Environmental Impacts of Carbon Dioxide Ocean Disposal: Plume Predictions and Time Dependent Organism Experience

by

Jennifer Ann Caulfield

Submitted to the Department of Civil and Environmental Engineering in partial fulfillment of the requirements for the degree of Master of Science in Civil and Environmental Engineering at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Abstract

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.

Each 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 determine the probabilistic exposure of passive organisms drifting through the plume. The mortality to zooplankton due to a time varying exposure to low pH was determined by using a toxicity model developed as part of the project coupled to the random walk model. The plume was described in terms of total organism mortality as well as spatial deficit of organisms.

Because pH is a stress with a threshold effect, it is possible to design injection scenarios that result in zero mortality. Dispersion methods, for example, were found to cause zero mortality, while possibilities also exist to design a droplet plume release that causes no mortality. 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. 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.

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Chapter 1

Introduction

Ocean disposal of power plant CO$_2$ emissions is one strategy that has been suggested to slow the rise of atmospheric CO$_2$ concentrations and avoid some of the possible effects of global warming. Currently a large fraction of atmospheric emissions find their way into the ocean; however, this process has a time scale of about a thousand years. Direct injection of CO$_2$ into the deep ocean has the potential to both reduce peak atmospheric CO$_2$ levels and to slow the rate of change of atmospheric concentrations—two factors that have been linked to large scale irreversible climate change.

This work has been done as part of a DOE sponsored project to evaluate the environmental impacts of ocean disposal of CO$_2$. The full topical reports and executive summary will be completed in September of 1996. The material covered in this thesis is limited to evaluating the near field impact of CO$_2$ disposal using a variety of different injection methods. The analysis includes a physical description of plume extent for the various cases. Time-varying organism exposure is also determined in a probabilistic sense for organisms that experience the plume, and mortality is calculated using a method [6] designed for exposure over a range of pH. This information provides several additional measures of impact. The dependence of impact on a variety of engineering and environmental parameters is explored, and recommendations are given on mitigating the possible negative effects of ocean disposal.

Basin and global ocean effects of CO$_2$ disposal at several possible injection sites
were studied by Scientific Applications International Corporation (SAIC) with a Mesoscale Ocean Dispersion Model using simulations over three years [2]. Longer term impact (hundreds of years) was studied using a Global Carbon Cycle Model.

Related work has been done by David Auerbach in developing the method used to evaluate the time varying exposures as well as in analyzing the legal and policy implications of ocean disposal of carbon dioxide emissions [6].

Finally, environmental impacts of various possible transportation methods will be explored in the final report [14].
Chapter 2

Scenarios and Loadings

2.1 Standard Power Plant

For this project, emissions of a standard power plant are taken as 130 kg/s carbon dioxide, where the standard power plant is a 500 $MW_e$ pulverized coal fired power plant with capture of 90% of the $CO_2$ with an energy penalty of 20%. Coal was chosen as a fuel because it produces 85% of the $CO_2$ emissions from power plants in the U.S. [3]. Because an individual power plant is the smallest unit considered, a moderate sized power plant of 500 $MW_e$ net power output (i.e. after capture) was chosen. This is a common size for coal plants and as emissions of multiple units of this size plant will also be considered, the results may be interpolated for cases that fall between the standard scenarios.

The standard emissions of a 500 $MW_e$ pulverized coal fired power plant were made consistent with the International Energy Agency (IEA) Greenhouse Gas R & D Programme studies, as follows:

- Mass flow (kg/s) 606.25
- Pressure (bar) 1.016
- Temperature($^\circ$C) 93.1
- Molecular Weight 29.2
Composition (molar 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$_2$ 666 mg/m$^3$ (STP)

These emissions have a mass flow of 115 kg/s carbon dioxide. The trace gases of sulfur dioxide and NO$_2$ 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 as standard. 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 process is 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% x (a-b)/a, where a = net power output with no CO$_2$ controls and b = net power output with CO$_2$ controls. The energy penalties quoted below include initial CO$_2$ 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 [15]:

