

Engineering Carbon Sequestration in the Ocean

Ian S F Jones and Chien Hsing Lu

Ocean Technology Group
University of Sydney,
N.S.W. 2006 Australia
Tel: (61 2) 93514585 – Fax (61 2) 93514584
Email: otg@otg.usyd.edu.au

Abstract

The ocean is a large sink of carbon dioxide released as a result of fossil fuel burning. This paper examines the impact of methods that might be used to increase this uptake of carbon dioxide by the ocean and the effect this will have on ocean alkalinity. There are three sequestration strategies for the ocean: direct injection, deliberate changes in alkalinity and Ocean Nourishment. Changes of alkalinity as a result of these strategies imply changes in carbon dioxide partial pressures. Once the stored carbon dioxide is again in contact with the atmosphere the changed partial pressures have implications for the longer-term sequestration of this carbon.

Introduction

Increasing concentrations of carbon dioxide in the atmosphere threatens to lead to rapid climate change. It is prudent to consider realistic ways of controlling this greenhouse gas. While a shift from fossil fuel use would be an effective strategy, the short term benefits of this abundant low cost energy make this unlikely in a world of rising population and increasing gross national product. An alternative strategy is to store the carbon dioxide away from the atmosphere. The ocean is already sequestering some one third of the fossil fuel carbon and if given enough time would capture most of the newly released carbon and incorporate in its carbonate pool.

The important issue for Greenhouse gas management is how to accelerate this oceanic carbon uptake in the near term. There are three approaches for engineering the storage of additional carbon in the ocean.

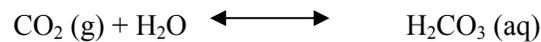
1. **Direct injection.** Carbon dioxide needs to be captured and compressed so it can be injected into the mid-depth of the ocean.
2. **Increase the alkalinity of the ocean.** The pH of the ocean has a strong influence on the solubility of carbon dioxide in sea water and Kheshgi (1995) pointed out how increasing the total alkalinity by one mole increases the carbon content by 0.89 moles (under typical surface ocean conditions). Thus he examined the impact of adding lime, CaO, to the surface ocean. Another approach studied by Caldeira and Rau (2000) uses bicarbonate.
3. **Enhanced photosynthesis** leads to more carbon being exported from the surface ocean. Ocean Nourishment is the concept of providing additional nutrients to surface ocean to sequester atmospheric carbon dioxide and to increase the sustainable fish catch. The rapid rise in population expected in the next 30 years will increase the demand for protein and the ocean is highly capable of being more productive. It is currently supplying only 6% of human protein.

The addition of reactive nitrogen and other nutrient will increase the primary production and stimulate the food web. As a result of the increased primary production, the atmospheric carbon dioxide is transferred to the ocean to be incorporated into the biomass that falls out of the photic zone. It is suggested by Jones and Otaegui (1997) that in a life cycle analysis, 1 tonne of nitrogen will sequester about 12 tonnes of carbon dioxide. Some of the consequence of large scale introduction of Ocean Nourishment are discussed in Jones (2000) while the issue of concern to the public are reviewed in Jones and Young (2001).

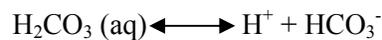
Carbon Chemistry

Carbon chemistry is one of the essential topics in understanding ocean sequestration of carbon since the chemistry of how carbon reacts with seawater and sea minerals affects the rate of ocean up-take. When the carbon concentration is in equilibrium between the atmosphere and the ocean, Henry's law says that there will be no carbon flux as there is no concentration gradient. It is natural to approach the equilibrium state and there is always carbon flow between the ocean and atmosphere towards this end. The ocean has the largest carbon storage capacity amongst the tree carbon reservoirs.

Carbon dioxide reacts with seawater and forms carbonic acid (H_2CO_3). The reaction can be represented by this equation:



Then carbonic acid is further dissociate in two steps and forms bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}),



These basic reactions allow us to calculate the concentration of carbon in the ocean and also predict the effect of additional carbon to the ocean in terms of total alkalinity, total carbon, pH and partial pressure of carbon dioxide. Takahashi et al (1980) published such a model.

Total carbon is the sum of the amount of inorganic carbon in the ocean. Carbon flux into the ocean occurs when atmospheric carbon dioxide concentration is increased. As a result, the pH of seawater decreases. It is stated by Kheshgi (1995) that, "For seawater at equilibrium with the atmosphere, increases in atmospheric CO_2 from a pre-industrial values of 285 to 350 μatm would have already decreases the pH by 0.079 and $[\text{CO}_3^{2-}]$ by 20 $\mu\text{mol/kg}$."

