Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary material: CO_2 capture by pumping surface acidity to the deep ocean

1 A simple approximation to CO_2 uptake efficiency

Addition of alkalinity to the ocean lowers pCO_2^{oc}, the partial pressure of CO_2, and thus subsequently more CO_2 is taken up from the atmosphere until pCO_2^{oc} = pCO_2^{atm} again. Dissolved inorganic carbon (DIC) exists in the ocean in an equilibrium between the three carbonate species, which can be written:

$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3{}^- + H^+ \rightleftharpoons CO_3{}^{2-} + 2H^+$

Introduction of alkalinity consumes H^+ ions and moves the above equilibrium to the right. Under normal ocean pH the vast majority of DIC is in the bicarbonate ($HCO_3{}^-$) form, thus addition of alkalinity allows for an approximately equimolar quantity of CO2 to enter from the atmosphere. However the actual amount is slightly smaller than 1: the intuition here is that for every mol of CO_2 entering the ocean we need ~1mol of alkalinity to convert all the CO_2 to bicarbonate, plus additional alkalinity to further convert some fraction to carbonate ions and pull the equilibrium over such that the concentration of CO_2 (and thus pCO_2^{oc}) returns to it's starting value. The unitless uptake efficiency η_{CO_2} can be calculated from the partial derivatives of pCO2 with respect to alkalinity and DIC and represents the slope of the pCO_2 isolines in an Alk vs DIC plot (see Figure S1).

$$\eta_{\mathrm{CO_2}} = -\frac{\partial p\mathrm{CO_2}}{\partial Alk} \Big/ \frac{\partial p\mathrm{CO_2}}{\partial DIC} \tag{1}$$

The carbonate system with equilibrium constants, K0, K1 and K2 is defined as:

$$[\mathrm{H_2CO_3}^*] = K_0 p\mathrm{CO_2} \tag{2}$$

$$K_1[\mathrm{H_2CO_3}^*] = [\mathrm{HCO_3}^-][\mathrm{H}^+] \tag{3}$$

$$K_2[\mathrm{HCO_3}^-] = [\mathrm{CO_3}^{2-}][\mathrm{H}^+] \tag{4}$$

where $[H_2CO_3{}^*] = [CO_2] + [H_2CO_3]$

A full carbonate system yields a complex expression for pCO_2 as a function of *Alk* and *DIC*, but we can easily estimate η_{CO_2} from a common approximation of *Alk* and *DIC*, which assumes that in the ocean $[H_2CO_3{}^*]$ is not a major contributor to the total inorganic carbon and that several minor species don't significantly contribute to alkalinity:

$$DIC = [\mathrm{H_2CO_3}^*] + [\mathrm{HCO_3}^-] + [\mathrm{CO_3}^{2-}] \approx [\mathrm{HCO_3}^-] + [\mathrm{CO_3}^{2-}] \tag{5}$$

$$Alk = [\mathrm{HCO_3}^-] + 2[\mathrm{CO_3}^{2-}] + \ldots \approx [\mathrm{HCO_3}^-] + 2[\mathrm{CO_3}^{2-}] \tag{6}$$

Combining all 5 equations, an expression is obtained for pCO_2, where we've contracted all the constants into one constant K.

$$p\mathrm{CO_2} = \frac{K_2[\mathrm{HCO_3}^-]^2}{K_0K_1[\mathrm{CO_3}^{2-}]} = K\frac{(2DIC - Alk)^2}{Alk - DIC} \tag{7}$$

Differentiating with respect to *Alk* and *DIC*, respectively, yields:

$$\frac{\partial p\mathrm{CO_2}}{\partial Alk} = K\frac{(Alk - DIC)^2 - DIC^2}{(Alk - DIC)^2} \tag{8}$$

$$\frac{\partial p\mathrm{CO}_2}{\partial DIC} = K\frac{Alk^2 - 4(Alk - DIC)^2}{(Alk - DIC)^2} \tag{9}$$

