Natural Marine CO$_2$ Sequestration: How Biological and Solubility Pumps Influence the Sequestration in the Black Sea and in the Eastern Mediterranean?

by

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Atmospheric CO\textsubscript{2} is increasing as mankind burns of fossil fuels. This presents serious environmental problems with respect to marine environments.

Forests and oceans naturally sequestrate (capture) about half of the atmospheric CO\textsubscript{2} (5 billions tons of CO\textsubscript{2} globally every year). The oceans portion decreased from 30% to 25% since 1960 (till 2006). Reasons:

- Strong winds and storms (Decrease in pCO\textsubscript{2})
- Increase in Sea Surface Temperature (Decrease in dissolution)
- Decrease in photosynthetic/primary organic matter production (Due to stratification)

\begin{center}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\hline
Land & 0.6 & 0.3 & 0.0 & 0.4 & 0.3 \\
Ocean & 0.2 & 0.3 & 0.3 & 0.2 & 0.2 \\
\hline
\end{tabular}
\end{center}

Canadell et al. 2007, PNAS
Source: Estimated emissions from fossil-fuel combustion and cement production of 9.1 Pg C, combined with the emissions from land-use change of 0.9 Pg C, led to a total emission of 10.0 Pg C in 2010 (Friedlingstein et al., 2010).

Sink: Of the remainder of the total emissions (5.0 Pg C), the ocean sink is 2.4 Pg C, and the residual attributed to the land sink is 2.6 Pg C (Le Quéré, 2009).

Accumulation in the atmosphere: Half of the total emissions (5.0 Pg C) remains in the atmosphere, leading to one of the largest atmospheric growth rates in the past decade (2.36 ppm) and the concentration at the end of 2010 of 390 ppm of CO2 (Conway & Tans, 2011).
Oceans are natural CO$_2$ sinks, and represent the largest active carbon sink on Earth. This role as a sink for CO$_2$ is driven by two processes:

1- The biological pump
2- The solubility pump
Dissolved CO$_2$ is taken up by marine phytoplankton driving a CO$_2$ flux from the atmosphere to surface waters. The organic matter produced is consumed by heterotrophic organisms and remineralized to CO$_2$ or exported as sinking organic matter.

This sinking fraction is also called as "Export Production", that actuates the removal of CO$_2$ from the atmosphere.

Biological pump is also important for the food production!
Production of organic matter

Dissolved constituents

\[ 106\text{CO}_2 + 16\text{NO}_3^- + \text{HPO}_4^{2-} + 139\text{H}_2\text{O} \leftrightarrow \text{C}_{106}\text{H}_{261}\text{O}_{109}\text{N}_{16}\text{P} + 138\text{O}_2 + 18\text{OH}^- \]

Suspended Organic Particles (Phytoplankton)
Export production of organic carbon is the engine that drives the biological pump, but it is also modulated by the export of inorganic carbon in the form of CaCO₃ particles and shells produced by a variety of marine organisms (like Coccolithophorids).

Export of calcium carbonate increases the alkalinity of surface water, thereby partially compensating for the CO₂ drawdown driven by the export of organic matter.

The efficiency of the biological pump is thus very much dependent on the relative proportion of organic and inorganic carbon leaving the surface mixed layer, which is controlled by ecological, biogeochemical and physical factors.
A distinguishing feature of the **Black Sea** is the high biological activity in the lower trophic food web structure as compared to neighboring **Aegean** and **Eastern Mediterranean** basins.

