Nonlinearities in seawater carbonate chemistry and the distribution of anthropogenic carbon uptake

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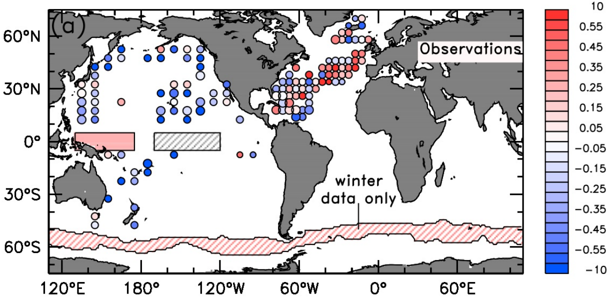
FUTURE OF OCEAN CO_2 SINK?

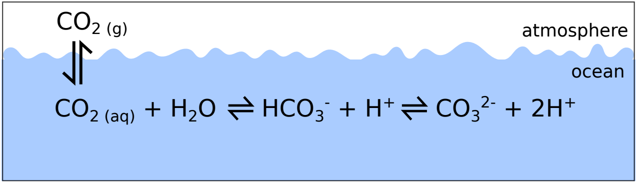
Currently, the ocean takes up ≈ 26% of anthropogenic CO_2 emissions (IPCC, AR5). But will that continue?



Trend in pCO_2^{ocean} - pCO_2^{air} (μatm yr^{-1}) between 1981 and 2007, Le Quéré et al., 2010

Trends in CO_2 uptake can be driven by changes in pCO_2^{atm}, by changes in ocean state (both long-term change and interannual), and by pecularities of ocean CO_2 chemistry

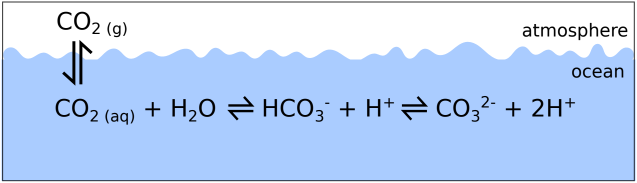
CO_2 in seawater



CO_2 reacts with water to H_2CO_3 and dissociates:

$$
\begin{aligned}
CO_2^{aq} + H_2O &\Leftrightarrow H_2CO_3 \\
H_2CO_3 &\Leftrightarrow HCO_3^- + H^+ \\
HCO_3^- &\Leftrightarrow CO_3^{2-} + H^+
\end{aligned}
$$

CO_2 IN SEAWATER



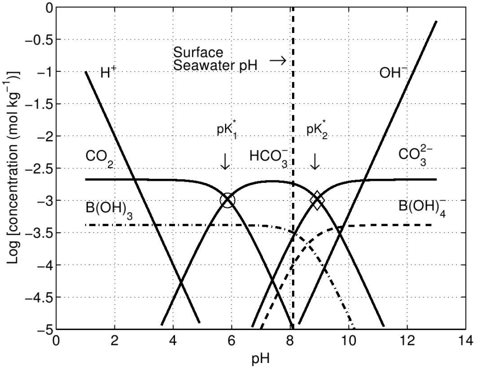
In equilibrium, we have the law of mass action for the dissociation reactions

$$K_1 = \frac{[\mathrm{HCO_3^-}][\mathrm{H^+}]}{[\mathrm{CO_2^*}]}$$

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

BJERRUM PLOT

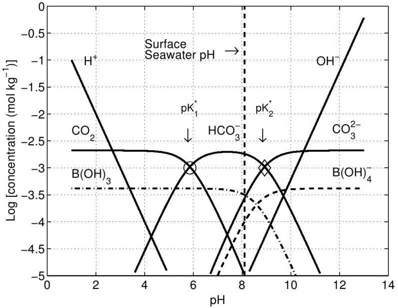
For a fixed total amount of *dissolved inorganic carbon* DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}], the concentration of the individual forms of carbon (y-axis) depends on the pH = -$\log_{10}$([H^+]) of the water (x-axis)



WHY SO MUCH CARBON IN THE OCEAN?

