reference to Midwater Organisms," Private conference report, Cambridge, MA.
- Ormerod, W.G., Webster, I.C., Audus, H., Riemer, P.W.F. (1993), "An Overview of Large Scale CO₂ Disposal Options," *Energy Conversion Management*, 34, 9, pp. 833-840.
- Oshumi, Takashi (1995), "Feasibility Study on CO₂ Storage in the Deep Sea" in Marine Technology and Science in Japan, Central Research Institute of Electric Power Industry.
- Paddock, R.A., Ditmars, J.D. (1983), "Initial Screening of License Applications for Ocean Thermal Energy Conversion OTEC Plants with Regard to Their Interaction With the

Environment," Technical Report ANL/OTEC-EV-2, Argonne National Laboratory, Chicago, IL.

Portmann, J.E. (1970), "Results of Acute Toxicity Tests with Marine Organisms, Using a Standard Method," *Marine Biology*, p.212-217.

Reed, A. (1975), Ocean Waste Disposal Practices, Noyes Data Corporation, London.

Reichle, D.E., Harwell, M.A., Kelly J.R., Kimball, K.D., Levin, S.A. (1989), Ecotoxicology: Problems and Approaches, Springer-Verlag, New York.

Revelle, R., Suess, H.E. (1957), "Carbon Dioxide Exchange Between the Atmosphere and Ocean, and the Question of an Increase in Atmospheric CO₂ During the Past Decades," *Tellus*, 9, p. 18.

Roemmich, D., and McGowan, J. (1995), "Climatic Warming and the Decline of Zooplankton in the California current," *Science*, 267, pp. 1324-1326.

Rose, C.D., Williams, G.W., Hollister, T. A., Parrish, P.R. (1977), "Method for Determining Acute Toxicity of an Acid Waste and Limiting Permissible Concentration and Boundaries of an Oceanic Mixing Zone," *Environmental Science and Technology*, 11 (4) 367-71.

Sarmiento, J.L. (1993), "Ocean Carbon Cycle," *C&E News*, May 31, p. 30-43.

Schubel, J.R., Coutant, C.C., Woodhead, P.M.J. (1978), "Thermal Effects of Entrainment" in Power Plant Entrainment, A Biological Assessment. Schubel, J.R., Marcy, Barton C. Jr. eds. Academic Press Inc., NY.

Shelford, V., Allee, W.C. (1913), "The Reactions of Fishes to Gradients of Dissolved Atmospheric Gases," *Journal of Experimental Zoology*, 14, pp 207-266.

Smith, A.D. and Roth, A.A. (1979), "Effect of Carbon Dioxide Concentration on Calcification in the Red Coralline Algae, *Bossiella orbigniana*" *Marine Biology*, 52, pp. 217-229.

Spencer, D.F. (1993), "Use of Hydrate for Sequestering CO₂ Deep in the Ocean," National Summer Conference of the American Institute of Chemical Engineers, Seattle, USA.

Sullivan, S.M., Sands, M.D., Donat, J.R., Jepsen, P., Smookler, M., and Villa, J.F. (1981), Environmental Assessment of Ocean Thermal Energy Conversion (OTEC) Pilot Plants, Lawrence Berkeley Laboratory, Report for the DOE W-7405-ENG-48.

Sumich, James L. (1992), An Introduction to the Biology of Marine Life, Wm. C. Brown Publishers, Iowa.

Sunda W., and Guillard R.L. (1976), "The Relationship Between Cupric Ion Activity and the Toxicity of Copper to Phytoplankton," *Journal of Marine Research*, 34,4, pp. 511-529.

Takahashi, T., Broecker, W.S., Bainbridge, A.E. (1981), "Supplement to the Alkalinity And Total Carbon Dioxide Concentration In The World Oceans," In Carbon Cycle Modeling, v. 16 of Scope. Wiley & Sons, New York.

United States Climate Change Action Plan (1994), available on the World Wide Web at (<http://gcrio.gcrio.org/USCCAP.toc.html>).

United States, Department of Energy (USDOE), Office of Fossil Energy (1994), "Meeting the Climate Challenge: Reducing Greenhouse Gases by More Efficient Use of Fossil Fuels," DOE/FE-0325.

United States Department of Energy (USDOE) (1996), Environmental Impacts of Ocean Disposal of CO₂, Final Report, DOE Grant # DE-FG22-94PC94227.

United States Environmental Protection Agency (USEPA), Office of Water Enforcement and Permits (1985), "Technical Support Document for Water Quality-based Toxics Control," Washington, DC.

Valiela, I. (1984), Marine Ecological Processes, Springer-Verlag, New York, p. 384.

Wellburn, A. (1988), Air Pollution and Acid Rain, Longman Group, UK.

Zirino, A., Yamamoto, S. (1972), "A pH Dependent Model for the Chemical Speciation of Copper, Zinc, Cadmium and Lead in Seawater," *Limnology and Oceanography*, 17, pp. 661-667.

Zobell, C.E. (1941), "Studies on Marine Bacteria. I. The Cultural Requirements of Heterotrophic Aerobes," *Journal of Marine Research*, 4, pp.42-75.

Topical Report 6

Legal and Political Aspects of CO₂ Ocean Disposal

**David I. Auerbach
Judith T. Kildow
Howard J. Herzog
E. Eric Adams**

**Massachusetts Institute of Technology
Energy Laboratory
77 Massachusetts Avenue
Cambridge, MA 02139-4307**

Table of Contents	Page
Chapter 1. Legal and Regulatory Framework	6-5
1.1 Introduction	6-5
1.2 International marine pollution control regimes	6-6
1.2.1 <i>The Law of the Sea</i>	
1.2.2 <i>The London Dumping Convention</i>	
1.2.3 <i>Regional agreements</i>	
1.3 National regimes - the U.S.	6-13
1.3.1 <i>National ocean dumping regulations</i>	
1.3.2 <i>National ocean discharge regulations</i>	
Chapter 2. Implications and Trends	6-19
2.1 Introduction	6-19
2.2 CO ₂ lake and dry ice scenarios	6-19
2.2.1 <i>U.S. dumping laws</i>	
2.2.2 <i>International laws</i>	
2.3 Dense and droplet plume scenarios	6-22
2.3.1 <i>U.S. regulations</i>	
2.3.2 <i>The Law of the Sea</i>	
2.4 Trends and analogies	6-25
2.4.1 <i>Ocean dumping in the NY Bight</i>	
2.4.2 <i>Radioactive waste</i>	
2.4.3 <i>Ocean Thermal Energy Conversion (OTEC)</i>	
2.4.4 <i>Acoustic Thermometry of Ocean Climate (ATOC)</i>	
2.4.5 <i>Warm water discharges from power plants</i>	
2.5 Trends in international laws	6-29
2.5.1 <i>The precautionary principle</i>	
2.5.2 <i>Systemic approaches</i>	
2.6 Conclusion	6-32
Chapter 3. Other Considerations	6-34
3.1 Introduction	6-34
3.2 Environmental monitoring	6-34
3.3 Implementation and siting	6-36
3.4 Public perception	6-36
3.5 Trends in fossil fuel use	6-37
3.6 Costs	6-39
Chapter 4. Conclusions	6-41
4.1 Introduction	6-41
4.2 Environmental impacts	6-41
4.3 Legal and other considerations	6-43
4.4 General conclusions	6-43
References	6-46

List of Figures

Page

Figure 3.1 CO₂ emissions over time for 5 major nations

6-38

Figure 3.2 Trends in total electricity generation from fossil fuels in OECD vs. non-OECD countries

6-38

List of Tables

Page

Table 2.1 Distance from discharge point to pH 7.0 and 7.5

6-24

Table 3.1 Cost estimates of various CO₂ reduction strategies

6-39

Chapter 1. Legal and Regulatory Framework

"Man has the fundamental right to freedom, equality, and adequate conditions of life, in an environment of a quality that permits a life of dignity and well-being and he bears a solemn responsibility to protect and improve the environment for present and future generations."

-Principle 1 from the Declaration on the Human Environment from the UN Convention of the Human Environment held in Stockholm, June, 1972.

1.1 Introduction

Ocean disposal of CO₂ presents a particularly interesting problem in international and national environmental regulation. As complex and multi-faceted as it is, this strategy has a single driving force: to reduce atmospheric concentrations of carbon dioxide in order to lessen the potential adverse impacts resulting from such concentrations. Strategies to reduce this atmospheric pollutant have been given high priority in international environmental conferences such as the UN Convention on Environment and Development in Rio De Janeiro in 1992, which have resulted in many national action plans and regulations to deal with CO₂ emissions (USCCAP, 1994). Ocean CO₂ disposal is a response to these calls for action and would likely be championed by many environmentalists interested in protecting the atmosphere and climate from further harm. Yet what makes the problem interesting is that while the strategy is in one sense simply a short cut to an inevitable long term equilibrium, this short cut may involve environmental benefits in one area at the expense of environmental harm in another.

Technically, ocean disposal of CO₂ is marine pollution. The 1972 Conference on the Human Environment in Stockholm and most subsequent marine pollution regimes including the Law of the Sea convention defines marine pollution as:

The introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) which results in or is likely to result in such deleterious effects as harm to living resources and marine life, hazards to human health, hindrance of marine activities, including fishing and other legitimate uses of the sea, impairment of quality or use of seawater, and reduction of amenities.

In a sense, the CO₂ disposal option reduces pollution in one sector of the environment while increasing pollution in another. To purely consider marine pollution regulations and ignore air pollution regimes seems incomplete. Yet while there are signs that international environmental regimes are moving toward multi-sector, all encompassing approaches to the environment, we

must currently consider CO₂ disposal in the context of marine pollution regulations (though these trends toward multi-media approaches will be discussed in Chapter 2). First, the relevant international treaties and regimes will be discussed followed by governing national laws and regulations using the U.S. as a focus.

1.2 International marine pollution control regimes

While CO₂ disposal would most likely be undertaken by an individual state if the strategy is to be used at all, international marine pollution regulations that may apply to CO₂ disposal are of primary importance for several reasons. On a fundamental level, the international environmental conferences, starting with the UN Conference on the Law of the Sea in 1958 have successfully encouraged the development of national legislation along the same general lines of the international agreements. Also, in many cases, international agreements themselves serve as the governing laws within national boundaries where no further specific national regulations exist. And the international agreements are the only governing rules for dealing with the high seas beyond national boundaries and for cases where activities from one state impact the interests of another state, both cases being relevant to some CO₂ disposal scenarios mentioned earlier. Finally, the approval or disapproval of the international community of any state's action might potentially affect that state in terms of international standing or reputation if a country were to violate the spirit of international guidelines or agreements.

1.2.1 The Law of the Sea

The agreement that first set the tone for addressing problems concerning the marine environment is the Law of the Sea. Begun in 1958 as a Conference of the United Nations, the first major area of concern was protection of the ocean floor and seabed in international water from nations seeking to extend their explorations as far as was economically feasible. A series of oil-spill disasters in the late 1960s and early 1970s provided impetus for the conference to meet again in 1972, where the concept of the 'heritage of mankind' was developed, implying that these waters and resources existed for the benefit of all states, and should thus be protected from exploitation by individual states. Negotiations eventually led to a treaty which was opened for signature in 1982, and was finally ratified in 1994 with the signature of the U.S. Over these years, the conference has developed in one sense as a general framework intended to guide regional and national laws, containing the principles and concepts of protection of the marine environment, while in some instances, it contains fairly specific and

enforceable provisions with respect to certain aspects of protection of the marine environment (it should be noted that the environmental issues make up only one part of the concern of the Law of the Sea).

The relevant sections of the Law of the Sea to ocean disposal are found in part XII, "Protection and Preservation of the Marine Environment." The two opening articles indicate from the outset a fundamental concept in international environmental conventions, namely, that while states are obligated to protect the environment as best they can, they retain the sovereign right to exploit their own resources as they see fit. Article 192 opens part XII stating, "states have the obligation to protect and preserve the marine environment," while article 193 follows with, "states have the sovereign right to exploit their natural resources pursuant to their environmental policies and in accordance with their duty to protect and preserve the marine environment." The obligation to protect as limited by sovereignty to exploit is a theme that reappears in many international conferences and often weakens their forcefulness.

Not surprisingly then, the international conferences are more obligatory and forceful when dealing with marine activity that impacts neutral territory or the interests of other states as opposed to activity within a state's exclusive economic zone, which extends 200 miles from the coast. As is stated in article 194 subpart 2,

States shall take all measures necessary to ensure that activities under their jurisdiction or control are so conducted as not to cause damage by pollution to other States and their environment, and that pollution arising from incidents or activities under their jurisdiction or control does not spread beyond the areas where they exercise sovereign rights in accordance with the Convention.

In the case of CO₂ disposal, however, as will be discussed later, it is not abundantly clear where to consider the boundary of influence of some of the disposal scenarios.

Article 194 is perhaps the most specific section in part XII, spelling out these obligations of states to protect the marine environment.

1. States shall take, individually or jointly as appropriate, all measures consistent with the Convention that are necessary to prevent, reduce and control pollution of the marine environment from any source, using for this purpose the *best practicable means at their disposal and in accordance with their capabilities* [emphasis added]...The measures taken pursuant to this part shall deal with all sources of pollution of the marine environment.
2. (quoted above)
3. ...These measures shall include, *inter alia*, those designed to minimize to the fullest possible extent:
 - a. the release of toxic, harmful or noxious substances, especially those which are persistent, from land-based sources, from or through the atmosphere, or by dumping;
 - b. pollution from vessels, in particular measures for preventing accidents and dealing with emergencies...preventing intentional and unintentional discharges....

c. pollution from installations and devices operating in the marine environment...

4. In taking measures to prevent, reduce or control pollution of the marine environment, States shall refrain from unjustifiable interference with activities carried out by other states in the exercise of their rights and in pursuance of their duties in conforming with the Convention. The measures taken in accordance with the Part shall include those necessary to protect and preserve rare or fragile ecosystems as well as the habitat of depleted, threatened or endangered species and other forms of marine life.

A few important concepts that arise from Article 194 are reinforced in other regulations as well. While we saw previously that the obligation not to cause damage when the pollution crosses sovereign boundaries into international waters or territories of other states was worded as "to take all necessary measures to ensure," when the pollution is within a state's jurisdiction the obligation in part 1 above is that states use, "best practicable means at their disposal." The latter is considerably weaker. Notice also that all forms of pollution, whether they be land-based, atmospheric in origin, etc. are mentioned in this clause without separate obligation. In later articles, distinctions will be made between forms of pollution with some more strongly discouraged than others. And finally, the mention of special protection required for fragile ecosystems and endangered species appearing in 194 part 4 is theme that is echoed in many national regulations.

Article 195 is an interesting clause, perhaps written to close potential loopholes, concerning the transformation of pollution. "In taking measures to prevent, reduce, and control pollution of the marine environment, States shall act so as not to transfer, directly or indirectly, damage or hazards from one area to another or transform one type of pollution into another." It appears that this clause, which subsequently appears in many regional and national regulations, refers not to physiochemical transformations of the pollutant but more to the type or location of the pollution. Speaking on article 195, Timagenis (1981) claims, "This rule gives specific expression to one aspect of the general obligation to protect the marine environment, and expands the rule of traditional law under which a State may not use or allow the use of its territory, including territorial sea, in a manner which may cause damage, including pollution, to third States" (p.37).

