

## Influence of carbon sequestration on biogeochemistry of carbon in the ocean

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### Abstract

Global weather is becoming warmer and temperatures may be increased by about 4°C by year 2100. This may have disastrous consequences on oceanic biogeochemistry of carbon. It is estimated that 1/4<sup>th</sup> of global mountain glaciers may be disappeared by 2050 if the similar rate of melting continues. Oceans are already absorbing less than half of anthropogenic carbon released to the atmosphere. There are several evidences that biological pump seems to be weakening in the major parts of the world ocean and strengthening in the low latitude regions especially equatorial, northern Indian Ocean and equatorial Atlantic. In the high latitude regions, where iron (Fe) is main controlling nutrient, primary production seems to be decreasing in the recent years where Fe fertilization might result in injection of atmospheric CO<sub>2</sub> into the ocean. On the other hand, it is also important to examine how increase in primary production artificially impacts other biogeochemical processes in the water column. The apparent oxygen utilization (AOU) seems to be the highest in the northern Indian Ocean where the higher sinking organic fluxes are observed and showed positive relationship. Therefore, enhanced primary production by Fe fertilization might result in formation of suboxic or anoxic conditions in the subsurface layer through increased sinking organic carbon fluxes. Such conditions are conducive for formation of another greenhouse gas, nitrous oxide, through denitrification. The alternative approach to sequester atmospheric CO<sub>2</sub> will be direct injection of CO<sub>2</sub> to the deep sea. Several laboratory experiments suggested that injection of liquefied CO<sub>2</sub> to the deep ocean has severe consequences on benthic organisms through decrease in pH. On the other hand, modeling efforts suggests that drastic decrease in pH due to direct CO<sub>2</sub> injection to deep sea is influenced by rate of discharge, droplet size, currents movement at the discharge region etc. Therefore, more studies are required to examine the factors that are influenced by these two strategies before they are ready to apply in the field.

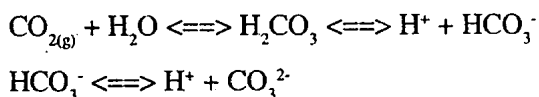
## Introduction

Since the beginning of the industrial period in the late 18<sup>th</sup> century, i.e., over the anthropocene (Crutzen and Stoermer, 2000), humankind has emitted large quantities of CO<sub>2</sub> into the atmosphere, mainly as a result of fossil-fuel burning, but also because of land-use practices, e.g., deforestation (Houghton and Hackler, 2002). Oceanic CO<sub>2</sub> levels are expected to rise during the next 2 centuries to levels not seen for past 10–150 million years by the uptake of atmospheric CO<sub>2</sub> in surface waters. Measurements and reconstructions of the atmospheric CO<sub>2</sub> history reveal, however, that less than half of these emissions remain in the atmosphere (Prentice et al., 2001). The anthropogenic CO<sub>2</sub>, which was not accumulated in the atmosphere, must have been taken up by the ocean, by the land biosphere, or by a combination of both. The relative roles of the ocean and land biosphere as sinks for anthropogenic CO<sub>2</sub> over the anthropocene are currently not known.

The absorption of CO<sub>2</sub> by the ocean involves complicated physical, chemical, biological and geological processes. The study of understanding biological and geochemical processes that regulate chemical equilibria at the Earth surface can be broadly termed as 'biogeochemistry'. Many of the climatically important gases influencing the Earth's radiation budget result from these processes occurring in hydrosphere, geosphere or atmosphere. Oceans form a major part of the hydrosphere on our planet as it covers 71% of the earth surface area and contains more than 97% of all water on the planet. Understanding biogeochemical processes in the oceans such as CO<sub>2</sub> uptake and release, exchange of biogenic trace gases, fluxes of particulate and dissolved organic carbon to different depths, variable bacterial activity and phytoplankton blooms, are critical to the global carbon cycling.

