

# Efficiency of Sequestering CO<sub>2</sub> in the Ocean

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## Abstract

Ocean disposal of CO<sub>2</sub> continues to be of great interest as a possible mitigation strategy for reducing atmospheric emissions of anthropogenic CO<sub>2</sub>. The ocean, and ultimately ocean sediments, naturally represents the single largest sink of CO<sub>2</sub>, and annually sequesters several gigatons of carbon from the atmosphere. The injection of additional CO<sub>2</sub> to artificially accelerate the use of the ocean as a sink for atmospheric CO<sub>2</sub> and avoid a short-term build-up of greenhouse gases has been investigated for over 20 years. Of central interest to the feasibility of ocean sequestration as a sink for anthropogenic CO<sub>2</sub> is the sequestration efficiency: i.e. over what period will a portion of the injected CO<sub>2</sub> remain in the ocean. Oceanic sites with long term sequestration characteristics are considered “efficient”. Without doing vast *in situ* field studies to investigate the sequestration characteristics of many oceanic environments, researchers have relied on ocean circulation and dispersion models to provide in-sight into the efficiency of ocean sequestration at different geographic locations and depths. These models, however, are complicated to implement and individual simulations provide characterization of only a small region of the world’s ocean. We present here a static analysis of high-resolution, global, dynamic parameters that mirror the advection and diffusion characteristics important for sequestration efficiency. The subsequent 3-dimensional sequestration efficiency map reveals the general sequestration characteristics of the entire ocean. Detailed sequestration characteristics and confirmation, however, must still be obtained through more complex dispersion modelling and direct *in situ* evaluations.

## Introduction: Ocean Sequestration Studies

The ocean represents the Earth’s single largest reservoir of natural CO<sub>2</sub>, and over 90% of all anthropogenic CO<sub>2</sub> released into the atmosphere will ultimately diffuse into the ocean. However, CO<sub>2</sub> gas transfer from the atmosphere to the deep ocean is a slow process, and equilibrium may take thousands of years. In fact, the recent acceleration of CO<sub>2</sub> concentrations in the atmosphere is due partly to the slow uptake of CO<sub>2</sub> by the deep ocean. Sequestration away from the atmosphere occurs only where seawater sinks away from the surface into the deep abyss. The slow circulatory nature of deep ocean currents dictates that gases dissolved into subducting water may remain away from contact with the atmosphere for centuries, or even millennia. This is the general premise behind ocean sequestration of CO<sub>2</sub>, where direct injection of CO<sub>2</sub> into the deep ocean might provide a temporary buffering of greenhouse gases from the atmosphere.

Historically, studies into ocean sequestration have taken one of three approaches: circulation modelling, laboratory studies, and feasibility (economic, legal, and logistical) investigations. More recently, experiments to directly inject small quantities of CO<sub>2</sub> into the ocean have been undertaken. The laboratory, economic, and direct injection studies continue to show us that with regard to many aspects, ocean injection of CO<sub>2</sub> is potentially feasible. Of particular interest are the recent direct injection studies (i.e. Brewer *et al.*, 1999), which have captured the behaviour of gas and liquid CO<sub>2</sub> in the deep ocean. These preliminary results are encouraging, suggesting that deep injection of liquid CO<sub>2</sub> may have only localized environmental impacts. Further, spontaneous hydrate formation may assist sequestration by slowing the

diffusion of CO<sub>2</sub> into the surrounding seawater. However, it is only through circulation and dispersion modelling that we can assess the longer-term impacts and likelihood that the injected CO<sub>2</sub> will remain sequestered out of the surface ocean and atmosphere.

A thorough review of CO<sub>2</sub> ocean sequestration modelling is presented by Dewey *et al.* (1996), and a more recent comparison of several Ocean Global Circulation Models (OGCMs) with carbon cycling is presented by Orr *et al.* (2000). Generally, these OGCM models have relatively coarse spatial resolution and attempt to predict the advection and diffusion of injected CO<sub>2</sub> as it circulates throughout the ocean basins. They consistently indicate, as one might expect, that deeper injection sites are more efficient than shallow sites, and that upwelling and convection regions of the ocean must be avoided. However, the scalar diffusion formulated in these coarse Eulerian models is usually parameterized to preserve the spatial structure of the temperature and salinity fields, which are maintained by boundary fluxes of heat and salt. The gradient diffusion parameterizations are not formulated for accurate tracer dispersion, and as such, typically over estimate the cross isopycnal diffusion of material (i.e. Xu *et al.*, 1999).