Total alkalinity is a measure of the charge that is able to take up anions in seawater. Increasing the total alkalinity in seawater increases the solubility of carbon dioxide.

Ocean carbon cycle

The essence of the ocean carbon cycle can be understood by considering a uniform temperature ocean in equilibrium with the atmosphere and in steady state. In our idealised ocean, water is subducted to the deep ocean with the dissolved inorganic carbon (DIC) in equilibrium with the atmosphere. As the water slowly moves through the ocean, organic detritus remineralises to nitrate and other inorganic material. This increases the DIC and lowers the alkalinity. When the water is eventually upwelled (after hundreds of years) it reaches the photic zone, rich in nutrients and with a higher carbon dioxide partial pressure than in the atmosphere. The carbon dioxide

starts to degas to the atmosphere, lowering the DIC. Once photosynthesis starts, carbon is exported from the photic zone as organic material and this again lowers the DIC. First the nutrients are converted to organic material, a process termed *new* primary production. Some of this organic material is exported to deep ocean, some remineralised in the upper ocean and again taken up by a second round of photosynthesis. This process continues until one of the nutrients is exhausted (mostly nitrogen, 80% of the ocean or iron, 20% of the ocean). The process is illustrated in Fig 1. shown below. Once one of the nutrients is exhausted, photosynthesis ceases and the low partial pressure of carbon dioxide in the water causes flux of carbon dioxide from the atmosphere into the surface ocean until equilibrium with the atmosphere is established. Then subduction starts the process all over again.

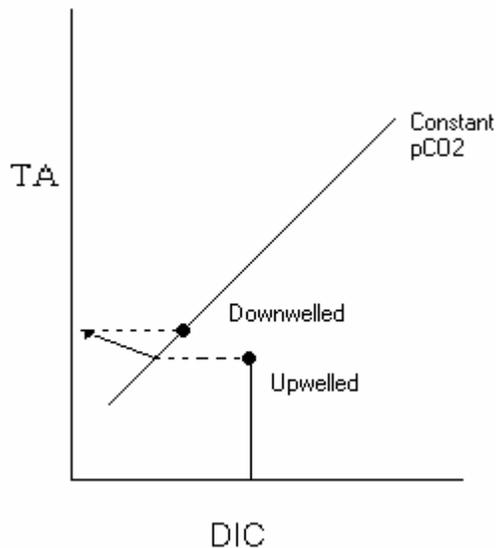


Figure 1 Shows the change in Dissolved Inorganic Carbon (DIC) in the surface ocean as upwelled water degases (Dotted line) undergoes photosynthesis (Solid line) and uptakes atmospheric CO₂ (Dotted line).

Three strategies

Direct injection

When carbon is directly injected into the mid-depth ocean in the form of carbon dioxide, the alkalinity is not changed but the pH decreases. When the dissolved carbon dioxide is upwelled into the surface ocean it degases and pH of the seawater returns to the earlier value of about 8.2. It takes some 400 hundred years after the injection to the depth of 1000m for most of the carbon to be back in the atmosphere. Alkalinity is not important in this sequestration strategy, as it undergoes no changes as a result of injection.

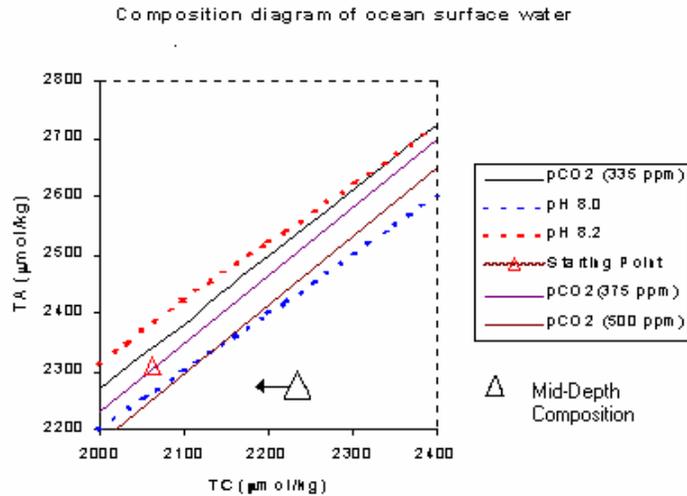


Figure 2: Composition of upwelled seawater after direct injection shown conceptually.

