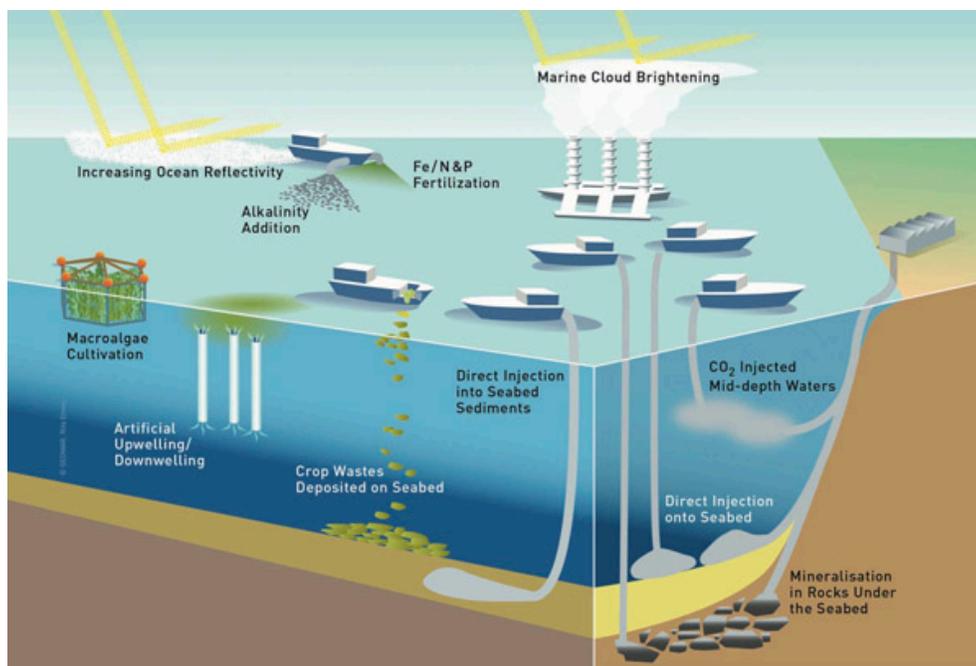


### III Geoengineering

Geoengineering has been suggested as a potential tool for addressing climate change and the Royal Society's definition of it has been widely accepted:

"The deliberate large-scale manipulation of the planetary environment to counteract anthropogenic climate change" (Royal Society, 2009).

Since this is a primer on oceanography, I will emphasize the role of the oceans in geoengineering. The following diagram illustrates some of the proposed, ocean based, geoengineering projects.



Different ocean geoengineering proposals. From GESAMP (2019).

First, two additional terms.

The **Redfield ratio** or Redfield stoichiometry is the consistent atomic ratio of carbon, nitrogen and phosphorus found in marine phytoplankton and throughout the deep oceans. The term is named for American oceanographer Alfred C. Redfield who in 1934 first described the relatively consistent ratio of nutrients in marine biomass samples collected across several voyages on board the research vessel *Atlantis*, and empirically found the ratio to be C:N:P = 106:16:1 (Redfield, 1934). While deviations from the canonical 106:16:1 ratio have been found depending on phytoplankton species and the study area, the Redfield ratio has remained an important reference to oceanographers studying nutrient limitation. A 2014 paper (Martiny, A.C. et al, 2014) summarized a large data set of nutrient

measurements across all major ocean regions spanning from 1970 to 2010 and reported the global median C:N:P to be 163:22:1. In the section on iron fertilization I will show the importance of adding iron to the ratio.

**Liebig law of the minimum**, often simply called Liebig's law or the law of the minimum, is a principle developed in agricultural science by Carl Sprengel (1840) and later popularized by Justus von Liebig. It states that growth is dictated not by total resources available, but by the scarcest resource (limiting factor).

## **Ocean Nourishment/Fertilization**

The issue of ocean fertilization is very controversial. If we were to support this, it will be critical to know what the controversies and potential problems are. Thus, I have reviewed this subject in some detail. This subject has also been reviewed in GESAMP (2019) (see below).

This is a type of climate engineering is based on the purposeful introduction of nutrients to the upper ocean – see Fe/N & P in the above illustration. It offers the prospect of both reducing the concentration of atmospheric greenhouse gases with the aim of slowing climate change and at the same time increasing fish stocks via increasing primary production. Each area of the ocean has a base sequestration rate on some timescale, e.g., annual. Fertilization must increase that rate but must do so on a scale beyond the natural scale. Otherwise, fertilization changes the timing, but not the total amount sequestered. However, accelerated timing may have beneficial effects for primary production separate from those from sequestration. (Lampitt, R. S. et al,2008).

