Mitigating the Atmospheric CO_2 Increase and Ocean Acidification by Adding Limestone Powder to Upwelling Regions

Presentation to

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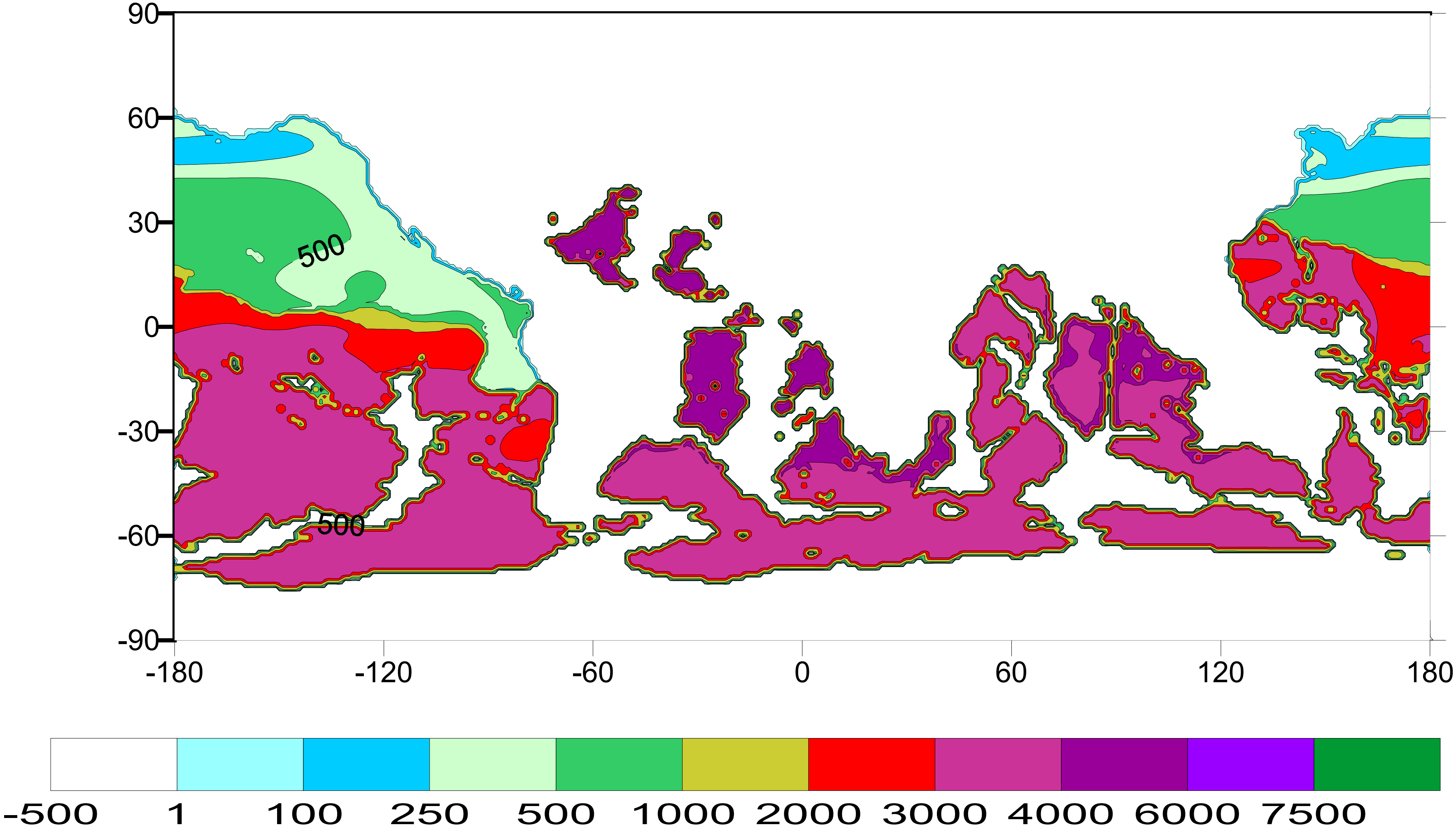
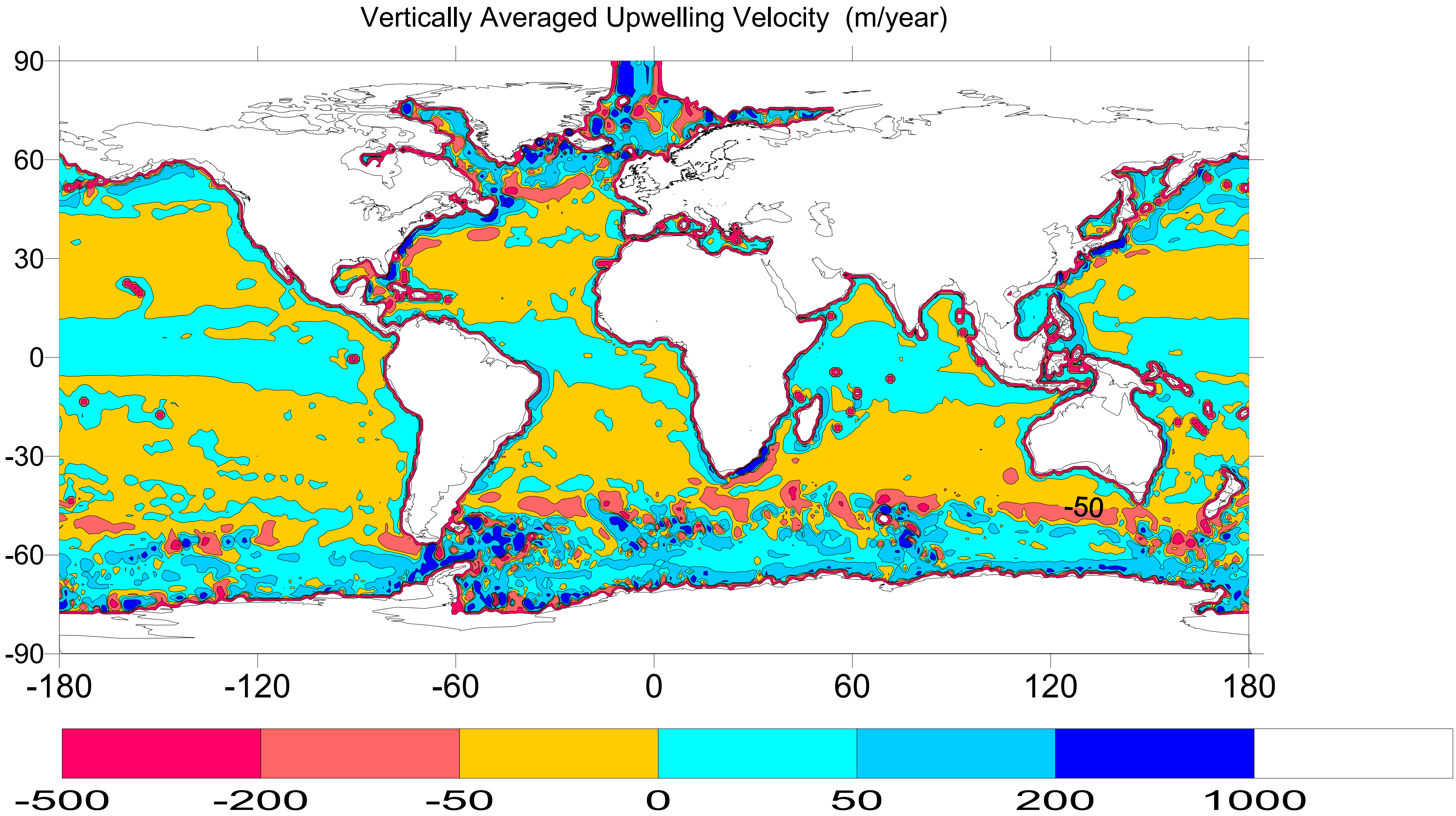
Basic Idea:

- Add finely ground (40-um radius) limestone powder to regions of the ocean where the boundary between saturated (upper) and unsaturated (lower) water wrt calcite is relatively shallow (250-500 m depth) and the upwelling velocity relatively large (50-100 m/year)
- The limestone powder will dissolve within the first few hundred meters of the saturation boundary, restoring CO_3^{2-}, increasing the pH, and reducing pCO_2
- When this water upwells to the surface, additional CO_2 will be absorbed from the atmosphere, pushing pH back down, thereby offsetting some of the beneficial increase in pH

