

THE POTENTIAL ROLE OF THE OCEAN IN COMBATING CLIMATE CHANGE

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Preface

The following extensive presentation is based on the feeling that the ocean should hold great promise for sequestering a sufficient amount of carbon dioxide to reverse the massive atmospheric accumulation of this greenhouse gas. The oceans occupy three fourths of the area of the earth and have already been shown to sequester 38 trillion tons of carbon dioxide by natural processes. Can this promise be realized or is it merely wishful thinking? Should we attempt this or give it up because the magnitude of the problem is too great, and too many objections have been voiced against this approach. To answer this question, it is important to review all relevant aspects of this complex subject. We start with an introduction to the basics of oceanography.

I. Introduction to Oceanography

Derived in part from various Wikipedia entries.

Understanding the biogeochemical cycling of carbon, nitrogen, phosphorus, oxygen and iron in the oceans is important in the context of using the oceans for the removal of man-made carbon dioxide from the atmosphere. The following provides some of that understanding. However, before discussing the potential use of micro- and macro- phytoplankton to help alleviate global warming, it is necessary to review basic aspects of **oceanography**.

The name **plankton** is derived from the Greek adjective (planktos), meaning errant, and by extension, **wanderer** or drifter, and was coined by Victor Hensen in 1887. While some forms are capable of independent movement and can swim hundreds of meters vertically in a single day (a behavior called **diel vertical migration**), their horizontal position is primarily determined by the surrounding water movement, and plankton typically flow with ocean currents. This is in contrast to **nekton** organisms, such as fish, squid and marine mammals, which can swim against the ambient flow and control their position in the environment.

Plankton are the diverse collection of organisms that live in large bodies of water and are **unable to swim against a current**. Planktonic organisms include bacteria, archaea, algae, protozoa and drifting or floating animals that inhabit the pelagic zone of oceans, seas, or bodies of fresh

water. Essentially, plankton are defined by their ecological niche rather than any phylogenetic or taxonomic classification.

Plankton are also often described in terms of size. These groups are megaplankton <20cm; macroplankton 2 to 20 cm; mesoplankton .2 to 20 mm; microplankton 20-200 μm ; nanoplankton 2-20 μm ; and picoplankton .2 to 2 μm ; and femtoplankton <.2 μm .

The species of these groups that will be discussed here are:

Macroplankton - krill, kelp, seaweed

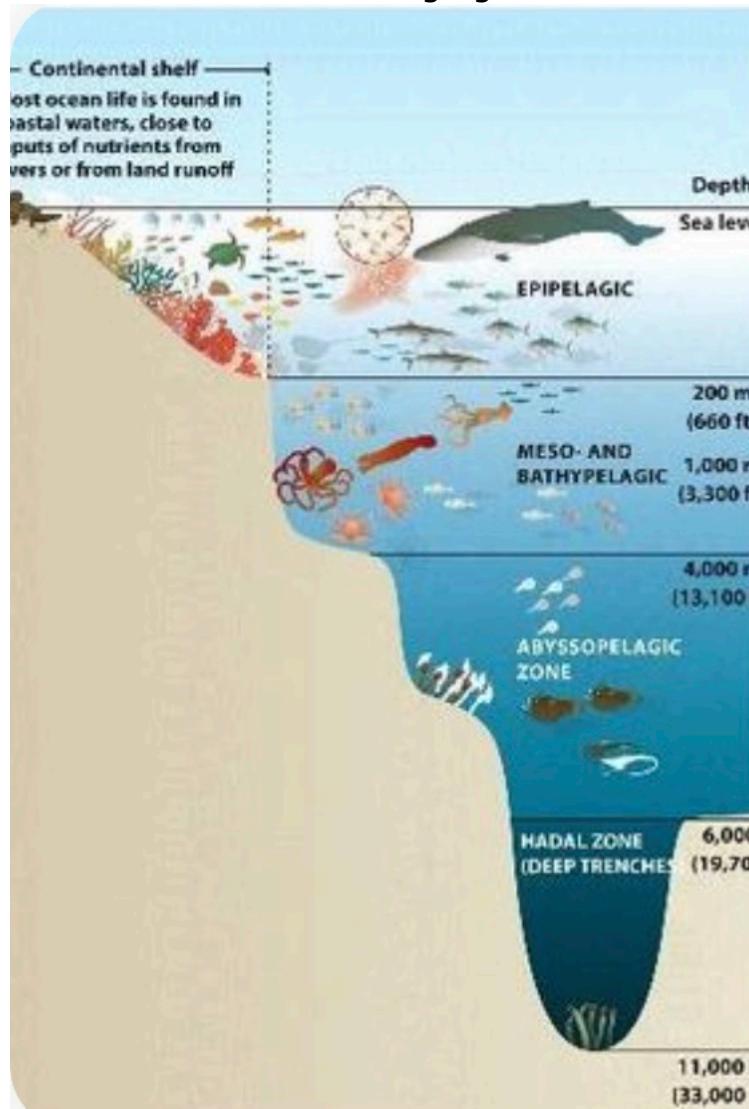
Microplankton – coccolithophores, copepods

Picoplankton – bacteria

Femtoplankton - viruses

Ocean Zones

These are illustrated in the following figure.



The different ocean zones.

Epipelagic zone

Epipelagic zone, photic zone, euphotic zone, or sunlight zone is the uppermost layer of the ocean that receives sunlight, enabling it to perform photosynthesis. It undergoes a series of physical, chemical, and biological processes that supply nutrients into the upper water column.

In the photic zone, the photosynthesis rate exceeds the respiration rate. This is due to the abundant solar energy which is used as a food source for primary producers such as phytoplankton. These phytoplankton grow extremely quickly. In fact, ninety five percent of the photosynthesis in the ocean occurs in the photic zone. Further down there is little to no

phytoplankton, because of insufficient sunlight. This zone extends down to about 200 meters.

Ninety percent of marine life lives in the photic zone. This includes phytoplankton (plants), including dinoflagellates, diatoms, cyanobacteria, coccolithophorids, and cryptomonads. It also includes zooplankton, the consumers in the photic zone. There are carnivorous meat eaters and herbivorous plant eaters. Next, copepods are the small crustaceans distributed everywhere in the photic zone and are one of the biggest groups of animals on the planet. Finally, there are nekton which are the largest and the most obvious animals in the photic zone, but their quantity is the smallest among all the groups.

The depth of the photic zone depends on the transparency of the water. If the water is very clear, the photic zone can become very deep. If it is very murky, it can be only fifteen meters deep.

Due to biological uptake, the photic zone has relatively low levels of nutrient concentrations. As a result, phytoplankton don't receive enough nutrients when there is high water-column stability (quiet seas).

The spatial distribution of organisms can be controlled by a number of factors. Physical factors include temperature, hydrostatic pressure, turbulent mixing such as the upward turbulent flux of inorganic nitrogen across the zone. Chemical factors include oxygen, nitrogen, phosphorus and trace elements such as iron. Biological factors include grazing and migrations. Upwelling carries nutrients from the deep waters into the photic zone, strengthening phytoplankton growth. The remixing and upwelling eventually bring nutrient-rich wastes back into the photic zone.

Mesopelagic zone

The **mesopelagic zone** also known as the **middle pelagic** or **twilight zone**, is the part of the pelagic zone that lies between the sunlight zone and the aphotic bathypelagic zones. It is defined by light and begins at the depth where only 1% of incident light reaches and **ends where there is no light**; the depths of this zone are between approximately 200 to 1000 meters (~660 to 3300 feet) below the ocean surface.

It hosts a diverse biological community that includes bristlemouths, blobfish, bioluminescent jellyfish, giant squid, and a myriad of other unique organisms adapted to live in a low-light environment.

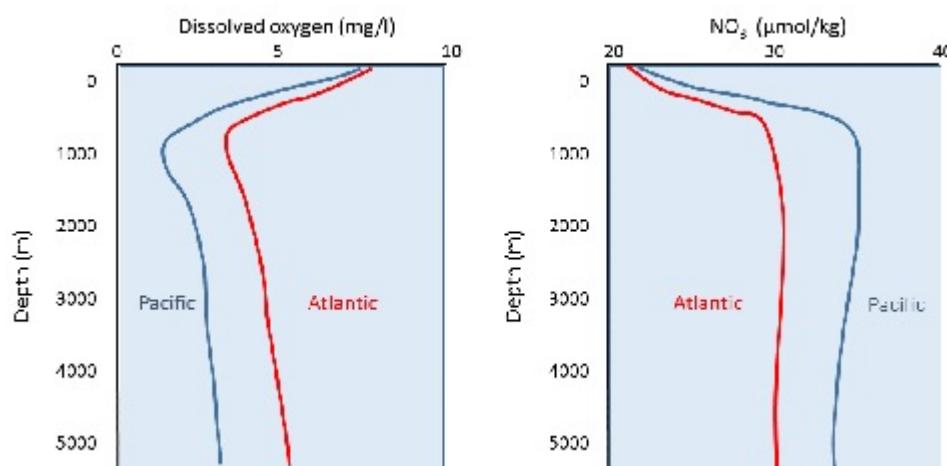
The mesopelagic zone includes the region of sharp changes in temperature, salinity and density called the **thermocline**, **halocline**, and **pycnocline**. The temperature variations are large; from over 20 °C (68 °F) at the upper layers to around 4 °C (39 °F) at the boundary with the bathyal zone. The variation in salinity is smaller, typically between 34.5 and 35 psu. The density ranges from 1023 to 1027 g/kg of seawater. These changes in temperature, salinity, and density induce stratification which creates ocean

layers. These different water masses affect gradients and mixing of nutrients and dissolved gasses. This makes this a dynamic zone.

Carbon The mesopelagic zone plays a key role in the ocean's biological pump, which contributes to the oceanic carbon cycle. In the biological pump, organic carbon is produced in the surface euphotic zone where light promotes photosynthesis. A fraction of this production is exported out of the surface mixed layer and into the mesopelagic zone. One pathway for carbon export from the euphotic layer is through sinking of particles which can be accelerated through repackaging of organic matter in zooplankton fecal pellets, ballasted particles, and aggregates. Mean particle sinking rates are 10 to 100 m/day.