A number of techniques, including fertilization by **iron**, **urea** and **phosphorus** have been proposed (Wikipedia, 2020 & below). Each of these three will be individually examined. Iron fertilization is the most controversial of all the ocean fertilization projects. Thus, I have reviewed it in some detail.

## **Iron Fertilization**

About 70% of the world's surface is covered in oceans. The part of these where light can penetrate is inhabited by algae (and other marine life). In some oceans, algae growth and reproduction is limited by the amount of iron. Iron is a vital micronutrient for phytoplankton growth and photosynthesis that has historically been delivered to the pelagic sea by dust storms from arid lands. This dust contains 3–5% iron and its deposition has fallen nearly 25% in recent decades.

Research expanded the Redfield constant to 106 C: 16 N: 1 P: .001 Fe signifying that in iron deficient conditions **each atom of iron can fix 106,000 atoms of carbon**, (Sundra & Huntsman, 1995) or on a mass basis, **each kilogram of iron can fix 83,000 kg** of carbon dioxide.

Therefore, small amounts of iron (measured by mass parts per trillion) in HNLC zones can trigger large phytoplankton blooms on the order of 100,000 kilograms of plankton per kilogram of iron. The size of the iron particles is critical. Particles of 0.5–1 micrometer or less seem to be ideal both in terms of sink rate and bioavailability. Particles this small are easier for cyanobacteria and other phytoplankton to incorporate and the churning of surface waters keeps them in the euphotic or sunlit biologically active depths without sinking for long periods.

As stated above, atmospheric deposition is an important iron source. Satellite images and data (such as PODLER, MODIS, MSIR) combined with back-trajectory analyses identified natural sources of iron-containing dust. Iron-bearing dusts erode from soil and are transported by wind. Although most dust sources are situated in the Northern Hemisphere, the largest dust sources are located in northern and southern Africa, North America, central Asia and Australia. (Mahowald, et al 2005)

Heterogeneous chemical reactions in the atmosphere modify the speciation of iron in dust and may affect the bioavailability of deposited iron. The soluble form of iron is much higher in aerosols than in soil (~0.5%). (Malowald, et al 2005; Fung et al,2000). Several photo-chemical interactions with dissolved organic acids increase iron solubility in aerosols. Among these, photochemical reduction of oxalate-bound Fe(III) from iron-containing minerals is important. The organic ligand forms a surface complex with the Fe (III) metal center of an iron-containing mineral (such as hematite or goethite). On exposure to solar radiation the complex is converted to an excited energy state in which the ligand, acting as bridge and an electron donor, supplies an electron to Fe(III) producing soluble Fe(II).

Consideration of iron's importance to phytoplankton growth and photosynthesis dates to the 1930s when English biologist Joseph Hart speculated that the ocean's great "desolate zones" (areas apparently rich in nutrients but lacking in plankton activity or other sea life) might be iron deficient. There was little scientific discussion recorded concerning this until the 1980s, when oceanographer **John Martin**, director of the Moss Landing Marine Laboratories, renewed controversy on the topic with his marine water nutrient analyses. His studies supported Hart's hypothesis. Some of these "desolate" regions came to be called "High Nutrient, Low Chlorophyll" (**HNLC**) zones.

To test this, known as the **Iron Hypothesis**, Martin he arranged an experiment using samples of clean water from Antarctica. Iron was added to some of these samples. After several days the phytoplankton in the samples with iron fertilization grew much more than in the untreated samples.

John Gribbin was the first scientist to publicly suggest that climate change could be reduced by adding large amounts of soluble iron to the oceans (Gribbin, 1988). Martin's 1988 quip four months later at Woods Hole

Oceanographic Institution, "Give me a half a tanker of iron and I will give you another ice age," drove a decade of research.