<table>
<thead>
<tr>
<th>Energy Source</th>
<th>Today</th>
<th>Future</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Coal</td>
<td>38%</td>
<td>22%</td>
</tr>
<tr>
<td>Gas</td>
<td>24%</td>
<td>15%</td>
</tr>
<tr>
<td>Advanced Coal</td>
<td>17%</td>
<td>10%</td>
</tr>
</tbody>
</table>

Considering that implementation of ocean disposal with the current energy penalty
for a coal plant would be neither environmentally nor 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 is summarized below:

<table>
<thead>
<tr>
<th>Net Energy Produced</th>
<th>Release of Carbon Dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>To Atmosphere</td>
</tr>
<tr>
<td>Without Capture</td>
<td>500 MWₑ</td>
</tr>
<tr>
<td>With Capture</td>
<td>500 MWₑ</td>
</tr>
</tbody>
</table>

2.2 Scenarios Considered

The emissions loadings that have been studied are multiples of the standard power plant. The impact of the emissions from one power plant will be studied in the near field, as will 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 due to economy of transport. The near field models will be injection technique specific and will provide information about the distribution of carbon dioxide species in an area on the order of 100 km around the point of injection. These local models will 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 released from a barge towed pipe,
- a droplet plume injected at 1000 meters, and
- a dense CO₂ seawater plume injected below 500 meters.
Chapter 3

Ambient Ocean

3.1 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 [39]. Profiles of temperature, salinity, total inorganic carbon, and total alkalinity are shown in Figure 3-1.

The total inorganic carbon is partitioned among carbonic acid, bicarbonate, and carbonate in the following manner [27]:

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

$$[H_2CO_3^*] = C_T/(1 + \frac{K_1}{[H^+]}) + \frac{K_1K_2}{[H^+]^2}$$

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

$$[CO_3^{2-}] = C_T/(\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1)$$
Figure 3-1: Average northern ocean values measured by GEOSECS expedition.
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 alkalinites. 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:

\[
TAlk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + [B(OH)_4^-] - \\
[H_3PO_4] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3]
\]

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

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

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

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

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 [25]. 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 3-2.
From these relationships an initial pH profile was calculated. As can be seen in Figure 3-3, 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 3-4 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, 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 3-4, which corresponds to the conditions at about 1000 meters, is a good description of the overall relationship between additional carbon dioxide resultant pH.
Figure 3-3: Initial ambient pH profile.

Figure 3-4: pH resulting from addition of carbon dioxide.
3.2 Physical Properties

3.2.1 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 OTEC sites in the late 1970's [7, 26, 13]. 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[2], 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 results in an underestimation of surface current speeds and a possible overestimation of deep ocean current speeds.

3.2.2 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 [34] (See Figure 3-5) 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, $\sigma_{rc}^2$, which is equivalent to $2\sigma_x^2$, where $\sigma_x^2$ 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 $\frac{\sigma_x^2}{4t}$ while the effective diffusivity is defined as $\frac{d \sigma_x^2}{dt}$. From these dye study observations, the one-dimensional equivalent effective diffusivity has been determined to be:

$$E_h \cong 0.006t^{1.3}$$  \hspace{1cm} (3.1)

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:

$$E_h \cong 0.0044l^{1.15}$$  \hspace{1cm} (3.2)

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

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 SF₆ as a tracer. Preliminary results indicate that the mixing after a year is of the same order as that predicted using Okubo’s relation [21, 43]. 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.

3.2.3 Stratification

Because of the importance of buoyancy effects in the mixing and distribution of excess CO₂ 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 3-1). The results of the calculation are shown in Figure 3-6.
3.3 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 5 a method to assess the experience of low mobility organisms is outlined and the range of experiences of a 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 4

Injection Scenarios

This chapter will quantify the physical impact of CO$_2$ 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 is a strategy which attempts to isolate all or a portion of CO$_2$ emissions from the environment. An example of an ocean disposal method which provides an element of isolation is a deep CO$_2$ lake [31, 29, 32]. This option is outside the scope of this work.