The next relevant section is Section 4 which ensures that, while states may act as they wish in their own areas, they have an obligation at least to monitor potential adverse impacts and inform the international community.

States shall, consistent with the rights of other states, endeavor, as far as practicable, directly or through the competent international organizations, to observe, measure, evaluate and analyze, by recognized scientific methods, the risks or effects of pollution of the marine environment. In particular, States shall keep under surveillance the effects of any activities which they permit or in which they engage in order to determine whether these activities are likely to pollute the marine environment.

Following this, many articles follow which define the separate forms of pollution along the above mentioned divisions, pollution from land-based sources, through the atmosphere, by vessels, by dumping, and through sea-bed activities. Articles appear for each form of pollution, declaring first and foremost that states establish national laws to prevent, reduce, and control pollution from the given source and enforce such laws. In these articles, the important distinction between land-based sources and ship-based sources of pollution appears. As Alan Boyle comments,

This basic unwillingness to accept a more demanding regulatory system is reflected in the provisions of the Law of the Sea Convention dealing with land-based and atmospheric sources of pollution. In contrast to the articles on dumping and pollution from ships, which require States to apply international standards contained in global treaties such as the London Dumping Convention, Articles 207 and 212 [which refer to land-based and atmospheric sources] refer only to the need to 'take account of international standards'. This is a significantly weaker and more uncertain standard of obligation...(Boyle, 1992, p.80).

In general, much of the force of the Law of the Sea lies in its call to states to establish their own laws or to appeal to existing ones. As is noted above, the call to heed regulations concerned with dumping from ships is stronger than the appeal to follow pollution regimes from other sources. Probably the most important and most restrictive regulation framework governing dumping from ships, is the international *Convention on the Prevention of Marine Pollution by Dumping of Wastes and other Matter*, commonly known as The London Dumping Convention (LDC).

1.2.2 The London Dumping Convention

This Conference met in 1972, again propelled in part by large scale disasters at the time and increasing awareness of man's impact on the marine environment. The convention has been more successful in terms of an easy ratification than the Law of the Sea mainly because its scope is limited to dumping of pollution from vessels which is easier to regulate than land based disposal and a clear concern of all states since wastes intended for dumping have greater potential for transboundary impact than land based pollution. So, while the convention is very strong, the dissolution scenarios of CO₂ ocean disposal would most likely not be under its jurisdiction. The definition of ocean dumping, as given in Article III of the convention states, "Dumping means: i) any deliberate disposal at sea of wastes or other matter from vessels, aircraft, platforms or other man-made structures at sea. ii) any deliberate disposal at sea of vessels, aircraft, platforms of other man-made structures at sea" (Timagenis, 1981, p.198).

The reason for the distinction between land-based and vessel-based pollution, which may effectively be indistinguishable but for the technical means of disposal is explained by Alan Boyle,

...in regard to this form of pollution [land-based], States did not wish to commit themselves to the same level of strong international control imposed on pollution from ships. The social and economic costs of such measures were seen as unacceptably high. The preferred solution was thus a weaker level of regulation, a resort to regional rather than global cooperation...(Boyle p.26).

Timagenis further explains the distinction,

Dumping differs from pollution caused directly from the land. Pollution from the land affects primarily the marine environment of the States concerned. Third States and the international community as a whole can only be affected indirectly where, under certain circumstances, pollution is liable to be transferred to other areas of the sea. On the contrary the pollutants dumped in the sea are introduced primarily in international waters. Dumping, therefore, is the object of a stronger international concern. Further, pollution from the land is well within the sovereignty of each particular State, national controls can be effectively used and international interference in this area is firmly defended against. Dumping, in contrast, is carried out from ships....which, as movable things, can be found in areas of the sea under the national jurisdiction of any State (Timagenis, p.118).

Thus, it appears that London Dumping conventions would be concerned only with the dry ice, towed pipe, and the CO₂ lake scenarios. Yet it is worthwhile to cover the convention in detail because the framework established for pollution control in the LDC is the same as in many of the subsequent regional and national agreements that do cover land-based pollution.

First of all, unlike the Law of the Sea, the LDC does *not* make the distinction between control of activities in territorial vs. international waters except in enforcement. It is generally assumed that ships will be more in danger of discharging into international waters than land-based sources, which interestingly, in the case of CO₂ disposal, is exactly the opposite of the truth given the discharge scenarios discussed.

The primary means of control, extended to all seas, are based on the seriousness of the pollutant involved, which are grouped into three classes called annexes. Annex I is a list of extremely dangerous substances which are completely prohibited from being dumped at sea except in trace amounts that would be "rapidly rendered harmless by physical, chemical or biological processes in the sea." These materials include organohalogen compounds, mercury, cadmium, oil, plastics, high-level radioactive wastes, and materials of chemical warfare.

Materials in Annex II are called the grey list, and require a special permit to be granted by the State in order for a party to dump these materials. Annex II includes wastes containing significant amounts of arsenic, lead, copper, zinc, cyanides, fluorides, beryllium, chromium, nickel, vanadium, other radioactive wastes not included in annex I, and large quantities of

acids or alkalis containing any of the above metals. Annex III includes all other matter or wastes, which require only a general permit in order to dump legally. This annex structure of classifying materials, and prohibiting some while requiring permits for others has been utilized in many regional and national regulations on dumping and discharge, often with the same grouping of substances.

CO₂ would most likely fall under annex III, as is assumed by Martin Angel (IEA , 1994), though one could argue that discharging CO₂ would have a similar impact as the dumping of a strong acid. The difference between the two is only in the type of permit required; the special permit for annex II materials require a separate application upon every instance of dumping, while the general permit for annex III materials only requires a one-time application and less stringent records concerning amount of materials dumped, impact monitoring, etc. In either case, a state wishing to dump CO₂ via the dry ice or CO₂ lake scenario would have to apply to the appropriate national authority for the issuance of a permit.

The LDC lays out many guidelines and criteria to be considered in the issuing of permits. Those that might apply to CO₂ disposal are paraphrased as follows:

A. Characteristics and composition of the matter

This section includes consideration of amounts and state of material, possible reactions and transformations, toxicity, persistence, and accumulation.

B. Characteristics of dump site and dumping method

Includes dumpsite, and proximity to other important areas such as spawning areas and areas containing other exploitable resources. Also includes physical characterization of dilution, dispersion, water characteristics, and other dumping which has gone on in the past in the location. Also mentioned is a note about monitoring, specifically, "In issuing a permit for dumping, Contracting Parties should consider whether an adequate scientific basis exists for assessing the consequences of such dumping, as outlined in the Annex, taking into account seasonal variations."

C. General consideration sand conditions

Includes possible effects on amenities, on marine life - especially commercially important life, on other uses of the sea such as fishing, observation, and conservation of special habitats. Also to be considered are practical availability of alternative land-based methods of treatment or disposal, or treatment to render the matter less harmful for dumping at sea.

The above considerations are all left to the discretion of the permitting state - no concrete requirements are given here. Thus, in a highly permissive permitting structure, the above might be interpreted as rather loose requirements, while a stricter regime may find the language more prohibitive.

A final interesting and possibly relevant aspect to the London Dumping Convention that is included in many regional and national treaties as well is the 'exceptions' section. In particular,

The provisions of Article IV shall not apply when it is necessary to secure of human life or of vessels...in cases of *force majeure* caused by stress of weather, or in any case which constitutes a danger to human life..., if dumping appears to be the only way of averting the threat and if there is every probability that the damage consequent upon such dumping will be less than would otherwise occur. Such dumping shall be so conducted as to minimize the likelihood of damage to human or marine life and shall be reported forthwith to the Organization.

This clause was most likely written in anticipation of potential storms or emergency leaks or contamination that could lead to endangerment of human life. Nevertheless, Timagenis believes, "it may provide a dangerous loophole to the whole control system, particularly in view of the fact that is not absolutely clear whether the substances ultimately dumped must have been loaded on board the ship when the events justifying the exception occurred, or the exception may equally apply when the substances are still on land." It is unlikely, though that this clause may be used to justify emergency CO₂ disposal under times of severe weather aberrations induced by the greenhouse effect because in this case, dumping would not be the only way to avert the threat, and that the immediate disposal of CO₂ would not improve the immediate emergency situation anyway.

1.2.3 Regional Agreements

The general concepts of annexes and permits found in the London Dumping Convention are echoed in many regional treaties that do attempt to regulate land-based pollution as well as vessel-based discharges. Some of the most relevant treaties are the 1974 Paris Convention covering the North-East Atlantic and the North Sea, the 1974 Helsinki Convention Covering the Baltic region, and the 1980 Athens Convention concerned with pollution in the Mediterranean. These conventions are all in force, and are quite effective, perhaps because of the smaller number of states involved (those bordering the waters in question) and the mutual self interest. Effective agreements such as these exist mainly only in Europe and in the South East Pacific where many nations border a body of water in relatively close proximity.

The Paris and Helsinki conventions, typical of the regional agreements, call for the eventual phase-out of discharges of all substances in the Annex I and II categories. With respect to annex III substances, the Helsinki Convention "sets out goals and criteria for minimizing pollution from municipal sewage, industrial waste, and waste water, including cooling water" (Boyle, 1992, p. 82). The goals of these conventions are generally quite restrictive, and would likely make CO₂ disposal much more difficult to obtain permits for in areas under the jurisdiction of these regional conventions than in areas outside of these regions.

1.3 National regimes - the U.S.

The existing regulatory structure in the U.S. will be analyzed as an example of a national regime that happens to be most relevant to the authors of this report. There will be considerable variation among nations, but many essential elements of the regulations will be the same.

Most relevant US legislation dealing with ocean dumping and discharges is found in the federal regulations under the jurisdiction of the Environmental Protection Agency mainly from the Clean Water Act (CWA) and the Marine Protection, Research and Sanctuaries Act (MPRSA). Among other acts that may be relevant are the Marine Mammal Protection Act (MMPA) and the Resource Conservation and Recovery Act (RCRA). RCRA is discussed briefly in relation to the transport and implementation of CO₂ disposal (i.e. pipe laying) in Topical Report 2. The MMPA is very protective of marine mammals some of which do venture to depths of 1000 m at times, but serious adverse impacts from CO₂ disposal are unlikely.

Yet, of first consideration should be perhaps the over-arching National Environmental Policy Act (NEPA). This Act, passed by Congress in 1970 was intended to ensure that any private or government sponsored project or action take into account and assess the potential environmental impact of the project. A detailed statement is required which must report on 1) the environmental impact of the proposed action, 2) any adverse environmental effects which cannot be avoided should the proposal be implemented, 3) alternatives to the proposed action, 4) the relationship between local, short-term uses of mans environment and maintenance and enhancement of long-term productivity, and 5) an irreversible and irretrievable commitments of resources which would be involved in the proposed action should it be implemented [U.S. Code, Title 102, pt. 2c]

Many of these assessment requirements appear in the EPA regulations as well, but it is important to list them here because many projects in the past have been held up via litigation because the environmental impact assessments were deemed inadequate with respect to this Act (Andersen, 1988). NEPA also specifies requirements for publishing the proposed act in the Federal Register whereby the public may comment and request special hearings. All comments must be responded to in the Environmental Impact Statement as required by NEPA, a process which can take many months in some instances.

Much of the force of the NEPA and many of the regulations of the EPA exist to ensure that complete and proper standards are used in estimating the environmental impact of the

proposed action. If we may now assume that a suitable environmental impact assessment of CO₂ disposal were able to be made, the potential impacts that would be assessed in such a statement (Topical Report 5 being essentially a preliminary statement of this sort) must now be considered with regard to the EPA regulations in the MPRSA and in the CWA as are found in the Code of Federal Regulations (CFR) sections 125 and 227 respectively. These would most likely be the binding laws in the U.S. by which CO₂ disposal would be evaluated, even if the U.S. Government itself were sponsoring and funding the action.

As in the international conventions, in the U.S. a distinction is made between dumping from vessels and discharge from land-based sources. The MPRSA covers the dumping regulations while the CWA contains regulations for ocean discharge. Thus, the CO₂ lake and dry ice scenario should be considered under the dumping regulations while the plume scenarios should be considered under the discharge regulations, which are somewhat less restrictive.

Before analyzing the regulations in detail, it is important to note that the US regulatory structure presented below is generally designed for smaller scale operations than CO₂ ocean disposal. There is some question whether the specific provisions outlined below would even apply to such a massive undertaking as CO₂ disposal or whether this policy would be evaluated separately under special circumstances. In the case that the regulations do apply, they will be considered below.

1.3.1 National Ocean Dumping Regulations

The regulatory structure concerning ocean dumping in the US is similar to that of the London Dumping Convention. Certain highly toxic materials are prohibited from being dumped outright, and all other materials are subject to the process of applications for permits which are reviewed by the appropriate regional administrator of the EPA. Also, as in the LDC, distinctions are made between types of permits; general permits are issued indefinitely for a given substance and location, while special permits expire after three years. Provisions are also made for emergency permits under the conditions noted above where emergency danger to human health exists. In a permit application, the party proposing the dumping must include information, as above in the LDC discussion, on the material, physical characteristics before and after dumping, the amounts, alternatives to dumping, and a thorough investigation of the environmental impacts. Notice of requests for general permits are published in the Federal Register while special permits are published in city and state newspapers near the area of the dumping in order that any interested parties may comment. Hearings are held at which

these parties may present objections, and at which the final decisions on the granting of permits are made.

The criteria for issuing permits are many and again involve many of the concepts encountered in the international marine pollution laws. Prohibited are essentially the same list of materials mentioned above in Annex I of the LDC, in addition to materials which would float, persist, or otherwise interfere with other legitimate uses of the sea such as fishing, navigation, etc. and materials which have unknown or insufficiently described impacts on the marine environment. The most general criterion for wastes not included in any special category is one based on the toxicity of the material and the dilution rate. "No wastes will be deemed acceptable for ocean dumping unless such wastes can be dumped so as not to exceed the limiting permissible concentration (LPC) as defined in 227.27" (where the LPC is defined as the maximum allowable concentration at a distance of 4 hours travel time from the discharge point e.g. 720 m in a 5 cm/s current).

This maximum allowable concentration is generally defined as one one-hundredth of the 96 hour LC₅₀ concentration for that substance although the rule is not without exception. If there are established water quality criteria for the substance, then as long as the concentration of material at the mixing zone boundary does not exceed that established value dumping is allowed. Further, in cases where "there is reasonable scientific evidence to justify use of an application factor other than 0.01...such alternative application factor may be used in calculating the LPC" (Section 227.27, a3). Rose *et al.* (1977) argues that there is indeed reasonable scientific evidence to use a factor other than 0.01 for acidic wastes because one one-hundredth of the LC₅₀ concentration for H⁺ toxicity would be a pH of greater than 8, which is far beyond the level of no harm. Still, his own criteria would allow for only a small pH change such as a few tenths of a unit at the mixing zone boundary.