Iron fertilization is the intentional introduction of iron to iron-poor areas of the ocean surface to stimulate phytoplankton production. This is intended to enhance biological productivity and/or accelerate carbon dioxide (CO<sub>2</sub>) sequestration from the atmosphere. (Wikipedia 2020 and below)

Iron is a trace element necessary for photosynthesis in plants. It is highly insoluble in sea water and in a variety of locations is the limiting nutrient for phytoplankton growth. Large algal blooms can be created by supplying iron to iron deficient ocean waters. These blooms can nourish other organisms. A number of experiments were launched to test the iron hypothesis. These were as follows:

**IRONEX I** Here 445 kg of iron were added to a patch of ocean near the Galápagos Islands. The levels of phytoplankton **increased three times** in the experimental area. The success of this experiment and others led to proposals to use this technique to remove carbon dioxide from the atmosphere as Gribbon had suggested.

**EisenEx** In 2000 and 2004, iron sulfate was discharged from the *EisenEx*. 10 to 20 percent of the resulting algal bloom died and sank to the sea floor.

The controversy about iron fertilization is well illustrated by some of the following cases.

**Planktos** was a US company that abandoned its plans to conduct 6 iron fertilization cruises from 2007 to 2009, each of which would have dissolved up to 100 tons of iron over a 10,000 km<sup>2</sup> area of ocean. Their ship *Weatherbird II* was refused entry to the port of Las Palmas in the Canary Islands where it was to take on provisions and scientific equipment.

In 2007 commercial companies such as **Climos** and **GreenSea Ventures** and the Australian-based **Ocean Nourishment Corporation**, planned to engage in fertilization projects. These companies invited green co-sponsors to finance their activities in return for provision of carbon credits to offset investors' CO<sub>2</sub> emissions.

**LOHAFEX** was an experiment initiated by the German Federal Ministry of Research and carried out by the German Alfred Wegener Institute (AWI) in 2009 to study fertilization in the South Atlantic. India was also involved. As part of the experiment, the German research vessel **Polarstern** deposited 6 tons of ferrous sulfate in an area of 300 square kilometers. It was expected that the material would distribute through the upper 15 meters (49 ft) of water and trigger an algal bloom. A significant part of the carbon dioxide dissolved in sea water would then be bound by the emerging bloom and sink to the ocean floor.

The German Federal Environment Ministry called for the experiment to halt, partly because environmentalists predicted damage to marine plants. Others predicted long-term effects that would not be detectable during

short-term observation (Lenton & Vaughan, 2009) or that this would encourage large-scale ecosystem manipulation. (Harrison, 2013).

A 2012 study deposited iron fertilizer in an eddy near Antarctica. The resulting algal bloom sent a significant amount of carbon into the deep ocean, where it was expected to remain for centuries to millennia. The eddy was chosen because it offered a largely self-contained test system. (Jones, 1996). As of day, 24, nutrients, including nitrogen, phosphorus and silicic acid that diatoms use to construct their shells, declined. Dissolved inorganic carbon concentrations were reduced below equilibrium with atmospheric CO<sub>2</sub>. In surface water, particulate organic matter (algal remains) including silica and chlorophyll increased. After day 24, the particulate matter fell to between 100 meters (330 ft) to the ocean floor. Each iron atom converted at least 13,000 carbon atoms into algae. At least half of the organic matter sank below, 1,000 meters (3,300 ft).

**Haida Gwaii project** In July 2012, the Haida Salmon Restoration Corporation dispersed 100 short tons (91 t) of iron sulphate dust into the Pacific Ocean several hundred miles west of the islands of Haida Gwaii near Vancouver. The Old Massett Village Council financed the action as a salmon enhancement project with \$2.5 million in village funds. The concept was that the formerly iron-deficient waters would produce more phytoplankton that would in turn serve as a "pasture" to feed salmon. Then CEO Russ George hoped to sell carbon offsets to recover the costs. The project was accompanied by charges of unscientific procedures and recklessness. George contended that 100 tons was negligible compared to what naturally enters the ocean.

Some environmentalists called the dumping a "blatant violation" of two international moratoria.(Karl et al, 2008). George said that the Old Massett Village Council and its lawyers approved the effort and at least seven Canadian agencies were aware of it. According to George, the 2013 salmon runs increased from 50 million to 226 million fish. However, many experts contend that changes in fishery stocks since 2012 cannot necessarily be attributed to the 2012 iron fertilization; many factors contribute to predictive models, and most data from the experiment are considered to be of questionable scientific value. (Jones, 2014)

**Restrictions** In 2007 Working Group III of the United Nations Intergovernmental Panel on Climate Change examined ocean fertilization methods in its fourth assessment report and noted that the field-study estimates of the amount of carbon removed per ton of iron was probably over-estimated and that potential adverse effects had not been fully studied (Metz et al, 2007).