4.1 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.
4.1.1 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 $CO_2$ 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 $kg/m^3$ [30], 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 of solid $CO_2$ in the ocean [30]. The laboratory rate is given in $g/s - cm^2$ by

$$\text{Mass Loss} = 6.6 \times 10^{-5} u + 2.6 \times 10^{-3}$$

(4.1)

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 4-1 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 [40] as

\[ l_m \approx K(C_D \ Area \ x_w)^{1/3} \quad (4.2) \]

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

$$E_{wake} \approx \frac{1}{2} \frac{d(t^2_{m})}{dt}$$  \hspace{1cm} (4.3)

The effect of the introduced turbulence on diffusivity is added to the ambient diffusivity, as described in Section 3.2.2 to yield the total diffusivity, $E_t$. The sum is then used to determine $\sigma^2$,

$$\sigma^2 = 2 \int E_t(t)dt + \sigma^2_o$$  \hspace{1cm} (4.4)

The distance $x$ is mapped using time $t$ and the ambient current speed, $u_a$. Figure 4-2 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,

\[ C(x, y) = \frac{\bar{M}/u_a}{\sqrt{2\pi\sigma}} \exp\left(\frac{-y^2}{2\sigma^2}\right) \]  \hspace{1cm} (4.5)

where \( \bar{M} \) 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 6.

**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 3.2.2).
Figure 4-3: pH 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.
Figure 4-4: Liquid CO₂ sprinkling from the pipe towed by vessel. from Ohsumi [33].

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 4-3.

4.1.2 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 [28, 17]. 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 4.1.1). It differs in that the vertical distribution is considered to be uniform over the depth range chosen,
the frame of 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 [45]. The wake due to the pipe can be considered to be two-dimensional, so that the mixing length is given by [40]

\[ l_m \approx 0.252(0.5 C_D d x)^{1/2} \]  

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 3.2.2).

The results for the base case are shown in Figure 4-5, where the distances given are relative to the pipe. The plume formed is very thin, only meters in the case of
Figure 4-5: pH 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.
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.

4.2 Droplet Plume

The first dissolution method considered is the formation of a droplet plume. At intermediate depths, liquid CO$_2$ is less dense than seawater and liquid CO$_2$ 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.

4.2.1 Physical Model

Plume Model

The near-field analysis of the droplet plume followed a modification of Liro et al. [22]. 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 CO$_2$ concentrations and to include the effect of dissolution on
plume water density using a relationship from Drange and Haugan[12].

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 CO$_2$ 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.

**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.* [19]. 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:

\[
\begin{align*}
l_H &= \frac{0.13\bar{S}Q_o N}{2u_a^2} \quad (4.7) \\
l_V &= \frac{1.2u_a}{N} \quad (4.8)
\end{align*}
\]

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:

\[
N = \left(\frac{\bar{S}}{\rho_a} \frac{\partial \rho_a}{\partial z}\right)^{\frac{1}{2}}
\]
where \( g \) is the acceleration due to gravity, \( \rho_a \) 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 4-6 is a best fit to the governing equations in this region [19, 35]. 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:

\[
b = l_H (9.2 + 6.3 \frac{x}{l_H})^{\frac{1}{2}} \tag{4.10}
\]

\[
h = \frac{l_V l_H \pi}{b} \tag{4.11}
\]

**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 [35] has been chosen 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...
Figure 4-6: Nondimensional half-width and half-thickness of the intermediate-field region for the case of linear stratification.
formulation based on Jirka's equations for linear stratification [35]:

\[ x_t = \left( \frac{u_0^2 l_H}{550 \alpha^3} \right)^{\frac{1}{2}} - 1.46 l_H \]  

(4.12)

\( \alpha \) is the coefficient of the effective diffusivity relationship to length scale, where \( E_h = \alpha L^{4/3} \). An appropriate \( \alpha \) can be chosen in order to make this relationship consistent with that of Okubo (See Section 3.2.2). 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 4.2.3. 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 \( cm^2/s \) 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:

\[ \frac{\partial c}{\partial t} = E_y \frac{\partial^2 c}{\partial y^2} \]  