<table>
<thead>
<tr>
<th>Region</th>
<th>Primary Production (\text{mgCm}^{-2}\text{d}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black Sea (Open waters)</td>
<td>112 - 587</td>
</tr>
<tr>
<td>Black Sea (NW and Shelf/Coastal Waters) (1960-2001)</td>
<td>405 - 2140</td>
</tr>
<tr>
<td>Eastern Mediterranean</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Upwelling Areas</td>
<td>800-1000</td>
</tr>
<tr>
<td>Open Ocean</td>
<td>&lt;100</td>
</tr>
</tbody>
</table>
The Black Sea is a unique marine environment representing the largest land-locked/semi-enclosed and deep (~2000 m) anoxic basin in the world. Its shelf region (<200m) is generally narrow and it enlarges at the north western corner. It has a very large catchment area, receiving extraordinary amount of nutrients, pollutants as well as fresh water from the rivers draining half of the Europe and some parts of Asia. The major rivers are the Danube, the Dniper and the Dniestr, all concentrated along the north western coast.
A distinguishing feature of the **Black Sea** is the high biological activity in the lower trophic food web structure as compared to neighboring **Aegean** and **Eastern Mediterranean** basins.

*Use of satellite images of phytoplankton concentration from NASA's Goddard Space Flight Center to examine the productivity of the ocean.*
<table>
<thead>
<tr>
<th>Basin</th>
<th>Area (%)</th>
<th>Global Production* Gt C y(^{-1})</th>
<th>% of Global Production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pacific Ocean</td>
<td>45</td>
<td>21</td>
<td>44</td>
</tr>
<tr>
<td>Atlantic Ocean</td>
<td>23</td>
<td>12.8</td>
<td>27</td>
</tr>
<tr>
<td>Indian Ocean</td>
<td>17</td>
<td>9.9</td>
<td>21</td>
</tr>
<tr>
<td>Southern Ocean</td>
<td>13</td>
<td>2.6</td>
<td>5.5</td>
</tr>
<tr>
<td>Arctic Ocean</td>
<td>1.2</td>
<td>0.33</td>
<td>0.7</td>
</tr>
<tr>
<td>Mediterranean</td>
<td>0.8</td>
<td>0.45</td>
<td>0.95</td>
</tr>
<tr>
<td>Black Sea</td>
<td>0.12</td>
<td>0.106**</td>
<td>0.22</td>
</tr>
</tbody>
</table>

- Although Black Sea is a small basin, it is highly productive area and unique area for effective natural sink for carbon!

* Carr et al., DSR, 2006  
** Yılmaz et al., 1998; Yayla et al., 2001; Yunev et al., 2002; Sorokin, 2002; Yılmaz et al., 2006

Export Production ~33 % in the Black Sea, which means ~35 tonnes C is exported annually. Approximately the same amount (~32 tonnes C y\(^{-1}\)) produced by chemoautotrophic activity at mid-water depths sinks down to bottom.
The flux of organic matter is the key element of the biological pump that eliminates carbon (CO$_2$) from the euphotic zone and delivers it to deeper layers.

Oxidation of organic matter results in consumption of oxygen and production of nitrate, phosphate, and CO$_2$ below the euphotic zone. This results in natural sequestration of CO$_2$ from the surface water and natural acidification (decreasing pH) of the suboxic zone and deeper layers.

Konovalov and Murray (2001) demonstrated that the observed decline in the content of oxygen in the 1970’s to 1990’s was stoichiometrically equivalent to oxidized organic matter that was produced in increasing quantities due to eutrophication and potentially due to increasing concentrations of CO$_2$. 
Some phytoplankton taxa (*Coccolithophores*) are more abundant at some locations and impacts the CO$_2$ exchange between oceans and atmosphere (e.g. Black Sea).

Rodriguez et al, 2001
Iglesias-Rodriguez et al. 2000
SeaWiFS data analyzed for the 1997-2000 period (Çokacar et al., 2001) provided new details on the duration, persistence, spatial extent of the *Emiliania huxleyi* (Coccolithophores) blooms in the Black Sea. A marked change in the appearance of the water is observed, and the colour turns a milky turquoise during intense blooms.