Alkalinity changes

To change the alkalinity of the ocean, the concentration of at least one of, carbonate, bicarbonate, and hydroxide ion has to change. The approximate expression of total alkalinity is:

$$TA = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{OH}^-]$$

In order to increase the total alkalinity, the concentrations of carbonate and bicarbonate have to have to become greater. This occurs when more carbon flows into ocean from the atmosphere to maintain the equilibrium state. This implies that the increase in total alkalinity lowers the partial pressure of carbon dioxide in the water and so enhances the ocean's ability to sequester carbon dioxide. As the carbon sequestered with changes in alkalinity stays in the form of inorganic carbon, the carbon sequestered stays in the ocean permanently.

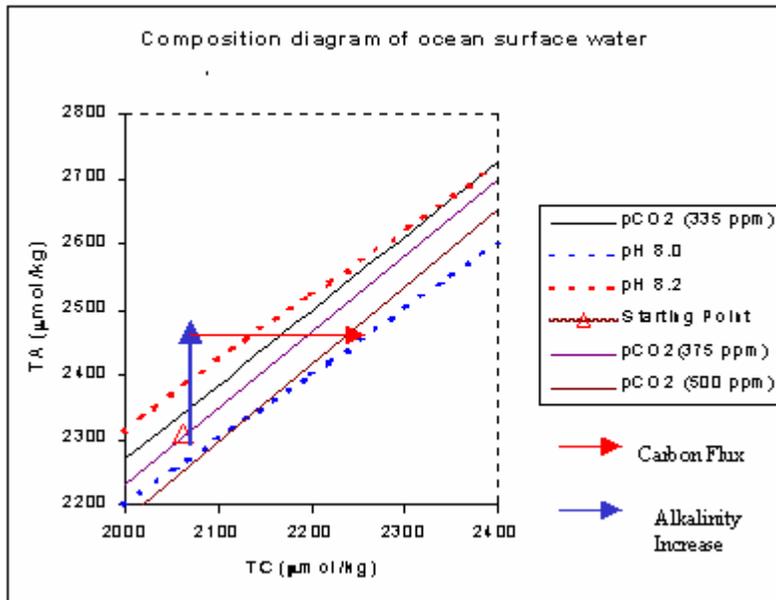


Figure 3: Composition of surface seawater after an alkalinity change and return to equilibrium with the atmosphere shown conceptually.

Ocean Nourishment

While the chemical reactions to direct injection or to alkalinity changes are relatively straight forward, the situation is more involved in the case of Ocean Nourishment. When nitrogen is added to waters in the photic zone with adequate other nutrients, additional DIC is converted to organic matter and exported from the surface layer of the ocean. This process changes the alkalinity and enhanced primary production.

When the sea is in equilibrium with the atmospheric $p\text{CO}_2$, a change in alkalinity of $1 \mu\text{mole/kg}$ induces a flux of carbon dioxide into the sea of approximately $1 \mu\text{mole of C}$. The first response of adding nitrogen in the form of NH_3 gas is to increase the pH and total. Since $1 \mu\text{mole of NH}_3$ changes the alkalinity about $1 \mu\text{mole}$,



$14 \mu\text{g of N/kg}$ (in the form of NH_3 gas) will lead to the flux of $12 \mu\text{g of C}$ due to the alkalinity change. Re-expressed we can say that approximate 17 gm of NH_3 added to the sea will cause the flux of 44 gm of CO_2 . Ammonia takes up $44/17$ times its weight in carbon dioxide. This process continues (in the absence of photosynthesis or subduction) until the equilibrium between $p\text{CO}_2$ and the atmospheric partial pressure is achieved.

With time the phytoplankton will be undertaking photosynthesis. This can be considered as following the equation: (after Redfield, 1963)



Thus the total carbon decreases while the consumption of OH^- ions means that the total alkalinity decreases. After photosynthesis, modelled as above, the total alkalinity has changed but one mole per mole of NH_3 and the carbon is now in the form of organic carbon which is eventually exported from the mixed layer under the influence of gravity. Again $p\text{CO}_2$ is lowered in the surface water and further carbon flux from the atmosphere.