Inserting these into the expression for η_{CO_2} and simplifying yields

$$\eta_{CO_2} = -\frac{\partial p\mathrm{CO}_2}{\partial Alk} \Big/ \frac{\partial p\mathrm{CO}_2}{\partial DIC} \approx -\frac{(Alk - DIC)^2 - DIC^2}{Alk^2 - 4(Alk - DIC)^2} = \frac{1}{3 - 2DIC/Alk} = \frac{1}{1 + 2[CO_3^{2-}]/Alk} \tag{10}$$

,

which yields ≈ 0.8 for stereotypical ocean values of DIC=2000µM and Alk=2300µM

Thus for every mol of alkalinity added, only $\sim$0.8 mols of CO_2 are absorbed until the partial pressure equilibrium with the atmosphere is restored. This limitation is inherent for all ocean alkalinity methods. A numerical calculation with a full carbonate system yields $\eta_{CO_2} \approx 0.81$ in close agreement the above approximate calculation.

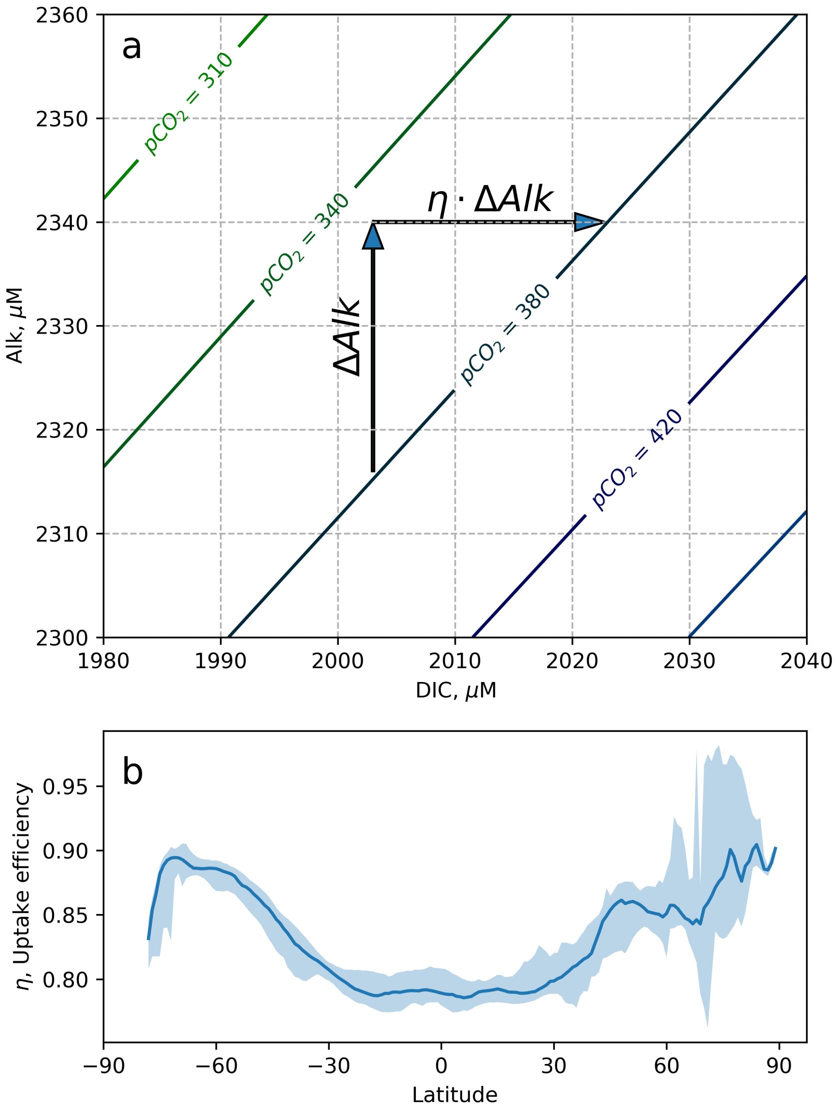

Figure S1 a) Plot of the partial pressure as a function of dissolved inorganic carbon (DIC) and total alkalinity (Alk). Addition of any given quantity of alkalinity ΔAlk to the surface will draw in additional ΔDIC = ηCO_2 ΔAlk until the partial pressure re-equilibrates. b) Graph of CO_2 compensation efficiency ηCO_2 as a function of latitude, calculated from GLODAPv2 data using pyCO2SYS. The worldwide average is ηCO_2= 0.81. Areas of higher efficiency at the poles will take up more CO_2 per mol of alkalinity added to the surface ocean and would a priori be preferred for alkalinization, however the practical amounts also depend strongly on currents, up/downwellings and the atmospheric CO_2 concentrations, thus the true uptake efficiency must be calculated using simulation (e.g. see Figure 5 in main text).