Black Sea, R/V Bilim April, 1998

*Photo by Ayşen Yılmaz*
Saharan dust, rich in nitrogen, iron and phosphorus, helps to fertilize the phytoplankton blooms that occur in the Black Sea.
Availabilty of Iron for the Fertilization of the Oceans

Dust (Fe$^{+3}$)

Dry Deposition

No Impact (Fe$^{+3}$)

No Light (Night)

Not enough Light

Rain carries Fe$^{+2}$ to the oceans

Photosynthetic oceanic production increases!
Emiliania huxleyi (Coccoliths) blooms

All phytoplankton (also Coccoliths) removes CO$_2$ to form organic matter and reduces atmospheric CO$_2$ by photosynthesis. However, Coccoliths also take up bicarbonate (HCO$_3^-$) to form their calcium carbonate (CaCO$_3$) shells and during this reaction CO$_2$ is released!

\[ \text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]

In this way, coccolithophore blooms may affect global warming negatively (by causing increased atmospheric CO$_2$).

However;
Coccoliths sink very rapidly!

If organic matter sinks faster than the time period necessary for bacterial decomposition, causes the depletion of the surface CO$_2$.

This co-transport of organic matter with coccoliths offsets the atmospheric CO$_2$ increase. This makes coccolithophore blooms act to oppose global warming, rather than to intensify it.
Carbon fluxes to Deep Oceans

The export of carbon through the biological pump from the surface to the deep ocean has a direct influence on the removal of CO$_2$ from the atmosphere. This is because the carbon is sequestered for only a few days to months in the surface while the carbon removed from the surface to deep waters takes hundreds of years to re-enter the atmosphere (Sarma et al., 2007).

Carbon Removal Processes:

- CO$_2$ absorption by surface ocean: ~1 yr (CO$_2$ + H$_2$O $\rightarrow$ H$^+$ + HCO$_3^-$)
- Mixing to deep ocean: ~300 yr
- Carbonate dissolution: ~6000 yr (CO$_2$ + CaCO$_3$ + H$_2$O $\rightarrow$ Ca$^{2+}$ + 2HCO$_3^-$)
- Silicate-rock weathering: ~300,000 yr (CO$_2$ + CaSiO$_3$ $\rightarrow$ CaCO$_3$ + SiO$_2$)
Carbon Transport to Deep Sea

**Solubility pump:** CO$_2$ is more soluble in cold, saline waters, such as those that sink in the North Atlantic. Thermohaline Circulation (THC) takes carbon out of surface and transfer into deep (Sinking waters hold lots of CO$_2$!!!)

Sabine et al. 2004, *Science*
2-Solubility Pump: Surface waters uptake of CO₂ by dissolution.

- Gas diffusion between ocean and atmosphere: Depends on concentration gradient between CO₂ (g) and CO₂ (aq).
- Solubility = f (Temperature, Salinity, Pressure)
- Key role of winds in determining (pCO₂) and rate of exchange.

Key reactions:

\[ \text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+ \]
\[ \text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+ \]
\[ \text{Ca}^{2+} + \text{CO}_3^{2-} \Rightarrow \text{CaCO}_3 \]

- If atmospheric CO₂ increases, pH decreases (waters becomes more acidic) and CO₃²⁻ decreases.
Anthropogenic CO$_2$ :

While the increase in surface ocean dissolved CO$_2$ is proportional to that in the atmosphere (equilibration after ~1 y), the increase in TCO$_2$ is not. This is a result of the buffer capacity of seawater.

As a consequence, the man-made increase of TCO$_2$ in surface seawater (ocean acidification) occurs not in a 1:1 ratio to the increase of atmospheric CO$_2$. Rather, a doubling of $p$CO$_2$ only leads to an increase of TCO$_2$ of the order of 10%.
There are also dramatic changes in the carbonate system in the Black Sea. The pH decreases from ~8.2 in the surface layer to 7.4 in the upper suboxic zone, while alkalinity remains constant (Goyet et al., 1991; Hiscock and Millero, 2006). The pH increases slightly through the suboxic zone and then decreases steadily in the deep water to a low value of 7.3.