In June 2007 the **London Dumping Convention** issued a statement of concern noting 'the potential for large scale ocean iron fertilization to have negative impacts on the marine environment and human health' but did not

define 'large scale'. It is believed that the definition would include research operations.

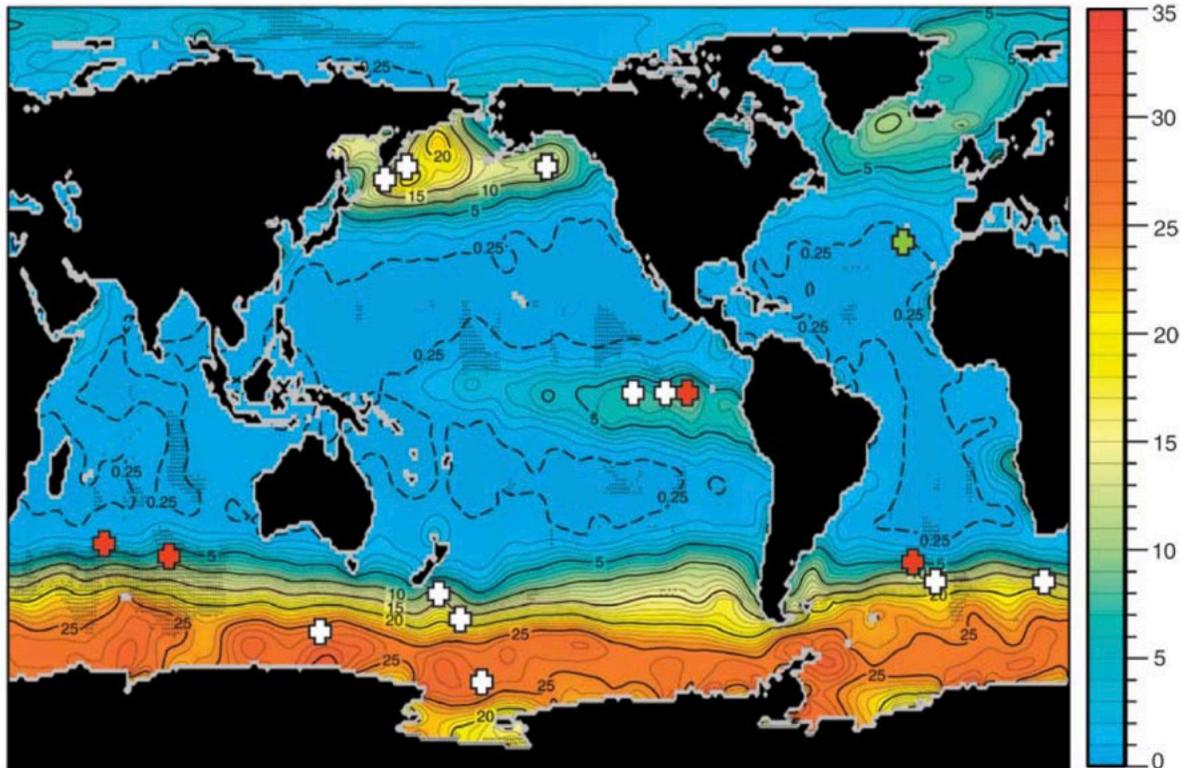
In 2008, the **London Convention/London Protocol** noted in resolution LC-LP.1 that knowledge on the effectiveness and potential environmental impacts of ocean fertilization was insufficient to justify activities other than research. This non-binding resolution stated that fertilization, other than research, "should be considered as contrary to the aims of the Convention and Protocol and do not currently qualify for any exemption from the definition of dumping".

On May 2008, at the **Convention on Biological Diversity**, 191 nations called for a ban on ocean fertilization until scientists better understand the implications.

In August 2018, Germany banned the sale of ocean seeding as carbon sequestration system the matter was under discussion at EU and EASAC levels.

Early results from shipboard fertilizations in high nutrient–low chlorophyll (**HNLC**) waters presented compelling but equivocal evidence that phytoplankton growth was limited by Fe availability (Martin, 1991). To be more convincing it was felt that larger (mesoscale) Fe addition experiments offered the best approach to resolve questions about the role of Fe in ocean productivity, C cycling, and climate. The main objective of was to test whether Fe enrichment would increase primary productivity in HNLC waters, but additional questions focused on how Fe enrichment would affect nutrient use and export (Martin 1990; Martin et al, 1994).