### What is biogeochemical cycling of carbon in the ocean?

Most of the oceanic CO<sub>2</sub> is present in dissolved forms of carbonic acid (in equilibrium with gaseous component, CO<sub>2</sub>), bicarbonate and carbonate ions, maintained through the equilibria



The gaseous component is less than 5% of the total dissolved inorganic carbon (DIC), which in surface layers of the ocean remains in equilibrium with that in air. Therefore, an increase in sea surface temperature (SST) or acidity would enhance the partial pressure of carbon dioxide (pCO<sub>2</sub>) in seawater and can result in its increased emission from the ocean. In addition to this, biological processes do also significantly influence surface pCO<sub>2</sub> levels through microbial respiration. These processes together with an estimated absorption of anthropogenic carbon from the atmosphere reflect the influence of ocean carbon processes on CO<sub>2</sub> levels in air.

Phytoplankton in the sunlit upper ocean absorbs atmospheric CO<sub>2</sub> and convert to organic carbon. Part of the organic carbon recycled in the upper ocean through microbial processes and the rest sinks down to the deep ocean and is called biological pump. In many areas of the ocean, particularly in tropics and subtropics, the strength of the biological pump is depended on the availability of nitrogen compounds. On the other hand, in some regions, micro nutrients, such as Iron (Fe), control primary production, since it serves as a cofactor for a wide variety of enzymes and redox catalysts (Raven, 1990; Tortell et al., 1999). Ecosystem-scale perturbation experiments have demonstrated

that low ambient Fe concentrations control phytoplankton growth, community composition and ecosystem function in large areas of the world's ocean, including the equatorial Pacific (Coale et al., 1996), the subarctic Pacific (Tsuda et al., 2003; Boyd et al., 2004) and the Southern Ocean (Boyd et al., 2000; Coale et al., 2004). In these regions, mesoscale "Fe enrichments" experiments have resulted in phytoplankton blooms and a switch in the ecosystem from recycling- to export dominated planktonic communities (Bishop et al., 2004; Buesseler et al., 2004).

Carbon, phosphorus and silica are used to build skeletal (eg. Carbonates, apatite and opal respectively) materials in some plankton. Phytoplankton is the starting material for secondary (zooplankton) and tertiary (fish) life forms in the ocean. About 90% of the organic material produced is recycled in the surface mixed layer because of microbial degradation. The remaining material sinks into subsurface layers (export flux) where it continues to decompose due to bacterial respiration. The skeletal debris consists of two varieties of crystal structure of calcium carbonate called aragonite and calcite. The aragonite is very sensitive to pH and pressure than calcite, therefore, aragonite saturation generally occurs in the shallower depth (~500 m) than calcite (>3000 m). Hence, changes in decomposition rates in the subsurface waters that lead to changes in pH, will have greater impact on aragonite dissolution. The remnant organic and skeletal materials reach ocean bottom and get deposited in the sediments. Even after deposition in sediments, these materials continue to be decomposed and dissolved due to which the materials are released back to seawater.

### **How Climate change affects these processes in the Ocean?**

Earth's atmosphere, hydrosphere and lithosphere has very delicate biogeochemical balance among different processes/systems. Disturbances in the system/process may result in drastic changes that can lead to either positive or negative feed backs. Here some of the processes that changed with time either naturally or anthropogenically for the past decades and its effect on biogeochemical carbon cycling are discussed. Such information will give us an idea on how carbon sequestration should be carried out and its possible feed backs.

- Based on the physical properties and mass of the world ocean as compared to other components of Earth's climate system, Rossby (1959) suggested that ocean heat content may be the dominant component of the variability of Earth's heat balance. Warming of the world ocean due to increasing atmospheric greenhouse gases was first identified in a report by Revelle et al (1965). Recently Levitus et al (2005) reported that world ocean heat content (0-3000 m) increased  $14.5 \times 10^{22}$  J corresponding to a mean temperature increase of  $0.037^{\circ}$  C at a rate of  $0.2 \text{ W/m}^2$  (per unit area of Earth's total surface area) from 1955-1998. Such increase in temperature has significant affect on biogeochemical processes in the ocean. The increased temperature, for instance, result in stratification (less mixing between upper few 10's meters of ocean with deep) that leads to less supply of nutrients to the surface. This severally affects phytoplankton production and structural change in the ecosystem. When new nutrients input reduce, phytoplankton production depends on the regenerated nutrients and it leads to switch over of ecosystem from export- to regenerated dominated plankton species.
- Gregg and Conkright (2002) observed the changes in chlorophyll concentrations between mean of 1979 to 1986 and 1997 to 2000 in the world oceans using remote sensing Coastal Zone Color Scanner (CZCS) and (Sea-viewing Wide Field of view Sensor (SeaWiFS) data. Global chlorophyll concentrations indicated a decrease from the CZCS record to the SeaWiFS by about 6%. Larger reductions occurred in the northern high