Average ocean pH ≈ 8.1 results in

1% CO_2
90% HCO_3^-
9% CO_3^{2-}



i.e. the ocean holds ≈ 100 times as much carbon as inferred from solubility of CO_2 alone, and ca. 50 times as much as the atmosphere

Until ca. 1955 it was assumed that this partitioning would remain constant: almost all anthropogenic emissions of carbon would dissolve in the ocean

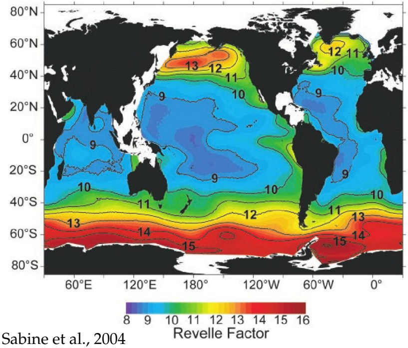
Roger Revelle (1909-1991)

Revelle and Suess, 1957:

- increasing CO_2 leads to $CO_2^{aq} + H_2O \Rightarrow$ $HCO_3^- + H^+ \Rightarrow CO_3^{2-} + 2H^+$
- this produces H^+ ions (acidification)
- and shifts the equilibrium towards higher CO_2 fraction in DIC
- the DIC increase is therefore smaller than that of CO_2

the ocean carbonate system is buffered!

BUFFERING = REVELLE FACTOR



Sabine et al., 2004

the Revelle factor

$$R = \frac{dCO_2}{CO_2} / \frac{dDIC}{DIC}$$

varies between 8 and 15

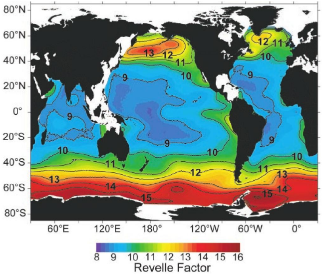
it increases with

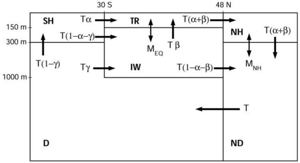
- increasing CO_2
- decreasing temperature
- increasing salinity/alkalinity

Implications for the North Atlantic

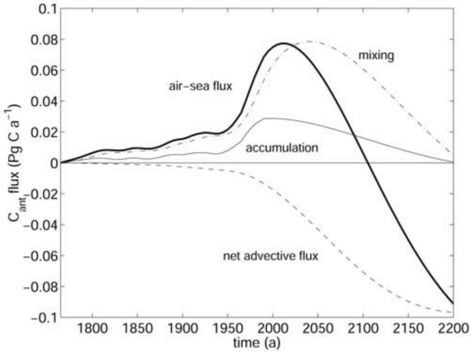
- R is lower in subtropical than subpolar North Atlantic
- for the same increase in CO_2, therefore, the increase in DIC is larger in subtropical N.A. than in subpolar
- overturning transports this increased DIC into subpolar N.A.
- reducing air-sea carbon flux there

Völker et al. (2002), box model with constant temperature, salinity and circulation: consequences of buffer factor differences on DIC uptake?



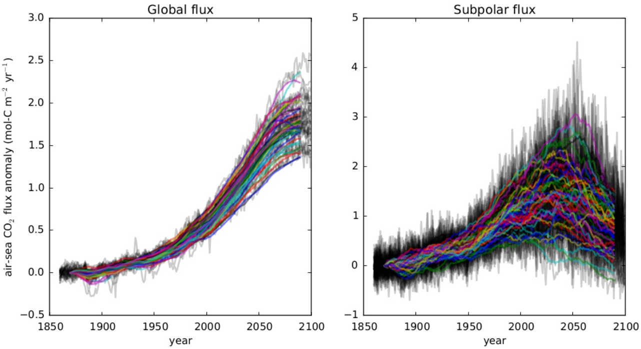


PEAK-AND-DECLINE CO_2 UPTAKE IN THE NORTH ATLANTIC!



advection of C_{ant}-rich water leads to a reversal in the carbon uptake in the subpolar North Atlantic. But: assuming constant climate

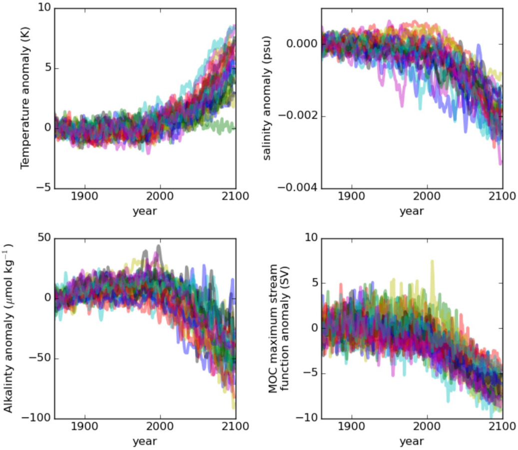
PEAK-AND-DECLINE UPTAKE IN EARTH-SYSTEM MODEL