Tracer release experiments by Ledwell *et al.* (1998, 2000) have shown that dissolved material does not spread steadily in all directions, as gradient diffusion in an Eulerian model dictates, but rather is advected along streamlines in the flow, and only weakly mixes across isopycnal boundaries. Accurate tracer modelling in complex flows can only be accomplished with a Lagrangian formulation, where by the dissolved material is tracked as diffusive “clouds”. This was the approach of Dewey and Stegen (1995) and the Mesoscale Ocean Dispersion Model (MODM), where clouds of dissolved CO<sub>2</sub> are tracked in a high resolution, time dependant, 3-dimensional ocean. The sequestration predictions of the MODM show more complex dispersion patterns of injected CO<sub>2</sub>, with generally weaker net diffusion and longer times before the CO<sub>2</sub> re-surfaces into the upper ocean.

## **Objective**

Our present study attempts to draw on the existing body of research into ocean sequestration and develop a first order predictive tool for evaluating ocean sequestration. Our goal is to develop a static 3-dimensional map of the global ocean that distinguishes regions by sequestration efficiency, measured as the fraction of injected CO<sub>2</sub> remaining in the ocean over time. Sites that keep the CO<sub>2</sub> away from the atmosphere for a long time have high sequestration efficiency.

## **Approach**

First, we will identify the important ocean parameters that govern dispersion of a dissolved substance, and then make a composite map from these quantities that distinguishes regions of potentially good and poor sequestration efficiency. Then we will compare the predictions of this map against past OGCM simulations and individual dispersion simulations using the MODM. Following Orr *et al.*, (2000) we define Sequestration Efficiency (their  $E_i$ ) as the ratio of the injected CO<sub>2</sub> retained by the ocean to the total amount of CO<sub>2</sub> injected.

First, the important oceanic processes dictating the nature and rate of dispersion of a material in the ocean are examined. Then 3-dimensional fields of the important ocean properties are combined to produce a composite map of sequestration efficiency. Several ocean regions representing a sample of the various levels of efficiency will be discussed. Direct comparisons against previously published sequestration efficiency estimates from OGCM and MODM simulations will be presented.

## **Advection-Diffusion: The Governing Equation**

The dispersion of a material in a fluid is governed by the Advection-Diffusion equation. For a concentration of substance  $C$ , the advection –diffusion equation can be written,

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} + V \frac{\partial C}{\partial y} + W \frac{\partial C}{\partial z} = \frac{\partial}{\partial x} \left( K_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_z \frac{\partial C}{\partial z} \right) \quad (1)$$

where  $(U, V, W)$  are the advection velocities of the flow in the  $(x, y, z)$  directions, respectively,  $(K_x, K_y, K_z)$  are the scalar diffusivities in the  $(x, y, z)$  directions, respectively, and  $\partial t, \partial x, \partial y, \partial z$  are the partial derivatives in time, and the  $(x, y, z)$  directions, respectively. It should be noted that in this form, the diffusion in any one direction need not be equal to the diffusion in another, and that the diffusion coefficients are not spatially homogeneous. Generally, these terms represent, from left to right, the rate of change of concentration with time, the advection of a scalar gradient in the  $x, y,$  and  $z$  directions, balanced by material diffusion in the  $x, y,$  and  $z$  directions. The parameterization of the diffusion terms in this form draws on the similarity of turbulent and molecular diffusion, where it is assumed that molecular diffusion will be negligible and that our  $K$ s are the consequence of turbulent motions. Simply stated, (1) tells us that the concentration of a material  $C$  will change as a result of advection (terms 2,3,4) and turbulent diffusion (terms 5,6,7).

To first order we can inspect the advection-diffusion equation and identify the flow characteristics that will lead to longer sequestration times. In particular, the horizontal advection terms  $(U, V)$  are likely to be the largest contributors to changes in the scalar ( $\text{CO}_2$ ) concentration, and will be largest near major ocean current systems (i.e. the Gulf Stream or the Kuroshio). Similarly, the vertical advection term  $(W)$  may be large near upwelling regions, or areas of vertical convection. Such regions will tend to disperse the  $\text{CO}_2$  vertically and are likely to accelerate the return of injected  $\text{CO}_2$  into the upper ocean. Similarly, regions of the ocean with vigorous turbulence and mixing will diffuse the  $\text{CO}_2$ , allowing it to spread over larger areas. In general then, we seek quiescent regions of the ocean, with weak currents and minimal mixing. However, identifying quiescent regions in the ocean is not easy and only partly contributes to sequestration efficiency. In particular, due to the non-linear nature of interactions between stratified sheared flows, internal waves, and turbulence, it is not obvious that we can easily identify regions of the ocean that will be void of mixing. To aid us in this parameterization, additional oceanic properties can be identified that play a role in sequestration efficiency.