latitudes. Conversely, chlorophyll in the low latitudes increased and mid-ocean gyres exhibited limited changes. These results may indicate facets of climate change, some of which may be related to regional oscillation behavior such as the PDO and ENSO. Some of the decadal changes can be attributed to observed changes in SST or meteorological forcing. Interestingly chlorophyll-a in the northern Indian Ocean were increased by 25% during winter and 55 to 60% during spring and summer monsoon periods.

- Observations in the eastern North Pacific indicate that apparent oxygen utilization (AOU; is a measure of oxygen utilized to decompose organic carbon in the deeper ocean) was increased by 20-25% over the two decades from 1980-1997 (Emerson et al 2001). They attributed that changes in the biological pump or upper-ocean ventilation resulted in enhanced sinking fluxes to the deep ocean resulting in higher oxygen consumption rates (higher AOU). On the other hand, similar increasing trend in AOU was also observed in the western North Pacific based on 4 decades time-series analysis and found to be due to changes in upper ocean ventilation resulting in decrease in intermediate water formation (Ono et al., 2001). Similar increase in AOU in the northwestern Indian Ocean (Sarma et al., 2002) is also associated with increase in chlorophyll-a concentrations suggesting that enhanced biological pump leads to intensification of oxygen minimum zone in the subsurface waters (100-1200 m). Such increase in consumption rates of oxygen result in accumulation of biogenic gases, such as CO<sub>2</sub>, and N<sub>2</sub>O. Since the average residence time of the intermediate waters is about <10 years (for example Sarma, 2002), the accumulated gases will be back to the atmosphere in short-time scale. That might have strong impact on atmospheric biogenic gas budgets. In addition to this, decrease in dissolved oxygen levels in the intermediate waters will have significant effect on mesopelagic plankton. Therefore, changes in surface primary production by natural or artificial processes will have significant impact on deep-ocean carbon cycling.
- Oceans absorb about half of the carbon released to the atmosphere. The Inter-governmental Panel on Climate Change (IPCC) estimates for the oceanic sink of anthropogenic CO<sub>2</sub> to be 2 PgC/y (Prentice et al., 2001). Sabine et al (1999) found that anthropogenic carbon inventory increased since GEOSECS (1970's) to WOCE (1995), for instance, Indian Ocean (north of 35 S) by 4 PgC (1 PgC=10<sup>15</sup> g). This result in upward translation of aragonite saturation horizon by 50 to 70 m in the Pacific and Indian Ocean in two decades (Feely et al., 2002 and Sarma et al., 2002). The dissolution of CaCO<sub>3</sub> neutralizes anthropogenic CO<sub>2</sub> and adds TA via the dissolution reaction: CO<sub>2</sub> + CaCO<sub>3</sub> + H<sub>2</sub>O → 2HCO<sub>3</sub><sup>-</sup> + Ca<sup>2+</sup>. Sarma et al (2002) observed that TA was increased at the depth of aragonite saturation horizon by 4 to 13 umol/kg in the Pacific and Indian Oceans. The increase in TA serves to enhance the seawater's capacity of CO<sub>2</sub> absorption from the atmosphere. However, the long-term changes in TA are unknown.
- Recently Le Quere et al (2007) observed that Southern Ocean sink of CO<sub>2</sub> has weakened between 1981 and 2004 by 0.08 PgC/y per decade relative to trends expected from the large increase in atmospheric CO<sub>2</sub>. This weakening was attributed to the observed increase in Southern Ocean winds resulting from human activities and projected to continue in the future.