Halloran et al., 2015

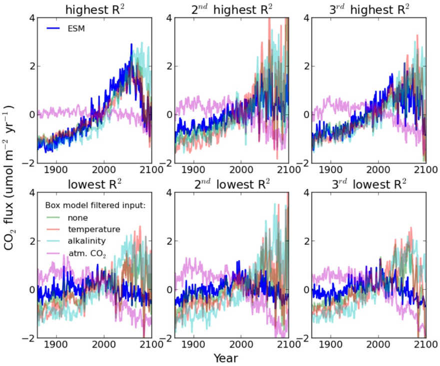
ensemble of scenario runs until end of 2100 with coupled atmosphere-ocean climate model: again reversal in carbon uptake in subpolar North Atlantic

MORE THAN JUST ONE FORCING



but this time, not only $p\mathrm{CO_2}$ changes, but temperature, overturning, salinity

USE A BOX MODEL TO SEPARATE MECHANISMS

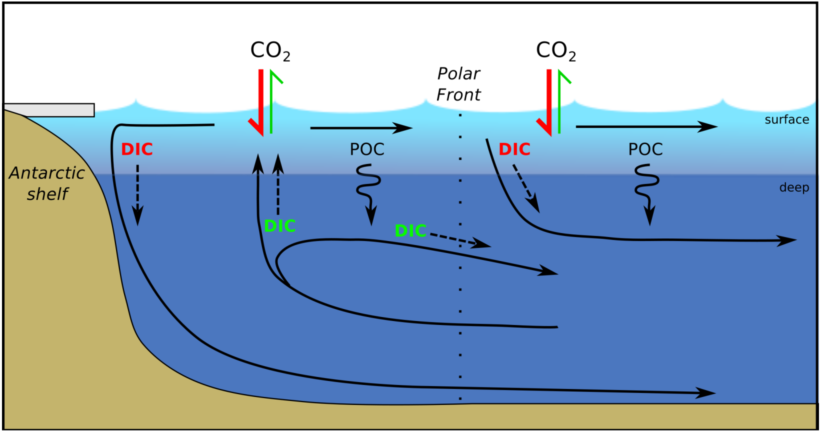


Halloran et al., 2015

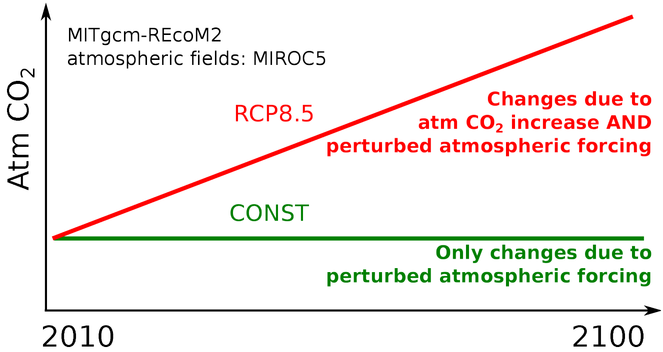
reproduce the earth system model output using the box model, forced with temperature, overturning, salinity from ESM?

identificaton of mechanism: keep one forcing constant

The Southern Ocean



Future of SO carbon sink

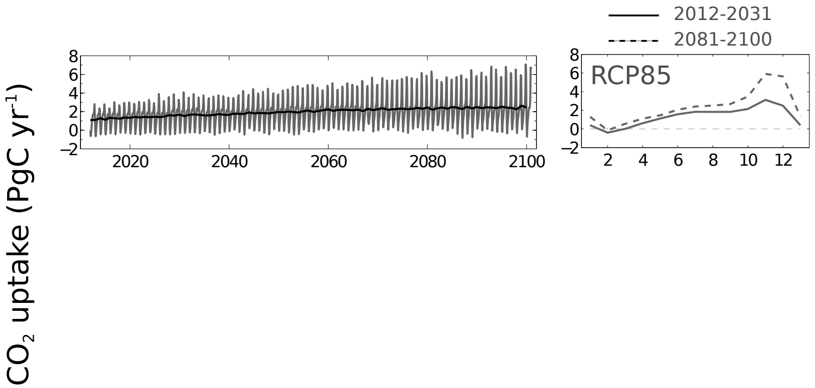


Hauck & Völker, 2015

scenario runs with global ocean/biogeochemical model (MITgcm/REcoM) until 2100; forced with atmospheric output from CMIP5 model and -optionally- with increasing $p\mathrm{CO}_2$