## Other Important Ocean Dispersion Parameters

Consistent with many of the findings on ocean sequestration, increased depth is perhaps the single most important parameter in long term sequestration. Given a sufficiently deep injection site, even in the presence of weak upwelling, the  $\text{CO}_2$  may remain away from the surface of the ocean for centuries. This is primarily because ocean currents and mixing generally become weaker with depth, and since our goal is to keep the  $\text{CO}_2$  away from the ocean surface, deeper injection sites tend to lead to longer sequestration. Similarly, weak stratification and regions susceptible to seasonal convection can lead to rapid venting of  $\text{CO}_2$ , even from great depths. Consequently, sites near deep convection regions, or that allow rapid advection into such regions, tend to be poor sequestration sites.

Two additional gradient quantities can lead to enhanced dispersion and accelerated out-gassing. These are regions of strong velocity shear, where flow instabilities are more likely, and regions with tilted isopycnal (constant density) surfaces. Flow instabilities tend to lead to either small-scale turbulence and mixing, in the case of strong vertical shears, or larger straining and stirring rates in regions of strong horizontal shear. Mixing and advection along isopycnal surfaces is more efficient than across isopycnal surfaces due to the suppressing influence of stratification. Subsequently, mixing and advection along tilted isopycnals can more rapidly lead to the venting of  $\text{CO}_2$  into the atmosphere.

The important oceanic properties for minimizing the dispersion of  $\text{CO}_2$  are summarized in Table 1. Turbulent mixing is represented in terms of turbulent kinetic energy dissipation ( $\epsilon$ ). Here we use  $\epsilon$  instead of diffusivity  $K$  because, to a good approximation, the dissipation of turbulent kinetic energy is proportional to turbulent diffusivity (Schmitt *et al.*, 1994) and is more readily measured and studied in the ocean. Vertical and horizontal density (isopycnal) gradients are given by  $r_z$  and  $r_x$ , respectively.

**Table 1** Ocean properties, the variable, influence on sequestration efficiency, and the typical range found in the ocean.