Oxygen Dissolved oxygen is a requirement for aerobic respiration, and while the surface ocean is usually oxygen-rich due to atmospheric gas exchange and photosynthesis, the mesopelagic zone is not in direct contact with the atmosphere. Organic matter is exported to the mesopelagic zone from the overlying euphotic layer, while the minimal light in the mesopelagic zone limits photosynthesis. The oxygen consumption due to respiration of most of the sinking organic matter and lack of gas exchange, often creates an oxygen minimum zone (**OMZ**) in the mesopelagic.

Nitrogen The mesopelagic zone, an area of significant respiration and remineralization of organic particles, is generally nutrient-rich. This is in contrast to the overlying euphotic zone, which is often nutrient-limited. The increase in Nitrogen content compared to a decrease in oxygen content at lower levels of the ocean is shown in the following figure.



Oxygen and Nitrogen by depth in the ocean.

Climate Change The mesopelagic region plays an important role in the global carbon cycle as it is the area where most of the surface organic matter is respired. Mesopelagic species also acquire carbon during their vertical migration to feed in surface waters, and they transport that carbon to the deep sea when they die. **It is estimated that the mesopelagic cycles between 5 and 12 billion tons of carbon dioxide from the atmosphere per year**, and until recently, this estimate was not included in many climate models (Economist, 2017). It is difficult to quantify the effects of climate change on the mesopelagic zone as a whole, as climate change does not have uniform impacts geographically. Research suggests that in warming waters, as long as there are adequate nutrients and food for fish, then mesopelagic biomass could actually increase due to higher trophic efficiency and increased temperature-driven metabolism. However, because ocean warming will not be uniform throughout the global mesopelagic zone, it is predicted that some areas may actually decrease in fish biomass, while others increase.

Water column stratification will also likely increase with ocean warming and climate change. Increased ocean stratification reduces the introduction of nutrients from the deep ocean into the euphotic zone resulting in decreases in both net primary production and sinking particulate matter.

Additional research suggests shifts in the geographical range of many species could also occur with warming, with many of them shifting poleward. The combination of these factors could potentially mean that as global ocean basins continue to warm, there could be areas in the mesopelagic that increase in biodiversity and species richness, while declines in other areas, especially moving farther from the equator.

Bathypelagic Zone

The **bathyal zone** or **bathypelagic** – from Greek, deep – (also known as **midnight zone**) is the part of the pelagic zone that extends from a depth of 1,000 to 4,000 m (3,300 to 13,100 ft) below the ocean surface. It lies between the mesopelagic above, and the abyssopelagic below. The average temperature hovers at about 4°C (39°F). Although larger by volume than the photic zone, the bathyal zone is less densely populated. **Sunlight does not reach this zone**, meaning primary production, if any, is almost nonexistent. There are no known plants because of the lack of sunlight necessary for photosynthesis.

Because of the lack of light, some species do not have eyes. Those possessing eyes in this zone include the viperfish and the frill shark. Many forms of nekton live in the bathyal zone, such as squid, large whales, and octopuses. Sponges, brachiopods, sea stars, and echinoids are also common in the bathyal zone. Animals in the bathyal zone are not threatened by predators that can see them, so they do not have powerful muscles. This zone is difficult for fish to live in since it is especially hard to find nutrients.

They have become very energy efficient, and many have slow metabolic rates to conserve energy. The fish are characterized by weak muscles, soft skin, and slimy bodies. The adaptations of some of the fish that live there include small eyes and transparent skin.

Abyssopelagic Zone

The **abyssopelagic zone** or **abyssal zone** name derives from "abyss" a Greek word meaning bottomless. At depths of 3,000 to 6,000 meters (9,800 to 19,700 ft), this zone **remains in perpetual darkness**. It alone makes up **over 83% of the ocean and covers 60% of the Earth**. The abyssal zone has temperatures around 2 to 3°C (36 to 37°F). The water along the seafloor of this zone is devoid of oxygen, resulting in a **death trap** for organisms unable to quickly return to the oxygen-enriched water above. This region also contains a **much higher concentration of nutrient salts, like nitrogen, phosphorus, and silica**, due to the large amount of dead organic material that drifts down from the above ocean zones and decomposes.

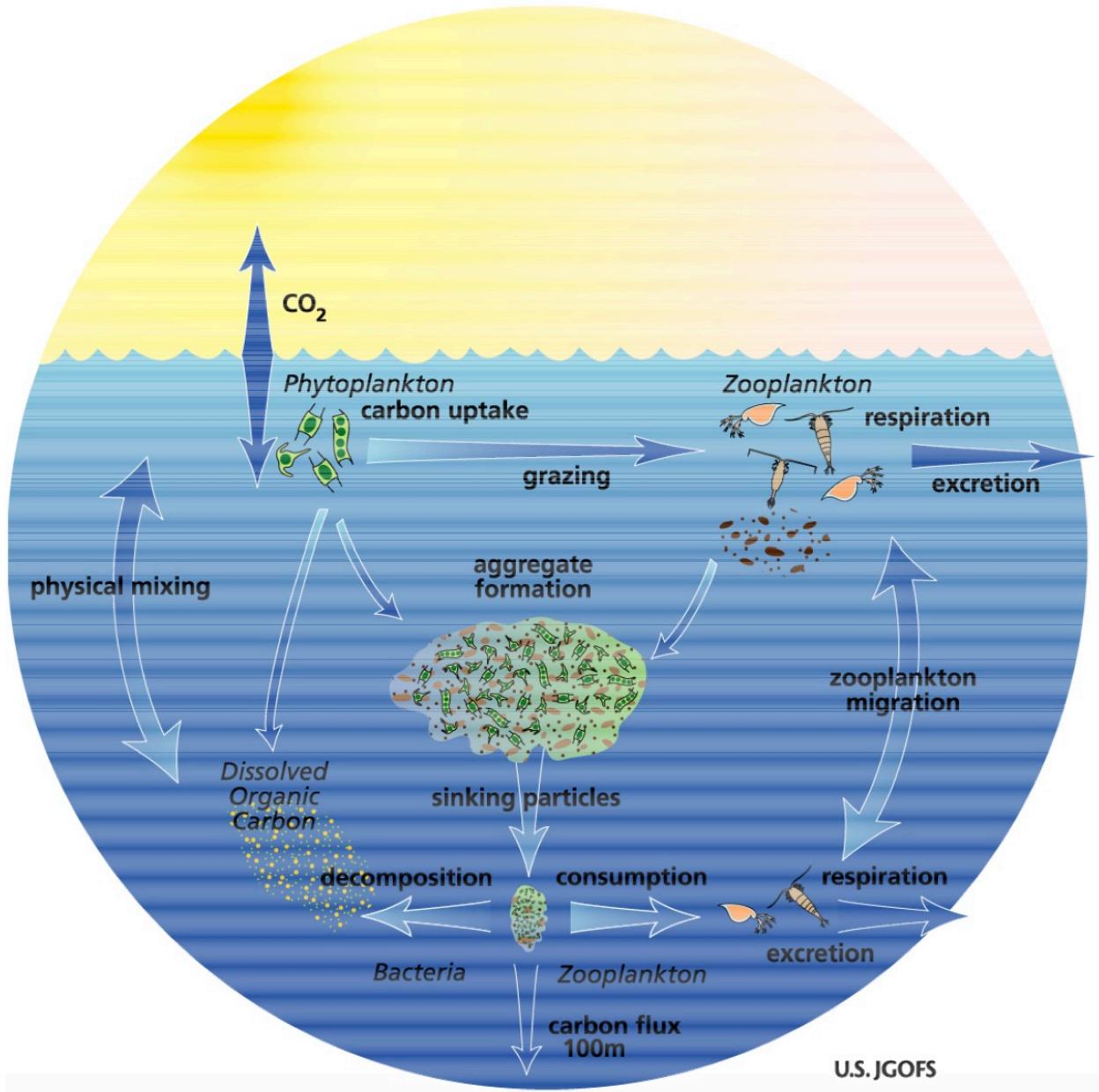
The abyssal zone is surprisingly made up of many different types of organisms, including microorganisms, crustaceans, molluscs, different classes of fishes, and a number of others that might not have even been discovered yet.

Hadal Zone

The area below the abyssal zone is the sparsely inhabited **hadal zone**. It contains the deep trenches or fissures that plunge down thousands of meters below the ocean floor. Next are some important oceanographic and marine carbon cycle terms.

Marine Carbon Cycle.

The following figure summarizes the principal elements of the marine carbon cycle.



Marine primary production is the **synthesis of organic compounds from atmospheric or aqueous carbon dioxide**. It principally occurs through the process of **photosynthesis**, which uses light as its source of energy, but it also occurs through **chemosynthesis**, which uses the oxidation or reduction of inorganic chemical compounds as its source of energy. Almost all life on Earth relies directly or indirectly on primary production. The organisms responsible for primary production are known as

primary producers or **autotrophs** and the form the base of the food chain (Wikipedia).

Water stratification or **water column stratification** is when water masses with different properties - **salinity (halocline), oxygenation (chemocline), density (pycnocline), temperature (thermocline)** - form layers that act as barriers to water mixing which could lead to anoxia, or anoxia plus increased hydrogen sulfide. These layers are normally arranged according to density, with the least dense water masses sitting above the denser layers. Water stratification also creates barriers to nutrient mixing between layers. This can affect the primary production in an area by limiting photosynthetic processes. When nutrients from the benthos cannot travel up into the photic zone, phytoplankton may be limited by nutrient availability. Lower primary production also leads to lower net productivity in waters. Wikipedia

DIC – dissolved inorganic carbon made up of bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and carbon dioxide (including both dissolved CO_2 and carbonic acid H_2CO_3). Carbonate and bicarbonate are the major species that combat ocean acidification.

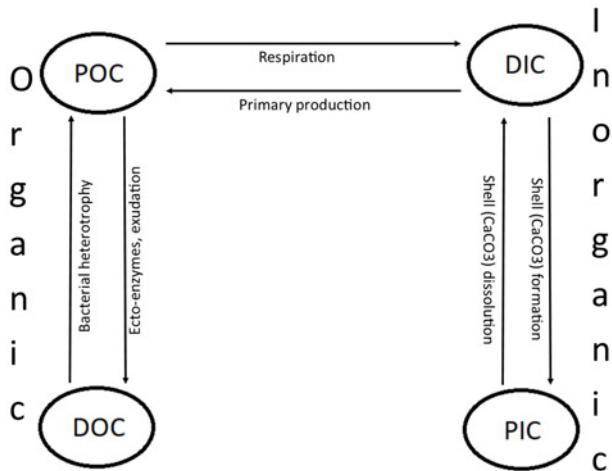
PIC – particulate inorganic carbon formed by combining calcium with CO_3^{2-} to form particulate CaCO_3 that makes up shells of various marine organisms.