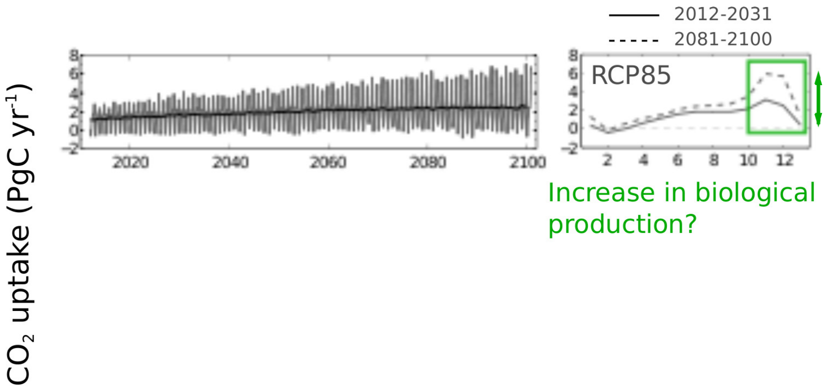
MITgcm-REcoM2 future simulation

CO_2 uptake, south of 30°S



MITgcm-REcoM2 future simulation

CO_2 uptake, south of 30°S



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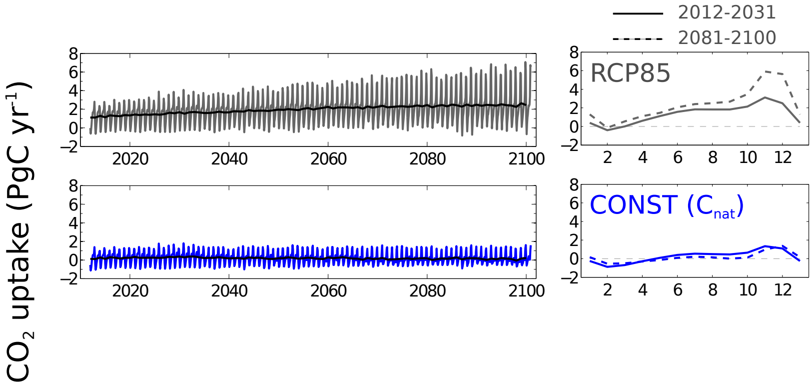

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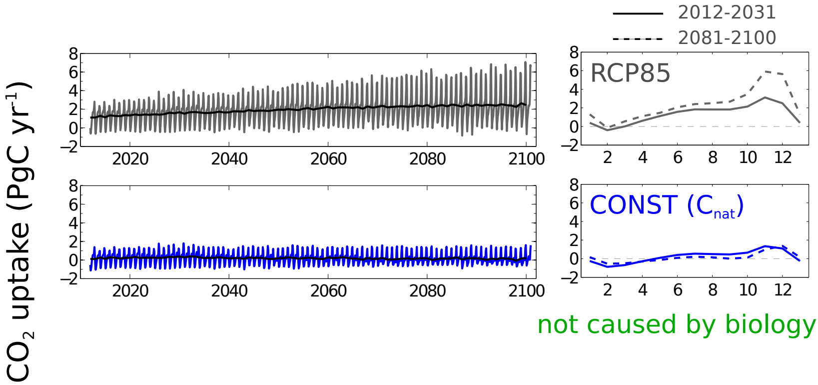
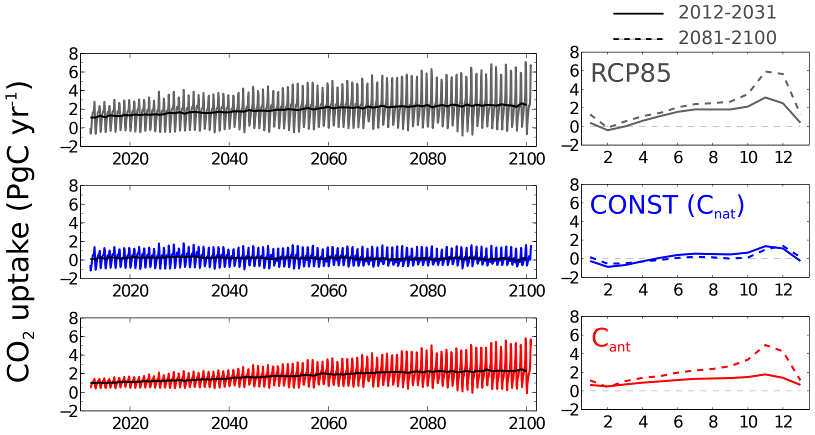