In summary, biogeochemistry of carbon is changing at least since last three decades due to climate change. The biological pump seems to be reduced on the global scale except in the tropical regions where it seems to be

intensified. As a result of higher surface production in the tropical regions and sluggish movement of intermediate waters in the subtropical/subarctic region due to reduced formation of intermediate waters, dissolved oxygen/AOU was decreased/increased in the intermediate layers. This might lead to formation of suboxic or anoxic conditions and will have significant influence on mesopelagic biota. Interestingly, increase in anthropogenic carbon in the ocean leads to dissolution of calcium carbonate skeletal material resulting in increase in TA. This is a positive feedback as increased TA serve to enhance the seawater's  $\text{CO}_2$  absorption capacity from the atmosphere. The main goal to the scientific community is to suggest the mechanism through which atmospheric  $\text{CO}_2$  can be reduced without disturbing the oceanic ecosystem. Therefore, the present trends in variations of biogeochemical properties should be taken into account when carbon sequestration experiments are planned in the ocean.

### Carbon Sequestration in the Oceans :

One of the most promising places to sequester carbon is oceans, which currently take up about half of the carbon emitted by human activity, roughly two billion metric tons each year. There are two strategies for enhancing carbon sequestration, 1) the enhancement of the net oceanic uptake from the atmosphere by fertilization of phytoplankton with micro- or macronutrients, and 2) the direct injection of a relatively pure  $\text{CO}_2$  stream to ocean depths greater than 1000 meters.

The long term effectiveness and potential environmental consequences of ocean sequestration by either strategy are unknown. Some modeling and experimental efforts were carried out to understand impact of direct  $\text{CO}_2$  injection on chemical and biological processes in the deep ocean. For instance, Chen et al (2005) observed that  $\text{CO}_2$  injection rate of 100 kg/s with 8mm diameter  $\text{CO}_2$  droplets from a fixed port at 858 m (20 m above the seafloor) into a current flowing at 2.5 cm/s will drop pH by 2.6 units. The pH decrease was found to 1.7 units when the liquid  $\text{CO}_2$  had an initial droplet diameter of 20 mm and injected at 1500 m from a towed pipe with a ship speed of 3 m/s. After 70 min the double plume developed into a single-phase passive plume with a vertical scale of 450 m and a horizontal scale larger than 150 m. This dispersion was attributed to the droplets' buoyant rise and dissolution, along with ocean turbulence, which together diluted the plume and reduced the decrease in pH to less than 0.5 units. Therefore, several investigations are still required to examine the disposal rate, size of the droplets, speed, and location in order to minimize drastic changes in pH due to direct injection of  $\text{CO}_2$  to deep-ocean. Nevertheless, small changes in pH will have greater impact on mesopelagic and benthic organisms. Shirayama and Thornton (2005) have done 6 months long manipulative experiments to examine impact of high  $\text{pCO}_2$  on shallow water benthic organisms that have calcium carbonate shells. They demonstrated that a 200 ppm increase in  $\text{CO}_2$  adversely affects the growth of both gastropods and sea urchins. Thus even moderate increases in atmospheric  $\text{CO}_2$  that could well be reached by the middle of this century, will adversely affect shallow water marine benthic organisms. More studies are recommended on influence of lowering pH on benthic organisms.

The alternative carbon sequestration in the ocean will be iron fertilization. The high latitude regions and equatorial Pacific are high nutrient and low chlorophyll (HNLC) regions where primary productivity is controlled by availability of iron. Several meso-scale experiments suggested that chlorophyll a increased by several fold when dissolved Fe injected to the system. For example, de Baar et al (2005) synthesized several Fe enrichment experiment conducted in different regions in the world ocean. They found that overall primary production was increased due to Fe fertilization and mainly larger phytoplankton (such as Diatoms) benefited from increased Fe concentrations.