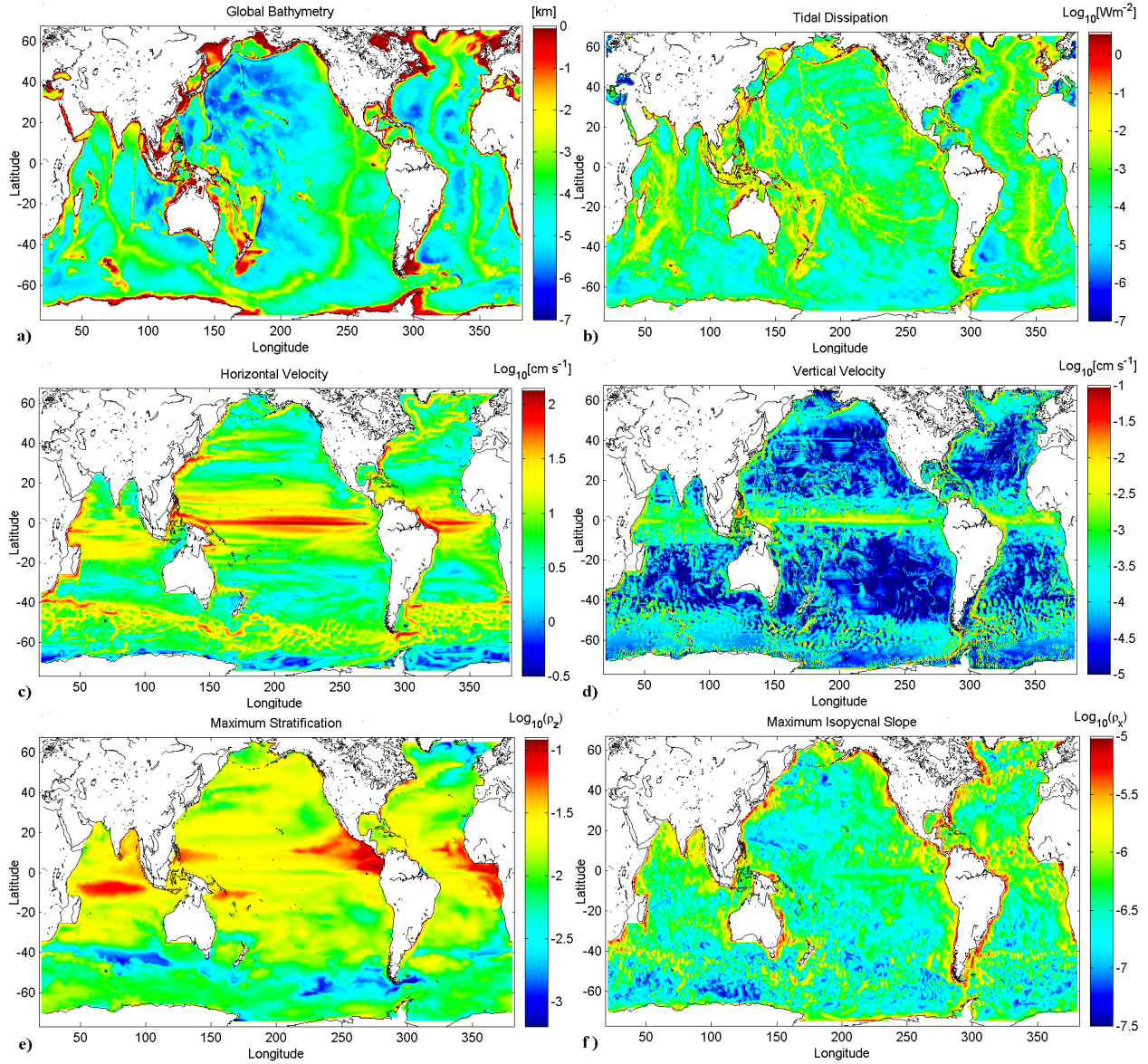
Ocean Property	Variable	Improve Sequestration	Range in Ocean
Depth	$Z$	Larger	0 – 8000 m
Horizontal Velocity	$U, V$	Smaller	0 – 2 m s <sup>-1</sup>
Vertical Velocity	$W$	Smaller	0 – 0.1 m s <sup>-1</sup>
Turbulent Mixing	$e$	Smaller	10 <sup>-7</sup> – 10 <sup>1</sup> W m <sup>-2</sup>
Stratification	$r_z$	Larger	10 <sup>-7</sup> – 10 <sup>-1</sup> kg m <sup>-4</sup>
Tilted Isopycnals	$r_x$	Smaller	10 <sup>-11</sup> – 10 <sup>-4</sup> kg m <sup>-4</sup>

### Normalized Sequestration Efficiency

From global data sets, measurements, and models, it is possible to construct global distributions of the important oceanic parameters that govern the advection and diffusion of an injected quantity in the ocean. Shown in Figure 1 are global maps of various quantities related to sequestration efficiency. Water depth (Figure 1a, Smith and Sandwell, 1997) is perhaps the most important parameter, where deeper sites are predicted to be better injection sites than shallow. However, as pointed out by Dewey and Stegen (1999), bottom roughness is also important, as it plays a significant role in dictating where mixing and turbulence are distributed (Ledwell, *et al.* 2000). Specifically, tides advect the stratified ocean across the ocean floor. Where the bottom is “rough” (generally the yellow and red regions of Figure 1a), energy is extracted from the tidal flow in the form of internal lee waves, which radiate away and subsequently dissipate through the generation of turbulence. Figure 1b is a global map of tidal dissipation considering both bottom and internal wave drag from rough bathymetry courtesy of Jayne and St. Laurent (2001). The results of Ledwell *et al.* (2000) would suggest that this map (Figure 1b) is a reasonable proxy for turbulent mixing throughout much of the water column, and therefore reduced sequestration efficiency.