**Mesoscale Experiments.** Beginning in 1993, thirteen research teams completed ocean trials demonstrating that phytoplankton blooms can be stimulated by iron augmentation (Boyd et al, 2014). The following figure shows the locations of these mesoscale experiments.



Annual surface mixed-layer nitrate concentrations in units of  $\text{mmol liter}^{-1}$ , with approximate site locations of Iron fertilization experiments (**white crosses**), natural bloom studies (**red crosses**), and a joint Fe and P enrichment study of the subtropical LNLC Atlantic Ocean (**green cross**). All areas that are not blue represent **HNLCs** (high nutrient, low chlorophyll) sites. (Boyd, et al 2014).

This era of mesoscale Fe enrichments started with IronEx I, where Fe and the conservative tracer  $\text{SF}_6$  would be added to HNLC surface waters. Watson et al (1991) outlined how these studies would be performed. They proposed that the use of 1,000 kg of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  would raise the concentration of Fe in a volume of water  $50 \text{ km}^2 \times 25 \text{ m}$  deep by 3  $\text{nmol kg/l}$ , which would be sufficient to have a substantial effect on productivity if Fe is in fact a limiting nutrient. This amount of  $\text{FeSO}_4$  would be dissolved in 7 t of water. The Fe solution would be pumped from a tank on the ship and be mixed with a flow of  $\text{SF}_6$  (sulfur hexafluoride)-tagged seawater from a separate tank just before release. In order to promote rapid initial mixing, the release would be made at a few meters depth into the wake of the ship's screws as it steamed ahead. In each survey, variables such as Fe, other nutrients,  $\text{K}_2\text{O}$ ,  $\text{O}_2$ ,  $^{14}\text{C}$  productivity, POC, Chl, dimethylsulfide, and other biogenic properties would be observed before and after and correlated with the amount of tracer. If the ratio of tracer to iron increased it would indicate there was an up take of iron. These experiments were termed FeAXs.

A further 11 FeAXs of similar design were undertaken in different HNLC regions (see above figure). These confirmed the capability to study pelagic

ecology and biogeochemical cycling in a discrete water parcel over time and space scales of weeks and kilometers. Complementary approaches include ship-based observations of persistent natural blooms within HNLC waters (above figure).

The most recent open ocean mesoscale trials of ocean iron fertilization were in 2009 (January to March) in the South Atlantic by project **Lohafex**, and in July 2012 in the North Pacific off the coast of British Columbia, Canada, by the **Haida Salmon Restoration Corporation** (HSRC).

Fertilization **occurs naturally** when upwellings bring nutrient-rich water to the surface, as occurs when ocean currents meet an ocean bank or a sea mount. This form of fertilization produces the world's largest marine habitats as at the Galapagos. Fertilization can also occur when weather carries wind-blown dust long distances over the ocean, or iron-rich minerals are carried into the ocean by glaciers, rivers and icebergs.

The mesoscale studies have verified that Fe enrichment enhances primary production from polar to tropical HNLC waters and **confirmed** that Fe supply has a fundamental role in photosynthesis (photosynthetic competence, diatom sinking, Fe uptake rates, and other physiological processes). They have also demonstrated reduced silica requirements of diatoms when relieved of Fe stress, confirming results from bottle experiments (Boyd et al, 2014).

The mesoscale findings suggested that iron deficiency was limiting ocean productivity and offered an approach to mitigating climate change as well. Perhaps the most dramatic support for Martin's hypothesis came with the 1991 eruption of Mount Pinatubo in the Philippines. Environmental scientist Andrew Watson analyzed global data from that eruption and calculated that it deposited approximately 40,000 tons of iron dust into oceans worldwide. This single fertilization event produced an easily observed **global decline in atmospheric CO<sub>2</sub>** and a parallel pulsed increase in oxygen levels (Watson, 1997).

One of the conclusions of the Boyd et al (2014) review was that improved experimental designs were needed to overcome the limitations of these mesoscale experiments, such as smaller and more frequent Fe doses, greater patch length scale ( $\gg 10$  km), and additional measurements that provide insight into the impact of Fe enrichment on climate (e.g., biogenic gases) or Fe cycling (e.g., fate of Fe). Detailed comparison of the biogeochemistry of differing natural blooms would also help to better understand the influence of a range of Fe:macronutrient stoichiometries on bloom dynamics and carbon biogeochemistry.