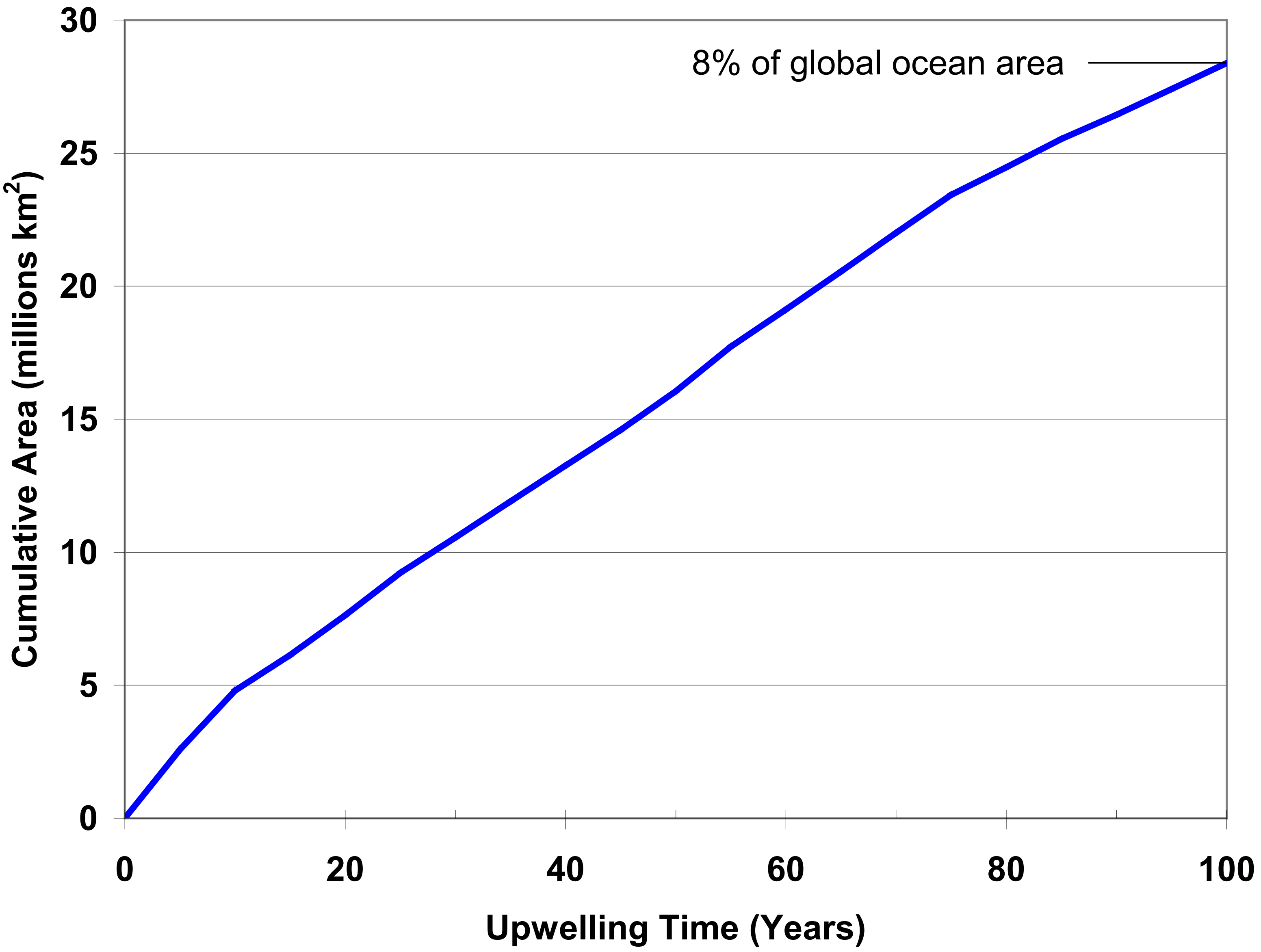
In the analysis to follow, I use the 7-component carbonate chemistry algorithm of Peng et al. (1987), and use global datasets on a $1^o \times 1^o$ latitude-longitude grid and at 33 depths for total dissolved inorganic carbon (TDIC), total alkalinity (TALK), dissolved phosphate, temperature, salinity, and upwelling velocity

Calcite Saturation Depth (m)





Vertically Averaged Upwelling Velocity (m/year)


30
25
20
15
10
5
0
Cumulative Area (millions km^2)
0
20
40
60
80
100
Upwelling Time (Years)
8% of global ocean area

The analysis to follow consists of 3 phases

- Simulation of the dissolution of falling $CaCO_3$ particles in a single column, calculation of the impact on mixed layer pCO_2 when the carbonate-enriched water upwells to the surface, and calculation of the amount of atmospheric CO_2 that would need to be absorbed in order to restore the original mixed layer pCO_2
- Analysis of the effect of feedback between atmospheric and mixed layer pCO_2
- Simulations with a global-scale coupled climate-carbon cycle model

Simulations with 5 Representative Columns

The reaction when $CaCO_3$ dissolves is

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \qquad (1)$$

This induces the following reactions:

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \qquad (2)$$

$$H_2CO_3(aq) \rightarrow H^+ + HCO_3^- \qquad (3)$$

$$CO_2 + H_2O \rightarrow H_2CO_3(aq) \qquad (4)$$

If reactions 2-4 are fully carried out, the net result is

$$\mathbf{CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-} \qquad \mathbf{(5)}$$

That is: **one mole** of CO_2 absorbed for every mole of $CaCO_3$ dissolved, and **no net effect on acidity.**

In reality, less than one mole of CO_2 is absorbed from the atmosphere for every mole of dissolved $CaCO_3$ entering the mixed layer, and there is a net reduction in acidity.

Why?

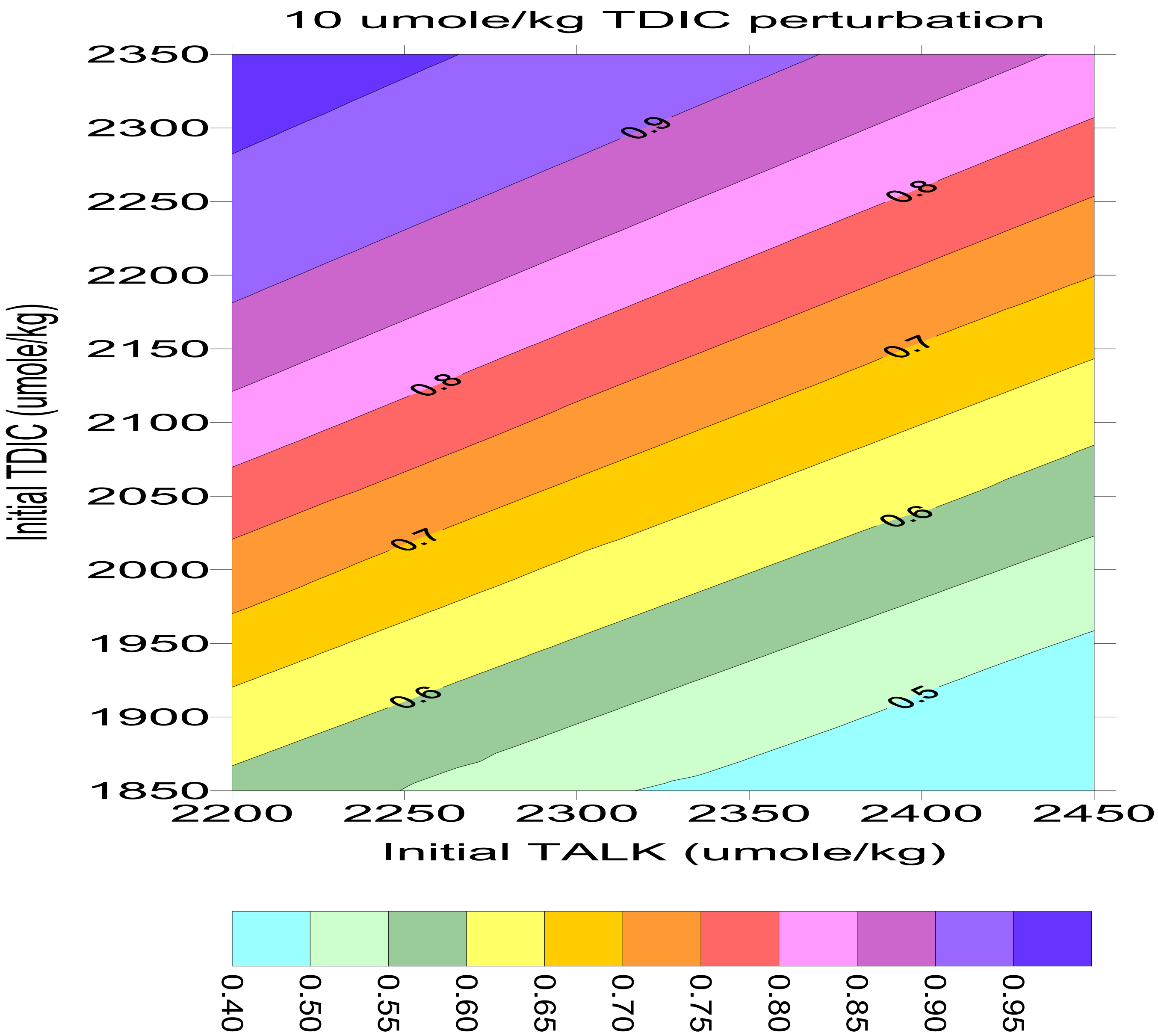
Because only as much CO_2 will enter the mixed layer from the atmosphere as is required to restore the initial pCO_2 difference between the mixed layer and atmosphere.

For fixed atmospheric pCO_2, the following applies after adjustment of mixed layer pCO_2 to the dissolution of $CaCO_3$:

$$\Delta TDIC_a \frac{\partial pCO_2}{\partial TDIC} + \Delta TDIC_p \frac{dpCO_2}{dTDIC} = 0$$

Thus, the molar ratio M_R is given by

$$M_R = \frac{\Delta TDIC_a}{\Delta TDIC_p} = -\frac{dpCO_2 / dTDIC}{\partial pCO_2 / \partial TDIC}$$


10 umole/kg TDIC perturbation
Initial TDIC (umole/kg)
2350
2300
2250
2200
2150
2100
2050
2000
1950
1900
1850
Initial TALK (umole/kg)
2200
2250
2300
2350
2400
2450
0.9
0.8
0.8
0.7
0.7
0.6
0.6
0.5
0.40
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95