POC, POM – particulate organic carbon or particulate organic matter formed by the conversion of DIC to POC through photosynthesis and chemoautotrophy. Along with dissolved organic matter, POM drives the lower aquatic food web by providing energy in the form of carbohydrates, sugars, and other polymers that can be degraded.

DOC, DOM – dissolved organic carbon or dissolved organic matter (Moran, 2016). It is defined operationally as any organic molecule that can pass through a 0.2 μm filter. The fraction remaining on the filter is the particulate organic carbon (**POC**).

DOC pool consists of **thousands of organic carbon compounds** with different biological turnover rates, biological availabilities, and biogeochemical features (Cherrier and Bauer, 2004). It plays important roles in all major element cycles, contributes to the storage of atmospheric CO_2 in the ocean, supports marine ecosystems, and facilitates interactions between organisms (Moran, 2016). **It is one of the largest pools of reduced carbon on earth**, comparable in size to the atmospheric CO_2 reservoir (Hansell, 2013). The flux of carbon through the marine DOC pool is mediated largely by microbial activity (see microbial carbon pump below) DOC can be converted into particulate organic carbon (POC) through heterotrophy and it can also be converted back to dissolved inorganic carbon (DIC) through respiration.

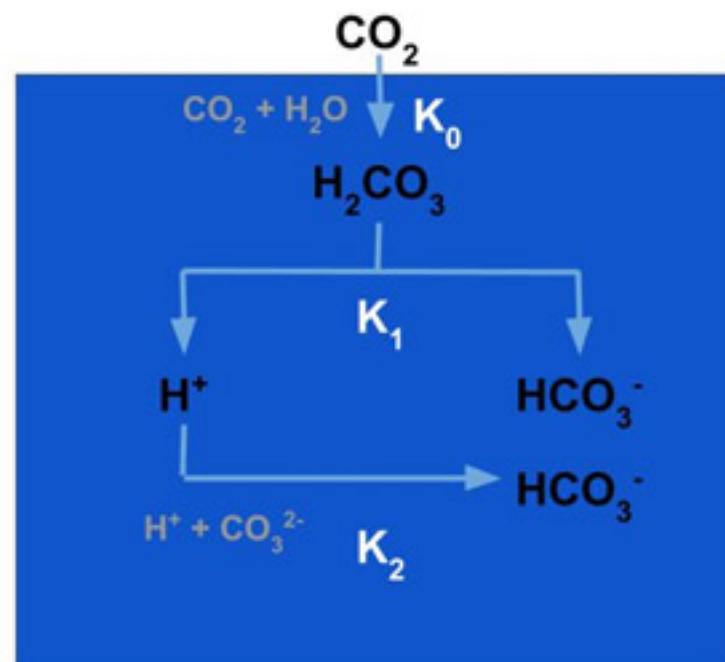
The inter-relationship between these is shown below.



The three main processes (or **pumps**) that make up the **marine carbon cycle**, a process that brings atmospheric carbon dioxide (CO_2) into the ocean interior and precipitates it to the ocean floor. These three pumps are: (1) the **solubility pump**, (2) the **carbonate pump**, and (3) the **biological pump**. The total active pool of carbon at the earth's surface for durations of less than 10,000 years is roughly 40,000 gigatons C (Gt C, a gigaton is one billion tons). About 95% (**~38,000 Gt C is stored in the ocean**, mostly as dissolved inorganic carbon (DIC) (Falkowski et al, 2013). The DIC is a primary controller of acid-base chemistry in the oceans.

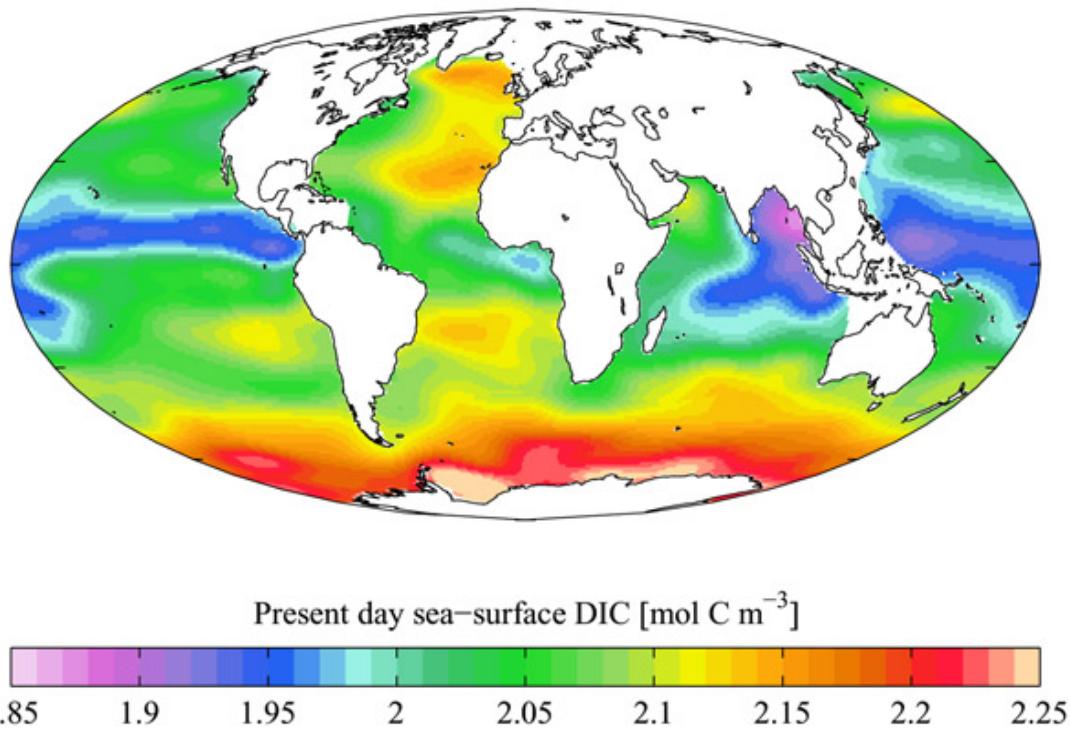
Solubility pump

DIC circulates throughout the whole ocean by **thermohaline** (temperature and salt) currents which facilitate the tremendous DIC storage capacity of the ocean. The chemical equations (see figure below) show the reactions that CO_2 undergoes after it enters the ocean and transforms into its DIC. These equations follow Henry's Law, that the amount of dissolved gas in a liquid is proportional to its partial pressure above the liquid.



First, carbon dioxide reacts with water to form carbonic acid H_2CO_3 . Carbonic acid rapidly dissociates into free H^+ hydrogen ion (technically hydronium ion H_3O^+) and bicarbonate ion HCO_3^- . The free hydrogen ion meets carbonate, already present in the water from the dissolution of CaCO_3 and reacts to form more bicarbonate ion HCO_3^- . It is predominately this bicarbonate that makes up the **carbonate alkalinity system**, the dominant contributor to seawater alkalinity.

Alkalinity is the capacity of water to resist changes in pH that would make the water more acidic. (It should not be confused with basicity which is an absolute measurement on the pH scale.) It is measured by titrating the solution with a monoprotic acid such as HCl until its pH changes abruptly, or it reaches a known endpoint where that happens. Alkalinity is expressed in units of meq/L (milliequivalents per liter), which corresponds to the amount of monoprotic acid added as a titrant in millimoles per liter.



Annual mean sea surface dissolved inorganic carbon (DIC) for the present day (1990s) from the Global Ocean Data Analysis Project (GLODAP) climatology.

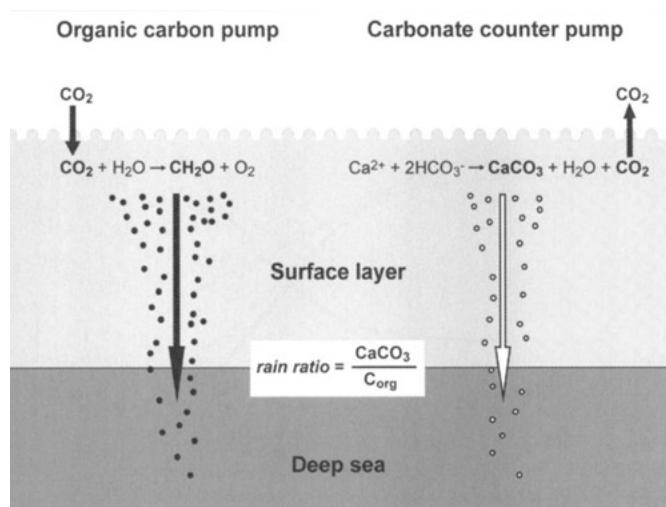
Because the **solubility of carbon dioxide increases when temperature decreases**, cold areas can contain more CO₂ and still be in equilibrium with the atmosphere. This accounts for the red areas in the Antarctic waters shown in the above figure. In contrast, **rising sea surface temperatures decrease the capacity of the oceans to take in carbon dioxide**. (Reville, 1957; Zebe, 2001). The North Atlantic and Nordic oceans have the highest carbon uptake per unit area in the world, (Takahasi, 2009) and in the North Atlantic deep convection transports approximately 197 Tg per year of non-refractory carbon to depth (Fontella, 2016).

Carbonate pump

The carbonate pump, sometimes called the carbonate counter pump, starts with marine organisms at the ocean's surface producing particulate inorganic carbon (PIC) in the form of **calcium carbonate** (calcite or aragonite, CaCO₃). This CaCO₃ is what forms hard body parts like shells. The formation of these shells decreases atmospheric CO₂ due to the production of CaCO₃ in the following reaction with simplified stoichiometry:



Coccolithophores, a nearly ubiquitous group of phytoplankton that produce shells of calcium carbonate, are the dominant contributors to the carbonate pump (Emerson, 2008). Due to their abundance, coccolithophores have significant implications on carbonate chemistry, in the surface waters they inhabit, and in the ocean below: **they provide a large mechanism for the downward transport of CaCO₃** (Rost, 2004). The air-sea CO₂ flux induced by a marine biological community can be determined by the **rain ratio** - the proportion of carbon from calcium carbonate compared to that from organic carbon in particulate matter sinking to the ocean floor, (PIC/POC). The carbonate pump acts as a negative feedback on CO₂ taken into the ocean by the solubility pump. It occurs with lesser magnitude than the solubility pump.