## **Methods**

There are two ways of performing artificial iron fertilization: ship based direct into the ocean and atmospheric deployment (Oeste, 2017).

**Ship based deployment** Trials of ocean fertilization using iron sulphate added directly to the surface water from ships are described above.

**Atmospheric sourcing** Iron-rich dust rising into the atmosphere is a primary source of ocean iron fertilization (Shaffer & Lambert, 2018). For example, wind-blown dust from the Sahara Desert fertilizes the Atlantic Ocean (Radford, 2014) and the Amazon rainforest (Lovett, 2010). The naturally occurring iron oxide in atmospheric dust reacts with hydrogen chloride from sea spray to produce iron chloride, which degrades methane and other greenhouse gases, brightens clouds and eventually falls with the rain in low concentration across a wide area of the globe. (Oeste, 2017). Unlike ship-based deployment, **no trials have been performed of increasing the natural level of atmospheric iron.** Expanding this atmospheric source of iron could complement ship-based deployment or prove to be better.

One proposal is to boost the atmospheric iron level with an iron salt aerosol (Oeste, 2017). Iron(III) chloride added to the troposphere could increase natural cooling effects including methane removal, cloud brightening and ocean fertilization, helping to prevent or reverse global warming.

**Volcanic ash** Volcanic ash is composed of glass shards, pyrogenic minerals, lithic particles and other forms of ash that release nutrients at different rates depending on structure and the type of reaction caused by contact with water (Olgun, et al 2011). In August 2008, an eruption in the Aleutian Islands deposited ash in the nutrient-limited Northeast Pacific. This ash and iron deposition resulted in one of the largest phytoplankton blooms observed in the subarctic (Hemme et al, 2010).

Volcanic ash adds nutrients to the surface ocean. This is most apparent in nutrient-limited areas. Research on the effects of anthropogenic and eolian (wind-driven) iron addition to the ocean surface suggests that nutrient-limited areas benefit most from a combination of nutrients provided by anthropogenic, eolian and volcanic deposition. (Duggen, S. et al, 2007). Some oceanic areas are comparably limited in more than one nutrient, so **fertilization regimes that includes all limited nutrients is more likely to succeed.** Volcanic ash supplies multiple nutrients to the system, but excess metal ions can be harmful. The positive impacts of volcanic ash deposition are potentially outweighed by their potential to do harm.

Clear evidence documents that ash can be as much as 45 percent by weight in some deep marine sediments. In the Pacific Ocean estimates claim that (on a millennial-scale) the atmospheric deposition of air-fall volcanic ash was as high as the deposition of desert dust. This indicates the potential of volcanic ash as a significant iron source.

In August 2008 the Kasatochi volcanic eruption in the Aleutian Islands, Alaska, deposited ash in the nutrient-limited northeast Pacific. This ash

(including iron) resulted in one of the largest phytoplankton blooms observed in the subarctic (Olgun et al, 2013). Fisheries scientists in Canada linked increased oceanic productivity from the volcanic iron to subsequent record returns of salmon in the Fraser River two years later (Parsons and Whitney, 2012).

Previous instances of biological carbon sequestration triggered major climatic changes, lowering the temperature of the planet, such as the Azolla event in the middle Eocene, 49 million years ago. Plankton that generate calcium or silicon carbonate skeletons, such as diatoms, coccolithophores and foraminifera, account for most direct sequestration. When these organisms die their carbonate skeletons sink relatively quickly and form a major component of the carbon-rich deep-sea precipitation known as **marine snow**. Marine snow also includes fish fecal pellets and other organic detritus, and steadily falls thousands of meters below active plankton blooms.

Of the carbon-rich biomass generated by plankton blooms, half (or more) is generally consumed by grazing organisms (zooplankton, krill, small fish, etc.) but 20 to 30% sinks below 200 meters (660 ft) into the colder water strata below the thermocline (steep temperature gradient). Much of this fixed carbon continues into the abyss, but a substantial percentage is redissolved and remineralized. At this depth, however, this carbon is now suspended in deep currents and effectively isolated from the atmosphere for centuries. The surface to benthic cycling time for the ocean is approximately 4,000 years.