Initial Profiles for 5 Representative Columns

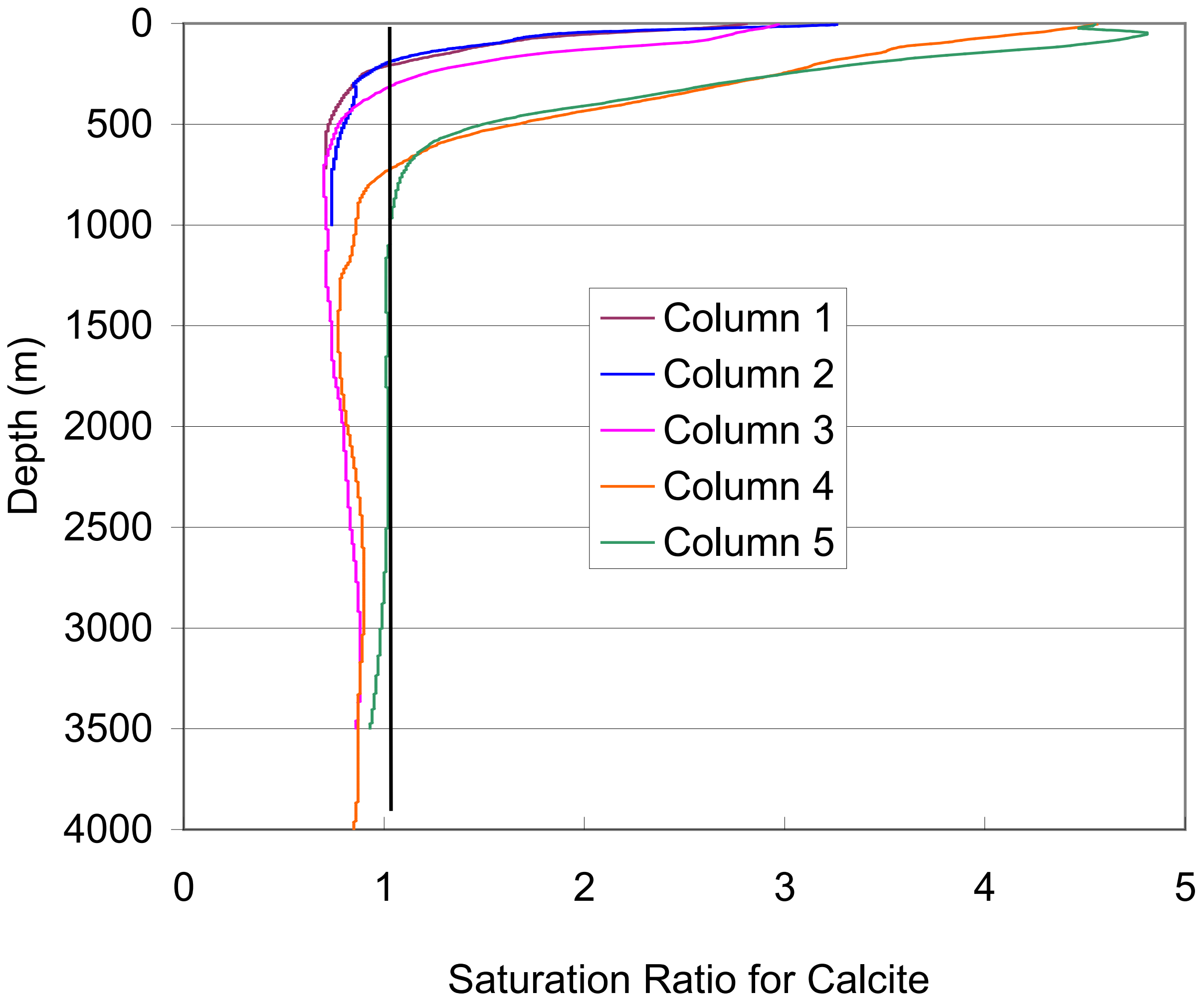
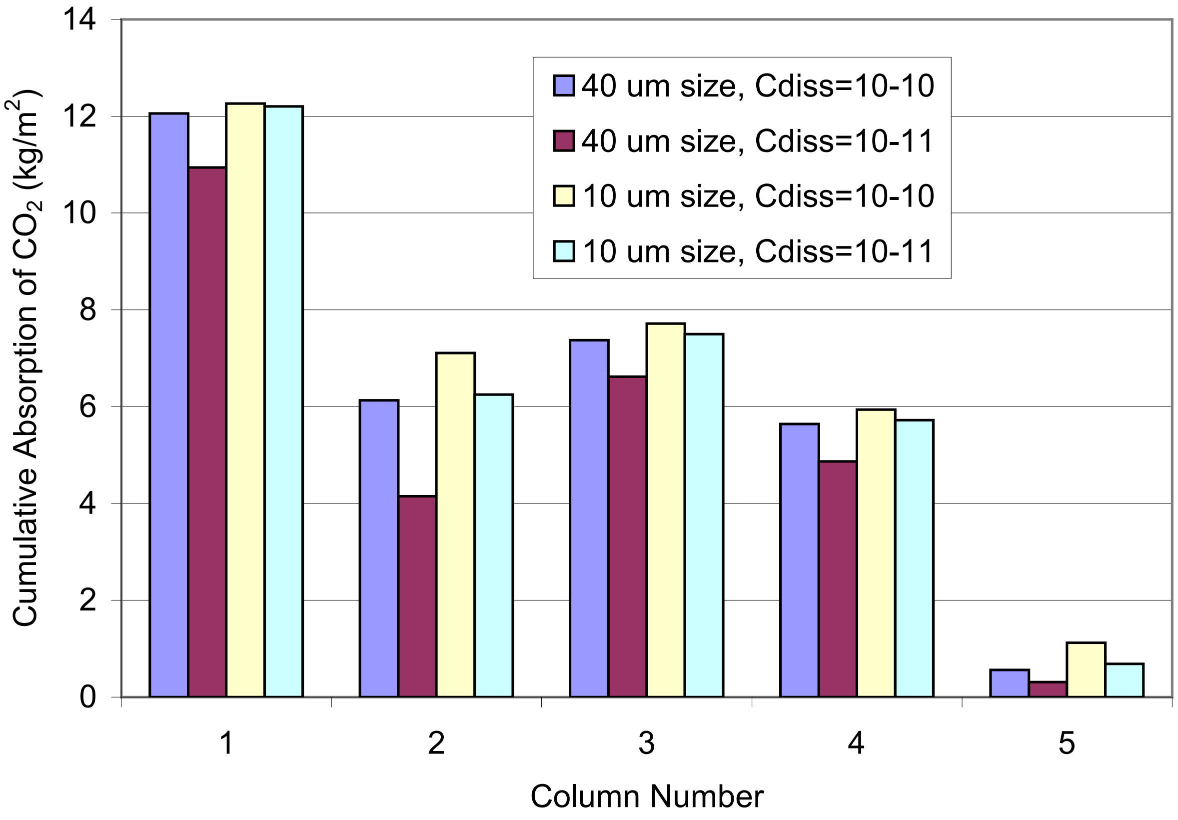


Table 3. Steady state impact on mixed layer properties of applying 200 gm/m^2/yr of $CaCO_3$ (assumed to be calcite) at 40 μm radius with $C_{dis} = 10^{-10}$ m/s/μmole/kg.

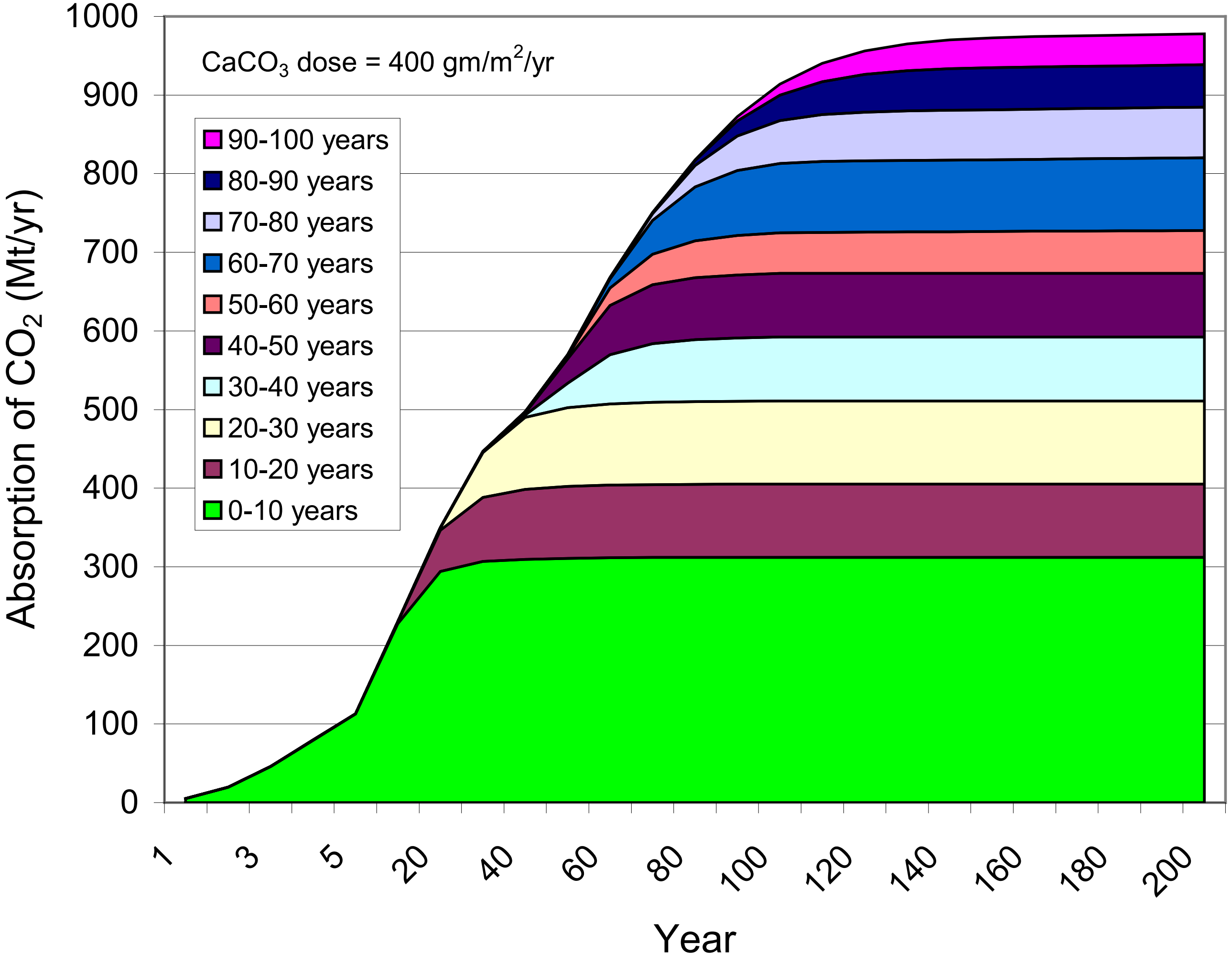
Column	Changes prior to absorption of atmospheric CO_2 (changes in TALK are twice those of TDIC)		Equilibrium adjustment of TDIC (μmole/kg)	Moles CO_2 absorbed over moles $CaCO_3$ added	Fraction of added $CaCO_3$ in the mixed layer (F)	Mass of CO_2 absorbed over mass of $CaCO_3$ added (R)
	TDIC (μmole/kg)	pCO_2 (μatm)				
1	39.8	-40.5	28.9	0.727	0.943	0.302
2	37.6	-27.5	26.2	0.696	0.501	0.153
3	44.4	-48.7	31.7	0.714	0.587	0.184
4	33.4	-26.7	20.5	0.613	0.522	0.141
5	8.5	-10.3	5.2	0.615	0.052	0.014
	Changes in pH			Changes in Supersaturation		
	Initial	Adjustment	Final	Initial	Adjustment	Final
1	0.073	-0.059	0.014	55%	-36%	19%
2	0.063	-0.050	0.013	63%	-34%	20%
3	0.078	-0.063	0.015	62%	-41%	22%
4	0.044	-0.033	0.011	51%	-28%	23%
5	0.012	-0.009	0.003	13%	-7%	6%