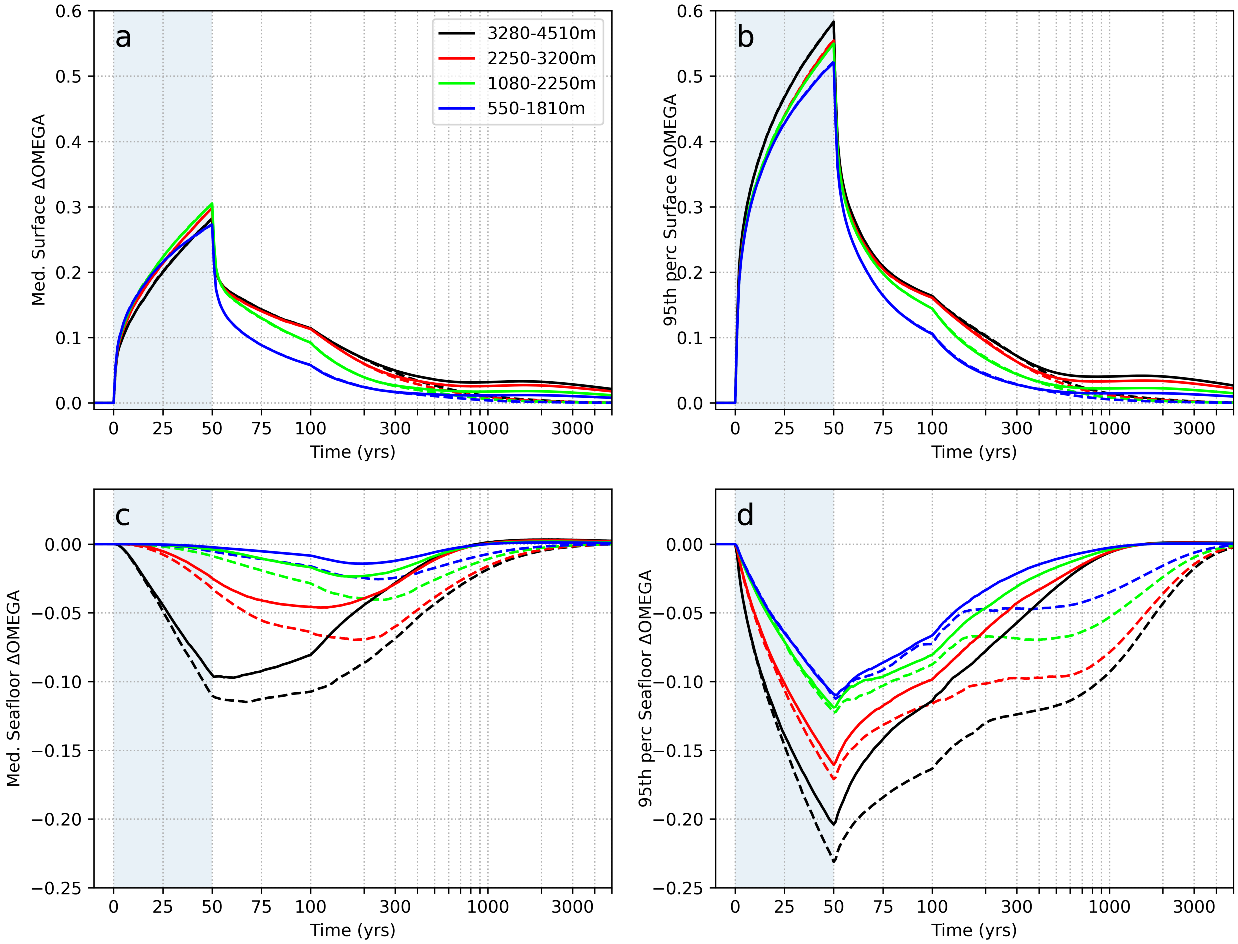

Figure S2 Median and 95%ile changes in calcite saturation (Ω) at the surface (a&b) (increased saturation) and at the seafloor (c&d) (decreased saturation) for the same runs. Analogous to Figure 3 in the main text.