(4.13)

The solution to this problem can be found by generalizing the solution originally given by Brooks [8] and for the case without decay, can be stated:

\[ \frac{c}{c_o} = \frac{1}{2} \left( \text{erf} \left[ \frac{y + b/2}{2b} \right] - \text{erf} \left[ \frac{y - b/2}{2b} \right] \right) \sqrt{\frac{24}{\left( \frac{12(2-n)E_{w0}x}{ab^2} + 1 \right) \frac{2}{\frac{2}{n} - 1}}} \]  

(4.14)
Figure 4-7: Definition sketch for Brooks' model.

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 3.2.2, $n$ is taken to be 1.15 based on empirical data.

4.2.2 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. [22]. However, to the extent that this report includes the effect of the dissolved $CO_2$ 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 4-8, increasing the number of ports leads to greater total entrainment. The base case chosen was ten ports per plant each
Figure 4-8: 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).
with a $CO_2$ 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 6 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 4-8 also shows the effect of larger initial droplet size. Liro et al. [22] calculated a maximum stable droplet radius of 1.25 cm for a liquid $CO_2$ 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 $CO_2$. As a result, 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
Figure 4-9: 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).
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 4-9 shows the ambient stratification for the region 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 p\^led layers is needed.

**Clathrate Hydrate Formation**

At intermediate depth there is a possibility of clathrate hydrate formation at the droplet-water interface [44, 16]. 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[44]. This study involved liquid CO\textsubscript{2} at rest, and its application to a droplet plume environment requires some caution; however, it does suggest that the effect may be significant. The base case mass transfer coefficient is that chosen by Liro et al. [22] based on studies by Clift et al. [9]

\[
K = 1.25\left(\frac{\rho_w - \rho}{\rho_w}\right)^{1/4}D^{1/2}d^{1/4}
\]  

(4.15)

where \(K\) is the mass transfer coefficient, \(g\) is the acceleration due to gravity, \(\rho_w\) is the density of water, \(\rho\) is the droplet density, \(D\) is the molecular diffusivity of CO\textsubscript{2}, and \(d\) is the effective droplet diameter.

Predicted rise and trap heights were found for releases between 800 and 2000 meter
Figure 4-10: 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.
depths for mass transfer rates of both one-half and one-tenth of the base case. The results are presented in Figure 4-10. 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 4-10. 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.

4.2.3 Thickness of the Intrusion Layer

Transition to Diffusion Model Occurring at Characteristic Length

In later analysis (See Chapter 6) 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 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 4-11. 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$^4$ 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 4-12. 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
Figure 4-12: Relationship between diluted flow and intrusion layer thickness in different environments with alternate transition assumption. The top figure shows 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$^4$. 
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 to that due to gravitational spreading, but the transition point used is that where vertical spreading becomes insignificant.

In the bottom graph of Figure 4-12 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 4-13 shows contour plots of the intrusion layer thickness resulting from a given diluted flow rate (100 $m^3/s$ on the left, 1000 $m^3/s$ 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.
Figure 4-13: 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 $m^3/s$.

4.2.4 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 3.2.3.
- 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 3.2.2).

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
Figure 4-14: pH 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.
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 4-14.

4.3 $CO_2$-Enriched Seawater Plume

Because dissolution of $CO_2$ increases the density of seawater, it is possible to form a negatively buoyant plume[12, 11]. 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 $CO_2$ must be a sizable fraction of the saturation concentration. As a result, injection would require some sort of initial mixing device [4]. 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.

4.3.1 Physical Model

Gravity Current Model

Earlier gravity current models [12, 11] 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 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 [37, 12, 11]. In this model, however, the aspect ratio was considered to be topography dependent and hence Coriolis force was neglected. The equations are as follows:

\[(AU)_\xi = E(Ri_o)WU\]  \hspace{1cm} (4.16)

\[(AU^2)\xi = Ag'sin\theta - \frac{C_DW}{cos\phi}U^2\]  \hspace{1cm} (4.17)

\[(AUg')\xi = -AU^N^2sin\theta\]  \hspace{1cm} (4.18)

\[(X)\xi = sin\theta\]  \hspace{1cm} (4.19)

where $\xi$ 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 4.9. The geometry assumed is shown in Figure 4-15. 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 $\theta$, and the side slope is $\phi$. $E$ 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.* [19], described in Section 4.2.1, 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 4.2.1. 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.