Cumulative Absorption after 200 Years

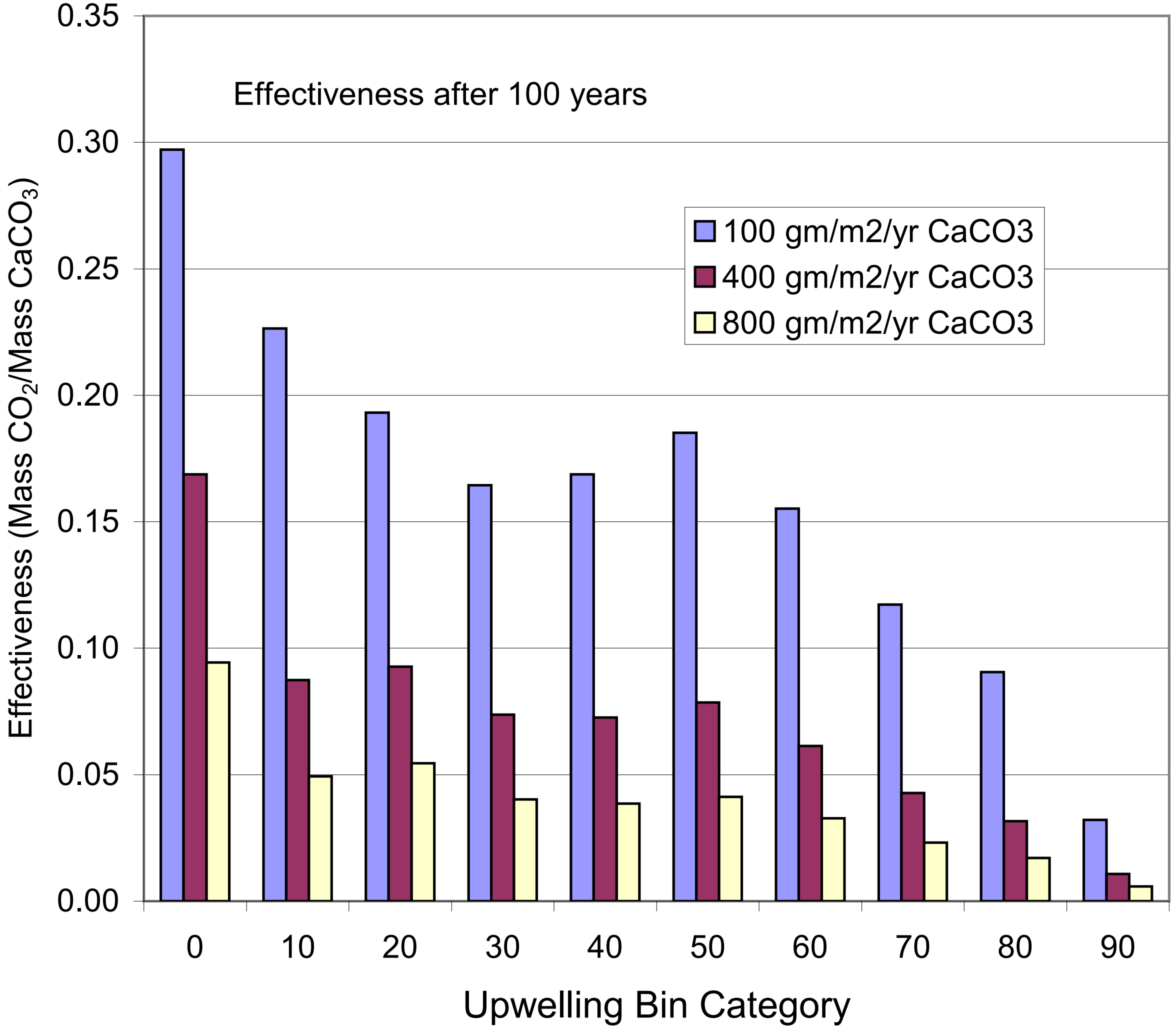


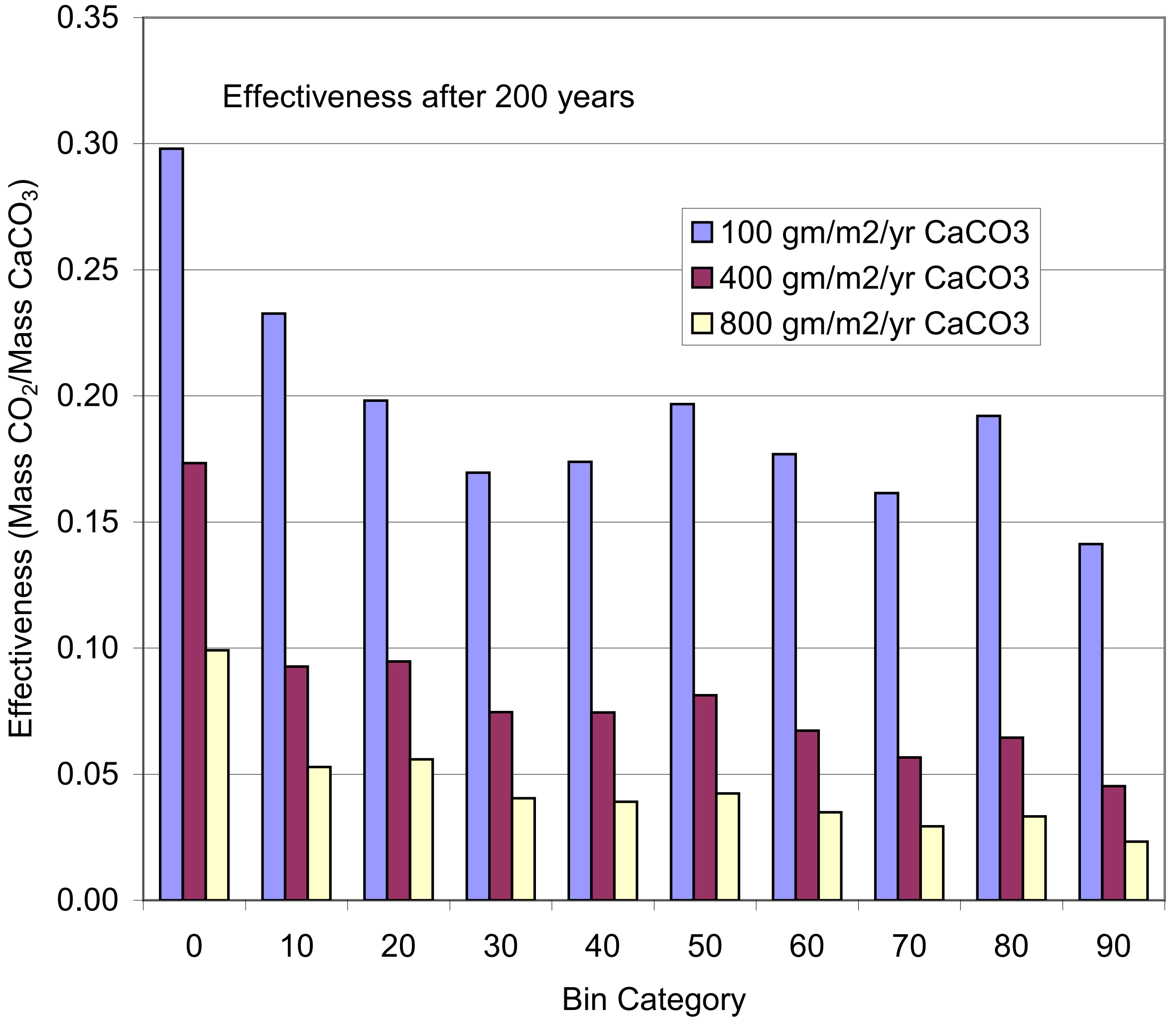
Simulations with all 3713 1^{o} x 1^{o} columns having an upwelling time of 100 years of less

Rate of absorption of CO_2 for one uniform rate of application of limestone powder, showing contributions from groups of columns with different upwelling times