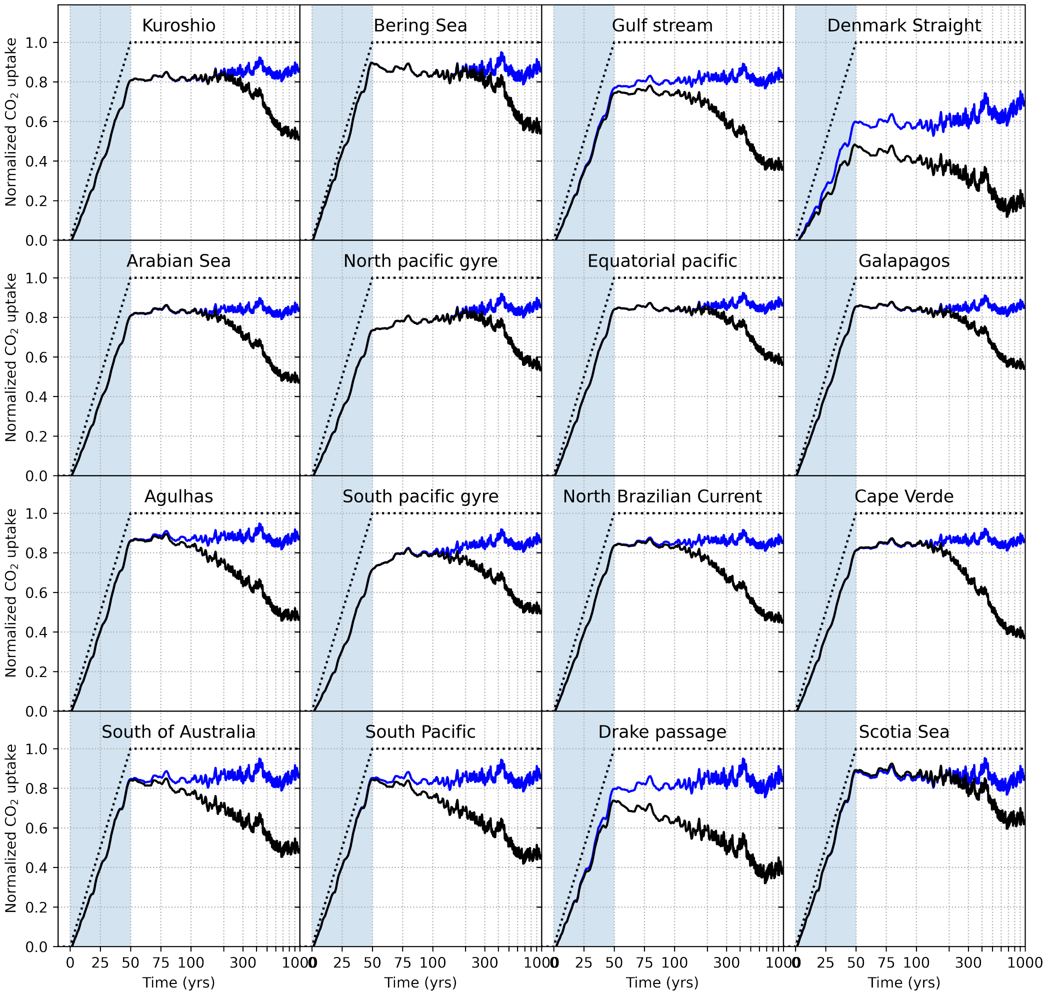

Figure S3 Time-resolved details for individual locations indicated in Figure 5, showing CO_2 uptake relative to the amount of acidity pumped (indicated by the dotted line). The black line shows the behaviour if acidity is pumped to depth and blue if the acidity is removed entirely (simple alkalinity addition). As expected the molar uptake ratio ηCO_2 is 80-85% and then decreases slowly as acidity returns to the surface. However some locations, such as the northern atlantic have markedly lower initial uptake ratios and are unadvisable for acidity pumping or alkalinity addition. Likewise the timescale of acidity return differs significantly depending on location.