4.3.2 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 4.2.1. 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 [41] and Lofquist[24], which is shown in Figure 4-16. Entrainment decreases as the Richardson number increases, where the overall
Richardson number is defined as

$$Ri_o = \frac{\Delta \rho \, gh \cos \theta}{\rho_a \, U^2} \quad (4.20)$$

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 [37], hence a $C_D$ of 0.02 was chosen for the base case. Sensitivity to this parameter is shown in Figure 4-17. 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.

**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 [23]. 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 4-18. 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 depth sunk.
Figure 4-18: 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.

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 4-18.

Initial Concentration and Loading

Using the base case topography, sensitivity to initial excess CO₂ concentration and loading was examined. In Figure 4-19 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 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
Figure 4-19: Distance (m) sunk by a CO₂ 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 CO₂ concentrations.

...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 4-20.

4.3.3 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 3.2.3.
- Initial excess CO₂ concentration: 12 kg/m³ (approximately 20% of saturation).
- Drag coefficient: 0.02.
- Ambient turbulence as parameterized by Okubo (See Section 3.2.2).
Figure 4-20: 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).

- One half of a symmetrical distribution due to effect of coastline.

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 m$^3$/s, and a pH of 5.5 versus 10000 m$^3$/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 m$^3$/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.
Figure 4-21: pH resulting from the ocean CO₂ disposal in a 5 cm/s current as a dense plume, the x-axis represents the coastline. Top: Emissions from one standard power plant. Bottom: Emissions from ten standard power plants.
<table>
<thead>
<tr>
<th></th>
<th>Volume of water with pH under 7 (km$^3$)</th>
<th>Distance to pH of 7 (km)</th>
<th>Minimum pH (after dissolution)</th>
<th>Minimum pH (diffusion regime)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dry Ice</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 plant</td>
<td>0.001</td>
<td>0.09</td>
<td>6.3</td>
<td>6.1</td>
</tr>
<tr>
<td>10 plants</td>
<td>1.1</td>
<td>2.2</td>
<td>5.8</td>
<td>7.4</td>
</tr>
<tr>
<td><strong>Towed Pipe</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1 plant</td>
<td>0.00004</td>
<td>0.2</td>
<td>6.5</td>
<td>7.2</td>
</tr>
<tr>
<td>10 plants</td>
<td>0.3</td>
<td>14</td>
<td>5.7</td>
<td>6.2</td>
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<tr>
<td><strong>Droplet Plume</strong></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1 plant</td>
<td>1.8</td>
<td>23</td>
<td>5.5</td>
<td>6.0</td>
</tr>
<tr>
<td>10 plants</td>
<td>130</td>
<td>60</td>
<td>5.5</td>
<td>6.0</td>
</tr>
<tr>
<td><strong>Dense Plume</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 plant</td>
<td>7.2</td>
<td>94</td>
<td>4.0</td>
<td>5.7</td>
</tr>
<tr>
<td>10 plants</td>
<td>510</td>
<td>690</td>
<td>4.0</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 4.1: Summary of results of modeled scenarios. Dry ice distance and pH values are from a depth of 1000 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 4-21.

### 4.4 Conclusions

Table 4.1 summarizes the base case scenarios with some appropriate physical properties of the resulting pH distributions. Depending on capture technology, levels of trace constituents of the emissions may be of concern. Figure 4-22 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 CO$_2$-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.
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 5

Organism Experience

5.1 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 [6]. Since organisms will experience a range of pH, their experience must be defined as pH experienced as a function of time.