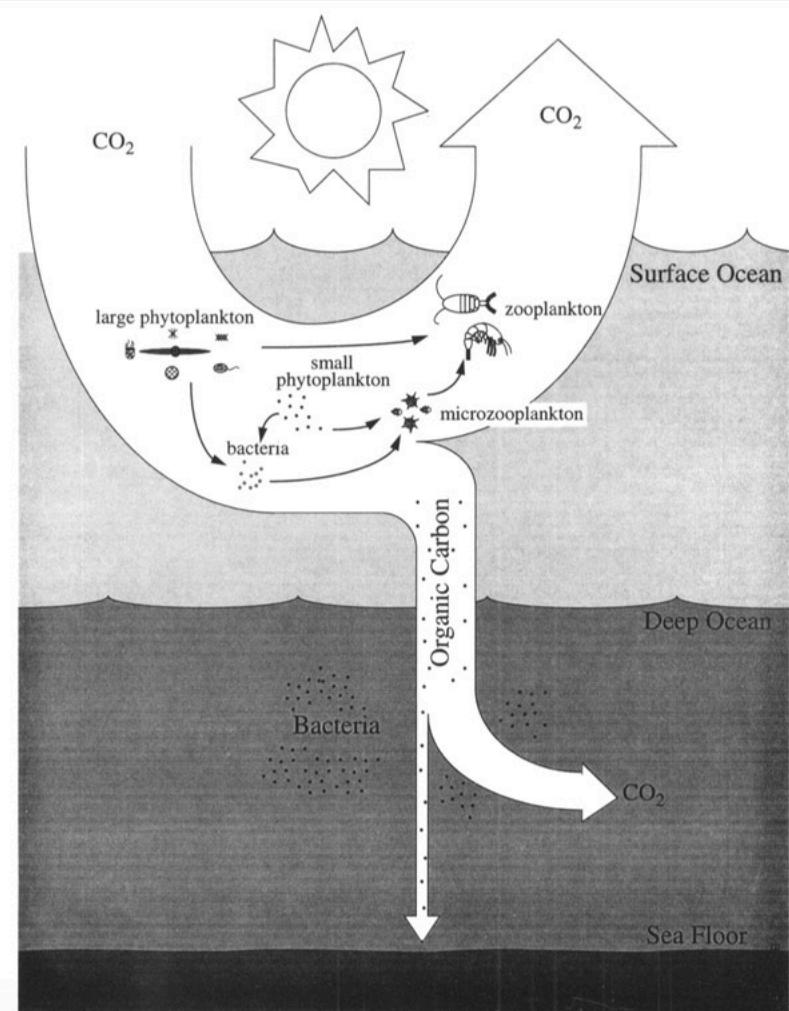
The biological carbon pumps: Photosynthetic production of organic matter in the surface layer and its subsequent transport to depth, termed organic carbon pump, generates a CO₂ sink in the ocean. In contrast, calcium carbonate production and its transport to depth, referred to as the calcium carbonate pump, releases CO₂ in the surface layer. **The relative strengths of these two processes (rain ratio)** largely determine the biologically mediated ocean-atmosphere CO₂ exchange.

Biological Pump

Particulate organic carbon, POC, created through biological production, can be exported from the upper ocean in a flux commonly termed the biological pump, where dissolved inorganic carbon (CO₂) is biologically converted into organic matter by photosynthesis



that then sinks and is, in part or whole, digested by heterotrophs.



Schematic of the "biological pump" which transports CO₂ from the atmosphere to the deep ocean. CO₂ is assimilated by phytoplankton through photosynthesis in the sunlit surface waters and converted to organic carbon. This phytoplankton biomass fuels a complex food web through which nutrients and CO₂ are recycled many times in the surface waters. The large phytoplankton are eaten by zooplankton and the small phytoplankton and bacteria are eaten by microzooplankton, which are in turn eaten by the zooplankton. Phytoplankton photosynthesize and excrete dissolved organic carbon which fuels the bacteria. In the open ocean, most of the CO₂ that is used in phytoplankton photosynthesis is ultimately released back into the atmosphere through their respiration, and that of the organisms who have eaten them. Some of the carbon finds its way to the deep ocean as zooplankton feces or pieces of dead organisms, where it is re-mineralized by bacteria back to CO₂. The net result is concentration of CO₂ (and nutrients) in the deep ocean.

Lability of DOM and DOC

In the following, DOC (dissolved organic carbon) and DOM (dissolved organic matter) will be used interchangeably depending on which term the author used. This group can be classified, based on how easily organisms can break them down for food, as labile, semi-labile, or refractory.

Labile DOM refers to the molecules that are consumed by microbes within hours or days of production. **Semi-labile DOM** is less reactive and persists in the surface ocean for weeks to years. **Refractory DOM** is the least biologically reactive and circulates through the major ocean basins on millennial time scales. Photosynthesis by phytoplankton is the primary source for labile and semi-labile molecules and is the indirect source for most refractory molecules (Moran 2016).

Labile molecules are present at low concentrations outside of cells (in the picomolar range). The very characteristics that define highly labile compounds make their study extremely challenging. They are consumed by microbes within hours or days of production and reside in the surface oceans, (Moran, 2016) where they contribute a majority of the labile carbon flux. Labile DOM can take the form of monocarboxylic and dicarboxylic acids, glycerols and fatty acids, and the nitrogen-containing metabolites taurine, choline, sarcosine, polyamines, methylamines, and ectoine. One-carbon compounds such as methanol as well as several sulfonates, have recently been added to the list. (Moran, 2016)

Semi-labile DOM Semi-labile molecules are much more difficult to consume, are able to reach depths of hundreds of meters below the surface before being metabolized (Hansell, 1998). Semi-labile DOM is operationally defined as the dissolved organic compounds that accumulate in surface waters over time frames of weeks to years but then disappear once exported to depth (Hansell, 1998). Why, exactly, these molecules resist degradation in the surface ocean where heterotrophic microbes are often limited by substrates and nutrients remains a mystery (Moran, 2016). One important factor may be that the full microbial community is needed to degrade the semi-labile DOM (Pedler et al, 2014).

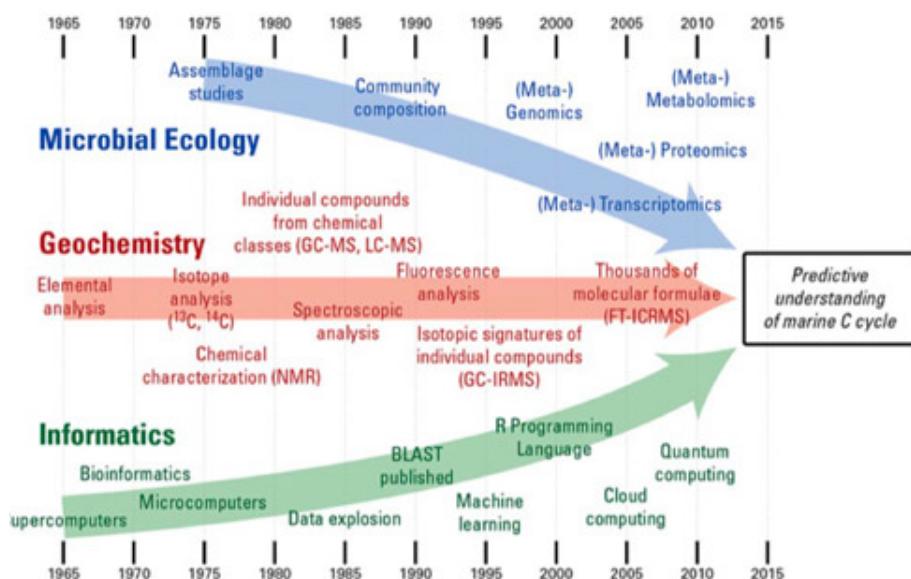
The DOM pool is now known to conservatively consist of tens to hundreds of thousands of different organic molecules (Kim S, et al, 2003), for which formulas are rapidly emerging (Hertkorn N, et al. (2006). The ocean microbiome has been estimated to consist of more than a hundred thousand different bacterial, archaeal, and eukaryotic taxa (Sunagawa S, et al.(2015); Gibbons SM, et al. (2013) with diverse ecological and metabolic strategies for producing and consuming fixed carbon (Ganesh S, et ak (2014).

At 662 Pg (Picograms or Gigatons (billion tons) Carbon, marine dissolved organic matter (DOM) is the largest ocean reservoir of reduced carbon, holding >200 times the carbon inventory of marine biomass (Hansell

et al. 2009). Most marine DOM results from photosynthesis in the surface ocean, and hence serves as substrate supporting vast heterotrophic prokaryote populations. The organic matter supporting these microbes is biologically labile and thus has a very short lifetime (hours to days), being quickly respired back to CO₂.

Refractory DOM A small fraction of the DOM produced escapes rapid mineralization, is transformed (biotically or abiotically) to resistant material, and accumulates as residual, biologically recalcitrant DOM, thus creating the enormous ocean inventory of dissolved organic carbon (DOC). This accumulated material has a wide range of lifetimes (months to millennia). DOM can store as much carbon as the current atmospheric CO₂ supply (Hansel, 2013).