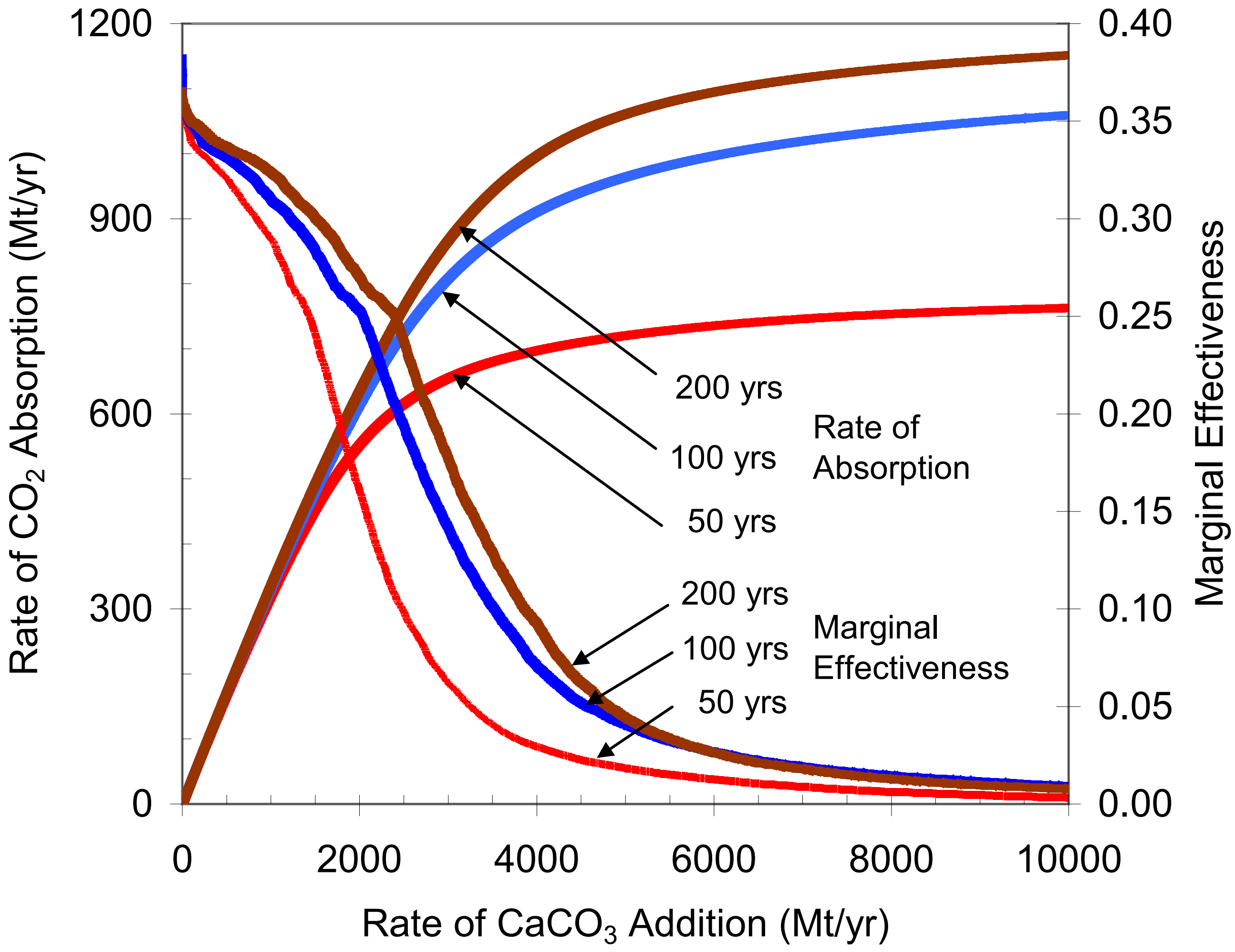
The effectiveness of adding limestone powder in terms of absorbing atmospheric CO_2 decreases with increasing rate of application, varies between columns in different upwelling bins, and varies over time


Effectiveness after 100 years
Effectiveness (Mass CO_2/Mass $CaCO_3$)
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
100 gm/m2/yr CaCO3
400 gm/m2/yr CaCO3
800 gm/m2/yr CaCO3
0
10
20
30
40
50
60
70
80
90
Upwelling Bin Category

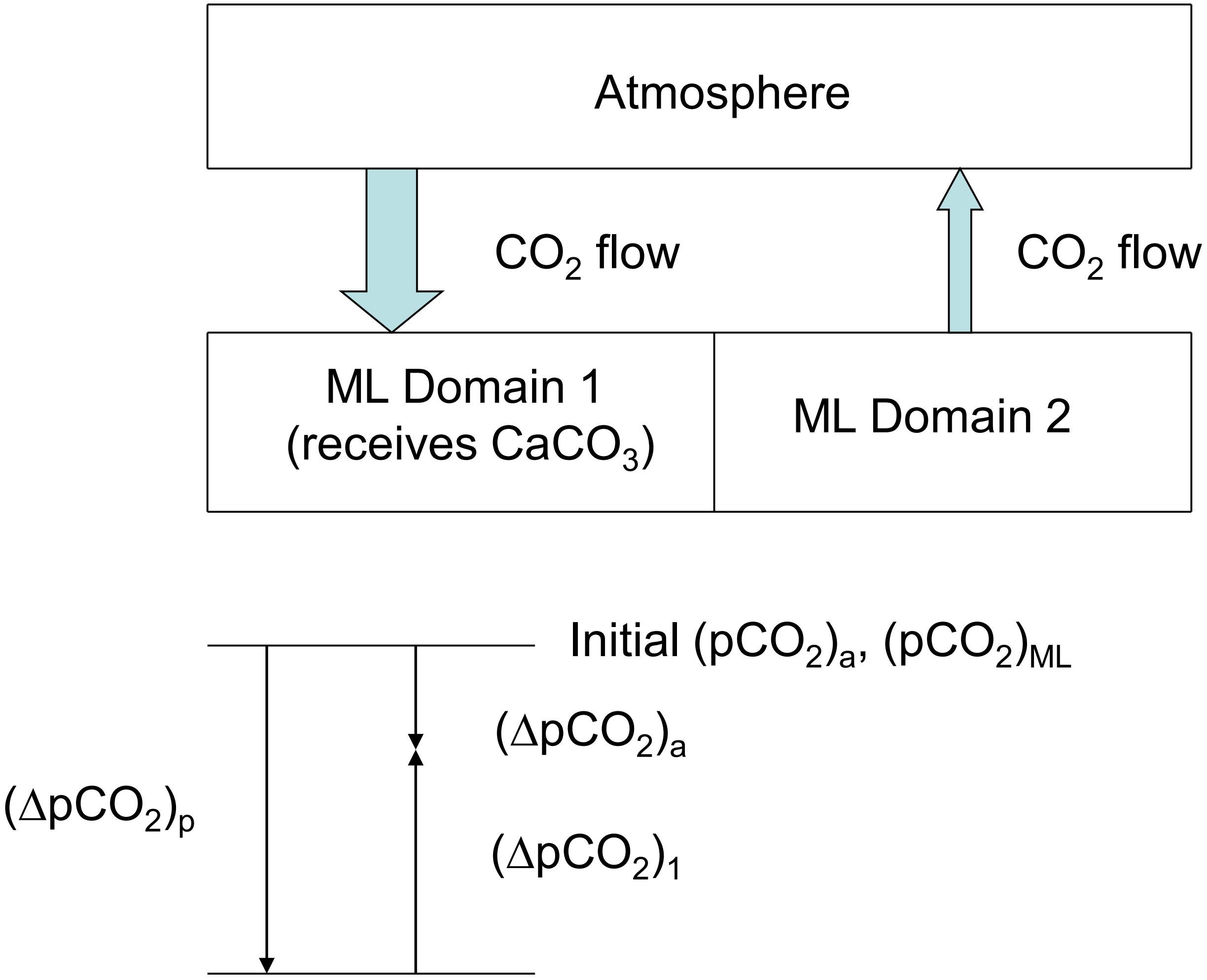

Effectiveness after 200 years
Effectiveness (Mass CO_2/Mass $CaCO_3$)
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
100 gm/m2/yr CaCO3
400 gm/m2/yr CaCO3
800 gm/m2/yr CaCO3
0
10
20
30
40
50
60
70
80
90
Bin Category

Optimization Strategy:

- Compute the marginal effectiveness of adding limestone powder in each of 3713 columns for successively greater rates of limestone addition
- Sort all of the column/limestone-increment combinations in order of decreasing effectiveness
- Prepare a plot of rate of absorption of CO_2 vs total rate of addition of limestone, as the rate of addition of limestone is increased according to the order established in step (2).