If the photosynthesis is involved with the production of calcium carbonate shells (CaCO_3) the $p\text{CO}_2$ will increase leading to degassing. This is counter intuitive as this process involves precipitation of carbon. The effect of the carbon precipitation decreases 2 units in Total Alkalinity and 1 unit in Total Carbon. Refer to the Figure 4 below. The $p\text{CO}_2$ moves from low pressure to high pressure when carbon is precipitated. Thus, carbon dioxide escapes to the atmosphere.

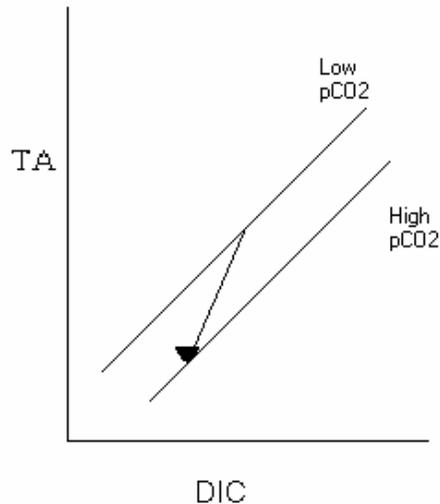


Figure 4: Precipitation of Calcium Carbonate

During the initial period of Ocean Nourishment, the export of carbon will be increased but the deep water in which the exported carbon is remineralised retains the its pre-ocean nourishment seawater properties. The extra remineralisation will lower the Total Alkalinity more than the pre-ocean nourishment level. When the post-ocean nourishment water is upwelled to be in communication with the atmosphere it would retain less DIC. It would be possible to compensate for low Total Alkalinity by adding by carbonate. This is a transient problem because high total alkalinity water is downwelled post ocean nourishment and eventually would take up more DIC then pre-ocean nourishment on returning to the surface.

There maybe advantages in combining Ocean Nourishment and Alkalinity change. For example, if ammonia scrubbing of flue gases yield ammonia bicarbonate it could be used to nourish the ocean and increase the Total Alkalinity for better sequestration efficiency. Nourishment with ammonia drives up the alkalinity initially by changing the pH. However, if bicarbonate ion is provided, the difficulties that might be associated with high pH can be avoided.

Conclusion

Ocean storage is a potentially important element in a climate manage strategy. The three approaches available to increase the rate of dissolution of atmospheric carbon dioxide in the ocean. When the atmospheric carbon dioxide partial pressure is increased the amount of carbon at equilibrium is also increased. At constant atmospheric partial pressure, direct injection of carbon dioxide affects the pH of seawater but doesn't store the carbon in the ocean permanently. However, changing the alkalinity allows more carbon dioxide storage in the ocean permanently at constant atmospheric carbon dioxide partial pressure. In the case of ocean nourishment, it retains additional the carbon as long as the nutrients are preserve in the ocean while the alkalinity of the ocean fluctuates but undergoes no long term change.

There maybe advantages in combining nitrogen nourishment with favourable alkalinity shift during the transient period when ocean nourishment is first implemented.

Reference

- Caldeira, K and G H Rau (2000) Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: geochemical implications. *Geophysical Research Letters*, **27**, 225-228.
- Jones, I S F (2001a) Ocean nourishment in the Humbolt Current. In ed. R Durie et al. CSIRO, Syd. ISBN 0643066721.
- Jones, I.S.F. & Otaegui, D. (1997) Photosynthetic greenhouse gas mitigation by ocean nourishment. *Energy Convers. and Mgmt*, **38S**, 379-384.
- Jones, I.S.F. (1996) Enhanced carbon dioxide uptake by the world's oceans. *Energy Conversion and Management*, **37**, 1049-1052.
- Jones I.S.F. and H. E. Young, (2001) The short and long term role of the ocean in Greenhouse Gas mitigation, Proc. 1st Nat Conference on Carbon Sequestration 2001.
- Jones I.S.F. (2001) The global impact of Ocean Nourishment, *Proc. 1st Nat Conference on Carbon Sequestration 2001*.
- Jones, I.S.F. and K. Caldeira (2003) Long-term ocean carbon sequestration with macronutrient addition. *Proc of this conference*.
- Kheshgi, H S (1995) Sequestering atmospheric carbon dioxide by increasing ocean alkalinity. *Energy*, **20**, 915-922.
- Redfield, A C, B H Ketchum and F A Richards (1963) The influence of organisms on the composition of sea water. *The Sea Vol 2*