There is another section of 227 which deals specially with acidic and alkaline materials that could also be relevant to CO₂:

In the dumping of wastes of highly acidic or alkaline nature into the ocean, consideration shall be given to: 1) the effects of any change in acidity or alkalinity of the water at the disposal site; and 2) the potential for synergistic effects of the formation of toxic compounds at or near the disposal site. Allowance may be made in the permit conditions for the capability of ocean waters to neutralize acid or alkaline wastes; provided, however, that dumping conditions must be such that the average total alkalinity or total acidity of the ocean water after allowance for initial mixing, as defined in 227.29, may be changed, based on stoichiometric calculations, by no more than 10 percent during all dumping operations at a site to neutralize acid or alkaline wastes [227.8].

What this means is that at a distance of about four hours travel time via the current from the release point, the acidity of the ambient ocean waters must be within about 10% of the natural value. The other criterion that applies involves the toxic affects of the materials released.

There are other factors to be considered before the issuing of a permit that may be especially relevant to the CO₂ lake scenario. Throughout the section on ocean dumping, it is stressed that to be avoided are persistent materials, materials that may result in long-term damage to the marine environment, and materials that may cause irreversible damage. For example, in the overall criteria for evaluating environmental impact, section 227.4, a permit for disposal will be issued as long as the disposal will present, "No unacceptable adverse effects on the marine ecosystem; No unacceptable adverse persistent or permanent effects due to the dumping of the particular volumes or concentrations of these materials..." The term, 'unacceptable' could allow for some interpretation to this clause, but later in 227.9, it is stated that "Substances which may damage the ocean environmental due to the quantities in which they are dumped...may be dumped only when the quantities to be dumped at a single time and place are controlled to prevent long-term damage to the environment or to amenities."

Finally, there is a great deal of emphasis on consideration of alternatives to dumping and on the potential for pretreatment of the material to be dumped before the issuance of a permit. It is not clear whether these considerations would be applicable to CO₂ disposal. There are certainly alternative strategies of reducing CO₂ emissions to the atmosphere (see Chapter 3) but these alternatives are generally so different in nature to ocean disposal that comparisons between alternatives given uncertainties present in climate change science are not very enlightening at this time. Comparisons with alternatives in a more specific sense, i.e. alternatives to ocean discharge once the CO₂ is collected, are also lacking as there do not exist other feasible disposal sites except for perhaps a small capacity in aquifers. The possibility of neutralization of the CO₂ with a base, for example is probably cost prohibitive, but may be a possibility requiring further study.

The 'dissolution' scenarios may be considered alternatives to CO₂ dumping scenarios in some respects. They serve as a different means to essentially the same end, but the difference in means is significant enough that a different set of regulations governs (though there is some overlap) and will now be analyzed.

1.3.2 National Ocean Discharge Regulations

The regulatory structure governing land-based ocean discharges as detailed in the CWA or section 125 of the CFR is somewhat different from the ocean dumping regulatory structure and does not follow the LDC guidelines of grouping materials into annexes. The

basic regulatory structure is the following: A party wishing to discharge materials to the ocean must show that the discharge would not result in *unreasonable degradation* to the marine environment. If the EPA administrator decides that unreasonable degradation will occur, no permit is issued. If it is determined that unreasonable degradation will not occur, a permit may be issued, "under conditions necessary to ensure that unreasonable degradation will not occur during the term of the permit." (USEPA, 1994, p.2). If it is determined that there is insufficient information to determine whether unreasonable degradation will occur, no discharge will be allowed unless the director can determine that:

- No irreparable harm will result from the discharge;
- There are no reasonable alternatives to the discharge; and
- The discharge will comply with certain permit conditions, including bioassay-based discharge limitations and monitoring requirements.

While much discretion is given to the administrator in the determination of unreasonable degradation and irreparable harm, fairly detailed guidelines are given to assist in these determinations, which will now be discussed.

The CFR, in section 125 gives seven guidelines to aid in evaluation of unreasonable degradation which are expanded as ten guidelines in the CWA. The general overriding statement governing unreasonable degradation is given in the section 403 regulations (USEPA, 1994).

[Unreasonable degradation is] significant adverse changes in ecosystem diversity, productivity and stability of the biological community within the area of discharge and surrounding biological communities, threat to human health through direct exposure to pollutants or through consumption of exposed aquatic organisms, or loss of aesthetic, recreational, scientific or economic values which is unreasonable in relation to the benefit derived from the discharge.

While the droplet and dense plume discharge scenarios would unlikely have an impact on human health, the biological community within the area of discharge may well be determined to suffer adverse changes. As this is uncertain, it would be instructive to examine the 10 guidelines used to assist in no unreasonable degradation determinations.

1) *Quantities, composition, and potential bioaccumulation or persistence of pollutants to be discharged...* In areas that do not contain sensitive species or unusual biological communities or are not important for surrounding biological communities, discharges containing primarily conventional pollutants may be of lesser concern if data indicate that there will be significant mixing with the receiving waters based on the flow of the discharge and the physical characteristics of the discharge site, such as water depth, density gradient, and turbulence.

It appears that CO₂ would not be considered a persistent or biocumulative substance based on its rapid conversion to the already abundant carbonates in seawater. The elaboration of this statement could potentially apply to CO₂ discharges, as the conditions of the statement seem to be met given our present knowledge, and thus CO₂ discharges may be deemed of little concern.

Guidelines 2, 3, and 4 maintain that detailed study and monitoring be done to assess the fate and transport of the pollutant, the potential for loss of species in the discharge area, particularly endangered species or those critical to the food chain, and the importance of the receiving area to regional ecosystems and communities, e.g. critical spawning areas, migratory pathways, etc. These conditions seem of somewhat minor relevance to CO₂ disposal as discharges would likely occur deep in the ocean, away from the coast, and in relatively featureless, homogenous areas.

Guidelines 5, 6, 7 and 9 refer to impacts on human health, marine sanctuaries and special areas, on recreational and commercial fishing, and on other uses of the ocean. These restrictions could likely be avoided by prudent CO₂ disposal but are certainly important to note as possible danger areas that must be avoided.

Guidelines 8 and 10 note that the party should be wary of specific state regulations concerning Coastal Zone Management or water quality criteria. While state regulations may be too specific to be discussed in the scope of this study, these regulations may include standards for pH which would likely mirror the often quoted EPA standard that pH should not persist below 6.5 (Knutzen, 1981).

The general criteria presented above for discharge and dumping are refined even further in the 1985 EPA Technical Support Document for Water Quality-Based Toxics Control (USEPA, 1985). These guidelines are meant as a non-binding aid to assessing toxicity or impact of a certain discharge. One focus of the guidelines is to define acute and chronic concentrations based on experimental assays (LC₅₀ values, etc.) that should not be exceeded for given periods of time. Another focus of the guidelines is in aid to modeling exposure and collecting toxicity data in the performance of an assessment of the type already done in this report. The defined concentration limits in these guidelines are generally very strict - set at levels to essentially ensure little or no mortality from the discharge. Yet it should again be stressed that the US regulatory structure above is generally designed for smaller scale operations than CO₂ ocean disposal, and there is some question whether the specific provisions outlined above would even apply to such a large-scale policy or whether the policy would be evaluated separately under special circumstances.

Chapter 2. Implications and Trends

"In dealing with any problem that is not amenable to simple or short-term solutions, such as environmental protection, well conceived strategies are indispensable. Nevertheless, to be effective, environmental strategies must be fitted to the scale and complexity of the problem, familiar to all sectors of society and firmly supported by political commitment.....The core of the problem is that rules and regulations for environmental protection, aimed at different environmental sectors and practices, are often developed in isolation from one another. This adds to the difficulty of choosing appropriate levels of control, increases the likelihood of imbalances between regulated sectors and practices and, in some instances, may benefit one sector of practice at the expense of another."

-R. G. V. Boelens, 1992

2.1 Introduction

The implications of the legal structures as described in Chapter 1 will now be further discussed in regard to CO₂ disposal. The dumping and discharge scenarios will be discussed separately as they are clearly treated differently under the national and international laws. The towed pipe scenario will be treated as a dumping scenario and would presumably be treated similarly to the dry ice scenario in the below discussions.

2.2 CO₂ lake and dry ice scenarios

Although it may seem like an arbitrary distinction because the same quantity of CO₂ is released in each scenario, these scenarios involve transport of the material by ship, and thus fall under the U.S. dumping regulations and the jurisdiction of the London Dumping Convention and the Law of the Sea. These regulations are generally stricter than the land-based discharge regulations, and might prove prohibitive.

2.2.1 U.S. Dumping laws

Whether CO₂ would be considered in Annex II or Annex III, a permit would be required before dumping would be allowed, so we must pay attention to the guidelines given for consideration in the granting of permits. It seems that the most relevant clause is that governing acidic discharges which was quoted at length in the previous chapter. The two conditions given are that at the boundary of the mixing zone, the pH can not be increased or depressed from its natural value by 10% and that the concentration can not be more than a

hundredth of the LC_{50} value. The definition of the boundary of the mixing zone is given in section 227.29 of the CFR as being about a four hours travel time (in an average current) from the discharge, which can be approximated as about 700 m distance from the release point if we use a 5 cm/s current.

These conditions are very strict and would not allow for a pH decrease of much more than a tenth of a unit. Rose and Williams' more liberal interpretation of the law for acidic materials would still only allow a deviation of a few tenths of a pH unit from ambient. (Rose and Williams, 1977). Even with the benign dry ice release scenario, the pH would deviate by more than a tenth of a unit 700 m away from the center of the vertical plume. Thus, if the letter of the law were followed, CO_2 disposal would probably be prohibited by almost any method of dumping. However, there are indications that the letter of the law might not be relevant to CO_2 dumping scenarios.

It has been mentioned earlier that the entire regulatory may not be relevant for a special large-scale case such as CO_2 disposal. Still, even in the dumping regulations themselves, there is a clause which might allow for a more scientifically based criteria than those given above. Part 2c of Section 227.9 states that

When there is reasonable scientific evidence to demonstrate that other methods of estimating a reasonable allowance for initial mixing are appropriate for a specific material, such methods may be used with the concurrence of EPA after appropriate scientific review.

Such methods may include the modeling efforts presented in this report and might establish the dry ice and towed pipe scenarios as safe with the CO_2 lake scenario as questionable.

Evidence supporting the fact that difficulties might be encountered with the CO_2 lake scenario and not with the dry ice scenario is found in sections 227.4 and 227.9. These sections state that permits may not be granted in the case of "unacceptable adverse or permanent effects." Section 227.9 states that substances only may be dumped when the dumping can be controlled so that there is no "long-term damage to the environment or amenities." The CO_2 lake indeed would result in permanent effects and long-term damage, even if these effects are deemed of minor importance, while the dry ice scenario would not.

2.2.2 International laws

The regulations in the London Dumping Convention could add some additional complications to attempts to dump CO_2 via the dry ice or CO_2 lake methods. They are especially important because these regulations would preside in any country that is party to the convention and does not have stricter national regulations on dumping. First, the clause on

the importance of monitoring adequacy could be a potential sticking point for either scenario in light of the difficulty of monitoring zooplankton losses as is discussed previously and in Chapter 3 of this report. Nevertheless, as the dry ice scenario appears to be free from potential harm, it would probably not be held to as strict monitoring requirements of a scenario with greater potential for harm.

The CO₂ lake scenario, on the other hand, would inevitably result in some degree of permanent damage to the ocean floor. This damage would unlikely affect 'other legitimate uses of the sea', but still is an 'adverse affect on marine life' which is something that must be considered in permitting decisions. This could be a holdup in permit requests in some instances, depending on the interpretation of the law by the state in question. It is also possible that the clause requiring consideration of 'treatments rendering the matter less harmful' would at least stir some debate over whether such treatments were feasible, e.g. neutralizing the CO₂ with an alkaline substance before dumping.

The provisions for enforcement are quite complicated, as distinctions must often be made between the state owning the vessel, the state where the vessel loads material to be dumped, and the state having jurisdiction over the area where the vessel wishes to dump. The enforcement provisions may be summarized as follows:

- State *x* may prohibit state *y* from dumping in *x*'s waters
- *X* may prohibit *y* from loading illegal materials off of *x*'s coast and dumping elsewhere
- *X* may prohibit *x*-flagged ships from dumping elsewhere
- But state *x* may *not* prevent state *y* from dumping in *y*'s own waters
- State *x*'s right to prohibit state *y* from dumping in the high seas is under dispute and unclear from the provisions (Timagenis, 1981, p.234)

These complex jurisdictional issues may result in interesting interactions or arrangements among states wishing to dispose of CO₂.

The Law of the Sea mandates that states take necessary measures to prevent, control and reduce pollution by dumping, but adds no further specific requirements that are more strict than the LDC and national laws on dumping, especially when the dumping is within a state's 200 mile limit. With the CO₂ lake and dry ice scenarios, this would almost certainly be the case.

Thus, it is likely that in the case of the dry ice and CO₂ lake scenarios, the most important factors determining whether such disposal would be allowable would be the seriousness of environmental impact, and it appears that the dry ice dumping might be deemed

allowable, while the CO₂ lake disposal would face many serious obstacles. Additionally, these scenarios are perhaps less likely to be favored than the droplet and dense plume scenarios for economic and other implementation feasibility reasons.

2.3 Dense and droplet plume scenarios

2.3.1 U.S. Regulations

The guidelines set forth in the ocean discharge regulations (section 125 of the CFR) are meant to assist in determination of whether unreasonable degradation of the marine environment would occur as a result of the discharge. If this can not be determined, the regulatory system has in place a temporary permit option. Most of these guidelines are in place to protect economic resources, sensitive ecosystems, etc. and would likely not be an issue with the plume disposal scenarios. However, the general statement requiring "no significant adverse changes in the....stability of the biological community" is somewhat vague, but given the assessment in Topical Report 5, one might determine that the predictions of zooplankton losses represent significant adverse changes. Still, given the many unknowns about the roles and sensitivities of deep ocean communities, it is very possible that an administrator would find that the determination of unreasonable degradation is impossible to make and would hence appeal to the insufficient information option.

In this case, a temporary permit may be issued (under strict monitoring requirements) *if* it were decided that no "significant undesirable effects occurring after the date of permit issuance which will not be reversed after cessation of modification of the discharge." Essentially, the discharge is allowed under a temporary basis, while monitoring is used to determine whether unreasonable degradation seems to be occurring - and this temporary situation is acceptable only if all parties are certain that no permanent damage will occur during this monitoring period. The important consideration here is the certainty that if during the trial period, if it was found that severe degradation was occurring, the discharge could be halted with no permanent damage. These decisions are again very vague and political, but there are guidelines to aid in decision making.

In the determination of no irreparable harm, discharges are classified into their potential to cause low, moderate, or high environmental damage. By the criteria given, the dissolution CO₂ discharge scenarios would most likely fall into the 'moderate potential threat' category (USEPA, 1994). The assignment of categories serves primarily to determine the level of monitoring required. In the moderate category, monitoring requirements are quite significant, including physical transport and tracer experiments to aid in plume modeling,

water quality chemistry measurements near and far field, and many biological survey studies, benthic and pelagic, to assess potential impact. It should be stressed that once a discharge is allowed, the assessment of impact and level of monitoring required is an iterative and dynamic process, as new information is gathered and interpreted. Permits may be revoked at any time by the administrator based on new monitoring information.