None of the existing models for the Black Sea account for the carbonate system, even though it is an extremely important component of the Black Sea biogeochemistry. The changes in the carbonate system of the Black Sea have not been numerically simulated, leaving an open question on the evolution due to human- and climate-driven changes in CO₂ and other boundary conditions in the Black Sea.
Carbonate Saturation

$\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3$

- Saturation state, $\Omega$ : A measure of how saturated the surface ocean is with respect to $\text{CaCO}_3$.

\[ \Omega = [\text{Ca}] [\text{CO}_3] / K_{sp} \]

($K_{sp}$: Solubility Product)

- If $\Omega > 1$, supersaturated: precipitation
- If $\Omega < 1$, undersaturated: dissolution

- Increase of atmospheric $\text{CO}_2$ causes the reduction in $\text{CO}_3$, so $\Omega$ decreases.
Climate Change and Carbonate Saturation Trends

<table>
<thead>
<tr>
<th></th>
<th>Glacial</th>
<th>Pre-industrial</th>
<th>Present</th>
<th>2XCO₂</th>
<th>3XCO₂</th>
<th>Change from pre-industrial to 3XCO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CO₂(g)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pCO₂</td>
<td>180</td>
<td>280</td>
<td>380</td>
<td>560</td>
<td>840</td>
<td>200%</td>
</tr>
<tr>
<td><strong>Gas exchange</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂(aq) + H₂O ↔ H₂CO₃</td>
<td>7</td>
<td>9</td>
<td>13</td>
<td>18</td>
<td>25</td>
<td>178%</td>
</tr>
<tr>
<td><strong>Carbonic acid</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂CO₃ ↔ H⁺ + HCO₃⁻</td>
<td>1666</td>
<td>1739</td>
<td>1827</td>
<td>1925</td>
<td>2004</td>
<td>15%</td>
</tr>
<tr>
<td><strong>Bicarbonate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO₃⁻ ↔ H⁺ + CO₃⁻²</td>
<td>279</td>
<td>222</td>
<td>186</td>
<td>146</td>
<td>115</td>
<td>-48%</td>
</tr>
<tr>
<td><strong>Carbonate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIC</td>
<td>1952</td>
<td>1970</td>
<td>2026</td>
<td>2090</td>
<td>2144</td>
<td>8.8%</td>
</tr>
<tr>
<td><strong>pH(sw)ₛ</strong></td>
<td>8.32</td>
<td>8.16</td>
<td>8.05</td>
<td>7.91</td>
<td>7.76</td>
<td>-0.4</td>
</tr>
<tr>
<td><strong>Ω(calcite)</strong></td>
<td>6.63</td>
<td>5.32</td>
<td>4.46</td>
<td>3.52</td>
<td>2.77</td>
<td>-48%</td>
</tr>
<tr>
<td><strong>Ω(aragonite)</strong></td>
<td>4.26</td>
<td>3.44</td>
<td>2.90</td>
<td>2.29</td>
<td>1.81</td>
<td>-47%</td>
</tr>
</tbody>
</table>

Fabry et al., 2008
At present surface waters of the Black Sea are supersaturated with respect to calcite and aragonite and the degree of saturation decreases with depth.

In the suboxic zone calcite is just above saturation while aragonite is just under saturation. However, the degree of saturation is not the only indicator of stress as experimental studies have shown that biological impacts are observed with decreasing saturation, even though a state of supersaturation persists in the Black Sea (Fabry et al., 2008).
Ocean Acidification

• The ocean absorbs anthropogenic CO\textsubscript{2} at a rate of 22 million tons per day, thus removing about 25\% of CO\textsubscript{2} emitted to the atmosphere each year and mitigating the harmful impact of this “greenhouse gas” on climate!