However the magnitude of responses to Fe enrichment showed large spatial variability (Kudo et al., 2006). On the contrary, two Fe enrichment experiments were conducted at Subarctic North Pacific and are called Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study (SEEDS). During SEEDS I experiment, significant increase in chlorophyll a and high phytoplankton growth rate (2.6 doublings per day) were found and concluded that the bioavailability of iron regulates the magnitude of the phytoplankton biomass and the key phytoplankton species that determine the biogeochemical sensitivity to iron supply of high-nitrate, low-chlorophyll waters (Kudo et al., 2006). The SEEDS II experiment was conducted in the same region and same season of SEEDS I. The results from SEEDS II showed both the iron-induced increase and subsequent decline in phytoplankton biomass. However, the iron-initiated bloom was much less intense than observed in SEEDS I. Chlorophyll-*a* concentrations increased only 2 to 3 times over initial values, and the drawdown of nutrients and  $p\text{CO}_2$  were small. The differences in results between SEEDS I and II were attributed to the fact that in natural ocean waters, zooplankton existed more than 10 times in the surface layer (high predation pressure) during SEEDS II whereas high multiplication rate phytoplankton types were not present. Therefore, the effect of Fe enrichment on marine primary production need not always uniform and it is depended on the existing ecosystem at the time of experiment. More studies are required to understand favorable setting for enhance primary production to Fe enrichment.

It is also important to examine potential consequences of carbon sequestration on the biogeochemical processes in the ocean. For instance, enhanced primary production in the sun-lit zone results in increased sinking organic carbon fluxes to the deep ocean where part of the organic carbon mineralizes by utilizing dissolved oxygen. Sarma et al (2006) observed that the highest AOU was observed in the northern Indian Ocean where higher sinking organic carbon fluxes were observed. Therefore, changes in sinking organic carbon flux have significant effect on subsurface oxygen utilization rates. It was already observed that, as discussed above, AOU is increasing due to increase in chlorophyll in the upper ocean. Increase in AOU in the subsurface layers might lead to formation of either sub-oxic or anoxic region where another greenhouse gas, nitrous oxide, is formed due to denitrification. This is especially important in the northern Indian Ocean and eastern tropical Pacific where suboxic conditions already exist in the subsurface layers (100-1000 m). For instance, Naqvi et al (2000) observed that increase in eutrophication along the west coast of India due to discharge of fertilizers by rivers resulting in formation of anoxia and sulphide formation. This leads to production several folds higher levels of nitrous oxide by denitrification process. This is one of the important feed backs from the oceans due to artificial enhancement in primary production. Therefore, it is important to take into account the impact of carbon sequestration strategies on 1) environmental consequences of long term ocean fertilization; 2) effectiveness of ocean fertilization on a large scale; 3) environmental consequences of direct injection of  $\text{CO}_2$  into the ocean in midwater or deep sea habitats; and 4) effectiveness of direct injection of  $\text{CO}_2$  for carbon sequestration to avoid disastrous consequences on ecosystem structure.

## Conclusion

Global weather is becoming warmer and temperatures may be increased by about  $4^\circ\text{C}$  by year 2100. This may have disastrous consequences on oceanic biogeochemistry of carbon. It is estimated that  $1/4^{\text{th}}$  of global mountain glaciers may be disappeared by 2050 if the similar rate of melting continues. Oceans are already absorbing less than half of anthropogenic carbon released to the atmosphere. There are several evidences that biological pump seems to be weakening in the major parts of the world ocean and strengthening in the low latitude regions. In the high latitude

regions, where Fe is main controlling nutrient, primary production seems to be decreasing in the recent years where Fe fertilization might result in injection of atmospheric CO<sub>2</sub> into the ocean. On the other hand, it is also important to examine how artificial increase in primary production impacts other biogeochemical processes in the water column. Direct injection of CO<sub>2</sub> to the deep sea is one of the potential mechanisms to remove CO<sub>2</sub> from the atmosphere. However, it is rather unclear how it affects mesopelagic and benthic organisms. Therefore, more studies are required to examine the factors that are influenced by these two strategies before they are ready to apply in the field.

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