1200
900
600
300
0
Rate of CO_2 Absorption (Mt/yr)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Marginal Effectiveness
0
2000
4000
6000
8000
10000
Rate of $CaCO_3$ Addition (Mt/yr)
200 yrs
100 yrs
50 yrs
Rate of Absorption
200 yrs
100 yrs
50 yrs
Marginal Effectiveness

Global-scale Interactions


Atmosphere

CO_2 flow

CO_2 flow

ML Domain 1
(receives $CaCO_3$)

ML Domain 2

Initial $(pCO_2)_a$, $(pCO_2)_{ML}$

$(\Delta pCO_2)_a$

$(\Delta pCO_2)_p$

$(\Delta pCO_2)_1$

Balance Equations:

Domain 1 pCO_2

$$\Delta(pCO_2)_1 - (\Delta pCO_2)_a + (\Delta pCO_2)_p = 0$$

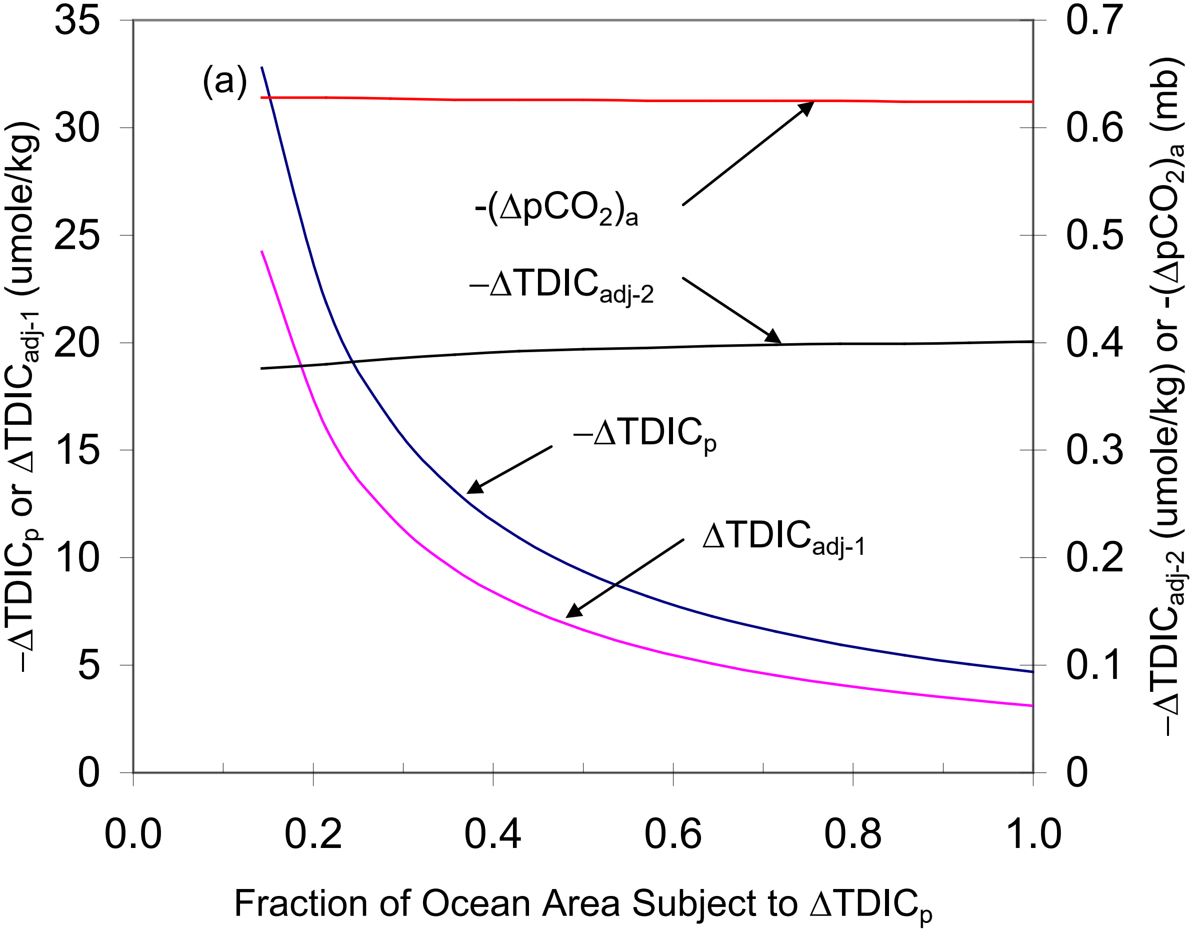
Domain 2 pCO_2

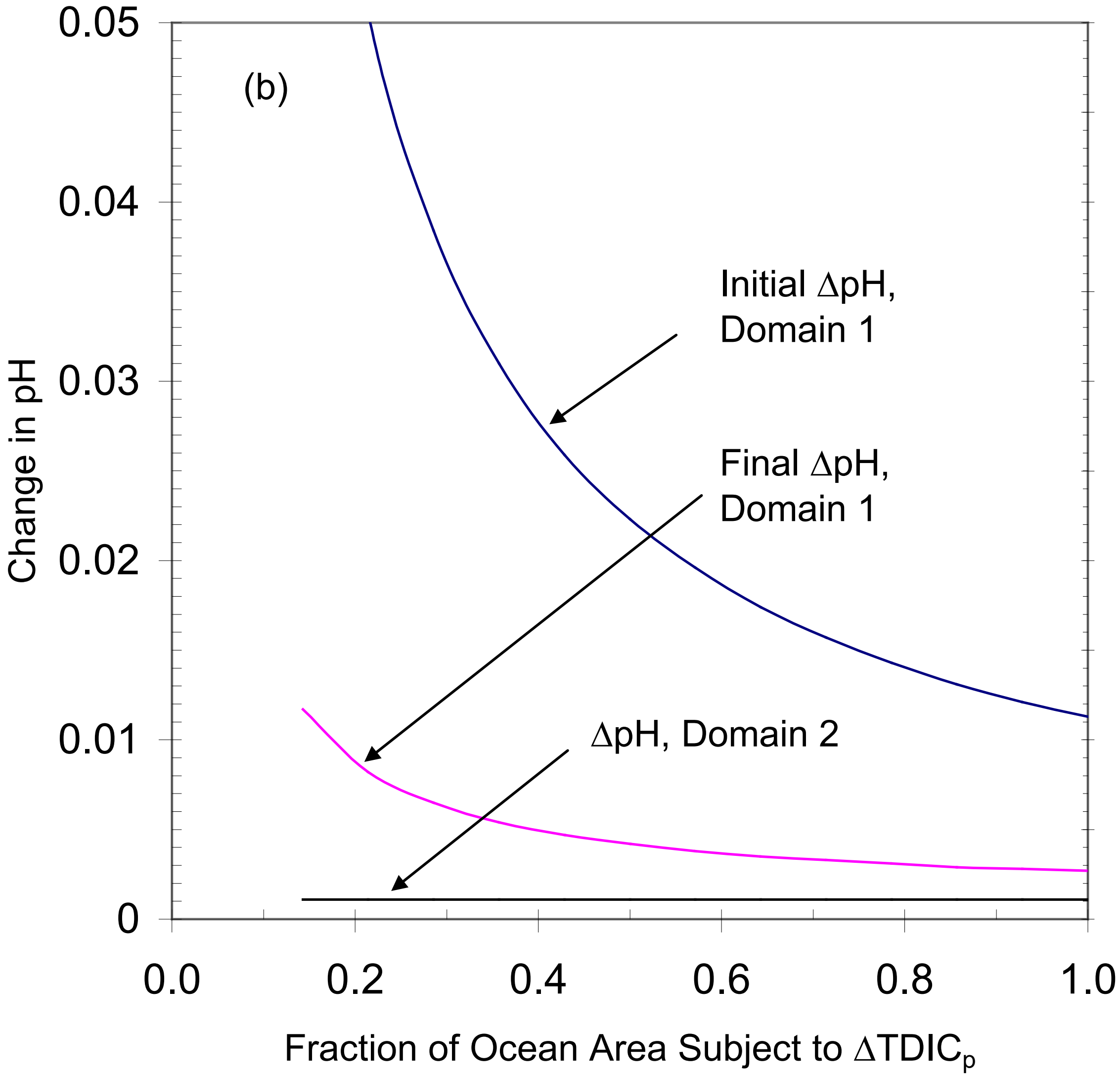
$$\Delta(pCO_2)_2 - (\Delta pCO_2)_a = 0$$

Conservation of mass

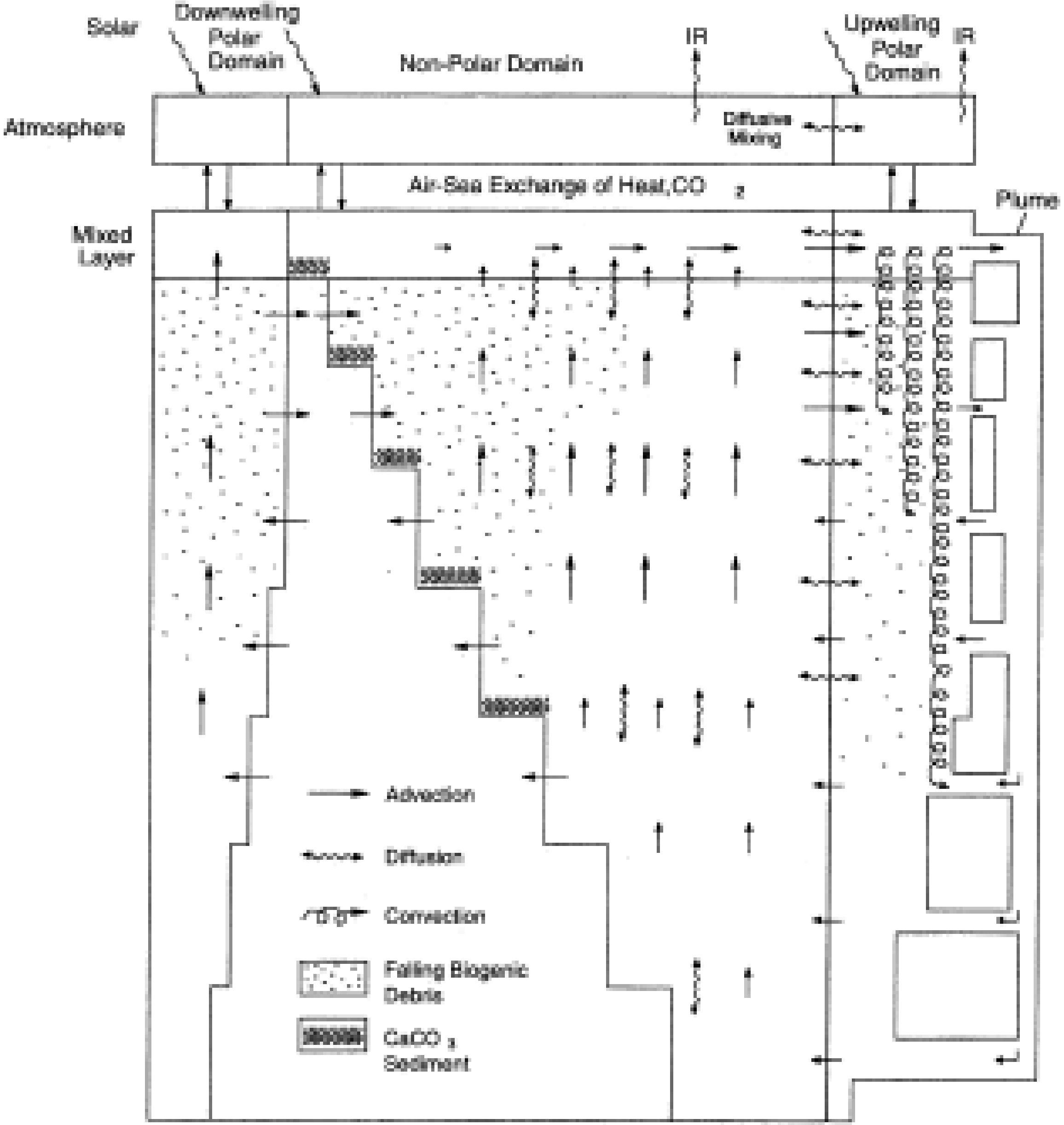
$$\Delta C_1 + \Delta C_2 + \Delta C_a = 0$$