not caused by biology

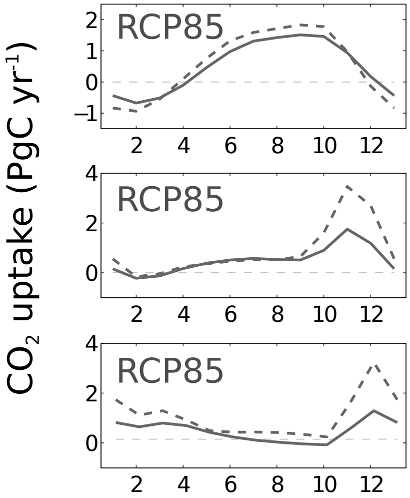
MITgcm-REcoM2 future simulation

CO_2 uptake, south of 30°S



MITgcm-REcoM2 future simulation

CO_2 uptake, subregions



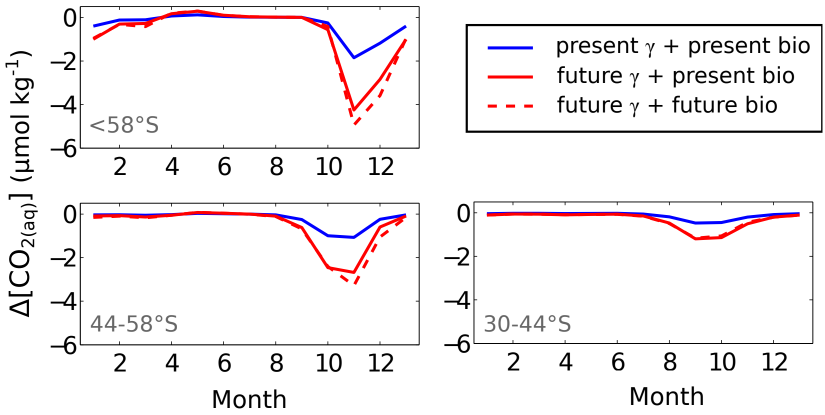
30 - 44°S

44 - 58°S

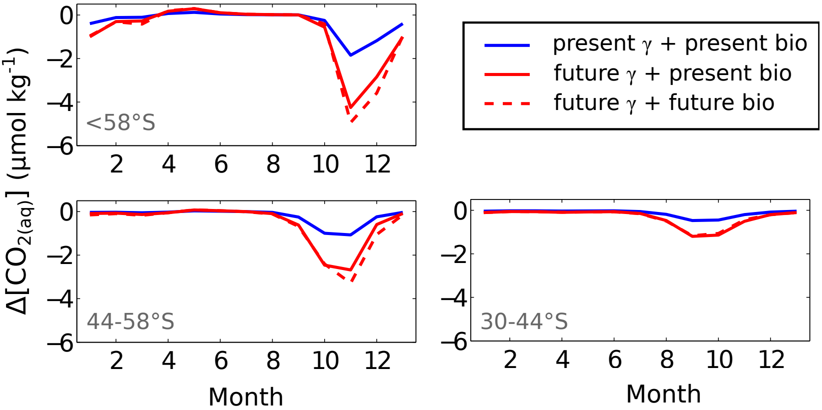
< 58°S

Large effect south of 44°S

Effect of buffer factor on $CO_{2(aq)}$



Effect of buffer factor on $CO_{2(aq)}$



Increasing Revelle factor (decreasing buffer capacity) of the ocean interacts with biology and leads to more CO_2 uptake per DIC draw-down by biology

CONCLUSIONS & IMPLICATIONS

- Revelle and Suess (1957): Buffering of the carbonate system limits anthropogenic carbon (C_{ant}) uptake
- North Atlantic:
  - Revelle factor depends on temperature: stronger buffering at high latitudes
  - subtropical Atlantic more important for C_{ant} uptake than subpolar
  - changes in Revelle factor due to acidification cause peak-and-decline C uptake in the North Atlantic
- Southern Ocean:
  - generally less C_{ant} uptake at higher Revelle factor - but larger C_{ant} uptake in regions with high seasonality
  - total $CO_{2(aq)}$ draw-down more than doubles due to change in buffer factor.
  - larger contribution of southern Southern Ocean to total C uptake
  - increasing seasonality of C uptake