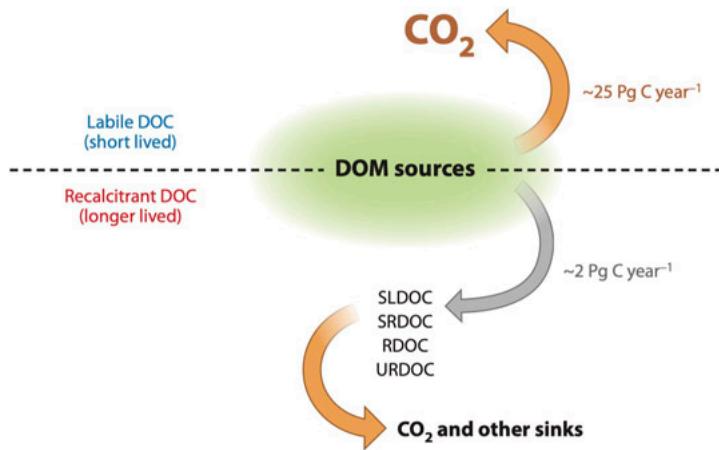
Refractory DOM can reach depths greater than 1000 m and circulates through the oceans over thousands of years.(Follett,2014;Moran, 2016; Hansell, 2013).These recent advances in understanding the marine carbon cycle have come from a wide range of technical advances (Moran et al, 2016).



Significant advances have occurred independently in three fields—microbial ecology, geochemistry, and informatics. They have positioned oceanographers for a deeper understanding of the ocean's carbon cycle. The integration of these three fields is yielding insights into the reactions at the foundation of the global carbon cycle. BLAST, basic local alignment search tool; FT-ICRMS, Fourier transform ion cyclotron resonance mass spectrometry; GCIRMS, gas chromatography isotope ratio mass spectrometry; GC-MS, gas chromatography mass spectrometry; LC-MS, liquid chromatography mass spectrometry; NMR, nuclear magnetic resonance spectroscopy. (Moran, et al,2016).

Over the course of a year, approximately 20 gigatons of photosynthetically-fixed labile and semi-labile carbon is taken up by

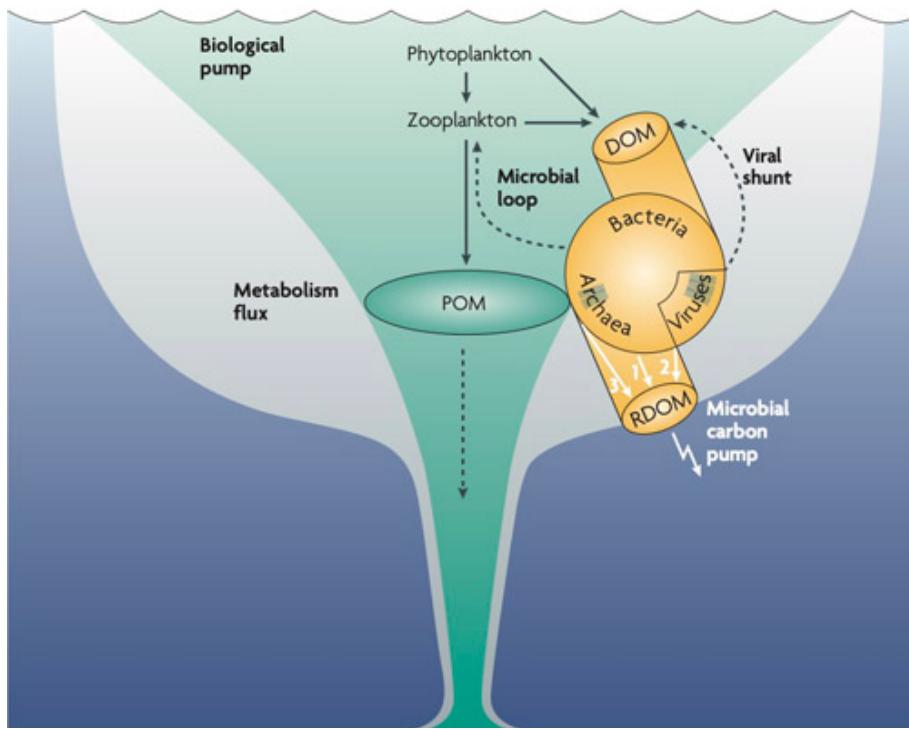
heterotrophs, whereas fewer than 0.2 gigatons of refractory carbon is produced. (Moran, et al, 2016). However, since refractory DOM is stable it is stored on the ocean floor, accumulating each year. On a global ocean basis, DOC undergoes net export to depths of >130 m at ~1.9 Pg C per year (Hansell et al. 2009) or ~20% of the global export production of ~10–13 Pg C per year (Laws et al. 2000, Dunne et al. 2007).



Two major classes of DOC exist in the ocean: labile DOC, which does not accumulate owing to rapid microbial turnover, and recalcitrant DOC, which serves as a reservoir of carbon until its eventual mineralization or removal by other processes. Recalcitrant DOC is subclassified as fractions, by shortest to longest lifetimes: semi-labile (SLDOC), semi-refractory (SRDOC), refractory (RDOC), and ultra-refractory (URDOC).

The majority of deep ocean refractory DOM likely represents the accumulation of metabolic products of ocean microbes that are refractory to further biological degradation, a phenomenon termed the “**microbial carbon pump**” (Jiao et al. 2010, Jiao & Azam 2011). Here marine microbes and their food web interactions effectively transform low concentrations of reactive carbon (LDOC and SLDOC) to high concentrations of RDOC, thus **building the huge marine DOC reservoir for carbon storage** (see following figure and legend).

Benner & Herndl (2011) employed tracers of bacterial input to estimate that the microbial carbon pump maintains ~155 Pg of RDOC and another 10 Pg of the less recalcitrant fractions. Thus, bacterial processing of organic matter may generate ~25% of the global DOC inventory and ~50% of SLDOC plus SRDOC.



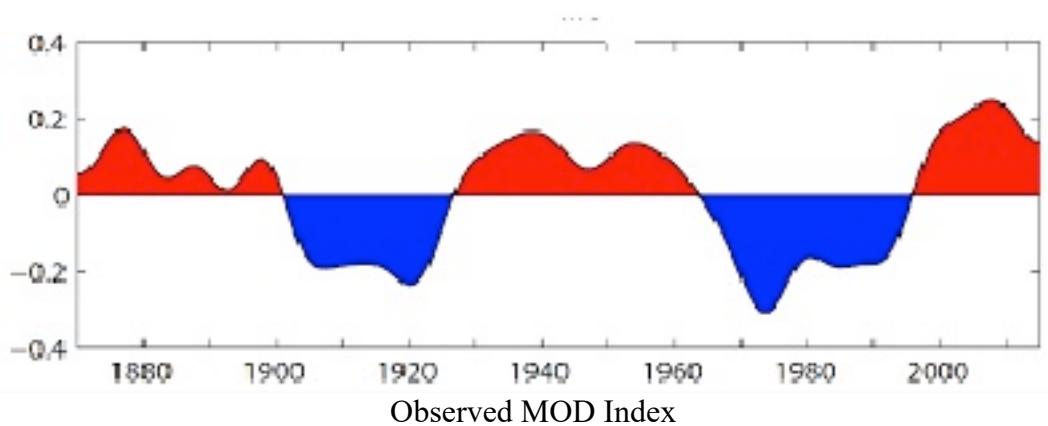
Major biological processes involved in carbon cycling in the ocean. The biological pump is a process where-by CO_2 in the upper ocean is fixed by particulate organic matter (POM) or as dissolved organic matter (DOM). The microbial loop is a pathway in the aquatic food web whereby DOM is taken up by bacteria and archaea, which are consumed by protists, which are in turn consumed by metazoans (not shown). The viral shunt reflects virus-mediated lysis of microorganisms, which returns the POM to the DOM pool. The proposed microbial carbon pump is a conceptual framework for understanding the role of microbial processes in the production of recalcitrant DOM (RDOM). RDOM can persist in the ocean for millennia and is therefore a reservoir for carbon storage in the ocean. Three major pathways have been identified in the **microbial carbon pump**: direct exudation of microbial cells during production and proliferation (path 1); **viral lysis** of microbial cells to release microbial cell wall and cell surface macromolecules (path 2); and **POM degradation** (path 3). The grey shading roughly indicates the total flux of carbon metabolism in the water column. (Jiao,N et al, 2010).

There are two additional terms that need to be explained. These are the following.

The **Atlantic Meridional Overturning Circulation (AMOC)** is an important component of the Earth's climate system, characterized by a northward flow of warm, salty water in the upper layers of the Atlantic, and a southward flow of colder water in the deep Atlantic. This ocean circulation system transports a substantial amount of heat from the Tropics and Southern Hemisphere toward the North Atlantic, where the heat is transferred to the atmosphere. Changes in this circulation have a profound impact on the global climate system which include, for example, changes in African and Indian monsoon rainfall, atmospheric circulation of relevance to hurricanes, and climate over North America and Western Europe.

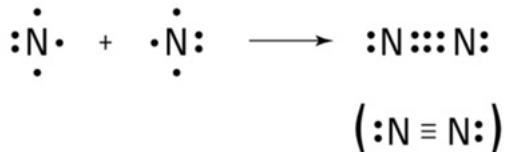
The **Atlantic Multi-decadal Oscillation (AMO)** also known as **Atlantic Multidecadal Variability (AMV)** is a mode of natural

variability occurring in the North Atlantic Ocean with an estimated period of 60-80 years. It is based upon the average anomalies of sea surface temperatures (SST) in the North Atlantic basin, typically over 0-80N. To remove the climate change signal from the AMO index, users typically adjust the SST data at each grid point.



The Marine Nitrogen Cycle

If the carbon cycle seemed complex, try this one. First, a note about the nitrogen triple bond.



A triple bond isn't quite three times as strong as a single bond, but it's a very strong bond. In fact, the triple bond in nitrogen is one of the **strongest bonds known**. This strong bond is what makes nitrogen very stable and resistant to reaction with other chemicals and why special a process like nitrogen fixation is needed to convert it to more readily used compounds. It's also why many explosive compounds (such as TNT and ammonium nitrate) contain nitrogen. When these compounds break apart in a chemical reaction, nitrogen gas is formed, and a large amount of energy is released.

The nitrogen cycle is the biogeochemical cycle by which nitrogen is converted into multiple chemical forms as it circulates among atmosphere, terrestrial, and marine ecosystems. The conversion of nitrogen can be carried out through both biological and physical processes. Important processes in the nitrogen cycle include **nitrogen fixation**, **ammonification**, **nitrification** and **denitrification**. The majority of Earth's atmosphere (78%) is atmosphere nitrogen, making it the largest source of nitrogen. However, atmospheric nitrogen has limited availability for biological use, leading to a scarcity of usable nitrogen in many types of ecosystems.