In summary, it is very difficult to determine at this time whether a dense-plume or droplet-plume discharge would be allowable under US regulations. Probably the dense plume would face larger barriers and stricter monitoring requirements as the ocean floor might be deemed a unique or sensitive biological area that should not be harmfully disrupted, as regions likely would be under the dense plume discharge. Still, given the uncertainty involved in environmental impact assessments for CO₂ effects, as this material has never before been discharged into the ocean in such quantities at such depths, there is a good chance that the determination of insufficient information would be made and that permitting might proceed cautiously under strict monitoring. Partly in anticipation of such a situation, discussions are currently underway on the possibility of a pilot-scale CO₂ ocean disposal experiment.

Analysis of the Law of the Sea regulations and recent trends in ocean discharge will further shed light on the prospects for implementation of these scenarios.

2.3.2 The Law of the Sea

Because the Law of the Sea Treaty is somewhat vague in its obligations, deferring specifics to the national and regional laws and other conventions dealing with the various aspects of marine pollution, it is a matter open to much interpretation whether the spirit of the Law of the Sea would be violated with CO₂ disposal. The general call to reduce, control and prevent pollution by the best practicable means is vague enough that one could argue that CO₂ disposal violates this spirit in deliberately polluting the marine environment with materials known to cause harm (and that the disposal is obviously preventable). One could also argue, though perhaps less effectively, that CO₂ disposal is a measure to prevent pollution of the surface oceans via atmospheric CO₂ in the spirit of article 194, part 1a, and to merely move the hazardous substance to a region of the ocean where it would cause less harm, molecule for molecule.

However the politics of the above arguments may play out, there are a few solid conclusions we may arrive at in evaluating CO₂ disposal in light of the Law of the Sea Treaty. It is clear that whether the effects of the disposal are entirely contained within a state's economic zone is important because the Law of the Sea Treaty essentially defers to the state in this case except to say that such state must inform others of what it is doing. To determine

whether the impacts will extend beyond the 200 mile limit, one may use data from the plume modeling efforts where the distance from the plume discharge to the farthest point where the pH would likely be below 7.0 or 7.5 has been calculated.

Scenario	Distance to pH 7.0 (mi.)	Distance to pH 7.5 (mi.)
1 plant droplet plume	14	47
1 plant dense plume	37	330
10 plant droplet plume	57	190
10 plant dense plume	422	1400

Table 2.1 Distance from discharge point to pH 7.0 and 7.5.

If we assume that the discharge point would most likely be between 10 and 100 miles off shore, the above table would suggest several interesting possibilities. First of all, it is unclear whether pH would even be used as an indicator for the extent of the plume impact. But as pH is a common indicator of water quality and the parameter in which the environmental impacts above have been assessed, it is not a bad assumption. Using pH 7.5 would be quite conservative, as it is very unlikely that an organism at the edge of the 7.5 contour would actually experience a negative impact. If 7.5 were indeed used, the dense plumes and the 10 plant droplet plume would extend their impact beyond the 200 mi. limit. If the mortality deficits as in Figures 3.3 and 3.4 of Topical Report 5 are used instead, mortality is found beyond 200 mi. for the same three scenarios and not for the one plant droplet plume. On the other hand, if pH 7.0 is used as the criterion, then all scenarios would be within 200 miles except the 10 plant dense plume.

However the extent of the plume is eventually measured, the 200 mile limit could be a factor ultimately influencing the design and scope of the CO₂ release system as the law clearly makes a distinction between pollution of sovereign waters and neutral waters (see article 194 above). Furthermore, if the CO₂ were found to enter the jurisdiction of another State, that state is given latitude under the Law of the Sea to bring charges against the polluting state.

The sections mentioning that special care be given to ecologically sensitive areas, endangered or threatened species, and persistent pollution are sensible calls that are repeated in many of the regional and national pollution regulations. It appears that CO₂ disposal at depths nearing 1000 m offshore would not conflict with these requirements as these habitats generally have little influence on surface processes and as CO₂ is not at all persistent the ocean. In fact, the average lifetime of CO₂ in the atmosphere is on the order of 10 to 100 years vs. minutes in

the ocean before it is transformed into carbonates which are extremely abundant naturally occurring substances in the ocean.

In summary, The Law of the Sea Treaty is somewhat vague in obligation, and would unlikely prohibit CO₂ disposal, though perhaps it would provide public interest groups opposed to CO₂ disposal with some ammunition as a point of attack.

2.4 Trends and analogies

Before making final conclusions about the potential permissibility of the CO₂ disposal scenarios given the current regulatory framework, we can gain a great deal of insight and perspective on the question of the potential approval of CO₂ disposal through a brief analysis of other similar cases that have occurred in recent years and of the direction that we seem to be moving in as a nation and as a global community. Important cases to consider in the US are those concerning the disposal of acidic industrial wastes, sewage sludge, dredged material, and warm water discharges from coastal nuclear power plants, and important international issues are those concerning Ocean Thermal Energy Conversion (OTEC), ocean disposal of nuclear waste, and the Acoustic Thermometry of Ocean Climate (ATOC) experiment.

2.4.1 Ocean dumping in the NY Bight

One of the most significant dumping operations in the US until recently was in the regions off of the coast of New York known as the New York Bight, where many industries routinely dumped large quantities of acidic by products of their operations into the surface waters from moving barges. The operations involved massive quantities of acid; from one titanium dioxide plant, it was estimated that 400 million liters of liquid equivalent to 2-4 M HCl was dumped in 1978 (Simpson *et al.*, 1981). Yet it is highly unclear as to whether significant adverse impacts on the marine environment ever resulted from such dumping. Swanson *et al.* (1977), reviewed many studies and noted that some indicated harmful accumulations of metals in some species of benthic organisms and an overall reduced benthic diversity. In contrast, Vaccaro *et al.* (1972) reported no significant difference in abundance or diversity in benthic or pelagic areas between areas within the dumping grounds and control areas outside.

Still, these operations have since been halted as the US along with most nations of the world endeavors to end the dumping of industrial waste indefinitely. This halt of dumping is part of a trend toward increasing protection of the marine environment as mentioned above. As Alan Boyle notes,

In 1990, the parties to the LDC followed suit, resolving to phase out all dumping of industrial waste by 1995 and calling on the parties to prohibit export of wastes for dumping by non-parties. If effected, this decision will largely end dumping at sea, at last by the parties to the convention (Boyle, p.84).

This trend is also evident in the case of disposal of sewage sludge, which had long been an accepted practice of the US and many other nations. Nearly six million tons of sewage sludge were being dumped in the NY Bight per year in the late 1970s, and although the adverse impacts of the biomatter are significant but not drastic, the sludge is often contaminated with heavy metals, pesticides, and other harmful materials that can have serious impacts on the marine environment (Bishop, 1983). Despite ongoing debate about the severity of harm from the materials, all sewage sludge dumping operations in the US have been banned. Britain is scheduled to end sludge dumping by 1998.

2.4.2 Radioactive Waste

The issue of low-level radioactive waste presents another interesting case. These waste products from nuclear power plants or uranium mining present little harm to the marine environment, and have traditionally be dumped in the ocean in large quantities; between 1946 and 1970, nearly 100,000 drums of radioactive waste were dumped into the oceans around the United States (Bishop, 1983). In a summary report estimating the risk of past dumping operations relative to other sources of risk, it was estimated that nuclear waste dumping posed a risk more than three orders of magnitude less than those from nuclear weapons testing fallout, Chernobyl fallout and civil nuclear site discharges (Calmet and Bowers, 1991). Yet despite this relatively low level of risk and increasing certainty in these estimates, such nuclear waste dumping has been banned since 1983. All parties to the LDC agreed to a voluntary moratorium on nuclear waste dumping until further evaluation of environmental as well as social and economic impacts could be made - in line with the tenets of the precautionary principle (see below).

Similarly, substantial efforts were made in the early 1980s to begin a program of emplacing high-level nuclear materials in safe encasements and sinking them beneath the ocean seabed. This emplacement would have been reversible and was implementable within existing safety standards and regulations, and with extremely small risk (Kildow, 1981). Yet again, the proposed strategy was eventually abandoned by the USDOE for several reasons. The agency was worried about transportation standards and potential hazards in transporting the materials. Second, because of the nature of the project, it was not practical to perform an *in situ* test without actually undertaking the natural risks of the normal implementation. And

finally, with recent work showing greater diversity of life than had been thought in the benthic regions that might be affected by the strategy, the agency decided that to attempt to prove that there would be no harm to benthic life and to fight perceived opposition from environmentalists and the press, would be too costly to justify.

These examples may all portend difficulties for CO₂ dumping, but it must be kept in mind that dumping of pollution is not quite analogous to CO₂ disposal. Most of the marine pollution regulations and trends are concerned with waste products that are more or less inevitable results of industrial or human processes. These wastes must be disposed of or used in some way, whether on land, or in the ocean. But as there are generally reasonable alternative to ocean disposal, a ban on ocean disposal of these waste products does not jeopardize the entire process or function that produced the waste in the first place. This is not the case with CO₂ disposal. The disposal of CO₂ in the ocean is fundamental to the process; CO₂ capture is not currently taking place, creating huge vats of waste CO₂ that must be disposed of in some way or another. Thus, the impacts of CO₂ disposal on the marine environment may be looked at in a different light from traditional marine pollution.

2.4.3 Ocean Thermal Energy Conversion (OTEC)

There are other examples of technologies which, similarly to CO₂ ocean disposal, use the resource of the ocean in a strategic capacity to produce an overall societal benefit, though simultaneously causing local adverse impacts on marine life. One example is the concept of Ocean Thermal Energy Conversion, a strategy which 'farms' the temperature difference between the surface ocean and the deep ocean by circulating huge volumes of water from the surface to about 1000 m depth. Many studies have been performed to assess the potential negative impacts on marine life of such a strategy and the results are not trivial. One assessment of a given site estimated that nearly 60 kgC / d of macro-zooplankton biomass would be entrained at the 1000 m intake vent.

Although the impacts from CO₂ disposal would be spread over larger areas, if we use the same assumptions of organism density at this depth, our estimates of biomass loss of macrozooplankton range from about 10 to over 1000 kg C / d for the one plant droplet and 10 plant dense plume scenarios respectively. In addition to this impact, the OTEC strategy results in significant loss of productivity as hordes of phytoplankton and surface zooplankton are entrained into the surface vents. Yet, given these impacts, it appears that the OTEC concept was never seriously challenged on marine pollution grounds (Avery and Wu, 1994). In fact, several plants are in operation today as demonstration facilities, despite low rates of energy efficiency. Perhaps working in OTEC's favor was the fact that the enhanced recirculation of

water from deep to shallow carries nutrients to the surface waters that stimulate growth and would likely overcome any surface losses in productivity.

2.4.4 Acoustic Thermometry of Ocean Climate (ATOC)

Another example of a technological use of the ocean that has been challenged on environmental grounds recently is the concept of Acoustic Thermometry of Ocean Climate (ATOC). Developed at the Scripps Institute of Oceanography, the concept would plant devices designed to produce periodic sound blasts deep in the ocean to monitor gradual changes in ocean temperature by measuring travel times between blasts (Holing, 1994). The plan was apparently close to implementation when pressure from the Natural Resources Defense Council (NRDC) and other interest groups succeeded in delaying the project significantly until a more comprehensive Environmental Impact Statement was prepared. They argued that the sound levels would be damaging to marine mammals which were especially protected under the Marine Mammal Protection Act, and that extensive monitoring requirements were needed in the form of experiments with marine mammals and noise sensitivity.

While there is some credibility to this concern, it is also true that the noise created by passing ships approaches similar decibel levels to those expected in the experiment. Yet the strength of opposition via the press, the internet, and environmental interest groups was very formidable in damaging the viability and threatening the eventual implementation of this project. This level of opposition was not anticipated by the Advanced Research Projects Agency, who have only now, after several years, been able to begin a scaled-back implementation of the plan (Kildow, 1996). Though not observed with the OTEC proposal, this type of opposition could be a serious force to be reckoned with in the case of CO₂ ocean disposal given the potential for harm to pristine environments. As the deep ocean is a very unknown and untested environment, there is much room for interest group opposition to effectively hamper and perhaps make impractical a project such as CO₂ ocean disposal through demands for proof of no harm.

2.4.5 Warm Water Discharges from Power Plants

A final case that should be briefly examined is the generally accepted warm-water discharges from coastal power plants that are known to kill substantial numbers of fish larvae and other passive aquatic organisms. In a summary of environmental impact assessments

performed mainly on power plants off of the Eastern Coast of the US, the estimates of impacts on local fish larval populations commonly exceed millions of deaths per day which amount to estimated losses of 1 to 5 % of the regional fish populations (Marcy *et al.*, 1978). Yet while studies such as these are common and the impacts predicted would have substantive effects on populations and even on fishing stocks and local economies, it is not generally suggested that this practice of warm water discharge cease.

With the above cases, while it is generally true that regulations serve well to restrict harmful uses of the ocean, it is apparent that some harmful uses of the ocean are allowed, while some likely benign ones are prohibited. Clearly, many other factors are involved in decisions, some of which will be discussed in Chapter 3. Yet there are definite trends over recent years toward use of the ocean for disposal which could be important to the future of CO₂ disposal.

2.5 Trends in international laws

2.5.1 The Precautionary Principle

In general, it can be said that CO₂ disposal would be more difficult in the future than today, all else being equal, in terms of the recent trends of international marine pollution laws. Boyle suggests there is "growing evidence that significant changes are occurring in international attitudes to the control of marine pollution." He cites that the 13th meeting of the London Dumping Convention in 1990 agreed "to work toward the progressive elimination of dumping at sea and to phase it out entirely by 1995." With regard to land-based pollution,

There is increasing emphasis on strengthening the control of this source, with the adoption of stricter measures at regional level...Finally, the so called 'precautionary principle' indicates a new priority for measures of environmental protection which has influenced developments in the Law of the Sea. What these changes indicate is a movement away from a system of limited impact control to one of stronger international supervision based on a fiduciary or custodial model of environmental protection. This model has two characteristic features: an enhanced role for international institutions the management of the marine environment for common benefit, and a reversal of the long-standing assumption that States are free to use the oceans for waste disposal purposes if there is no proof of likely harm resulting (Boyle, p.84).

The precautionary principle, which appears to be gaining in acceptance and impact would essentially say that the parties proposing to dump matter into the ocean would have to show conclusively that no harm would result from such dumping. Though not yet codified into the international laws, under this approach, prohibited would be "waste categories where there is reason to assume that long-term harmful consequences could occur" (Boyle, p.85). In the

Assessment Procedure for impact assessment proposed as a recent development in the LDC, "if the assessment reveals that adequate information is not available to determine the likely environmental effects of the proposed dumping, then a permit would not be granted" (Peet, 1991). In addition to the increased acceptance of the precautionary principle, international as well as national trends are moving toward the goal of elimination of waste disposal at sea entirely, especially industrial and sewage wastes that are known to have at least local impacts. These trends are more apparent in the case of ocean dumping and uses with international implications. Such trends could especially threaten the feasibility of a large-scale CO₂ discharge via ships or into international waters.