This chapter will provide a brief overview of the method used to evaluate mortality due to time varying pH exposures (Section 5.2), and some general background on relative diffusion (Section 5.3), and will describe three approaches to defining organism experience (Section 5.4). Because the most accurate stochastic method is relatively complicated and computationally intensive, two simpler methods are also explored. The limitations of the simplified approach are explained and results obtained using the stochastic method are presented in Section 5.6.

5.2 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 [6]. The results are shown in Figure 5-1.

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 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 5-2 where the stress level is represented by equivalent hours at pH of 6.5.

More information about this method can be found in David Auerbach’s Master’s Thesis [6].

5.3 Relative Diffusion of Organism and Plume

Because vertical diffusivities are so much smaller than horizontal diffusivities (See Section 4.2.1), 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
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 5-1). 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 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 3.2.2, empirical correlations of the variance ($\sigma_{rc}^2$) of mass distribution with time were presented. These were based on observations from point releases of dye. Diffusivity, $E$, is defined as

$$ E \equiv \frac{d \sigma_{rc}^2}{dt} $$  \hspace{1cm} (5.1)

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

$$ E = a\sigma^m t^n $$  \hspace{1cm} (5.2)

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 a slightly different shape (fourth moment) but 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}
Figure 5-3: Schematic of scale dependent diffusion (from Richardson [36]).

The scale dependent nature of natural turbulence was first described by Richardson [36]. Figure 5-3 is that used by Richardson [36] 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

$$\frac{\partial q}{\partial t} = \frac{\partial}{\partial l} \left( F(l) \frac{\partial q}{\partial l} \right)$$

(5.3)

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 [38] 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 [34] (See Section 3.2.2) 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 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 [18].

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 \( \frac{1}{4} \frac{d}{dt} \left( \sigma_{xx}^2 \right) \), 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 3.2, becomes

\[
E = 0.001811.5 \quad \text{(5.4)}
\]

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 5-4, 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 5-4)

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, \( y_o \), is at a distance \( y \), then Equation 5.3 becomes

\[
\frac{\partial p}{\partial t} = \frac{\partial}{\partial y} \left( F(y) \frac{\partial p}{\partial y} \right) \tag{5.5}
\]

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

\[
\frac{\partial p}{\partial t} + \frac{\partial}{\partial y} \left( \frac{\partial F}{\partial y} \right) = \frac{\partial^2}{\partial y^2} \left( F(y)p \right) \tag{5.6}
\]
where \( \frac{\partial \Phi}{\partial y} \) is the apparent or "pseudo" velocity.

### 5.4 Possible Approaches

The following three approaches attempt to take into account the variation of exposure with time due to the relative horizontal position of the plume centerline and the organisms considered. As in the physical descriptions, vertical variation is neglected as it is expected to be minimal, and its exclusion leads to more conservative results.

#### 5.4.1 Stochastic Simulation

Although no general analytical solution exists for Equation 5.3, 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 is then determined from the spatial distribution of pH. Each experience could then be integrated over time as described in Section 5.2 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 is divided 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 accurately 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 variation in time (distance); in the case of the one plant droplet plume scenario, this time step was one day. The grid set up for the one plant droplet plume scenario is superimposed on the pH contours in Figure 5-5. 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 each path times the number of organisms expected to have traveled this path. When the number of pathways becomes too large, the experiences are grouped according to stress level (i.e. equivalent hours at a given pH), and each set of organisms continues its probabilistic journey through the plume.

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

Because the stochastic method is computationally intensive, different formulations of an "average" experience were attempted. The first 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, $y_0$, from the plume centerline. This average position can be determined from the pseudo velocity described earlier.

A variation of this method was to use the probability distribution of the separation distance. When this information is combined with the information obtained from the physical modeling in Chapter 4, the experience can be integrated spatially to obtain a representative pH at every point in time for a given entrance position. This is illustrated schematically in Figure 5-6, where the plane perpendicular to the current at the point of injection has been 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 $(y_0, z_0)$. 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. A sample probability distribution is shown on a spatial concentration map in Figure 5-6. For the entrance position and point of time chosen, the average concentration can be expressed as,

$$\bar{c}(y_0, z_0, t) = \int c(y, z_0, x/u)p(y, z_0, x/u)dy$$  \hspace{1cm} (5.7)

This average experience can then be integrated with respect to time (see Section 5.2) to give an "average" mortality.