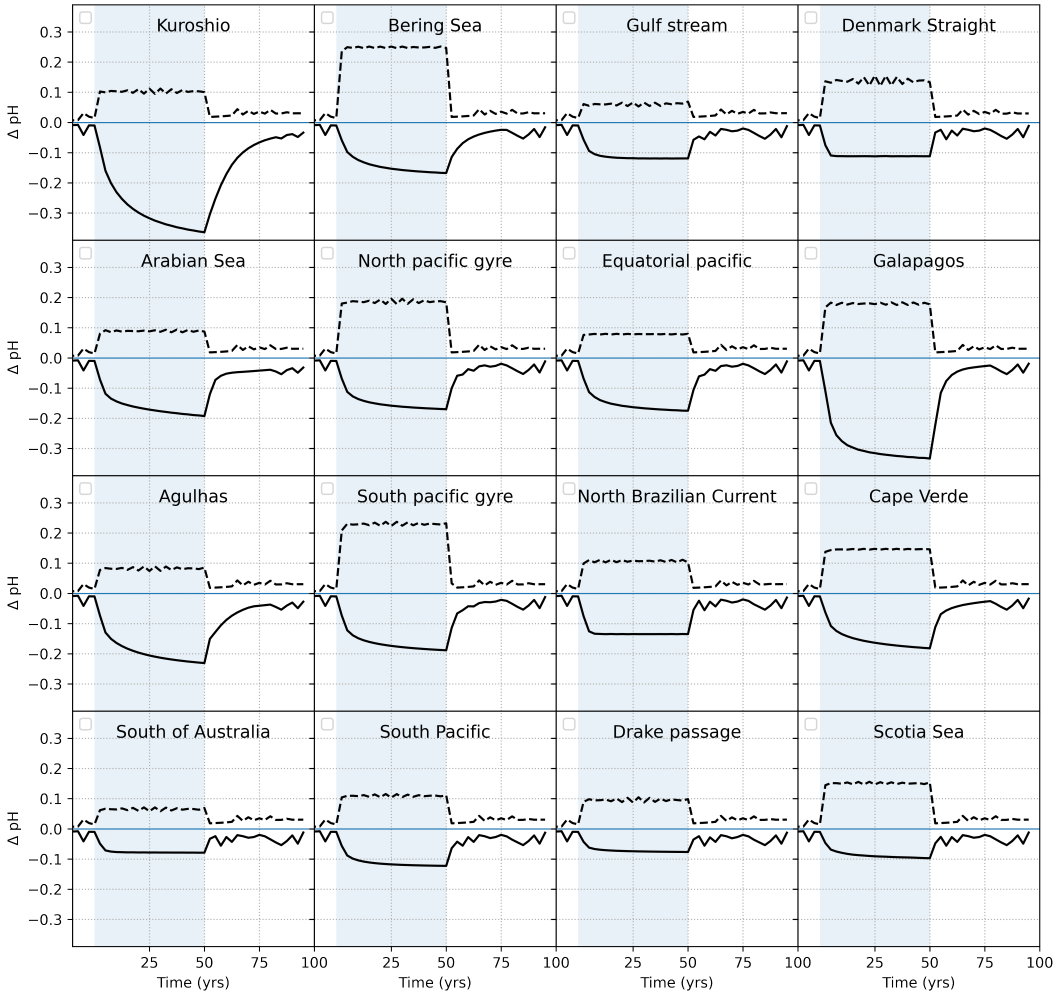

Figure S4 Depth plots of changes in calcite saturation (Ω) at the end of the pumping period (50yrs) for globally uniform acid pumping to 2-3km depth. In some locations, likethe Gulf stream and Denmark Straight, sinking surface waters pull surface alkalinity into deeper waters where it can't be neutralized by atmospheric CO_2 (e.g) and explain the significantly reduced uptake efficiency in these areas (Figure 5, main text). Surface-omega changes are also lower in the southern ocean, perhaps due to the consistent high circum polar winds which reduce the ocean-atmosphere equilibration time for CO_2.