2.5.2 Systemic Approaches

Yet, let us return again to the opening quote by R.V. Boelens which calls for a rational, global multi-sector approach to global multi-sector problems such as climate change and CO₂ disposal. Is it possible that many of the details of marine pollution laws may be glossed over or that the exception clauses be invoked for a problem of this magnitude? If the benefits of nutrient redistribution in the case of OTEC are able to counterbalance the negative effects of entrainment of deep-water zooplankton, could the atmospheric benefits of CO₂ disposal have bearing in the evaluation of its overall environmental impact assessment? While the scientific knowledge that the ocean and atmospheric systems are intimately linked has not pervaded the policy world in terms of systemic approaches to environmental regulation, there are stirrings in this direction, and it is the opinion of many that such approaches should be the rule.

It could be argued that to decouple the oceans from the atmosphere as in the previous sections would be quite naive. We have long known that nearly half of anthropogenically produced carbon is already taken up by the oceans and that the two media are in constant flux in both directions with respect to CO₂. Marine pollution conventions are primarily concerned with the effects of deliberate oceanic disturbances on human life, but this concern clearly is apparent in the other direction as well. Many of the most serious potential consequences of climate change involve disruptions of oceanic currents and flows, or sea-level rise. Further, several studies have recently documented huge losses in zooplankton populations near the California coast which have been attributed to climate change effects (Barry *et al.*, 1995, Roemmich *et al.*, 1995).

One example of the recognition of the ocean-atmosphere linkage is apparent in Article 17 of Agenda 21 from the Rio Declaration, the section dealing with the marine environment. The first paragraphs states, "The marine environment - including the oceans and all seas and

adjacent coastal areas - forms an integrated whole that is an essential component of the global life-support system and a positive asset that presents opportunities for sustainable development." Section E definitively opens, "The marine environment is vulnerable and sensitive to climate and atmospheric changes." These and similar statements would suggest that regulations affecting one area should be integrated with or conscious of others. As Douglas Cormack states in his discussion of pollution from land-based sources,

Recently, the concept of best practical environmental option has been introduced, together with that of integrated pollution control in an attempt to ensure that the claims of all environmental media are considered in an integrated manner....The notion that different regions have differing capacities per se to absorb pollution in a sustainable manner and additionally are subject to varying degrees of stress or lack of stress by current practices needs to be remembered if proper use of is be made of available resources (Cormack, 1992, p.17).

This statement certainly speaks of the type of systemic approach that would allow CO₂ disposal to be viewed in a wider context of overall environmental benefit.

These comprehensive approaches to international environmental problems are also supported by the Global Environmental Fund (GEF) which is concerned with providing funding for problems of this nature.

The GEF has been established to deal with the financing of activities which are transboundary in nature. The GEF implicitly assumes a degree of common ownership of the environment; its operational modalities are embraced by a sense of managing a shared resource and addressing a set of common concerns. The GEF is a unique experiment - the largest today - with funds committed at about \$1.5 billion to be earmarked for projects over the next three years. The GEF supports innovative demonstration investments, technical assistance and policy assistance in four areas of concern: global warming, ozone depletion, protection of biodiversity, and protection of international waters, both marine and freshwater....It is a 'breathing space' in which we can truly and substantively help assess the financial economic, institutional and policy ramifications of a global environmental strategy.....(Ian Johnson p.70).

Yet on a somewhat discouraging note, Calmet and Bewers note that progress in systemic approaches is very slow and such approaches are not well accepted, resulting in what they see are sub optimal solutions to the problem of radioactive waste disposal.

There exist strong pressures to protect the seas as well as other sectors of the environment, with the result that all disposal options appear unacceptable in the public eye. The absence of holistic perspectives in current debates in marine environmental protection fora, including those within regional and international conventions, constitutes misdirected good intentions. Both the declaration of the 1972 Stockholm conference and the report of the World Commission on the Environment and Development make clear the need to take account of the effects of management action in one sector upon other sectors of the environment to ensure that there is an overall benefit to the environment and man. This principle is being ignored in the current action to foreclose marine disposal options, since no prior comparison

with assessment of the consequences in other environmental sectors is being undertaken. This is a recipe for future problems, ignores scientific rationale, and points to the urgent need for a holistic international mechanism for overall environmental protection that is consistent with the elements of sound waste management (Calmet and Bowers, 1991, p.430).

If the example of low-level nuclear waste disposal is followed with CO₂ disposal, then it would likely be many years before such a strategy would hope to gain acceptance from the international community, and renegade disposal by individual states with international disapproval would be even more unlikely to take place than a concerted international effort and endorsement.

2.6 Conclusion

How are we to look at CO₂ disposal then, in relation to other types of discharges or dumping operations, or more importantly perhaps, how would it be viewed by policy-makers and those who assess environmental impacts? This is certainly a large-scale international issue, perhaps of the order of importance of nuclear waste disposal or sewage sludge disposal. Yet at the same time, it would likely be implemented as a land-based discharge, which generally are dealt with nationally and with much more lax standards. Locally, CO₂ disposal might appear like just another power plant discharging heat or an OTEC operation exchanging water.

In the isolated case of a plant interested in discharging CO₂, under the regulation of the USEPA it would appear that there would be some hurdles to be overcome before such a discharge would be permitted. The dumping scenarios would meet with the strict dumping regulations discussed above and the recent trends to discontinue practically all dumping at sea except for perhaps fish spoils and dredged materials (these materials are 'natural' originating from the ocean and have little impact themselves. Is CO₂ 'natural' to the ocean in this sense?). The plume scenarios may be permitted after significant study, surveying and monitoring, but could still be subject to forceful opposition, as the environmental impacts we predict appear to make the discharge questionable in light of much of the regulatory language as discussed above.

Still, national regulations are only one part of the future of this proposal. The quantities involved in CO₂ disposal and the simple fact that an effect on the global climate is the driving force to the strategy make this issue an international one. While trends suggest a recent and future tightening of use of the ocean for disposal purposes, other trends suggest increased willingness to consider large-scale environmental problems in global contexts and interdisciplinary fora. The prospects for ocean CO₂ disposal would be obviously worsened by the former and improved by the latter. In any case, with such a complex strategy, many

agencies and many levels of many governments would likely be involved in any approval process, possibly bogging the strategy down in years of bureaucratic negotiations.

There are many other issues which could influence the eventual negotiations over this policy including public perception and, of course, economics. While not the focus of this work, these and several other important factors in the fate of CO₂ ocean disposal are briefly discussed in Chapter 3.

Chapter 3. Other considerations

3.1 Introduction

What does the future hold for ocean disposal of CO₂? Part of the answer to this question relies on issues other than environmental impacts and legal implications. Factors not yet mentioned are implementation and siting difficulties, environmental monitoring requirements, public perception, the relative attractiveness of alternative strategies, and of course, a large component of all of these, the costs of CO₂ disposal.

3.2 Environmental monitoring

For any of the discussed CO₂ ocean disposal scenarios, it will inevitably be important that a comprehensive plan be placed forth by the proposers as to how they might monitor the marine environment for potential impact. Though monitoring requirements would vary among states and scenarios, most of the regulatory frameworks contain basic monitoring elements which would be necessary in all cases. These basic elements generally consist of baseline studies to assess natural conditions, a short term intensive monitoring program to assess impacts in the short term or in a pilot scale demonstration, and a long-term program.

All of these elements may prove difficult in the case of CO₂ disposal as the depths involved require advanced technology and the deep ocean is relatively unstudied thus far. A background study may prove the most difficult. The entire area potentially affected by the CO₂ disposal would have to be assessed qualitatively and quantitatively and with respect to seasonal variation. Many ongoing survey programs could be useful toward this endeavor, but there would clearly be many gaps that would have to be filled in with specific studies (IEA, 1994). Angel suggests that perhaps three years of data would be necessary to establish a baseline, though even this may be optimistic.

More pessimistically, Glover *et al.* (1971) discussed ongoing (1948-1969) monitoring experiments in the North Atlantic in a paper which attempted to provide a background of zooplankton populations. The data showed tremendous variability, leading the authors to conclude,

The present state of knowledge of variability in the field and the present level of monitoring the natural environment are inadequate for the detection and identification of the sources of variation and, especially, for the separation of natural processes from all but the most obvious consequences of pollution incidents (Glover *et al.*, 1971).

It is possible that there would be less variability in populations in the deep ocean (the above sampling was done at 10 meters depth), and that modern technology would make for more accurate assessment, but the difficulties in separating minor impacts from background variation should be recognized.

With respect to the details of monitoring, there are many techniques presently in use for sampling organisms of all sizes and kinds. The Clean Water Act in the US details many standard practices and approaches for monitoring zooplankton and benthic populations involving sampling with bottles, nets and trawls, and bottom corers (USEPA, 1994). Sampling periods are suggested, as are key variables and indicators of ecosystem health or constancy. Biomass values are becoming less important, and more emphasis is placed on numbers and distributions of species. Measures such as the number of species that make up 75% of all individuals in a class (dominance) can be useful in assessing ecosystem stress.

In addition, the Act emphasizes the importance of looking for impacts on other affected levels in the food chain - in the case of deep water zooplankton, one would want to assess changes in the nekton population that would have relied on the zooplankton as well as changes in the amounts of detrital materials upon which the zooplankton feed. Such effects would reach to the benthic regions where materials might accumulate. In monitoring benthic affects one would also be sure not only to assess effects on regions directly in contact with CO₂, but neighboring regions laterally and vertically, where secondary ecosystem effects might be felt.

With respect to deep water monitoring, there are many special techniques that would be useful to the purpose of monitoring effects of CO₂ disposal. Mesh nets would be appropriate for larger plankton and micronekton, though much data is already available through standing surveys currently being conducted (Ormerod, 1994). For smaller organisms, acoustic and optical counting techniques can provide relatively cheap abundant information, though this data would not be species specific. For sampling of benthic regions, special deep-water trawling systems are available for measuring the larger organisms that dwell on the ocean floor. For the microscopic species and those dwelling below the surface, special coring methods are mentioned. More qualitative methods such as photography and use of Robotically Operated Vehicles (ROV's) are also suggested.

It is possible that only a monitoring program that is very regionally specific and confined may detect a change in populations due to CO₂ disposal, yet if larger scale changes are not even detectable, then the monitoring program may be judged less useful. Many details of a monitoring program have yet to be worked out, and the stringency required to carry out the monitoring could vary greatly, delaying a pilot proposal for many years depending on the administrator.

3.3 Implementation and siting

A clear result from other work on the feasibility of CO₂ disposal is that the scenarios involving tanker transport of CO₂ offshore (the dry ice, towed pipe, and CO₂ lake scenarios) would involve many more complications than the dissolution scenarios (Herzog *et al.*, 1995). In order to transport CO₂ offshore via tanker, the CO₂ arriving from power plants would have to be collected and stored at coastal facilities. These facilities would have to comply with environmental regulations and would be very costly, especially in that they would require a large excess capacity to store CO₂ in the case of delays in its shipment offshore. Extra precautions would have to be taken to insure against accidental releases of CO₂ which is quite toxic to humans if released in large quantities in the storage and tanker loading process. The transport of CO₂ via pipes as in the dissolution scenarios also involves safety and pipe-laying difficulties, but these are universally less costly and would involve fewer precautions and regulations than those for tanker transport (Topical Report 2).

A potential problem with all scenarios is the practical availability of disposal sites. Dan Golomb has performed an assessment of available sites with the criterion that 1000 m of depth must be reached within 300 km offshore, and found the number of available disposal sites to be somewhat restricted. The United States would allow perhaps three sites off of the East Coast (the Hudson, Delaware, and Hatteras canyons), a site in the Gulf of Mexico and several West Coast sites. Western Europe would afford several Atlantic sites, but for the countries of Europe with no Atlantic coast and most of Eastern Europe, there would be few to no options. The Pacific and Indian oceans offer many potential sites as continental shelves are generally more narrow than in the Atlantic, with Japan perhaps in the best situation practically for CO₂ ocean disposal. Still, it should be noted that in many of these locations where several nations share a border with a body of water in close proximity, there are often strict regional agreements on dumping and discharge in existence which could create additional roadblocks.

3.4 Public perception

Public perception of ocean CO₂ disposal is also likely to play a large part in the future of this strategy. Because the project is large in scale and would involve definite environmental risks, no matter how small, lobbying efforts against the strategy could be significant at the local, national, and international levels. In a collection of articles published in Marine Policy entitled "General issues affecting land-based sources of marine pollution," the contribution from Greenpeace voiced concern that "numerous coastal ecosystems have been ruined, others

are at risk, and there are growing signs that the seaward reach of pollution is extending beyond continental shelves, into the deeper ocean." (Curtis, 1992). It is likely that Greenpeace and many other NGOs would stand categorically against ocean CO₂ disposal as presenting an unacceptable risk to the marine environment. Their power in forcing expensive monitoring experiments and lengthy legal challenges should not be underestimated. Still, much of their force is derived from the level of public rage and outcry, which could depend on how the project is presented and perceived, and filtered through the media.

At worst, CO₂ disposal could be presented as an example of the industrialized world, having disrupted one environment recklessly for hundreds of years, suddenly realizing that actual self-harm might result, and as a consequence, turning to another pristine environment to pour its excesses.

Yet, CO₂ ocean disposal may also be presented in a very benign light. We know that the ocean and the atmosphere will eventually come to long-term equilibrium with respect to CO₂. In this equilibrium, the eventual partitioning of CO₂ between atmosphere and ocean will be in the ratio of approximately 1:10. But with CO₂ entering the atmosphere at today's rapid rate, the current system is unable to reach equilibrium and thus CO₂ concentrations in the atmosphere are higher than they would be if the system could equilibrate. Thus, CO₂ ocean disposal is in a sense a means to facilitate the equilibrium process that will take place eventually by placing the CO₂ directly where it is eventually headed. In this placement, it is assumed, the CO₂ would cause less environmental damage than if it were allowed to reach the ocean slowly by means of the atmosphere as is currently the process.

3.5 Trends in fossil fuel use

One objection to CO₂ ocean disposal that may carry a good deal of weight is that the strategy does not require a reduction of total CO₂ produced, which would be the ultimate goal of many policy makers and NGOs. However, recent indications show that solutions calling for fewer emissions may be extremely difficult to implement.

Figure 3.1 CO₂ emissions over time for 5 major nations (NAS, 1992).

In Figure 3.1 we see that emissions of CO₂ are rising in most countries and the rise is most rapid in developing countries such as India and China. This rise is largely due to simple increases in energy demand, which translate into increases in fossil fuel use. In many developing countries in fact, the fastest rising energy source is coal, which also happens to be the fuel with the most CO₂ emitted per unit of energy produced. Figure 3.2 shows trends in uses of fossil fuels for electricity generation in OECD and non-OECD countries.

Figure 3.2 Trends in total electricity generation from fossil fuels in OECD vs. non-OECD countries. From IEA Energy Statistics and Balances of Non-OECD Countries, 1990-1991.