Strong advection by horizontal currents (Figure 1c) and vertical motion (Figure 1d) (5 year mean fields from Semtner and Chervin, 1992), either upwelling or convection is also likely to lead to poor regions of sequestration efficiency. In these maps (1c and 1d), the maximum value in the water column has been plotted. In addition, due to the dynamic range, the logarithm of the current speed is contoured. If the CO<sub>2</sub> is injected near a strong ocean current, it will advect and spread over a large portion of the ocean, and, more likely than not, will eventually encounter a region of upwelling or vertical convection. Vertical motion permits the CO<sub>2</sub> to re-surface and out-gas into the atmosphere. Large velocities (horizontal or vertical) are typically undesirable for sequestration efficiency. In a few unique down-welling locations (i.e. Mediterranean outflow), broad regions of negative (downward) vertical velocities may assist sequestration efficiency. Deep convection at high Latitudes tends to mix the CO<sub>2</sub> vertically, sending some CO<sub>2</sub> into the deep ocean with the sinking cold water, while at the same time mixing a significant portion of the CO<sub>2</sub> up to the ocean’s surface (Bacastow and Dewey, 1996; Orr *et al.*, 2000).

Finally, density gradients, both vertical (Figure 1e) and horizontal (Figure 1f) (Levitus *et al.*, 1994) can influence sequestration efficiency. Strong stratification ( $r_z = \partial r / \partial z$ , Figure 1e) can suppress turbulent mixing and reduce vertical diffusion, thereby improving the sequestration efficiency. Regions of the ocean with strong horizontal density gradients (tilted isopycnal surfaces,  $r_x = \partial r / \partial x + \partial r / \partial y$ , Figure 1f), are likely to be regions of enhanced vertical advection and dispersion, leading to poor efficiency. These quantities are also plotted in Log<sub>10</sub> format, due to their large dynamic range, and the maximum at each geographic location has been contoured (i.e. maximum value throughout water column).



**Figure 1** Global distributions of various oceanic properties related to dispersion and sequestration efficiency: a) Ocean bathymetry, showing water depth in [m]. b) Tidal energy dissipation, a regional proxy for ocean mixing [ $W m^{-2}$ ]. c) Maximum horizontal current speed [ $cm s^{-1}$ ]. d) Maximum vertical velocity [ $cm s^{-1}$ ]. e) Maximum vertical stratification [ $kg m^{-4}$ ]. f) Maximum horizontal isopycnal slope [ $kg m^{-4}$ ].

Most of these ocean properties ( $U$ ,  $V$ ,  $W$ ,  $\rho_z$ ,  $\rho_x$ ) have a 4 dimensional structure, varying in both the horizontal and vertical directions, as well as time. Our goal is to develop a static (time independent) composite, 3 dimensional map of these parameters which could then be used as a first order indication of regions more likely to have improved sequestration efficiency. Two obvious methods are available for constructing this composite map. First is through a dimensional analysis, where by a dimensionless quantity (i.e. sequestration efficiency) is sought from a set of the important dimensional parameters (i.e. McCormack and Crane, 1973). Second is through a simple linear model of the important parameters. In this paper, we shall investigate the latter.

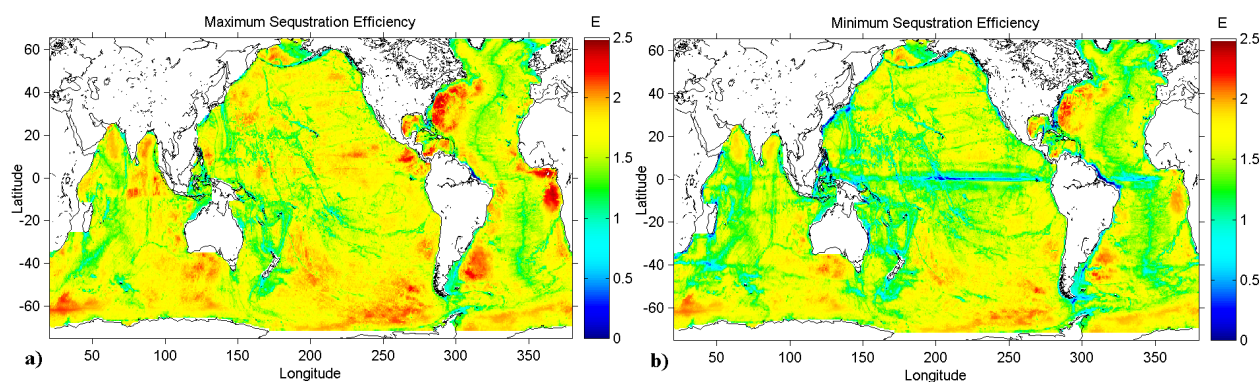
To first order, a simple proxy for sequestration efficiency may be constructed by a weighted sum of the normalized parameters in Table 1. Since each parameter has a different unit (dimension) and either a dynamical or a hydrographic origin, the quantities must first be normalized. For a parameter  $x$ , this may be accomplished by applying  $x' = 2((x - x_{min}) / (x_{max} - x_{min}) - 0.5)$ , where  $x'$  is now the normalized