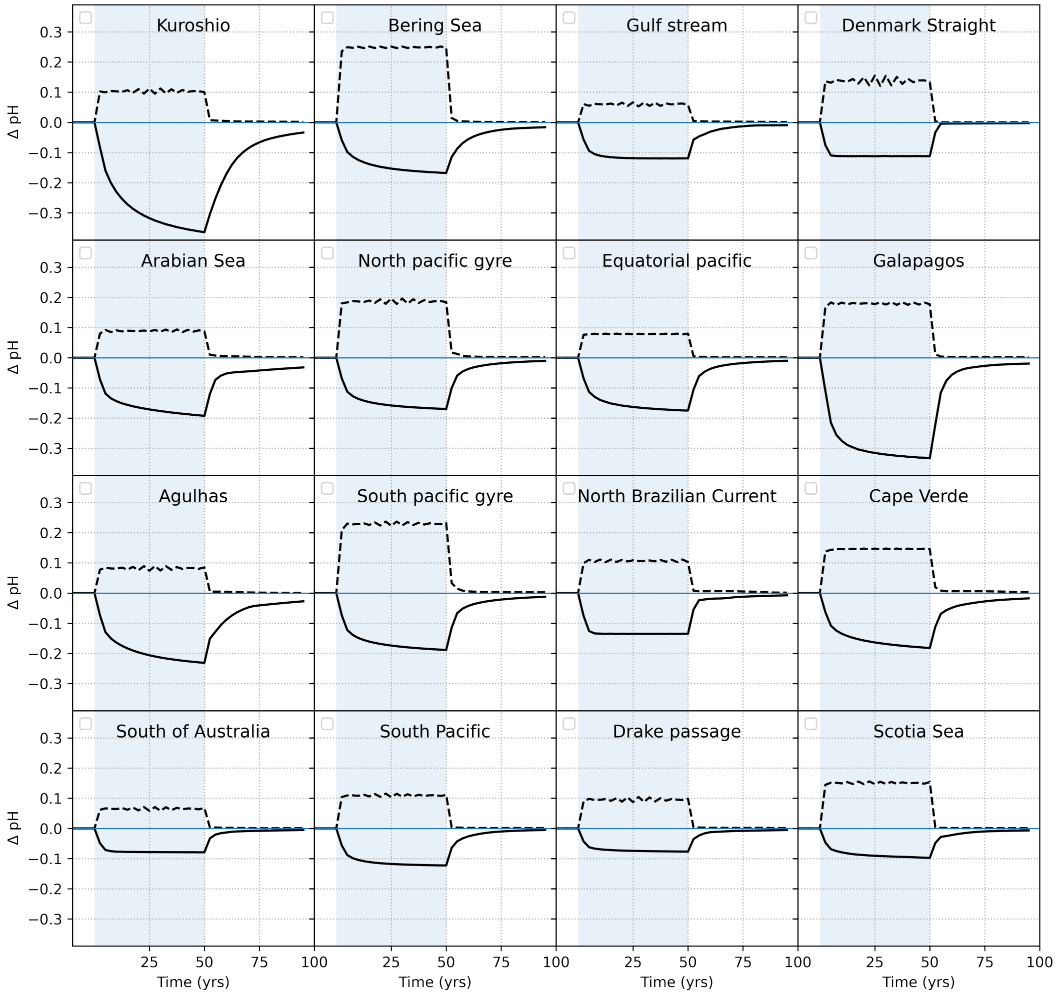

Figure S5 Time-resolved pH changes for individual locations indicated in Figure 5, showing ΔpH extrema at the surface (dashed) and at depth (solid) for the pumping time and 50 years beyond. In each simulation acidity was pumped at just one grid point, with a pumping density of 0.54mol/km2/s (approximately equivalent to 200tC/km2/yr). Note that because in each simulation acidity pumping was only performed at one location, the perturbation can diffuse and dilute horizontally