The trends show that we can expect moderate growth or a near leveling off at best in the future unless radical policies are enacted to slow emissions rates. Even conventional policies have not been successful to date. In the US, the many strategies called for in the Clinton Climate Change Action Plan aimed at mainly increased efficiency of fossil fuel use and conservation efforts have failed to significantly slow the rate of US emissions even though

many of the policies claim a positive return on investment (Hileman, 1996). Continued ineffectiveness of mitigation policies requiring usage reductions could make strategies such as CO₂ disposal more attractive in the future.

3.6 Costs

At the present time, CO₂ capture with ocean disposal is very expensive relative to many other mitigation strategies. While costs of disposal itself are not high, estimated as on the order of \$5 to 10 per ton of CO₂ avoided for injection at 500 - 1000 m, costs of capture, compression and transport dominate. Total costs today for a system utilizing the dissolution type scenarios have been estimated to be between \$22 and \$80 per ton CO₂ avoided (Ormerod, 1994). The cost of \$22 per ton avoided would correspond to an increase in the price of producing electricity by about a third, though who would actually bear this cost could vary considerably depending on the financing mechanism utilized.

The costs of other strategies from several sources are shown in Table 3.1. The accounting systems used by the different authors were different so the estimates are not perfectly comparable. Yet what is apparent from the table is that aside from efficiency options which are universally accepted as very low cost, the costs of CO₂ ocean disposal are comparable to many other strategies under consideration.

Option	Net cost (\$ per ton CO ₂ avoided)	Emissions reduction Potential (Mt CO ₂ /yr)
Vehicle efficiency ^a	0	900
Industrial energy management ^a	0 - 10	500
Reforestation ^a	10 - 99	200
Stimulation of ocean biomass with iron ^a	5 - 99	7000
Coal switch to natural gas ^b	17 - 46	850 (in the U.S.)
Coal switch to solar PV ^b	90	400 (in the U.S.)
Coal switch to nuclear ^b	28 - 69	1500 (in the U.S.)
CO ₂ ocean disposal ^c	22 - 80	4000 (one thousand 500MW _e coal-fired power plants)

Table 3.1 Cost estimates of various CO₂ reduction strategies

^aEstimates from NAS, 1992. ^bEstimates from Rubin *et al.*, 1992. ^cEstimates from Ormerod, 1994.

Still, these are hypothetical estimates which ignore practical difficulties in carrying out these strategies. Phytoplankton growth stimulation with iron is not yet a proven concept, and the estimate of emissions reduction potential is thus purely hypothetical. It should also be kept

in mind that the cost estimates for CO₂ disposal are also quite uncertain. As this concept is still new and little research has been put into its development, there is a great deal of room for cost reduction as opposed to some of the efficiency measures which have been heavily researched for many years. The costs of SO₂ scrubbing, for example, have decreased by a factor of 5 to 10 from initial cost estimates (O'Neill, 1996).

Chapter 4. Conclusions

4.1 Introduction

Of the many feasibility questions surrounding the concept of CO₂ ocean disposal, this study has attempted to address two of those which have received little attention to date; the environmental impacts and legal/political implications.

While there are uncertainties in attempting to predict effects on such a complex system as the deep sea environment, the toxicological methodology utilized above goes beyond simple qualitative guesses in evaluating the potential effect of a toxin on affected organisms. Indeed, this analysis goes further still in assessing the potential impact of CO₂ ocean disposal on the marine environment by interpreting the results from the study in larger environmental and political contexts.

The methodology reviewed and the methods used to work exposure time concepts into impact assessment will undoubtedly prove to be of value to similar endeavors and is already being considered by the Massachusetts EPA office in a possible modification to water quality standards. The concept of a threshold LC₀ curve combined with a methodology to evaluate gradual impacts in the potential to cross this curve could prove important in future attempts to minimize impacts through engineering solutions.

The results of the assessment suggest the following conclusions:

4.2 Environmental impacts

- **The severity of adverse impacts on marine life near the disposal sites is strongly dependent on the dispersion of the CO₂. Given the effluents from a 500MW_e coal fired plant:**

- If released as dry ice cubes, impacts would be negligible on marine fauna. Minimal impacts on phytoplankton growth are possible.

- If released as a deep water plume, significant numbers of zooplankton may not survive, though this would depend on the dispersion of the plume.

With a more concentrated plume (the dense plume scenario) containing effluents from 10 power plants, our results indicate that a volume of approximately 1000 km³ close to the release point might become devoid of 50% of its natural abundance of zooplankton life forms and a volume of approximately 5000 km³ might see a reduction by at least 10% from the natural value. These impacts are quite large - 5000 km³ is nearly one fourth the dimensions of the Baltic Sea, for example. Yet again, if the same amount of CO₂ is released as a more dispersed droplet plume, only 26 km³ are predicted to become devoid of at least 10% of natural zooplankton populations. And if this 10 plant droplet plume release is dispersed further as 10 individual non-overlapping releases, the combined 10% deficit volume is reduced to near 1 km³. Taking this concept to its ultimate implication, *if each single plant release is dispersed via optimally spaced diffusion ports as in the towed pipe scenario, the impact might be reduced to nil.*

- If released below 3000 m forming a CO₂ lake, local devastation of the benthic community is inevitable, though the impacts would most likely be contained to a small, localized area.
- **Large scale impacts reaching far beyond the immediate release region (within several hundred km of release) are unlikely to occur as the 'sink' capacity of the ocean for CO₂ is extremely large.**
- **Surface dwelling phytoplankton are probably more sensitive to pH change than deep water zooplankton which suggest that there could actually be environmental benefits from diverting CO₂ from the atmosphere (from which it is absorbed to the ocean surface) to the deep ocean.**

Such benefits may be too small to register, however, and would only be temporary at best because in the long run the ocean - atmosphere circulation system will bring all CO₂ to equilibrium. But it is important to stress that any environmental impact statement assessing impacts of CO₂ disposal must assess impacts against the background of a no-action scenario. The no action scenario in this case could involve significant impacts in marine ecosystems via large CO₂ flux from atmosphere to ocean lowering surface pH.

It should be remembered that the significance of the predicted regional impact and the effect on larger ecosystems is very difficult to estimate, may be even more difficult to monitor, and will inevitably be subject to varied interpretations. Little is known about the role of deep-

sea zooplankton, as man has thus far had limited capacity to impact or even study life at this depths, although these regions are receiving more attention recently and this project could serve to stimulate further research in this area.

4.3 Legal and other considerations

- The dry ice, CO₂ lake, and towed pipe scenarios would meet with more difficult implementation and legal barriers because they involve transport by vessels and therefore 'ocean dumping'. International conventions on dumping would be relevant as well as national regulations.
- The plume scenarios would likely face less significant legal barriers to implementation, most of which would be national in origin.
- None of the strategies are clearly outright illegal, nor are they clearly unobjectionable. Because of the vagaries of the laws and the lack of precedents for such a project, there is much room for interpretation in the laws as to the legality of the scenarios and many decisions would likely be open to political pressure.
- Given the uncertainty involved in knowledge of the deep ocean, any disposal scenario would not likely be implemented before considerable further research was done on possible impacts, and still, the strategy would likely be approved only on a trial basis at first. Monitoring requirements could be substantial, involving many years of study and resources - investments which could ultimately doom the project if political and interest group pressure were to force the most strictest requirements to be applied.
- The direction of recent trends in environmental regulation and specifically ocean disposal suggests that approval of this strategy may become more difficult in the future, though there also appears to be an increased willingness to consider multi-media approaches.

4.4 General Conclusions

Ocean disposal of CO₂ as a policy option appears to be in the process of being considered as a mainstream option and distinguished from more fantastic, less feasible strategies such as iron fertilization and solar reflection. These latter strategies are theoretically unproven and would be extremely impractical and nearly impossible to implement. CO₂ ocean

disposal, on the other hand, is theoretically very sound, and indeed, aquifer disposal of CO₂ will become a reality later this year in Norway. The cost estimates for CO₂ ocean disposal are quite high relative to strategies such as conservation and efficiency (electricity prices would be increased by perhaps a third in the current economic situation), but are not particularly high relative to greater reliance on renewable or nuclear energy sources, for example.

Implementation times would be long as well and legal barriers may be significant, but these are factors which are subject to change given political situations in the future. Under a carbon tax, CO₂ ocean disposal can actually become an attractive option in many situations as is currently being demonstrated in Norway.

It is likely that to some decision makers the potential for or perception of environmental impact, is one of the most serious holdups to the CO₂ ocean disposal strategy. This study has shed some light on these impacts and may serve as a stimulant to other work which may ultimately establish with near certainty that CO₂ ocean disposal is possible with trivial environmental impacts. What environmental impacts might be considered as trivial is open to interpretation, of course. Martin Angel, in his overview study of environmental implications of CO₂ ocean disposal states, "A working hypothesis might be that 1% of any oceanic ecosystem might be sacrificed for the avoidance of a tangible disruption of a global process or a more valuable natural resource." (IEA, 1994). The 10-plant dense plume scenario which is predicted to be by far the most severe in terms of environmental impact in this study would not approach such a figure of 1%. If implemented in 10 separate locations in the North Atlantic (100 plants' worth) the overall impact would be predicted in this study to be a 0.1% loss of zooplankton in a relatively small slice of ocean (900 - 1100 m), a much smaller loss than the 1% figure of Angel.

When compared with a no-action scenario, there are even possible environmental benefits to the marine environment (aside from reductions in climate change) in that a smaller CO₂ flux from atmosphere to surface ocean could mitigate pH decrease in surface waters where it is expected to have a larger adverse impact than in the deep ocean.

But even if it could be established with fair certainty that there would be little or no adverse impact to the marine environment due to CO₂ ocean disposal, it cannot be ignored that the concept of this solution would still likely be unacceptable to some. This solution is ultimately an end of pipe solution as opposed to pollution prevention. Worse, the pipe end would lead to one of the world's last untouched environments which would raise red flags in the eyes of many. Many international guidelines and national regulations are written to acknowledge these flags and to discourage this type of solution. In fact, trends seem to be tending toward even greater discouragement. While the strategy would probably not be discarded outright for the sake of any current regulations or conventions, these regulations

could be used to prevent ocean disposal of CO₂ from ever being implemented if opposition were strong enough. Or the simple fact that environmental and legal concerns are even present with this strategy while others (such as efficiency in fuel use) would not raise such concerns, could be a discouraging factor.

Currently, CO₂ disposal represents a huge investment for the opportunity to trade one uncertainty for another. One would be achieving an unquantifiable environmental benefit (from lower atmospheric CO₂ concentrations) and trading this uncertain benefit for more uncertainty in possible ocean disruptions. Thus, to become more viable, these three factors must continue to move in the direction in which they are currently headed; the costs and potential for environmental damage of CO₂ ocean disposal must continue to decrease while the perceived damage due to global climate change must continue to increase.

Even at best, CO₂ ocean disposal would be a highly complicated, costly strategy that alone could not save the world from rising CO₂ concentrations in the atmosphere - the fact that only 1/3 of world CO₂ emissions come from power plants and that not all of these are conveniently near deep-water dumpsites limits the efficacy of this strategy. Still, if and when the time comes that nations find themselves with very strong incentives to control CO₂ emissions, each will evaluate the many available options and likely use a battery of many options simultaneously. Each option would have large economic and social costs, and the number of available effective options is likely to be very limited. For many, ocean disposal of CO₂ would be out of the range of consideration; but for others with favorable economic, political, and geographic conditions, it may very well be a realistic option to be used in combination with other mitigation strategies. As it is hard to predict the near future of these trends, this option should be kept on the playing field (in some countries, it is already considered a major player) as a viable strategy in a crisis, and the larger unknowns - environmental impacts and technology of deep ocean disposal and monitoring - should be further researched.

References

- Andersen, L.F. (1988), "Ocean Iron Fertilization as Greenhouse Mitigation: A Question of Ecology and Ethics?," Master's Thesis, Massachusetts Institute of Technology, Cambridge.
- Avery, W.H., Wu, Chih (1994), Renewable Energy From the Ocean: A Guide to OTEC, Oxford University Press, UK.
- Barry, J.P., Baxter, C.H., Sagarin, R.D., Gilman, S.E. (1995), "Climate-related Long-term Faunal Changes in a California Rocky Intertidal Community," *Science*, 267, pp. 672-675.
- Bishop, P.L. (1983), Marine Pollution and its Control, McGraw Hill, USA.
- Boelens, R.G.V. (1992), "From Policies to Science: Strategies for Marine Environmental Protection," *Marine Pollution Bulletin*, 25,4, pp. 14-17.
- Boyle, A.E. (1992), "Protecting the Marine Environment," *Marine Policy*, March, p.79-92.
- Calmet, D.P., and Bewers, J.M. (1991), "Radioactive Waste and Ocean Dumping," *Marine Policy*, 15, 6, pp. 413-430.
- Cormack, Douglas (1992), "Scientific and Technical Background," *Marine Policy*, January, pp. 5-19.
- Curtis, Clifton (1992), "Views of Greenpeace," in General Issues Affecting Land-Based Pollution, *Marine Policy*, January, pp. 67-68.
- Eng, William (1996), USEPA Region I, Personal Communication.
- Glover, R.S. (1971), Robinson, G.A., Colebrook, J.M., "Plankton in the North Atlantic - An Example of The Problems of Analyzing Variability in the Environment," *Bulletin of Marine Ecology*, pp. 439-445.
- Herzog, H.J., Adams, E.E., Auerbach, D., Caulfield, J. (1995), "Technology Assessment of CO₂ Ocean Disposal," Massachusetts Institute of Technology (MIT) Energy Laboratory, MIT-EL 95-001, Cambridge, MA, USA.
- Hileman, Bette (1996), "U.S. Unlikely to Achieve Goal of Stabilizing Greenhouse Gas Emissions," *C&E News*, Jan. 15, pp. 14-15.
- International Energy Agency (IEA), The Greenhouse Gas R&D Programme (1994), "The Disposal of Carbon Dioxide from Fossil Fuel Fired Power Stations," IEAGHG/SR3.
- Johnson, Ian (1992), "Cross-sectoral Issues Affecting Land-Based Pollution," *Marine Policy*, January, pp. 69 - 71.
- Kildow, J.T. (1981), Social Science Research Agenda for Subseabed Disposal of High Level Nuclear Waste and Spent Fuel Program, Final Report, Sandia Laboratories, NM, USA.
- Kildow, J.T. (1996), Personal Communication.

Knutzen, J. (1981), "Effects of Decreased pH on Marine Organisms," *Marine Pollution Bulletin*, 12, pp. 25-29.

Marcy, B.C. Jr. (1978), "Effects and Impacts of Physical Stress on Entrained Organisms," in Power Plant Entrainment, A Biological Assessment, Schubel, J.R., Marcy, B.C. Jr. Eds., Academic Press, New York, USA.

National Academy of Sciences (NAS), National Academy of Engineering, Institute of Medicine (1992), "Policy Implications of Greenhouse Warming: Mitigation, Adaptation, and the Science Base," National Academy Press.