Unfortunately, because mortality is a non-linear function of low-pH exposure, both these methods suffer from the problem that the result depends on the designation of the initial plane. This can be shown by redefining the initial plane in Figure 5-6 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. Since the effect of pH are non-linear (see Figure 5-1), averaging this experience with another that is most likely further away from the plume centerline during the same time period would underestimate the effect on the population.

### 5.4.3 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 dense plume scenario is much longer than the other scenarios, the inaccuracy due to large spatial organism distributions is much larger than in the other scenarios. For this reason, an impartial 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.

5.5 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 [10]. The simplest form for a single species population is:

\[
\frac{dN}{dt} = rN(1 - \frac{N}{K})
\]  

(5.8)

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 normal-
ized by the equilibrium population, so that

\[
\frac{d N}{dt K} = r \frac{N}{K} (\text{deficit})
\]  

(5.9)

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 [20] 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 (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 [42]. 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 [20]. 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.
5.6 Organism Experience for Scenarios Analyzed using the Stochastic Approach

Because the exposures due to the dispersion methods 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.

5.6.1 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 5-8. 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 before which there is no mortality. 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 5-8), 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 5-2)

5.6.2 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 not fall below the mortality threshold. As a result the level of mortality and the corresponding deficit are much higher. Figure 5-9 (top) illustrates the resulting zooplankton deficit using the stochastic method to evaluate the one plant base case
Figure 5-8: Deficit of zooplankton caused by the base case one plant droplet plume scenario (top). Deficit of zooplankton caused by the base case ten plant droplet plume scenario (bottom).
Figure 5-9: Deficit of zooplankton caused by the base case one plant dense plume scenario (top). Deficit of zooplankton caused by the base case ten plant dense plume scenario (bottom).
<table>
<thead>
<tr>
<th></th>
<th>Integrated Total Mortality (km²)</th>
<th>Maximum Mortality Flux (m³/s)</th>
<th>Highest Spatial Deficit (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dry Ice</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 plant</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>10 plants</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td><strong>Towed Pipe</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 plant</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10 plants</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td><strong>Droplet Plume</strong></td>
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<td>1 plant</td>
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<tr>
<td>10 plants</td>
<td>800</td>
<td>46900</td>
<td>95</td>
</tr>
</tbody>
</table>

Table 5.1: Summary of expected zooplankton mortality for various base case plumes

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 5-9 (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 5-1) or Figure 5-2 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.

### 5.7 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 are shown in Table 5.1. Mortality flux and integrated total mortal-
ity 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 4.1, with the biological impacts assessed in Table 5.1, 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 will be explored in Chapter 6, with particular attention paid to the area around the mortality threshold.
Chapter 6

Impact Model Sensitivities

Although scenario-specific sensitivities related to the physical dimensions of the plumes were explored in Chapter 4, 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 6.1. Section 6.2 illustrates the factors that correlate most strongly with impact, in Section 6.3 the differences among the base cases are explained in terms of these parameters, and in Section 6.4 ways of eliminating the near-field impact of the droplet plume are explored.