parameter with a range between -1 and 1, and  $x_{\min}$  and  $x_{\max}$  are the global minimum and maximum values of a parameter, respectively. For dynamic quantities with a naturally large ranges of values, the logarithm of the parameter may be normalized. The normalized quantities  $x'$  are dimensionless and may be summed arithmetically. The contribution for each parameter, however, need not have equal weighting, leading to an efficiency parameter,

$$E = \alpha z' + \beta u' + \gamma w' + \delta \epsilon' + \phi \rho'_z + \gamma \rho'_x \quad (2)$$

where the composite parameter for sequestration efficiency ( $E$ ) is the weighted ( $\alpha, \beta, \gamma, \delta, \phi, \gamma$ ) sum of the normalized ocean parameters ( $z', u', w', \epsilon', \rho'_z, \rho'_x$ ). Weights can be derived objectively through exhaustive sequestration efficiency simulations using a global carbon cycle model. The objective analysis of sequestration efficiency remains an on-going study. Choosing the weights can be done subjectively, where by parameters deemed more important to sequestration are given slightly higher weights (i.e. 1) than parameters believed to be less important (i.e. 0.5). Here we present preliminary results of our subjective analysis with weights of ( $\alpha=0, \beta=-1, \gamma=-1, \delta=-1, \phi=0.5, \gamma=-0.5$ ). A zero weight for depth has been selected to emphasise dynamic characteristics of the ocean, where it is assumed that deeper injection is generally better than shallow injection.



**Figure 2** Sequestration efficiency based on a weighted sum of the six ocean parameters presented in Figure 1. a) The maximum value in the water column at each geographic location, and b) the minimum value. Higher (red) values would suggest better injection locations with regard to sequestration efficiency.

The sequestration efficiency maps shown in Figure 2 reveal many of the dominant ocean characteristics evident in the parameter fields (Figure 1). Some features of interest include: the generally good sequestration efficiencies predicted for sites beyond the continental slope off the east coast of the United States, the poor sequestration efficiencies near the mid-ocean ridges caused by enhanced mixing over rough topography, and the poor sequestration along the equator where persistent upwelling exists. Specific maps for any given depth (i.e. 1500m), have similar features, revealing geographic differences in relative sequestration efficiency. Some features (Figure 2) are not easily interpreted. Specifically, the Southern Ocean (Latitudes less than  $40^\circ$  S) is believed to be a relatively poor region for long term sequestration due to the vertical motions associated with deep convection. The present analysis does not directly include a parameter field for convection, separate from the inclusion of mean vertical velocities. Including seasonal air-sea temperature differences as a dynamic parameter may reduce the efficiency of the Southern Ocean and North Atlantic regions. Further comparisons against previous OGCM and dispersion model simulations will be presented at the meeting.

True sequestration efficiency can only be evaluated through detailed dispersion modelling and *in situ* observations. Tracer dispersion is inherently a Lagrangian process, and the sequestration characteristics of the injection site are only part of the story. Once injected, the  $\text{CO}_2$  is advected by the 3-dimensional, time-varying ocean currents, which take it (albeit slowly for deep sites), away from the injection location. As time progresses, the  $\text{CO}_2$  is advected far from the injection site, and is therefore exposed to a path integral of sequestration efficiencies along a stream line in the flow. It is this very non-linear, turbulent life history which complicates the modelling and predictive skill of ocean sequestration studies.

## Preliminary Conclusions

Preliminary results are presented of an on-going analysis of ocean sequestration efficiency based on global characteristics of the ocean. Direct comparisons between the sequestration efficiency predicted by this linear parameterization and fully developed circulation and dispersion models, is on going. Some of these results will be presented at the meeting. In particular, the sequestration efficiencies ( $E_i$ ) predicted by the Lagrangian Mesoscale Ocean Dispersion Model (MODM) appear to be better than those from course resolution OGCMs. In other words, the MODM typically predicts a better buffering capacity for the ocean, with less cross-isopycnal mixing. This is believed to be due to the overly dispersive nature of Eulerian diffusion parameterizations in the OGCMs.

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