leading to a faster return to baseline than shown in Figure C, where pumping was done uniformly across the entire ocean and at a much larger total rate.

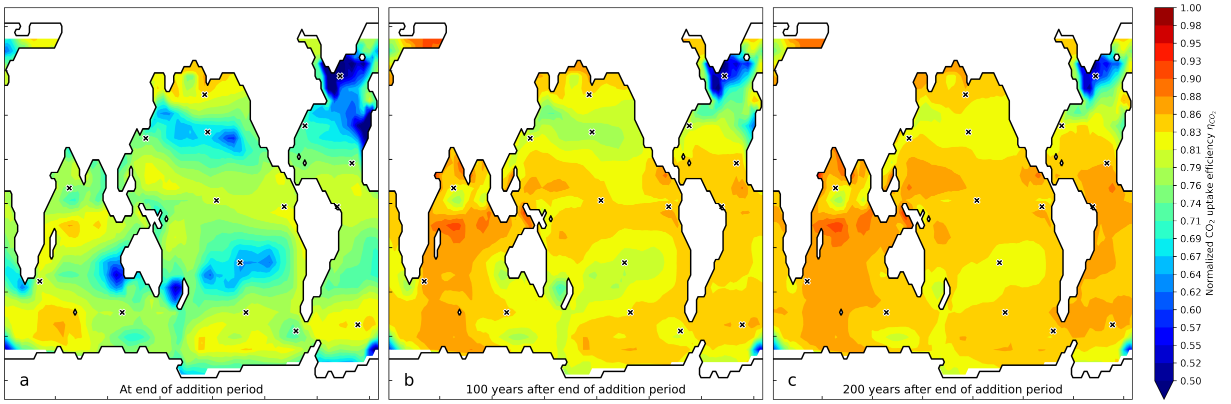

Figure S6 Uptake efficiency upon addition rather than pumping. Analogous to Figure 5 in main text. There exists significant variation in uptake efficiency which any practical ocean alkalinization scheme will need to take into account to maximize early rapid uptake of CO_2 and balance against costs of alkalinity transport.