Nitrogen is present in the environment in a wide variety of chemical forms including organic nitrogen. Bacteria are a key element in the cycle, providing different forms of nitrogen compounds able to be assimilated by higher organism's ammonium (NH_4^+), nitrite (NO^{2-}), nitrate (NO^{3-}), nitrous oxide (N_2O), nitric oxide (NO) or inorganic nitrogen gas (N_2).

The following are the differences between ammonia (NH_3) and ammonium (NH_4^+).

Differences between ammonia and ammonium

- Ammonia is a weak base and is un-ionized. Ammonium is ionized.
- Ammonia gives out a strong smell. Ammonium does not smell at all.
- Ammonia is toxic or harmful to aquatic organisms. Ammonium is not harmful to aquatic organisms.
- Ammonia and ammonium help the plants in nitrogen fixation.
- Ammonia (NH_3) is widely used for producing fertilizers, cleansing products, plastics, pesticides and explosives. Ammonium (NH_4^+) is also used in the production of fertilizers and explosives. It is used in rocket propellant and also in water filters and in food preservatives.
- When ammonium salt solution (like NH_4Cl) is treated with a strong base, it produces ammonia. And if ammonia is mixed in water, a portion of it changes back to ammonium.

Nitrogen fixation

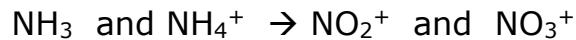


The conversion of nitrogen gas (N_2) into nitrates and nitrites through atmospheric, industrial and biological processes is called nitrogen fixation. Atmospheric nitrogen must be processed, or "fixed", into a usable form to be taken up by plants. Between 5 and 10 billion kg per year are fixed by lightning strikes, but most fixation is done by free-living or symbiotic bacteria known as **diazotrophs**. These bacteria have the **nitrogenase** enzyme that combines gaseous nitrogen with hydrogen to produce ammonia, NH_3 , which is converted by the bacteria into other organic compounds. Most biological nitrogen fixation occurs by the activity of Mo-nitrogenase, found in a wide variety of bacteria and some Archaea. Mo-nitrogenase is a complex two-component enzyme that has multiple metal-containing prosthetic groups. An example of free-living bacteria is *Azotobacter*. Symbiotic nitrogen-fixing bacteria such as *Rhizobium* usually live in the root nodules of legumes (such as peas, alfalfa, and locust trees). They form a mutualistic relationship with the plant, producing ammonia in exchange for carbohydrates. Because of this relationship, legumes will often increase the nitrogen content of nitrogen-poor soils. A few non-legumes can also form such symbioses.

Assimilation Plants can absorb nitrate (NO_3^-), or ammonium (NH_4^+) from the soil by their root hairs. If nitrate is absorbed, it is first reduced to nitrite ions (NO_2^-) and then ammonium ions for incorporation into amino acids, nucleic acids, and chlorophyll. In plants that have a symbiotic relationship with rhizobia, some nitrogen is assimilated in the form of ammonium ions directly from the nodules. It is now known that there is a more complex cycling of amino acids between Rhizobia bacteroids and plants. The plant provides amino acids to the bacteroids so ammonia assimilation is not required and the bacteroids pass amino acids (with the newly fixed nitrogen) back to the plant, thus forming an interdependent relationship. While many animals, fungi, and other heterotrophic organisms obtain nitrogen by ingestion of amino acids, nucleotides, and other small organic molecules, other heterotrophs (including many bacteria) are able to utilize inorganic compounds, such as ammonium as sole N sources.

Ammonification When a plant or animal dies or an animal expels waste, the initial form of nitrogen is organic. Bacteria or fungi convert the organic nitrogen within the remains back into ammonium (NH_4^+), a process called ammonification or **mineralization**.

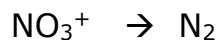
Nitrification



The conversion of ammonium and ammonia to nitrate is performed primarily by soil-living bacteria and other nitrifying bacteria. In the primary stage of nitrification, the oxidation of ammonium (NH_4^+) is performed by bacteria such as the *Nitrosomonas* species, which converts ammonia to nitrites (NO_2^+). Other bacterial species such as *Nitrobacter*, are responsible for the oxidation of the nitrites (NO_2^+) into nitrates (NO_3^+). It is important for the ammonia (NH_3) gas to be converted to nitrates or nitrites because ammonia gas is toxic to plants.

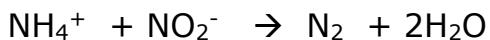
Where groundwater recharges stream flow, nitrate-enriched groundwater can contribute to eutrophication, a process that leads to high algal population and growth, especially blue-green algal populations. Since 2006, the application of nitrogen fertilizer has been increasingly controlled in Britain and the United States. This is occurring along the same lines as control of phosphorus fertilizer. Its restriction is considered essential to the recovery of eutrophied waterbodies.

Denitrification refers to all processes that convert reactive forms of nitrogen to molecular nitrogen (N_2). Most often this involves the following:



i.e. the reduction of nitrates NO_3^- back into nitrogen gas (N_2). This process is performed by bacterial species such as *Pseudomonas* and *Paracoccus*, **under anaerobic conditions**. They use the nitrate as an electron acceptor in the place of oxygen during respiration. The denitrifying bacteria use nitrates in the soil and the ocean to carry out respiration and consequently produce nitrogen gas, which is inert and unavailable to plants and escapes back into the atmosphere. This is an important process since it is responsible for the depletion of nitrogen in some parts of the ocean.

Anammox (Anaerobic ammonia oxidation) is the **anaerobic** oxidation of ammonium, NH_4^+ , to N_2 , using nitrite, NO_2^- , as an electron acceptor.



Anammox bacteria in the marine environment were first discovered in 2003, although a role for anaerobic ammonium oxidation had been postulated much earlier. Across **OMZ regions, anammox has been shown to be the principal mode of nitrogen loss**. Anammox rates have been shown to strongly correlate with the export of organic matter. This correlation is the result of sinking organic matter being remineralized and releasing ammonium, one of the key substrates needed for anammox (Bristow,L.A. et al, 2017).

Nitrogen fixation is the primary source of plant-available nitrogen in most ecosystems. However, in areas with nitrogen-rich bedrock, the breakdown of this rock also serves as a nitrogen source.

Nitrate reduction is also part of the **iron cycle**. Under anoxic conditions $\text{Fe}(\text{II})$ can donate an electron to NO_3^- and is oxidized to $\text{Fe}(\text{III})$ while NO_3^- is reduced to NO_2^- , N_2O , N_2 , and NH_4^+ depending on the conditions and microbial species involved.

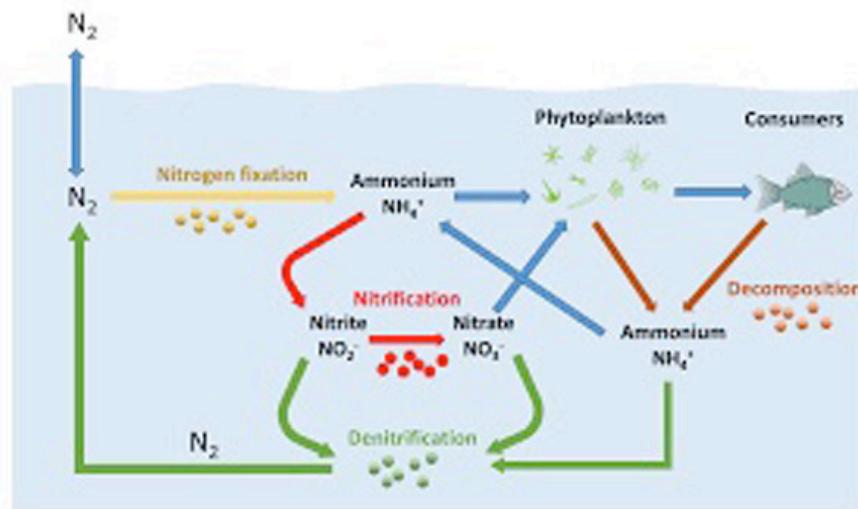
The following are terms often used in discussions of nitrogen in the water. **DON** = dissolved organic nitrogen **PON** = particulate organic nitrogen. DON is defined as material that can pass a $0.2\text{-}\mu\text{m}$ filter, while PON is the material that is retained on the filter. PON includes both dead organic matter and living organisms that are larger than $0.2\text{ }\mu\text{m}$. DON includes a variety of organic molecules and compounds, ranging from small organic molecules like urea and amino acids, to peptides and proteins, but does also include viruses and small bacteria. Another important nitrogen pool in aquatic environments is dissolved inorganic nitrogen (**DIN**), which consists of ammonium, nitrate, and nitrite. Thus, the content of total dissolved nitrogen (**TDN**) is made up by DIN and DON.

Diazotrophs

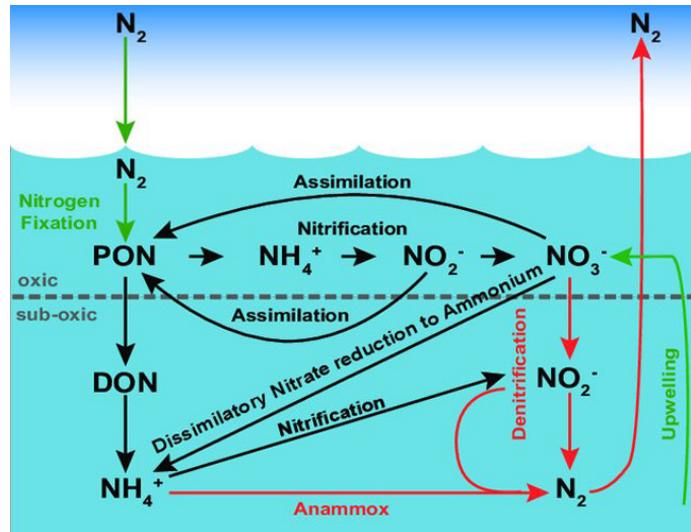
Diazotrophs are **bacteria and archaea** that fix **atmospheric nitrogen gas** into a more usable form such as ammonia. They are able to grow without external sources of fixed nitrogen. Examples of organisms that do this are *rhizobia* and *Frankia* (in symbiosis) and *Azospirillum*. All diazotrophs contain iron-molybdenum or -vanadium nitrogenase systems. The word diazotroph is derived from the words *diao* ("di" = two + "azo" = nitrogen) meaning "dinitrogen (N_2)" and *troph* meaning "pertaining to food or nourishment", in summary N_2 utilizing. Diazotrophs are scattered across bacteria taxonomic groups and a couple of archaea. Fixation is shut off when other sources of nitrogen are available, and, for many species, when oxygen is at high partial pressure.