Impact of Dissolving 2 Gt $CaCO_3$ into the Mixed Layer of Domain 1



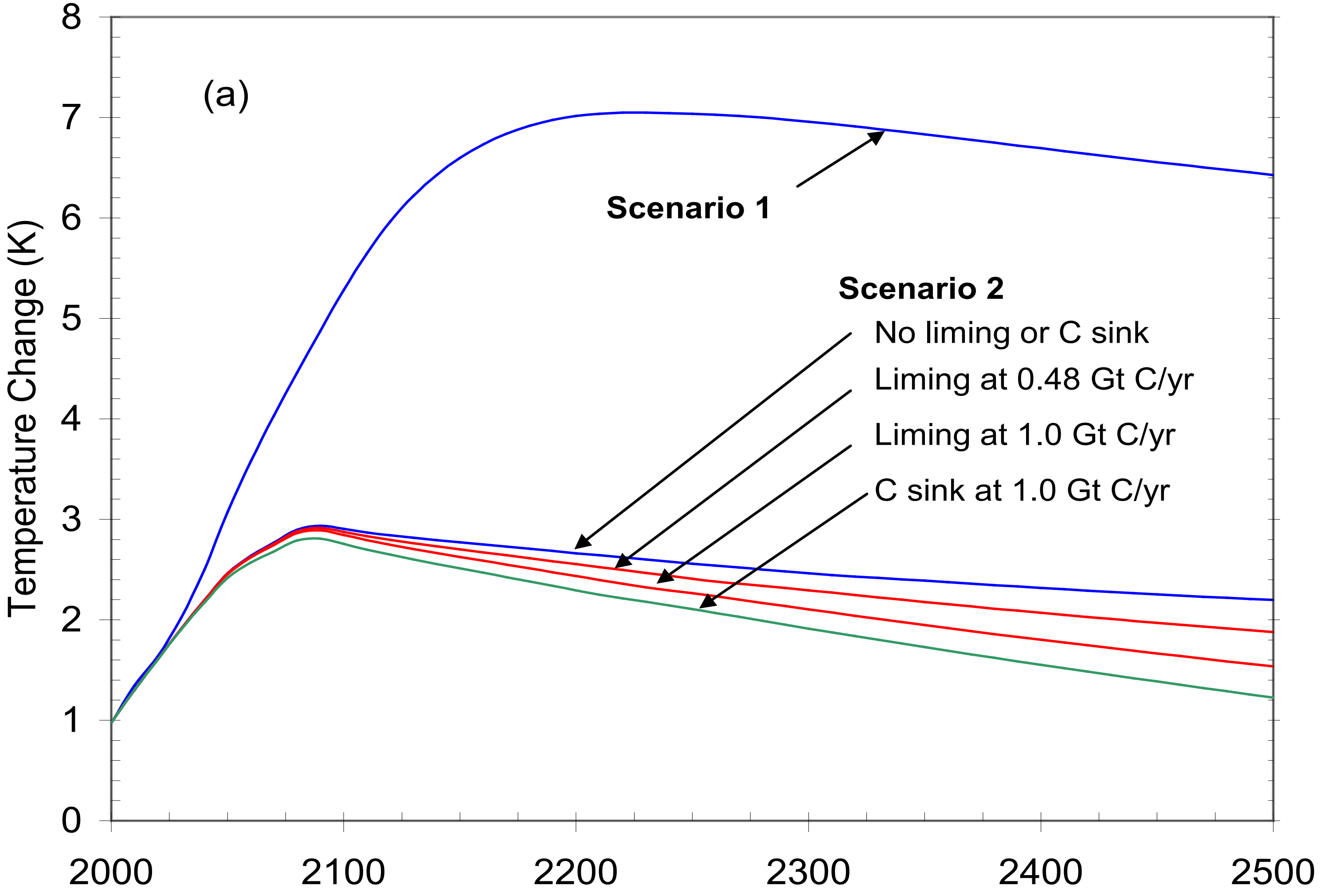

(b)
Change in pH
0.05
0.04
0.03
0.02
0.01
0
0.0
0.2
0.4
0.6
0.8
1.0
Initial ΔpH, Domain 1
Final ΔpH, Domain 1
ΔpH, Domain 2
Fraction of Ocean Area Subject to ΔTDIC$_p$

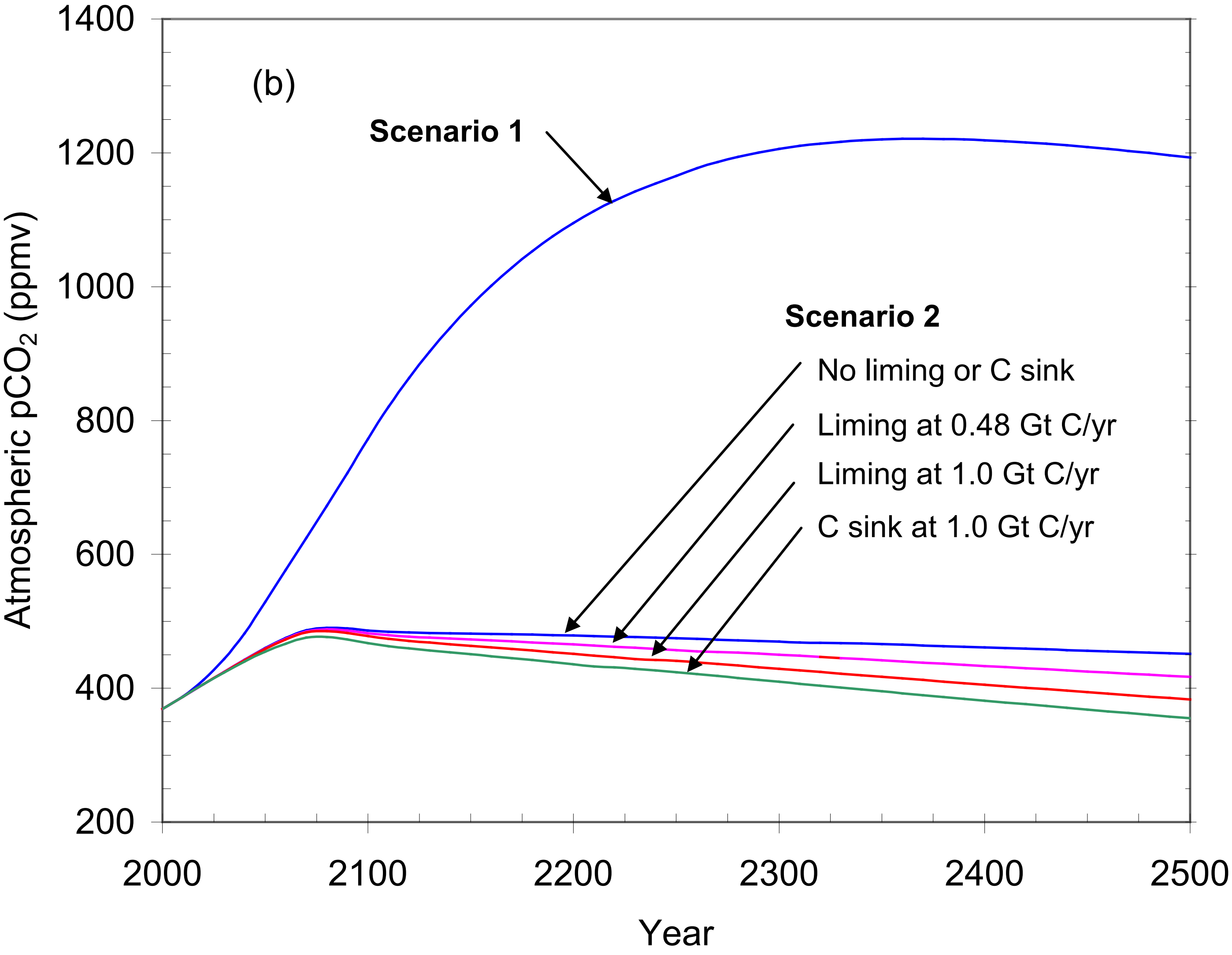
Simulations with a coupled climate-carbon cycle model