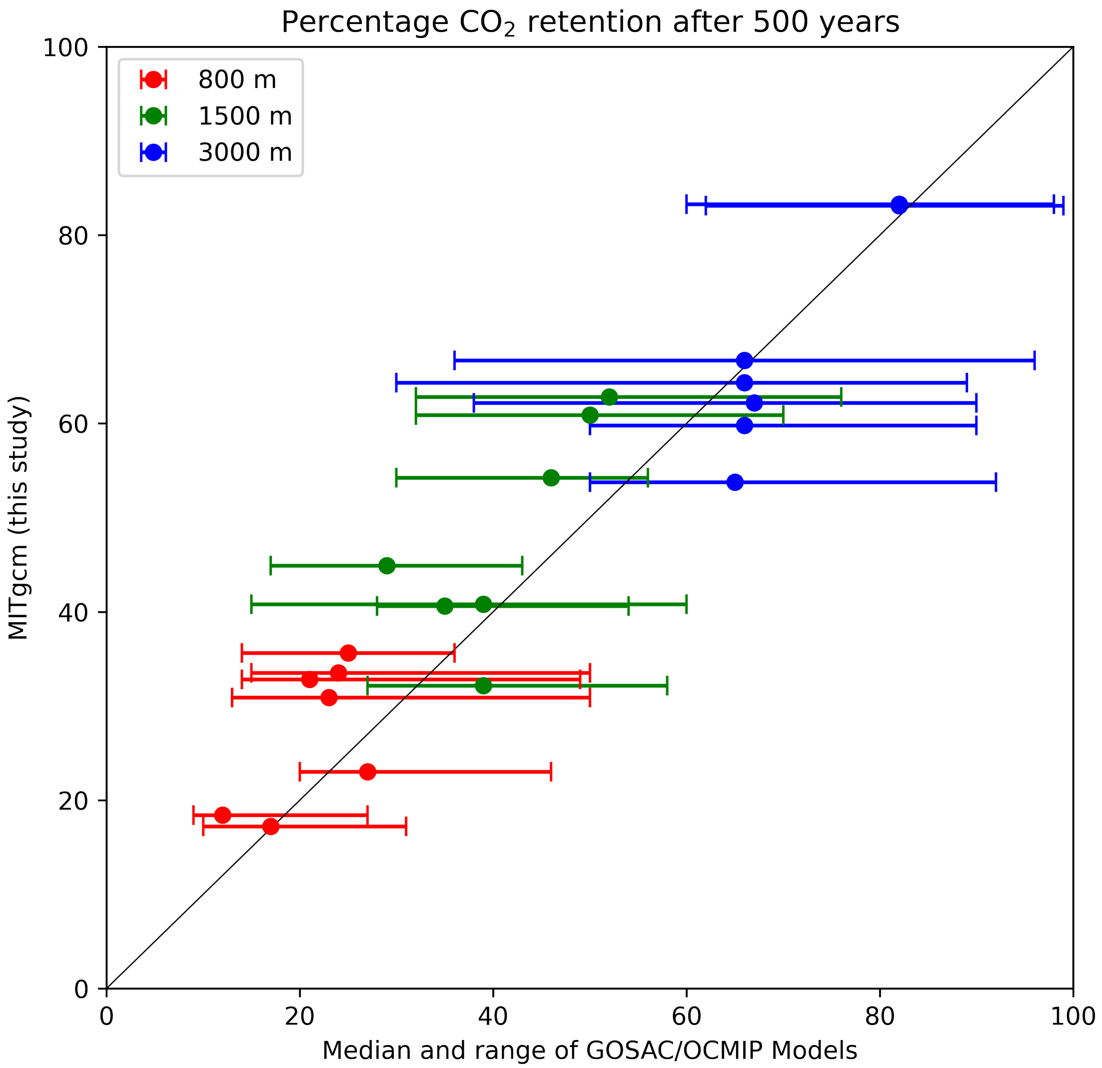

Figure S7 Comparison of CO_2 retention with results from a multi-model comparison (Orr et al. 2001) which used models of comparable resolution to simulate direct CO_2 injection. We ran our acid-pumping model for the 7 locations (Bay of Biscay, New York, Rio de Janeiro, San Francisco, Tokyo, Jakarta and Bombay) and three depths (800m, 1500m and 3000m) used used in the above study, to within the precision allowed for by the 15 vertical levels in our model. To match the conditions as closely as possible, calcium carbonate compensation was turned off. Since in our simulations we do not directly inject CO_2 into deep waters, we instead use the maximum absorbed CO_2 (shortly after the pumping period ceases) as 100% and calculate the retention efficiency going forward as a percentage of that peak. The plot shows the calculated retention efficiency after 500 yrs in our model against the median times observed in the 9 models tested as part of the above study (with the error bars indicating the range observed between the 9 models). We see that, in general, there is good agreement for almost all locations and depths, though we note that there is considerable uncertainty in the OCMIP models.