Figures of the Marine Nitrogen Cycle

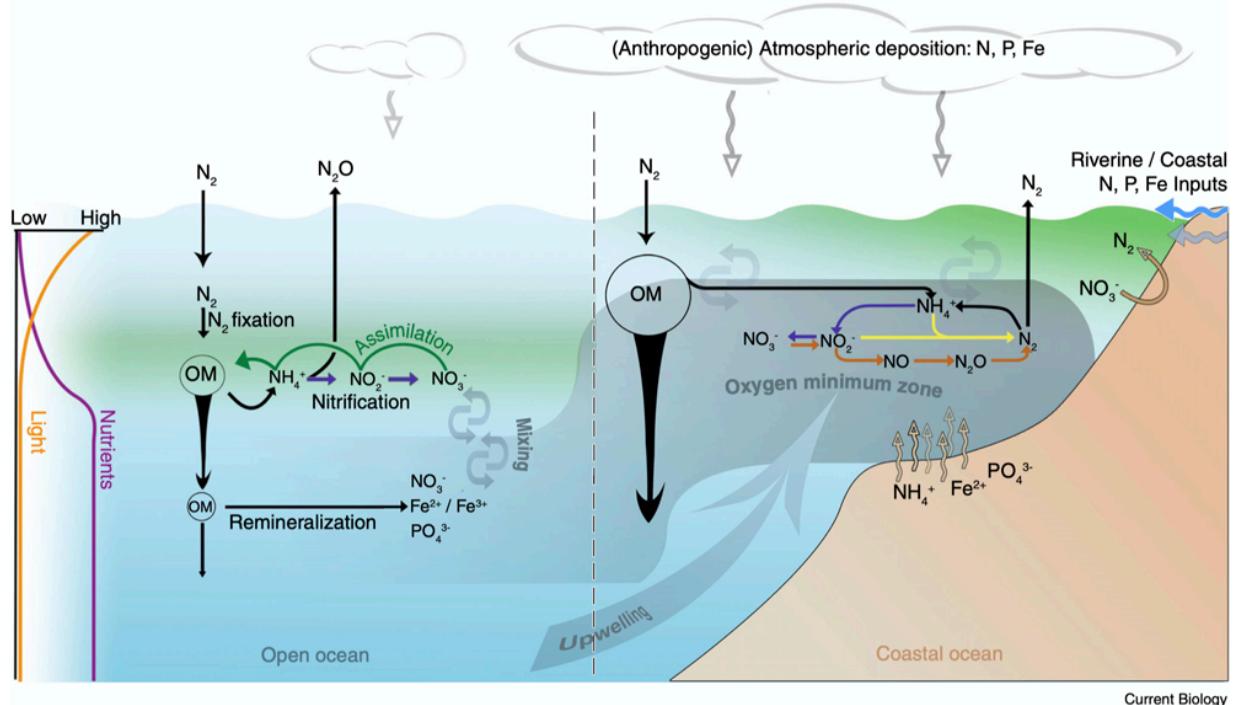
The following three figures illustrate the marine nitrogen cycle. It takes three to fully explain this complex cycle.



The marine nitrogen cycle showing the central role of phytoplankton. Wikipedia, 2020.



Chemistry of nitrogen in the ocean. PON particulate organic nitrogen
DON dissolved organic nitrogen (Sollai, et al, 2015).



Schematic showing nitrogen cycle processes occurring in the **open ocean** (left) and the **coastal ocean**, with an oxygen minimum zone (right). Depth profiles (far left) show typical distributions of light and nutrients (nitrate and phosphate) in the open ocean that can lead to the **formation of a deep chlorophyll a maximum (green shading)**. The processes depicted in the open ocean also occur in the coastal ocean. In the presence of an **OMZ (oxygen minimal zone)**, denitrification and anammox lead to nitrogen loss. Independent of an OMZ, **sedimentary (gray) denitrification results in significant nitrogen loss**. The processes of **anammox (yellow)**, **assimilation (green)**, **denitrification (orange)** and **nitrification (blue)** are shown by arrows. Nitrate, NO_3^- ; iron, Fe^{2+}/Fe^{3+} ; phosphate, PO_4^{3-} ; ammonium, NH_4^+ ; nitrite, NO_2^- ; nitrous oxide, N_2O ; nitric oxide, NO ; **organic matter, OM**. (Bristow, L. A. et al 2017)

The nitrogen cycle is an important process in the ocean as well as on land. While the overall cycle is similar, there are different players and modes of transfer for nitrogen in the ocean. Nitrogen enters the water through the precipitation, runoff, or as N₂ from the atmosphere. Nitrogen cannot be utilized by phytoplankton as N₂ so it must undergo nitrogen fixation which is performed predominately by cyanobacteria. Without supplies of fixed nitrogen entering the marine cycle, the fixed nitrogen would be used up in about 2,000 years. Phytoplankton need nitrogen in biologically available forms for the initial synthesis of organic matter. Ammonia and urea (CH₄N₂O) are released into the water by excretion from plankton.

Nitrogen sources are removed from the euphotic zone by the downward movement of the organic matter. This can occur from sinking of phytoplankton, vertical mixing, or sinking of waste of vertical migrators. The sinking results in ammonia being introduced at lower depths below the euphotic zone.

Bacteria are able to convert ammonia to nitrite and nitrate but they are **inhibited by light** so this must occur below the euphotic zone. Ammonification or Mineralization is performed by bacteria to convert organic nitrogen to ammonia. Nitrification can then occur to convert the ammonium to nitrite and nitrate. Nitrate can be returned to the euphotic zone by vertical mixing and upwelling where it can be taken up by phytoplankton to continue the cycle. N₂ can be returned to the atmosphere through denitrification.

Geographical Ocean Distribution of Nitrogen

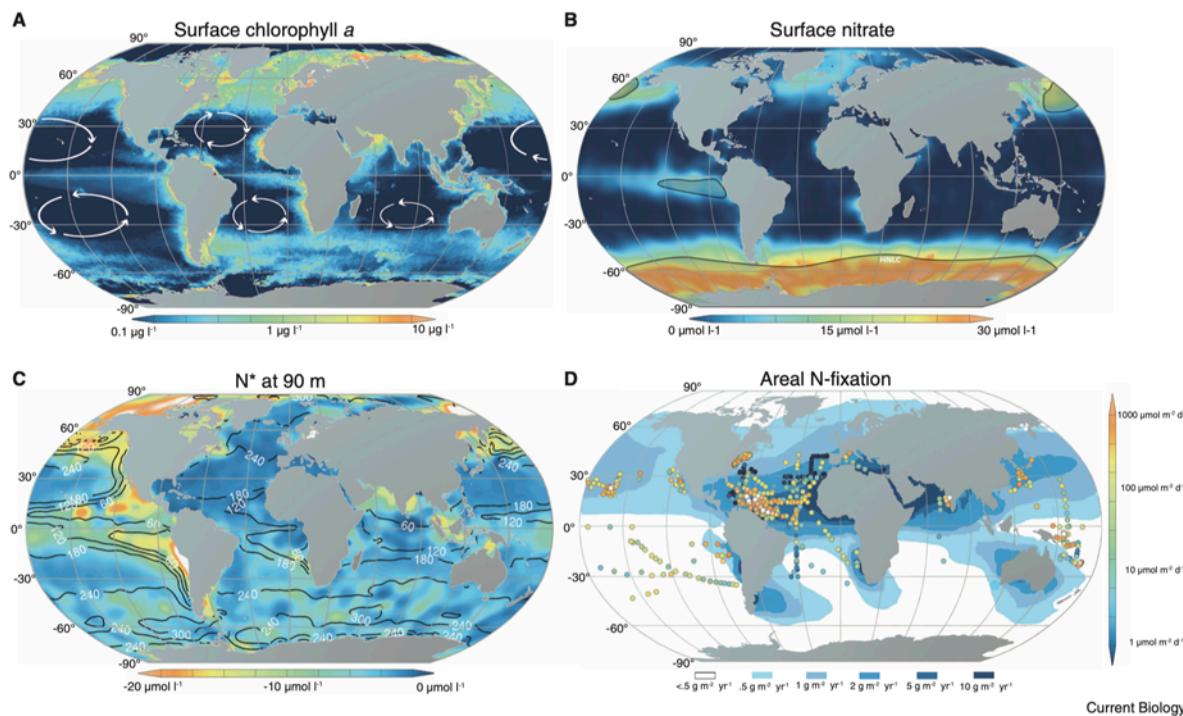
The nutrients in the ocean are not uniformly distributed. Areas of upwelling provide supplies of nitrogen from below the euphotic zone. Coastal zones provide nitrogen from runoff and upwelling occurs readily along the coast. However, the rate at which nitrogen can be taken up by phytoplankton is decreased in oligotrophic waters year-round and temperate water in the summer resulting in lower primary production. The distribution of the different forms of nitrogen varies throughout the oceans as well.

Nitrate is depleted in near-surface water except in upwelling regions. Coastal upwelling regions usually have high nitrate and chlorophyll levels as a result of the increased production. However, there are regions of high surface nitrate but low chlorophyll that are referred to as **HNLC (high nitrogen, low chlorophyll)** regions. The **best explanation for HNLC regions relates to iron scarcity in the ocean**, which may play an important part in ocean dynamics and nutrient cycles. The input of iron varies by region and is delivered to the ocean by dust (from dust storms) and leached out of rocks. Iron is under consideration as the true limiting element to ecosystem productivity in the ocean.

Ammonium and nitrite show a maximum concentration at 50–80 m (lower end of the euphotic zone) with decreasing concentration below that depth. This distribution can be accounted for by the fact that nitrite and

ammonium are intermediate species. They are both rapidly produced and consumed through the water column. **The amount of ammonium in the ocean is about 3 orders of magnitude less than nitrate.** Between ammonium, nitrite, and nitrate, nitrite has the fastest turnover rate. It can be produced during nitrate assimilation, nitrification, and denitrification; however, it is immediately consumed again. Wikipedia

The following figure illustrates some of the critical aspect of the distribution of nitrogen and other nutrients in the oceans of the world.