6.1 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 6.1.
<table>
<thead>
<tr>
<th></th>
<th>Integrated Total Mortality (km$^3$)</th>
<th>Maximum Mortality Flux (m$^3$/s)</th>
<th>Highest Spatial Mortality Deficit (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base Case</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Droplet Plume</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 plant</td>
<td>0.45</td>
<td>307.00</td>
<td>11</td>
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<tr>
<td>10 plants</td>
<td>162.00</td>
<td>27500.00</td>
<td>69</td>
</tr>
<tr>
<td><strong>Dense Plume</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 plant</td>
<td>10.60</td>
<td>1980.00</td>
<td>50</td>
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<tr>
<td>10 plants</td>
<td>800.00</td>
<td>46900.00</td>
<td>95</td>
</tr>
<tr>
<td><em>with .25 decrease in pH curves</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Droplet Plume</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 plant</td>
<td>0.03</td>
<td>19.00</td>
<td>0.86</td>
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<tr>
<td>10 plants</td>
<td>72.80</td>
<td>12650.00</td>
<td>50</td>
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<tr>
<td><strong>Dense Plume</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 plant</td>
<td>3.40</td>
<td>730.00</td>
<td>32</td>
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<tr>
<td>10 plants</td>
<td>387.00</td>
<td>23070.00</td>
<td>79</td>
</tr>
<tr>
<td><em>with .25 increase in pH curves</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Droplet Plume</strong></td>
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<tr>
<td>1 plant</td>
<td>2.06</td>
<td>1221.00</td>
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<tr>
<td>10 plants</td>
<td>248.00</td>
<td>47890.00</td>
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</tr>
<tr>
<td><strong>Dense Plume</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1 plant</td>
<td>17.00</td>
<td>3985.00</td>
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</tr>
<tr>
<td>10 plants</td>
<td>113.00</td>
<td>77210.00</td>
<td>99</td>
</tr>
</tbody>
</table>

Table 6.1: Sensitivity of integrated mortality and maximum mortality flux to the determination of the pH-Mortality curves for the base case dissolution scenarios.
As expected, lowering the pH curves by a quarter of a unit (raising them on the graph in Figure 5-1), 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 5-2, 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.

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.

### 6.2 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 6-1 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 per area, where the mass loading per area is defined as the
Figure 6-1: Steps for determining biological impact from injection scenario.

- Size of independent injection
- Dilution from near field mixing
- Thickness, \( h \), from intrusion model

- Chemistry
- Far field mixing

- Probability of organism paths
- pH-Mortality curves

Injection Scenario

Independent Mass Loading

Time to pH 7

Biological Impact
Figure 6-2: Relationship between time to a centerline pH of 7 and total mortality per 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.

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, these two values are plotted in Figure 6-2 for simulations involving a range of initial concentrations, 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,

\[
K = \frac{d}{dt} \frac{\sigma^2}{2} = a\sigma^n
\]  

(6.1)

where \( \sigma \) is the standard deviation, \( a \) is a constant, and \( n \) is the exponent that reflects the time dependence of the diffusivity, then

\[
t = \frac{\sigma_f^{2-n}}{a(2-n)} - \frac{\sigma_o^{2-n}}{a(2-n)}
\]  

(6.2)

where \( \sigma_f \) is the final \( \sigma \), and \( \sigma_o \) is the initial \( \sigma \). If a \( \sigma_7 \) 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

\[
\sigma_7 \approx \frac{\dot{m}}{u h C_7} = \frac{\text{Mass Loading}}{C_7}
\]  

(6.3)

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 6-3, 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 \( \sigma_o \), which is dwarfed by the \( \sigma_7 \) in most scenarios that lead to mortality.

Looking at Figure 6-2 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
Figure 6-3: 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$^3$. 
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 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 4.2.3 discusses the uncertainties around the ultimate thickness of the intrusion layer formed, and possible leverage points. Section 4.2.2 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.

6.3 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 6-4. It can be seen that the dense plume cases are more serious than the corresponding droplet plume cases. Although the initial concentrations are 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 6-4 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 6-5. Even though longer exposure times begin to show diminishing returns in terms of mortality flux for the more severe scenarios (See Figure 6-4), 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. 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.

6.4 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 CO₂ 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 ef-
Figure 6-5: Total integrated mortality due to the base case scenarios.

Figure 6-6: Schematic of independent droplet plume injections. The required horizontal spacing is $\lambda_h$, and the required vertical spacing is $\lambda_v$. 
Table 6.2: 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.

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 6.2 show the 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 7

Summary, Conclusions, and Recommendations for Future Research

7.1 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 [6]. 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.

7.2 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 MWₑ 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 6.4), 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.

7.3 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 entrainment 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