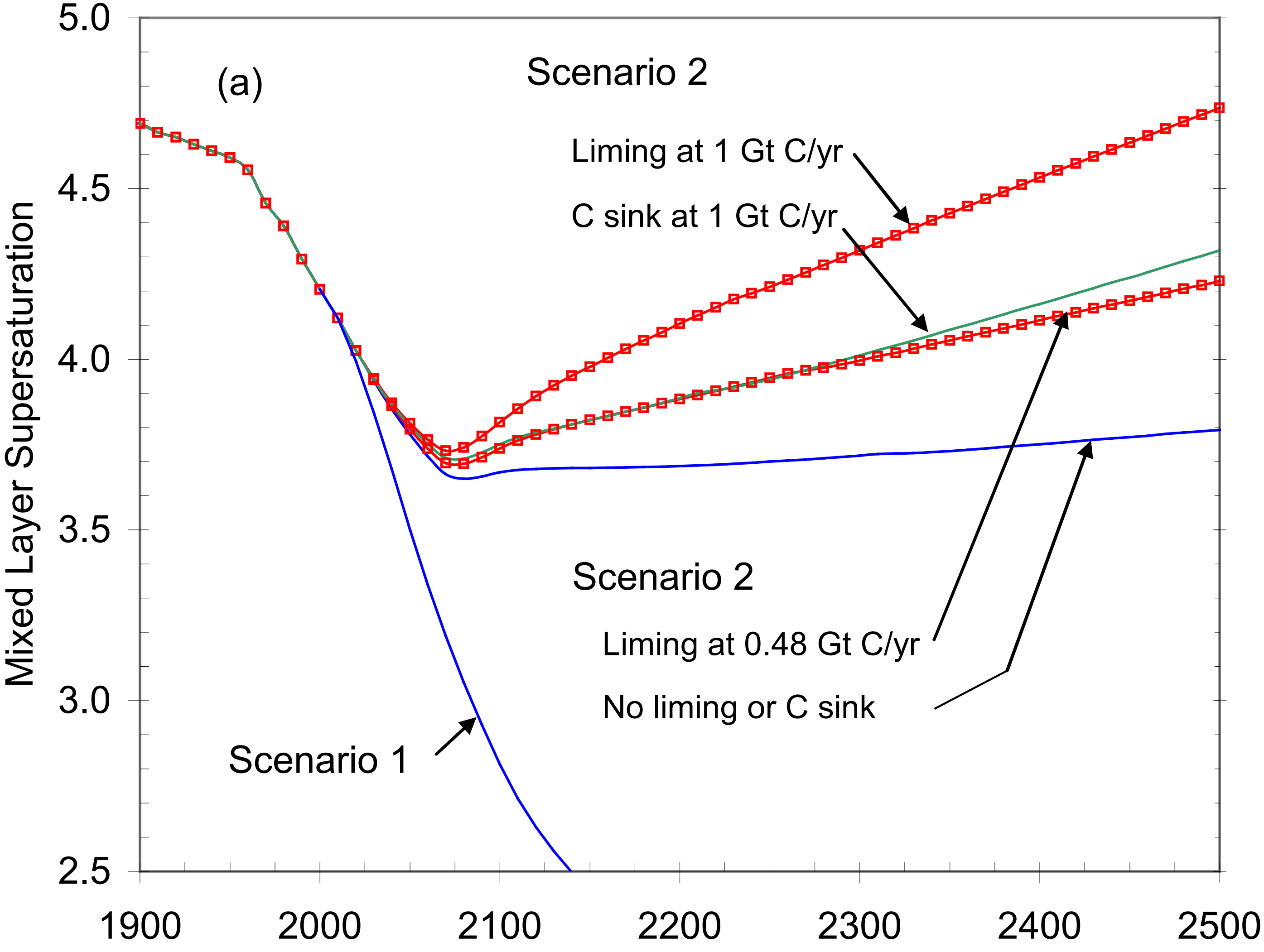

Solar
Downwelling Polar Domain
Non-Polar Domain
IR
Upwelling Polar Domain
IR
Atmosphere
Diffusive Mixing
Air-Sea Exchange of Heat, CO2
Plume
Mixed Layer
Advection
Diffusion
Convection
Falling Biogenic Debris
CaCO3 Sediment

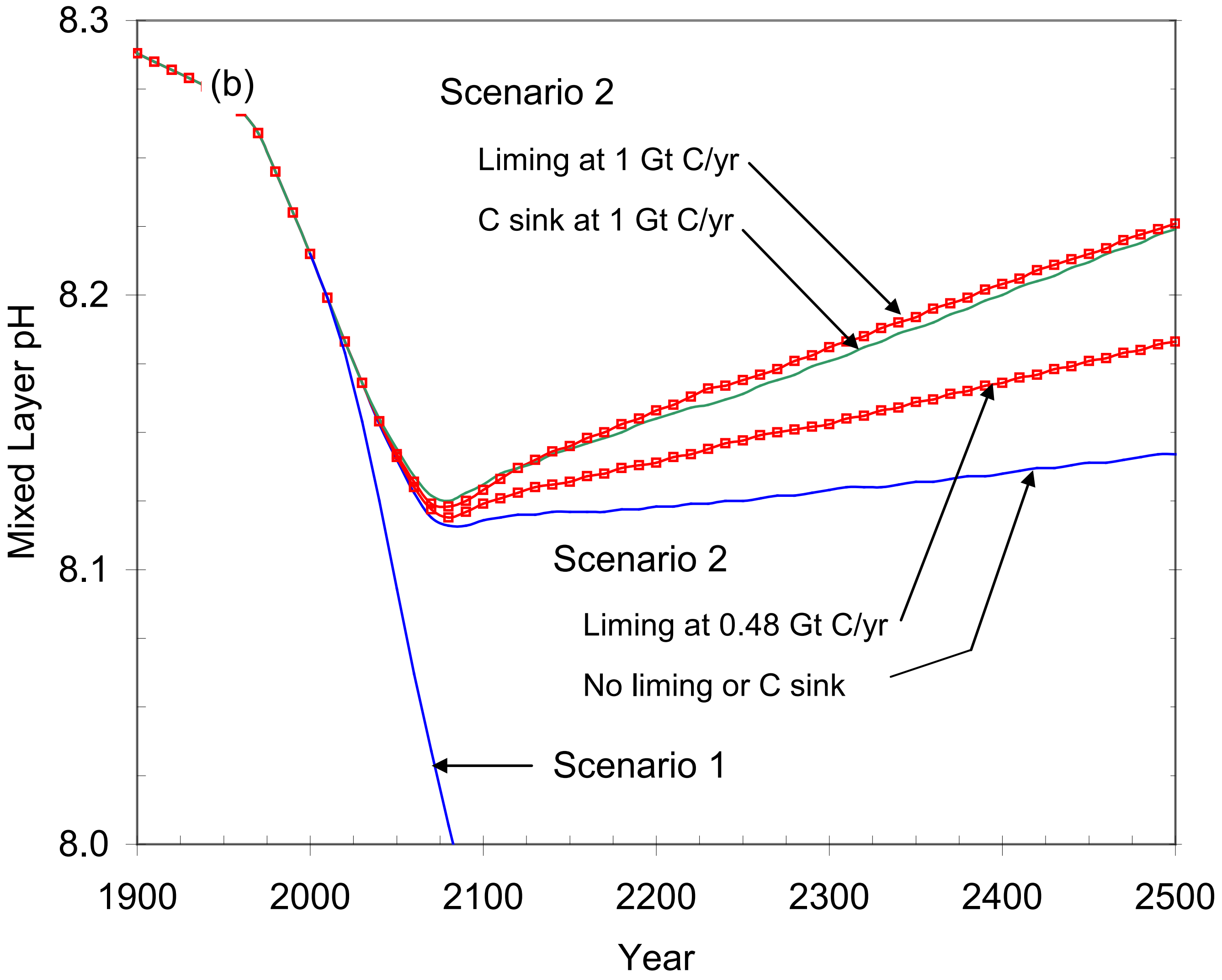
Scenarios and Assumptions

- Scenario 1: Fossil fuel CO_2 emission peaks at 17.5 Gt C/yr in 2100, then declines by 1%/yr
- Scenario 2: Fossil fuel CO_2 emission peaks at 7.5 Gt C/yr in 2010, drops to zero by 2100, and stringent reductions in emissions of other GHGs or precursors occur
- Climate sensitivity of 3 K


(a)
Temperature Change (K)
0
1
2
3
4
5
6
7
8
2000
2100
2200
2300
2400
2500
Scenario 1
Scenario 2
No liming or C sink
Liming at 0.48 Gt C/yr
Liming at 1.0 Gt C/yr
C sink at 1.0 Gt C/yr


(b)
Scenario 1
Scenario 2
No liming or C sink
Liming at 0.48 Gt C/yr
Liming at 1.0 Gt C/yr
C sink at 1.0 Gt C/yr
Atmospheric pCO2 (ppmv)
1400
1200
1000
800
600
400
200
2000
2100
2200
2300
2400
2500
Year


5.0
4.5
4.0
3.5
3.0
2.5
Mixed Layer Supersaturation
1900
2000
2100
2200
2300
2400
2500
(a)
Scenario 2
Liming at 1 Gt C/yr
C sink at 1 Gt C/yr
Scenario 2
Liming at 0.48 Gt C/yr
No liming or C sink
Scenario 1


8.3
8.2
8.1
8.0
Mixed Layer pH
1900
2000
2100
2200
2300
2400
2500
Year
(b)
Scenario 2
Liming at 1 Gt C/yr
C sink at 1 Gt C/yr
Scenario 2
Liming at 0.48 Gt C/yr
No liming or C sink
Scenario 1

Conclusions

- Phasing out CO_2 emissions by 2100 has the single largest impact in reducing the ocean acidification that will otherwise occur
- Extraordinary additional measures (adding 4 Gt limestone/yr to the ocean for > 200 years) provides a modest additional benefit
- Compared to sequestering 0.5 Gt C/yr in soils or in geological strata, adding 0.5 Gt C/yr of dissolved $CaCO_3$ to the mixed layer (by adding 4 Gt/yr of limestone powder) has
- - about twice the effect of ML supersaturation,
- - about the same effect on ML pH, and
- - about ¾ the effect on atm pCO_2 and ΔT