Oneill, Erin (1996), MIT Energy Laboratory, Personal Communication.

Ormerod, W.G., Webster, I.C., Audus, H., Riemer, P.W.F. (1993), "An Overview of Large Scale CO₂ Disposal Options," *Energy Conversion Management*, 34, 9, pp. 833-840.

Peet, Gerard (1991), "London Dumping Convention: Obsolete or Effective?," *Marine Pollution Bulletin*, 22,2, pp. 56-58.

Roemmich, D., and McGowan, J. (1995), "Climatic Warming and the Decline of Zooplankton in the California current," *Science*, 267, pp. 1324-1326.

Rose, C.D., Williams, G.W., Hollister, T. A., Parrish, P.R. (1977), "Method for Determining Acute Toxicity of an Acid Waste and Limiting Permissible Concentration and Boundaries of an Oceanic Mixing Zone," *Environmental Science and Technology*, 11 (4) 367-71.

Rubin, E.S., Cooper, R.N., Frosch, R.A., Lee, T.H., Marland, G., Rosenfeld, A.H., Stine, D.D. (1992), "Realistic Mitigation Options for Global Warming," *Science*, 257, pp. 148-266.

Simpson, D.C., O'Connor, T.P., Park P.K (1981), "Deep Ocean Dumping of Industrial Wastes," Ch. 12 in Marine Environmental Pollution, Dumping and Mining, Richard A. Geyer ed., Elsevier, Netherlands.

Swanson, R. (1977), "Status of Ocean Dumping Research in New York Bight," *Journal of the Waterways, Port, Coastal and Ocean Division ASCE*, 103, pp. 9-24.

Timagenis, G.J. (1981), International Control of Marine Pollution, volumes 1 and 2, Oceana Publications, USA.

United States Climate Change Action Plan (USCCAP, 1994), available on the World Wide Web at (<http://gcio.gcio.org/USCCAP.toc.html>).

United States Environmental Protection Agency (USEPA), Office of Water Enforcement and Permits (1985), "Technical Support Document for Water Quality-based Toxics Control," Washington, DC.

United States Environmental Protection Agency (USEPA), Office of Wetlands, Oceans and Watersheds, (1994), "CWA Section 403: Procedural and Monitoring Guidance," Washington, DC.

Vaccaro, R.F., Grice, G.D., Rowe, G.T., Wiebe, P.H. (1972), "Acid-Iron Waste Disposal and the Summer Distribution of Standing Crops in the New York Bight," *Water Research*, 6, pp. 231-256.

Appendices

**Jennifer A. Caulfield
E. Eric Adams
Sharon W. Ho**

**Massachusetts Institute of Technology
Energy Laboratory
77 Massachusetts Avenue
Cambridge, MA 02139-4307**

Introduction

Following are five brief appendices which describe additional calculations and other information which didn't fit into the topical reports.

Appendix 1 describes the model we used to predict water column impacts from a deep lake injection. This analysis complements that of the other four injection scenarios (dry ice, towed pipe, droplet plume and dense plume) described in Topical Report 3.

Appendix 2 summarizes the benthic impacts expected from all five injection scenarios. Along with corresponding water column impacts, these form the basis for our conclusions in Volume 1 concerning the relative near field impacts of different injection scenarios.

Appendix 3 describes a simple box model of the effect on global average atmospheric CO₂ concentration and global average ocean pH associated with the CO₂ injection from 1000 standard power plants of the type described in Topical Report 1. Though far less detailed than the 3-D numerical simulations described in Topical Report 4, the box model provides insight into limiting conditions to be expected if ocean CO₂ disposal were to be enacted on a large scale.

Appendix 4 addresses a question of safety which is sometimes asked in connection with ocean CO₂ disposal: is it possible that a violent eruption could occur, similar to the one at Lake Nyos in Cameroon, which killed 1700 people? In this appendix we explain why such an eruption would not occur.

Finally, Appendix 5 provides an update relative to the discussion in Topical Report 6 concerning the London Dumping Convention. As of this writing (August 1996), the convention is being revised, and the new wording could have an effect on the regulation of CO₂ which is discharged to the ocean through any scenario involving transport by tanker.

Appendix 1: Near-Field Perturbations Resulting from the Deep Lake Injection Scenario

Formation of a deep CO₂ lake on the ocean floor is an injection scenario that can be considered an isolation strategy. This type of lake would be stable at depths greater than about 3700 meters, where liquid CO₂ becomes more dense than both ambient and CO₂ saturated seawater. Although this form of injection presents many engineering problems, it has clear advantages in terms of effective CO₂ sequestration due both to its depth and its ability to isolate a fraction of the emissions during the time that the lake is growing towards its steady state.

To simulate the growth of the deep lake over time, it was necessary to choose a topography for the basin in which the CO₂ liquid would be deposited. Curves were fit to data from the Nishinosima Trough, a deep ocean basin off the coast of Japan (T. Oshumi & N. Nakashiki, CRIEPI, Abiko, Japan, personal communication). Volume and area were determined as functions of distance of the lake surface from the ocean floor. The equations for volume and radius of a lake with equivalent circular surface area were determined separately for a better data fit, and are as follows:

$$Volume (km^3) = 221 * depth (km)^{2.18} \quad (1)$$

$$Radius (km) = 10.93 * depth (km)^{0.472} \quad (2)$$

The actual data points and the fit equations are shown in Figure 1.

The input to the lake is the emissions from either one or ten standard power plants, and the flux out is the diffusion rate through the clathrate hydrate crust. The base case current assumed at these depths is 3 cm/s, and this leads to a CO₂ mass transfer velocity of 2.67×10^{-7} m/s (Hirai *et al.*, 1996). The actual flux of CO₂ is equal to the mass transfer velocity times the difference between the saturation concentration of CO₂ and the ambient concentration in the surrounding waters. For this model the ambient concentration was assumed to be zero.

The rate at which the lake grows and the surface area of the lake at equilibrium depend on the number of plants contributing CO₂. The one plant case essentially reaches equilibrium after about 200 years (See Figure 2). The radius required to maintain steady conditions is 1.9 km. When ten plants contribute emissions, the lake does not begin to reach equilibrium for

more than 1000 years, and the steady state lake needs ten times the surface area of the one plant lake, resulting in a steady-state radius of 5.9 kilometers (See Figure 3). The rate at which CO₂ is isolated, or retained, is the difference between the flux in and the flux out. The former is simply the emissions from the contributing power plants, while the latter depends on the area of the lake and will change as the lake grows until the lake reaches equilibrium and no further isolation occurs. For the one plant case, the isolation component has decreased to only 10% after 50 years, while for the 10 plant case it takes closer to 1000 years for the lake to reach this level of retention. Figures 4 and 5 illustrate this process for the two cases.

The CO₂ leaving the lake is transported by advection and diffusion. It was decided to model the lake as ten finite line sources (See Figure 6). Each line source underwent horizontal diffusion as described by the modified Brooks' solution presented in Topical Report 3.

Diffusivity in the vertical direction was assumed to be constant with a value of 0.01 m²/s, the same value used by Nakashiki in the lower 100 meters of his model (Nakashiki, 1993). In order to obtain the three dimensional concentration of CO₂ from each discretized source, the Brooks solution was multiplied by the following factor to account for vertical diffusion.

$$\text{vertical factor} = \frac{1}{\sqrt{4\pi \times E_z/u}} e^{\frac{-z^2 u}{4E_z x}} \quad (3)$$

The sum of the additional concentration at a point from each of the ten sources was used to calculate resultant pH. The resultant pH values were not very low, and so it was decided to ignore any possible dissolution from calcium carbonate sediments on the ocean floor; this omission leads to conservative results. This type of ocean disposal of CO₂ is not expected to continue long enough for the lake to reach equilibrium, and so the values after 50 years of disposal were chosen as representative. The results are shown in Figure 7 for the one plant case, and in Figure 8 for the ten plant case. The same values presented in Table 1 of Topical Report 3 for the other scenarios are tabulated below for the deep lake scenarios after 50 years of disposal: the volume of water with a pH less than 7, the distance from the upstream end of the lake to the point where the pH reaches 7 again, and the minimum pH. In this case the two values given for minimum pH are the same since there are no near-field mixing processes.

	Volume of water	Distance to	Minimum pH	Minimum pH
	with pH under 7	pH of 7	(after	(diffusion
	(km^3)	(km)	dissolution)	regime)
Deep Lake				
1 plant	0.34	6	6.4	6.4
10 plants	3.9	15	6.2	6.2

A quick analysis of the centerline experience from the one plant deep lake scenario shows that this scenario will not result in mortality in the water column using the data in Topical Report 5. The centerline experience for the ten plant case shows finite mortality, so the probabilistic pathway method described in Chapter 2 of Topical Report 3 was used to evaluate the impact. Since the plume resulting from the deep lake underwent vertical diffusion, the same diffusion was taken into account when calculating the organism paths. It is in part due to this vertical diffusion that the mortalities resulting from this scenario are so low. The results are presented below.

	Integrated Total	Maximum Mortality	Highest Spatial
	Mortality (km^3)	Flux (m^3/s)	Deficit (percent)
Deep Lake			
1 plant	0	0	0
10 plants	0.03	840	0.7

Clearly, the impact on the benthic community surrounding the lake also needs to be taken into account; this impact will be considered and compared to the benthic impact from the other scenarios in Appendix 2.

References

Shuichiro Hirai, Ken Okazaki, Yutaka Tabe, Kunio Hijikata, and Yasuo Mori (1996) "Dissolution rate of liquid CO_2 in pressurized water flow and effect of clathrate film." Submitted.

Norikazu Nakashiki and Takashi Ohsumi (1993). "Simulation of near-field behavior of CO_2 from a source on the deep-sea floor." In *Proc. of The Int. Symp. on CO_2 Fixation and Efficient Utilization of Energy*, pages 331-336.

Figure 1: Volume, radius, and area of ocean floor basin assuming a circular shape. Results from theoretical curve compared to actual numbers.

Figure 2: One plant case, volume and area versus time.

Figure 3: Ten plant case, volume and area versus time.

Figure 4: One plant case, percent retention.

Figure 5: Ten plant case, percent retention.

Figure 6: Diagram of theoretical deep lake model. The liquid carbon dioxide fills the basin and dissipates via advection and diffusion. The lake is divided into 10 continuous line sources and downstream ocean CO_2 concentration distribution is calculated via Brooks model modified to account for vertical diffusion.

Figure 7: pH Distribution for a one power plant deep lake after 50 years. Distance defined from the upstream edge of the lake. The lake has a diameter of 3.5 km and there is a 3 cm/s current in the x-direction.

Figure 8: pH Distribution for a ten power plant deep lake after 50 years. Distance defined from the upstream edge of the lake. The lake has a diameter of 7.2 km and there is a 3 cm/s current in the x-direction.

Appendix 2: Benthic Impacts Due to the Various Injection Scenarios

In addition to water column effects, some of the proposed scenarios result in negative impacts associated with the contact of low pH water with benthic communities. For the dense plume this will occur in the area of the gravity current as well as the area of the slope along which the current intrudes and diffuses. In the case of the deep lake and dry ice scenarios, the impact will come from both the contact with low pH water and the loss of area of the sea floor in direct contact with liquid CO₂. The towed pipe scenario allows certain water depths to be targeted and consequently is able to avoid impact to the ocean floor. As schematized, the droplet plume would also distribute CO₂ only to intermediate water depths; however, this form of injection could certainly be used in scenarios that would distribute the CO₂ close to the ocean floor (See Topical Report 3).

Table 1 describes the benthic impacts for the various scenarios. Mortality is assumed to be 100% in the area covered by liquid CO₂, while mortality for regions in contact with low pH water is estimated using the mortality curves described in Topical Report 5 by extrapolation at very long times (on the order of 100 years).

Examining the results in Table 1, it can be seen that the dense plume scenario has the largest potential benthic impact. As a fraction of the area affected, the area of depression in which the plume descends is quite small. The area affected outside of the gravity current depends on the vertical thickness of the affected ocean layer, the slope of the ocean floor at the intrusion depth, and the length of the plume. The large area that results is in part due to the fact that the plume is schematized as intruding and then diffusing along a coast with a shallow slope (2°). With a steeper local slope or a current that was slightly offshore, this impact would be much smaller. If the droplet plume were to occur in a similar environment, benthic impact would result; however, these impacts would still be substantially lower due to the shorter length and the higher initial pH expected with this scenario.

In the case of the deep lake, about one-third of the predicted mortality results from direct loss of the sea-floor needed to form the lake (see Appendix 1). The remaining area is due to the low pH water in contact with the ocean floor around the deep lake.

Injection Scenario	Number of Plants	Benthic Impacts	
		Physical Dimensions (km ² < pH 7)	Total Mortality (km ²)
Dry Ice	1	3	3
	10	33	46
Towed Pipe	1	0	0
	10	0	0
Droplet Plume	1	0	0
	10	0	0
Dense Plume	1	62	75
	10	450	540
Deep Lake	1	24	34
	10	94	120

The benthic impact for the dry ice scenario depends on the size of the cubes and the depth of the ocean floor at the release site. In order to insure that the majority of CO₂ in the dry ice cubes reaches the ocean floor, the cubes need to be quite large. At most disposal locations, a fraction of each cube will reach the ocean floor where it will form a liquid puddle with a hydrate skin and dissolve in a manner similar to that of the deep lake. If the cubes are modeled as falling in the same general area of the ocean floor, a single deep lake would form. The areas presented in Table 1 result from this assumption where the ocean floor is at a depth of 4000 meters. If, however, the cubes were to be widely distributed and form individual puddles, the puddles would cover more bottom area. Although then would dissolve more quickly, the overall impact would be greater and would depend on the time needed for recovery of the benthic community after the remainder of the cube dissolved. If the ocean floor were located at depths shallower than about 2800 m, the liquid CO₂ would be less dense than seawater, and would tend to mix with the overlying seawater instead of forming a stable pool.

The magnitude of the benthic impact varies substantially among scenarios and is dependent on the conditions at the disposal site. In no case is the area large compared with the total area of the ocean floor, so that the primary concern may be avoiding unique or highly productive areas.

Appendix 3: A Simple Box Model

Topical Report 4 documents regional scale and global scale 3-D numerical models which are used to examine the impacts of the ocean disposal of CO₂ from ten and one hundred standard power plants, respectively. In this appendix we describe a much simpler model which is used to illustrate, in an approximate global average sense, the impacts associated with CO₂ addition from approximately one thousand power plants. This magnitude of CO₂ addition represents a likely upper bound on the amount of anthropogenic CO₂ which could be sequestered, so the simulations serve as an environmental endpoint to compare ocean impacts associated with increased acidification with atmospheric impact avoided.

Three disposal scenarios are considered. (1) Ocean dissolution of 130,000 kg/s CO₂ which corresponds to one thousand 500 MW_e coal plants with a 20% energy penalty, or approximately one-sixth of the world's current anthropogenic production of CO₂; (2) same as above but without the energy penalty; (3) same as above but assuming the CO₂ is isolated (*e.g.* geologically such as in an aquifer) rather than dissolved in the ocean. These three scenarios are compared with the limiting conditions of atmospheric disposal (base case or business-as-usual) and an equilibrium case in which atmospheric and ocean concentrations are always in balance. In all simulations future CO₂ emissions follow the projection of the U.S. Electric Power Research Institute (Hidy and Spencer, 1994) of 3800 Gt carbon over the 200 years whereby total emissions continue to rise over the first 100 years, then decline in the following 100 years, with no emissions after 200 years.