Current Biology

Patterns of growth related to nutrient limitation.

- A)** Distribution of surface **chlorophyll a** ($\mu\text{g per L}$). White arrows depict the location and circulation direction of the open ocean **gyres**.
- B)** **Surface nitrate concentrations** ($\mu\text{mol per L}$) and approximate locations of the **high-nutrient low-chlorophyll (HNLC)** regions within the black lines.
- C)** **N^*** (calculated as $\text{N}^* = (\text{NO}_3^- + \text{NO}_2^-) - 16 * \text{P}^+$) 2.9 $\mu\text{mol per kg}$; (Gruber and Sarmiento, 1997) and **oxygen concentrations (black contour lines)** at 90 m water depth. This depth was chosen to highlight the shelf regions and OMZs; however, positive N^* as a result of N_2 fixation is often not observed at this depth.
- D)** Depth-integrated N_2^- fixation rates (circles, scale bar to the right of the panel; $\mu\text{mol per m}^2 \text{ per day}$; modified from Luo et al., 2012, zero values excluded), with blue shading showing regions of **dust deposition** (scale bar below; adapted from Jickells et al., 2005). Data in panels A-C from World Ocean Atlas, 2013 v2.

OMZ - Oxygen Minimal Zones

Warming and acidification are no longer enough to describe the upheavals in the marine world. There is a **third component: deoxygenation**, i.e., the depletion of oxygen in certain zones of the Ocean.

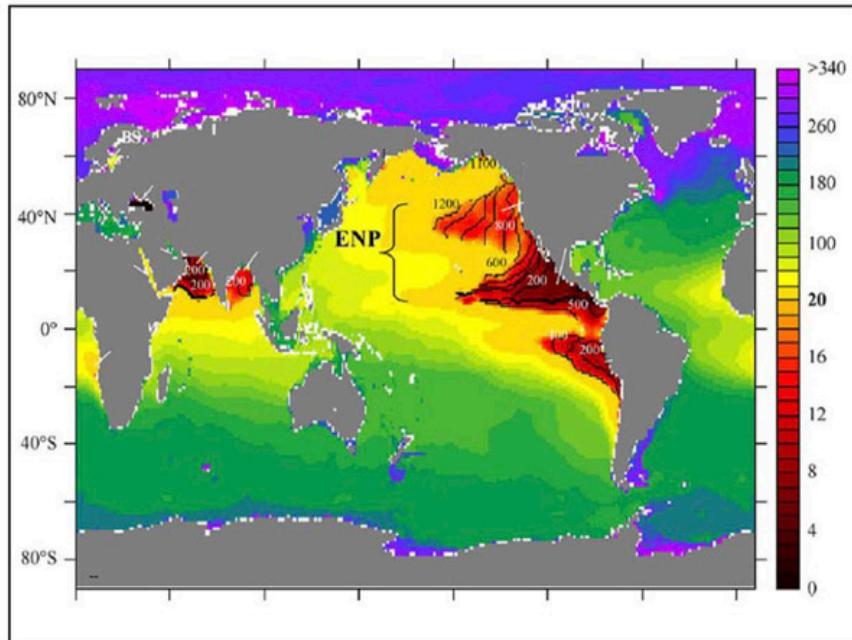
The ocean is often called “the blue lung of the planet” – comparable to a huge forest. The billions of micro-algae inhabiting the ocean’s surface waters inject as much oxygen into the atmosphere via photosynthesis as all the world’s forests. However, in certain oceanic regions, mostly located at depths between 100 and 500 meters, oxygen is critically lacking. Like temperature, salinity and nutrients, the concentration of dissolved oxygen is very heterogeneous in the ocean.

In general, oxygen concentration decreases with depth. In some ocean regions, a convergence of certain natural phenomena sometimes gives rise to OMZs — “oxygen minimum zones”. Cold waters rising up from the depths are low in oxygen but rich in nutrients and CO₂. They cause phytoplankton blooms on the surface. At greater depths the degradation of all this organic matter consumes a large amount of oxygen and sometimes completely depletes the water. Paradoxically, although life develops with difficulty in the OMZ, just a few hundred meters above we find the most productive areas of the ocean that correspond to great fishing zones. The problem is that ocean circulation does not properly resupply these OMZs, and oxygen eventually becomes exhausted. The largest deoxygenated zones are found along the eastern coasts of the Pacific and Atlantic Ocean. Two other famous OMZs are located in the Bay of Bengal and in the Arabian Sea. (pink-red areas in the map below)

What are the impacts of this lack of oxygen on the distribution and diversity of life? If you could dive into an OMZ, what would you find there? These more acidic and oxygen-free waters host mostly microorganisms, especially Archaea and anaerobic bacteria (Deutsch et al, 2011). Organisms that need more oxygen (fish for example) cannot survive here, while others with less intense metabolisms or capable of capturing oxygen from the water, can withstand relatively low concentrations.

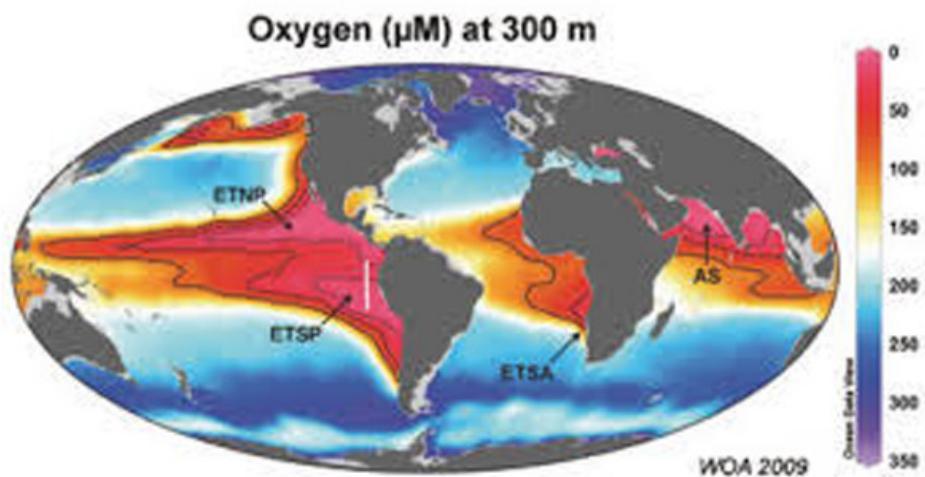
Another problem related to these OMZs is that molecules such as methane (CH₄), nitrous oxide (N₂O) or hydrogen sulphide (H₂S) are the metabolic products of the anaerobic bacteria and Archaea living here. CH₄ and N₂O are major greenhouse gases (respectively 80 and 300 times more detrimental than CO₂). As for H₂S, it is toxic to certain marine organisms.

Clearly if we were planning to fight climate change by adding nutrients to certain areas of the ocean to enhance phytoplankton growth, it will be important to avoid areas of severe oxygen depletion, since this environment would be lethal to new growth. These areas were mapped on a global scale by Paulmiera and Ruiz-Pino (2008). Their world map is as follows:



World distribution of low oxygen zones, OMZs.

A map of the oxygen concentration at a depth of 300 meters is published by NOAA.



© World Ocean Atlas 2009 nodc.noaa.gov

OMZs are also keys to understanding the present unbalanced nitrogen cycle and the oceans' role on atmospheric greenhouse control. OMZs are the main areas of nitrogen loss (as N_2 , N_2O) to the atmosphere through denitrification and anammox (see Nitrogen cycle above). They could even indirectly mitigate the oceanic biological sequestration of CO_2 .

OMZs have been mainly known for playing an essential role in the global nitrogen cycle, in which various chemical species, according to their degree of oxidation (e.g. ammonium, NH₄; nitrite, NO₂; nitrate, NO₃; nitrous oxide, N₂O; dinitrogen, N₂), and different bacterial processes intervene. Under oxygen conditions, but also at the upper boundary (oxycline) of an OMZ, nitrification transforms NH₄ into NO₃. But **OMZs are especially associated with denitrification, which is a bacterial process occurring only in O₂ deficient regions** (Codispoti et al., 2001). **Denitrification converts NO₃, one of the main limiting nutrients in the ocean, into gaseous nitrogen (N₂O, N₂) which is lost to the atmosphere and contributes to the oceanic nitrate deficit** (N/P % 14.7; e.g., Tyrrell, 1999).

Recently, a previously unknown process in the ocean has been observed, first in sediments and then in the water column in the OMZs (Kuypers et al., 2003) involving the anaerobic oxidation of NH₄ using NO₂ (**anammox**). This imposes a complete revision of the global nitrogen cycle (e.g., Arrigo, 2005). **OMZs are also involved in** the cycle of very important climatic gases (Palmier and Ruiz-Pino, 2009):

- **production of 50% of the oceanic N₂O** (e.g., Bange et al., 1996);
- **production of H₂S** (e.g., Dugdale et al., 1977) and CH₄ (e.g., Cicerone and Oremland, 1988), episodically or for OMZs in contact with sediments.

- **limitation of atmospheric CO₂ sequestration by the ocean** - directly as an end-product of remineralization (Paulmier et al., 2006) or indirectly through limitation of total primary production due to the N loss (see hypothesis of Falkowski, 1997);

- **potential DMS consumption** due to higher bacterial activity (Kiene and Bates, 1990).

- Chemically, OMZs are associated with **acidification** (low pH % 7.5 SWS; Paulmier, 2005), and reduced conditions (Richards, 1965) favoring reduced chemical species (e.g., Fe(II) or Cu(I) potentially stimulating photosynthesis or N₂O production (Palmier and Ruiz-Pino, 2009)).

Hypoxia development in areas of the world's coastal ocean is accelerated by human activities, primarily increased nutrient loads, that have set in motion a cascading chain of events related to eutrophication. With an ever-increasing population, the inputs of nutrients to coastal systems will continue to escalate, especially in developing countries, as the application of nutrients for growth of crops to sustain human needs and the burning of fossil fuels in response to industrialization will continue, and coastal hypoxia will be more widespread and frequent than is presently the situation.

All of the above was presented to help understand the relevant terminology. Now for the essence of it all – the phytoplankton itself.