• This valuable service provided by the ocean, however, may have a high ecological cost. When CO\textsubscript{2} dissolves in seawater, carbonic acid is formed. This phenomenon, called as “Ocean Acidification (OA)”, decreases the availability of carbonate (CO\textsubscript{3}^{2-}), making it more difficult for many marine organisms to construct their hard parts (shells) out of calcium carbonate minerals.
Ocean Acidification

**Ocean Acidification**

**OCEAN ACIDIFICATION**

1. Atmospheric carbon dioxide

   ![Diagram of atmospheric carbon dioxide dissolving into water](image)

   - Dissolved carbon dioxide
   - Water
   - Carbonic acid: $\text{H}_2\text{CO}_3$
   - Hydrogen ions: $\text{H}^+$
   - Bicarbonate ions: $\text{HCO}_3^-$
   - Carbonate ions: $\text{CO}_3^{2-}$
   - Deformed shells

   Source: University of Maryland

   pH = $-\log_{10}[\text{H}^+]$

**Variation in pH Levels in the World’s Oceans**

- Less acidic: 8.20, 8.15, 8.10, 8.05, 8.00, 7.95
- More acidic

- Arctic Ocean
- North Pacific Ocean
- North Atlantic Ocean
- Indian Ocean
- South Pacific Ocean
- South Atlantic Ocean
- Antarctic Ocean

- **Northern Hawai (ALOHA Stations)-Surface pH (Doney, Science 2010)**

- **Graphs showing trends in $\text{pCO}_2$ and pH**
  - Air $\text{pCO}_2$ trend = $+1.69 \pm 0.03$ μatm y$^{-1}$
  - Sea $\text{pCO}_2$ trend = $+1.88 \pm 0.15$ μatm y$^{-1}$
  - In situ pH trend = $-0.0019 \pm 0.0002$ y$^{-1}$
Ocean Acidification

If atmospheric CO$_2$ increases from e.g. 390 ppm today to 900 ppm in 2100, the pH will decrease by 0.4-0.5 units. This will cause 3 times increase in H$^+$ concentrations in sea water for the first time with in the last 20 x 10$^6$ years (Raven et al., 2005).
Consequences of Ocean Acidification:

• A decrease in pH causes a decrease in carbonate ion (CO$_3^{2-}$) concentration, a species used by many organisms to make their CaCO$_3$ shells. Many species of calcifying and non-calcifying organisms are sensitive to higher CO$_2$ levels. This removal will have a cascading effect, altering the species composition and abundance of phytoplankton in the World’s ocean.

• Ocean acidification alters inorganic and organic seawater chemistry beyond the carbonate system (e.g., the concentrations of the major ions of seawater, the C/N ratios of plankton, Burkhardt et al., 1999).

• Decreases in primary productivity are likely to further exacerbate rising CO$_2$ levels in the Earth’s atmosphere by creating a positive feedback. If productivity is reduced, less CO$_2$ will be removed from the atmosphere, resulting in an increase in atmospheric CO$_2$ concentration. This increase will enhance ocean warming and acidification, both of which may lead to further reductions in primary productivity.
Effect of higher CO$_2$ on Coccolithophores

- Increased calcification at low CO$_2$
- Increased deformation at high CO$_2$ (Due to decrease in CO$_3^{2-}$ concentration)

Riebesell et al. 2000
Ocean acidification due to the flux of CO$_2$ from the atmosphere is a problem. This will result in a lower carbonate mineral saturation state and impact the biological community structure all the way through the Black Sea fisheries industry (Orr et al., 2005).

In addition, recent studies (Brewer and Peltzer, 2009) have suggested that increasing atmospheric CO$_2$ has the potential to result in expansion of the suboxic zone.

The Black Sea has a high CO$_2$ assimilation capacity because of its high alkalinity and long residence time. Both of these problems represent potentially serious Environmental Security problems with consequences are very difficult to predict.

Brewer and Peltzer (2009) recently showed that the domain of low oxygen waters, which is controlled by the ratio of pO$_2$/pCO$_2$, can be expanded due to increasing CO$_2$ as well as increased consumption of O$_2$. 
Wanna reduce CO² emissions? Go hold your breath for an hour or two.

Thanks...