The model represents a one-dimensional ocean which absorbs CO₂ from the atmosphere based on differences in partial pressures. The decay function is based on the 3-D ocean model of Maier-Reimer and Hasselman (1987). Reduced buffering capacity is modeled by an increasing fraction of emissions remaining in the atmosphere as a function of cumulative emissions (Sarmiento, 1993). Release of injected CO₂ to the atmosphere is based on the 1-D evasion model of Kheshgi *et al.*, (1994) which uses a global average for both upwelling velocity and vertical diffusivity. All injected CO₂ is assumed to be ultimately released to the atmosphere, where it is eventually re-absorbed by the ocean based on the above decay function. At a depth of 1000 m the ocean residence time of the injected CO₂ is 250 years. The predicted atmospheric

concentrations without CO₂ capture modeled by Cole *et al.* (1993) are used to calibrate the model. The corresponding change in the ocean inventory of carbon species was calculated assuming that all other fossil fuel emissions are divided between atmospheric and ocean inventories (i.e., no change in the terrestrial inventory). pH was evaluated by assuming a uniform ocean concentration of each carbonate species. Equilibrium reference values were tied to the emissions scenario using the predicted partitioning values for perturbations in total carbon dioxide in the air/ocean system as evaluated by Sarmineto (1993). This represents the equilibrium state of the system based on cumulative emissions as of the year specified. The "equilibrium distribution" line represents the equilibrium partitioning with the baseline scenario. In assessing the approach to equilibrium for the cases with different cumulative emissions, the corresponding equilibrium states were used.

As can be seen in Figure 1, the release of 3800 Gt of fossil fuel carbon will lead to an overall pH change in the ocean of approximately one-half of a pH unit at system equilibrium. The difference in the ocean impact of the baseline case and the ocean dissolution cases is largest at 200 years when fossil fuels are exhausted. At this point in time, the difference is 0.06 pH units if no energy penalty is considered and 0.09 when a 20% energy penalty is assessed. Isolation of one-sixth of current emissions cuts the peak atmospheric concentrations as effectively as ocean dissolution without additional decrease in ocean pH compared with the baseline scenario. The continued benefits of isolation are seen after 200 years as the system approaches equilibrium. The net decrease in ocean pH at equilibrium will be only 85% of that of the baseline case.

Figure 2 illustrates the atmospheric response to CO₂ emissions over time for the same scenarios. Isolation or ocean dissolution of one-sixth of current emissions could reduce peak atmospheric concentration of CO₂ by 14%. Lower atmospheric concentrations of CO₂ continue as the system approaches equilibrium. At 400 years the difference between the base case and other ocean dissolution cases is still about 11%. As the system approaches equilibrium, the significant decrease in final atmospheric concentrations expected with isolation begins to be seen (100 ppm lower than the equilibrium line), as does the final difference in atmospheric concentrations that will result from the energy penalty of capture (45 ppm higher than the equilibrium line).

In conclusion, ocean dissolution of a fraction of fossil fuel emissions has the potential to significantly lower peak atmospheric concentrations of CO₂ at the expense of a far-field decrease in average ocean pH. For this example

where one-sixth of current anthropogenic CO₂ emissions are discharged at an ocean depth of 1000 m, these changes are 14% and 0.09 pH units when an energy penalty of 20% is assessed. The concept of direct ocean dissolution of CO₂ is motivated by the assumption that the benefit of the reduction in atmospheric concentrations of CO₂ more than offsets the cost of capture and disposal as well as the detriment to the global ocean environment caused by the additional decrease in pH. Of course, spatial pH changes must be evaluated as well, particularly the variation in the vertical. For example, Haugan and Drange (1995) suggest that ocean disposal of CO₂ will likely result in less pH change—compared with business as usual—at the ocean surface where the greatest biological productivity takes place. Isolation of a fraction of the emission would also result in *less* global average pH change as well as significantly lower peak atmospheric concentrations of CO₂. From a purely environmental standpoint this is the best option.

References

- Cole, K.H., G.R. Stegan and G.L. Simmons (1993) "The capacity of the deep oceans to absorb CO₂." *Energy Convers. Mgmt* 34:991-998.
- Haugan, P. M. and H. Drange (1995) "Effects of CO₂ on the ocean environment." *Energy Convers. Mgmt* 37:1019-1022.
- Hidy, G.M. and D.F. Spencer, (1994) "Climate alteration: a global issue for the electric power industry in the 21st century." *Policy* 22:1005-1027.
- Kheshgi, H.S., B.P. Flannery, M.I. Hoffert and A.G. Lapenis (1994). "The effectiveness of marine CO₂ disposal." *Energy*, 19(9):967-974.
- Maier-Reimer, E. and K. Hasselmann (1987) "Transport and storage of CO₂ in the ocean—an inorganic ocean-circulation carbon cycle model." *Clim. Dyn.* 2 63-90.
- Sarmiento, J.L, (1993) "Ocean carbon cycle." *C&EN*: 30-43 (May 31, 1993).

Figure 1 Impact of various ocean disposal scenarios on ocean pH.

Figure 2 Impact of various ocean disposal scenarios on atmospheric CO₂ concentrations.

Appendix 4: The Possibility of a "Lake Nyos Type" Eruption

Introduction

In August of 1986 an explosive release of carbon dioxide from Lake Nyos in Cameroon killed over 1700 people. This release appears to have been triggered by a relatively small disturbance that lifted carbon dioxide-saturated water up to a depth of oversaturation at which point CO_2 came out of solution as a buoyant vapor (Zhang, 1996; Ladbury, 1996). Ocean disposal of CO_2 also involves relatively large quantities of carbon dioxide in the water column, and so there are superficial similarities to the deep lake injection scenario, and possibly the dense plume injection scenario. It will be shown, however, that the requisites for this type of "Limnic Eruption" are not met by either scenario.

Lake Nyos is a vertically stratified lake with a depth of about 200 meters. It is located in a volcanically active region and CO_2 diffuses up through the water column from cooling magma at the bottom of the lake. The lake does not experience annual turnover, and several chemoclines are present. The first is located at a depth of only 7 meters, and separates water that is essentially fresh, from water with a large amount of dissolved CO_2 . It is estimated that at saturation Lake Nyos contains about 1 km^3 (STP) of CO_2 , and that at present the lake is 25% saturated (Oskarsson, 1990). The eruption in 1986 released about $(1-3) \times 10^8 \text{ kg}$ of CO_2 over a period of about 4.5 hours (Zhang, 1996), so that it is thought that the lake was close to saturation, and possibly even over-saturated, over a significant depth before the eruption.

It is not known exactly what triggered the eruption; however, hypotheses include the sinking of cold rain water, a heavy flood, an internal wave, or a landslide (Zhang, 1996). It is thought that mixing started to occur across a chemocline at a depth of about 40 meters. As CO_2 -enriched water was lifted, more and more CO_2 was released from solution until the disturbance began to lift water from deeper depths, and the mixing became even more vigorous. It is worth noting that not all of the available CO_2 was liberated. It is postulated that the eruption terminated as the column began to entrain shallow, unsaturated water.

In summary, a Lake Nyos - type eruption requires:

- A large, concentrated, carbon dioxide inventory.
- Some sort of trigger or perturbation that lifts saturated or under-saturated water to a region where it is over-saturated and the CO₂ released from solution is positively buoyant.
- Positive feedback. As CO₂ enriched water moves up, more and more CO₂ is released from solution causing greater buoyancy leading to more water movement, more CO₂ release, etc. If this feedback is not present, mixing with ambient water will stop the eruption.

Deep Lake

Clearly, a deep CO₂ lake on the ocean floor meets the first requirement of a significant carbon dioxide inventory. Examining the remaining two criteria, however, it appears unlikely that a mechanism exists to trigger or sustain such an eruption.

In the case of a deep lake, the trigger needed to begin any disturbance would have to be much bigger than the relatively small perturbation that initiated the Lake Nyos eruption. The Lake Nyos event was initiated at a relatively shallow depth; consequently, CO₂ came out of solution in the vapor phase and was a strong source of positive buoyancy. A deep lake would be located at a minimum depth of about 3700 meters so that the liquid CO₂ in the lake is more dense than the CO₂ saturated seawater above the lake; any CO₂ that came out of solution due to a disturbance would contribute negative buoyancy and act to restore the stable lake. In order to trigger instability, the disturbance would have to be great enough to move a significant amount of CO₂ up to a depth of about 2800 meters where the ambient conditions are such that the liquid CO₂ coming out of solution would be slightly positively buoyant.

If we assume that a volcanic or seismic event might be strong enough to trigger instability, we still need a mechanism for this instability to grow before an eruption is possible. The Lake Nyos eruption was made possible by strong positive feedback. Even with the assumption that we are able to lift the saturated seawater up into a region where the CO₂ released is positively buoyant, both the acceleration due to this buoyancy and the feedback experienced are orders of magnitude smaller in the deep ocean. The three principal reasons are that below about 500 meters the stable form of CO₂ is liquid, and even in the region where this liquid is positively buoyant, the density difference is not nearly as great as between seawater and CO₂ gas. The second reason is that the saturation gradient in the deep ocean is not

very steep. For each meter lifted in the deep ocean, very little additional CO_2 is released. Finally, unlike in the Lake Nyos case, the surrounding ambient water is very much undersaturated so that any mixing causes redissolution of the CO_2 and loss of the buoyancy force. The saturation gradient, the buoyancy force, and the resultant feedback in terms of additional acceleration per meter rise for a parcel of water that undergoes no mixing are shown in Figure 1. It can be seen that the level of positive feedback in the deep ocean is orders of magnitude smaller than in the shallow ocean (depths similar to those in Lake Nyos), making it very difficult for any disturbance to propagate up to the shallow region.

If it were possible for this type of disturbance to occur without any mixing, a small stable source of buoyancy would be sufficient; however, it is not conceivable to expect a parcel of water to rise several kilometers without either causing some turbulence, and hence mixing, or rising so slowly that diffusion would begin to play some role. It is also important to note that in the Lake Nyos case water that mixed with the initial disturbance was also near saturation and did little to dilute the source of potential buoyancy, while in the case of the deep lake, the ambient CO_2 levels for most of the depth are very low.

If disturbance to the deep lake were to be created, the most appropriate scenario would be the creation of a short term, high CO_2 flux droplet plume. Ambient seawater entrained into this plume could conceivably draw denser liquid CO_2 from a lake upwards into the plume. The situation can be analysed by reference to studies of selective withdrawal in a rotating fluid (Whitehead *et al.*, 1977, Whitehead, 1980), treating the plume entrainment as a point sink. Assuming a density difference of 1% between the liquid CO_2 in the lake and the ambient seawater at the sink location 1000 meters above the lake surface the approximate plume entrainment flow required to entrain even a fraction of the more dense liquid CO_2 1000 meters below would need to exceed $20000 \text{ m}^3/\text{s}$ for a disturbance that lasted about a day. (A longer disturbance would need a smaller flow.) For comparison, a droplet plume produced from the CO_2 emitted by 100 standard power plants would entrain a total of about $1000 \text{ m}^3/\text{s}$, a large percentage of which will come from recirculation. Hence, it can be safely concluded that any disturbance to the deep lake would not generate the feedback necessary for a Lake Nyos type eruption.

Dense Plume

Since the dense plume is the most concentrated of the other forms of

release, it will also be examined for instability.

The total amount of CO₂ available to be released if the whole plume water mass were suddenly lifted to the water surface without undergoing mixing is only 3.2×10^6 kg in the ten plant base case—two orders of magnitude less than the amount that was actually released in the Lake Nyos event. Even if the plume were to start off at 50% saturation, as opposed to the 25% saturation assumed in the base case model scenarios, it dilutes so quickly that the total inventory available is only slightly greater— 3.4×10^6 kg. This is only about 7 hours worth of one standard power plant's emissions, so it is less than would most likely be stored in a tank in the case of barge transport, or about the amount that would be contained in about 10 km of 40 in diameter pipeline.

The available CO₂ is very dilute. In order to release this store, 5.6×10^6 m³ of water would need to be lifted from a depth of about 1000 meters to a depth of about 200 meters where the water becomes oversaturated so that CO₂ gas comes out of solution and contributes buoyancy. A disturbance of this magnitude is highly unlikely.

As with the deep CO₂ lake, any sort of sustained disturbance due to a small quantity of CO₂ establishing a "conduit" like that created in Lake Nyos is implausible due to distance between the inventory depth and the depth at which the disturbance could become self propagating.

References

- Zhang, Y. (1996) "Dynamics of CO₂-driven lake eruptions", *Nature* 379, 57-59.
- Ladbury, Ray (1996) "Model sheds light on a tragedy and a new type of eruption" *Physics Today*, 20-22.
- Oskarsson, Niels (1990) "Carbon Dioxide burst of Lake Nyos, Camaroon modelled as periodic supersaturation in a counter current reactor." *J. Volcanic Geotherm.* 42, 307-318.
- Whitehead, John A., Jr. and Porter, D.L. (1977) "Axisymmetric critical withdrawal of a rotating fluid." *Dynamics of Atmospheres and Oceans* 2, 1-18.
- Whitehead, John A., Jr. (1980) "Selective withdrawal of rotating stratified fluid." *Dynamics of Atmospheres and Oceans* 5, 123-135.

Figure 1: CO_2 saturation gradient as a function of depth (top). Buoyancy (m/s^2) of the stable pure form of CO_2 as a function of depth (middle). Positive feedback in terms of additional acceleration due to a one meter rise ($m/s^2\cdot m$) of a parcel of CO_2 saturated water (bottom).

Appendix 5: Revisions to the London Dumping Convention

As of this writing, the London Dumping Convention (LDC) is undergoing revisions which could be implemented as early as late 1996. The revisions would appear to significantly affect the way in which CO₂ discharged from a ship (*e.g.* dry ice, towed pipe or deep lake scenario) is treated. Note that the LDC applies to pollutants dumped to the sea from a ship (or an aircraft), but not those conveyed to sea via pipe.

As described in Topical Report 6, the LDC currently classifies marine pollutants according to their severity by assigning them to one of three annexes ranging from most hazardous (Annex I) to least hazardous (Annex III). CO₂ is not listed on any of the annexes, but would most likely have been assigned to Annex III. Under the proposed revisions, the list of annexes would be replaced by a "reverse" list which identifies pollutants which are *exempted* by the Convention. In principle, it would violate the Convention to discharge any industrial pollutant which causes an impact to the marine environment and is not on the "reverse" list. CO₂ is clearly an industrial pollutant which causes some impact to the marine environment and *it is not on the list*. Procedures are being included for amending the list. At a minimum, however, this would place the burden of proof on the jurisdiction(s) that wished to discharge the CO₂ to demonstrate that such disposal is environmentally reasonable.