**Limitations** The maximum possible result from iron fertilization, assuming the most favorable conditions and disregarding practical considerations, is 0.29W/m<sup>2</sup> of globally averaged negative forcing (Lenton & Vaughan, 2009). offsetting 1/6 of current levels of anthropogenic CO<sub>2</sub> emissions. These benefits have been called into question by research suggesting that fertilization with iron may deplete other essential nutrients in the seawater causing reduced phytoplankton growth elsewhere in other words, that iron concentrations limit growth more locally than they do on a global scale.

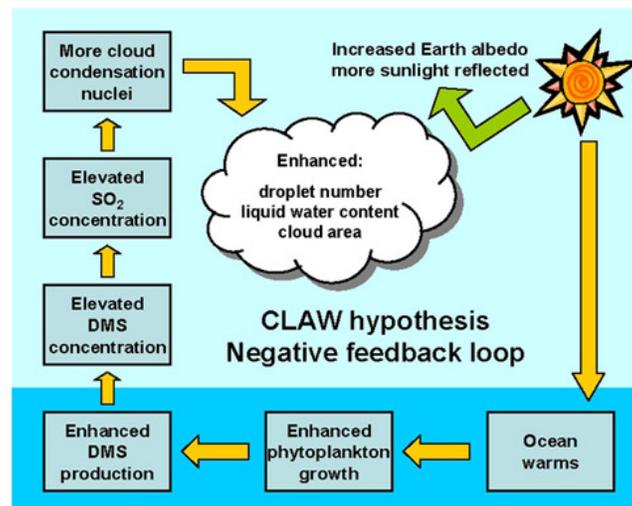
Evaluation of the biological effects and verification of the amount of carbon actually sequestered by any particular bloom involves a variety of measurements, combining ship-borne and remote sampling, submarine filtration traps, tracking buoy spectroscopy and satellite telemetry. Unpredictable ocean currents can remove experimental iron patches from the pelagic zone, invalidating the experiment.

The potential of fertilization to tackle global warming is illustrated by the following. If phytoplankton converted all the nitrate and phosphate present in the surface mixed layer across the entire Antarctic circumpolar current into organic carbon, the resulting carbon dioxide deficit could be compensated by uptake from the atmosphere amounting to about 0.8 to 1.4

gigatons of carbon per year. This quantity is comparable in magnitude to annual anthropogenic fossil fuels combustion of approximately 6 gigatons. The Antarctic circumpolar current region is one of several in which iron fertilization could be conducted—the Galapagos islands area is another potentially suitable location.

### Dimethyl sulfide and clouds

Some species of plankton produce dimethyl sulfide (DMS), a portion of which enters the atmosphere where it is oxidized by hydroxyl radicals (OH), atomic chlorine (Cl) and bromine monoxide (BrO) to form sulfate particles, and potentially increase cloud cover. This may increase the albedo of the planet and so cause cooling—this proposed mechanism is central to the **CLAW hypothesis** named after Robert J Carlson, James Lovelock, Meinrat Andreae and Stephen G. Warren (Carlson, et al 1987). This is one of the examples used by James Lovelock to illustrate his Gaia hypothesis.



Elements of the CLAW hypothesis.

During the SOFeX (Southern Ocean Fe eXperiment) DMS concentrations increased by a factor of four inside the fertilized patch. Widescale iron fertilization of the Southern Ocean could lead to significant sulfur-triggered cooling in addition to that due to the CO<sub>2</sub> uptake and that due to the ocean's albedo increase, however the amount of cooling by this particular effect is very uncertain (Wingenter et al(2004).

### Financial opportunities

Beginning with the Kyoto Protocol, several countries and the European Union established carbon offset markets which trade certified emission reduction credits (CERs) and other types of carbon credit instruments. In

2007 CERs sold for approximately €15–20/ton CO<sub>2</sub>. **Iron fertilization is relatively inexpensive** compared to scrubbing, direct injection and other industrial approaches, and can theoretically sequester for less than €5/ton CO<sub>2</sub>, creating a substantial return. Scientists have reported a 6–12% decline in global plankton production since 1980. A full-scale plankton restoration program could regenerate approximately 3–5 billion tons of sequestration capacity worth €50–100 billion in carbon offset value. However, a 2013 study suggested the cost versus benefits of iron fertilization may put it behind carbon capture and storage with carbon taxes. (U of Sydney Press Release 2013).

### **Sequestration definitions**

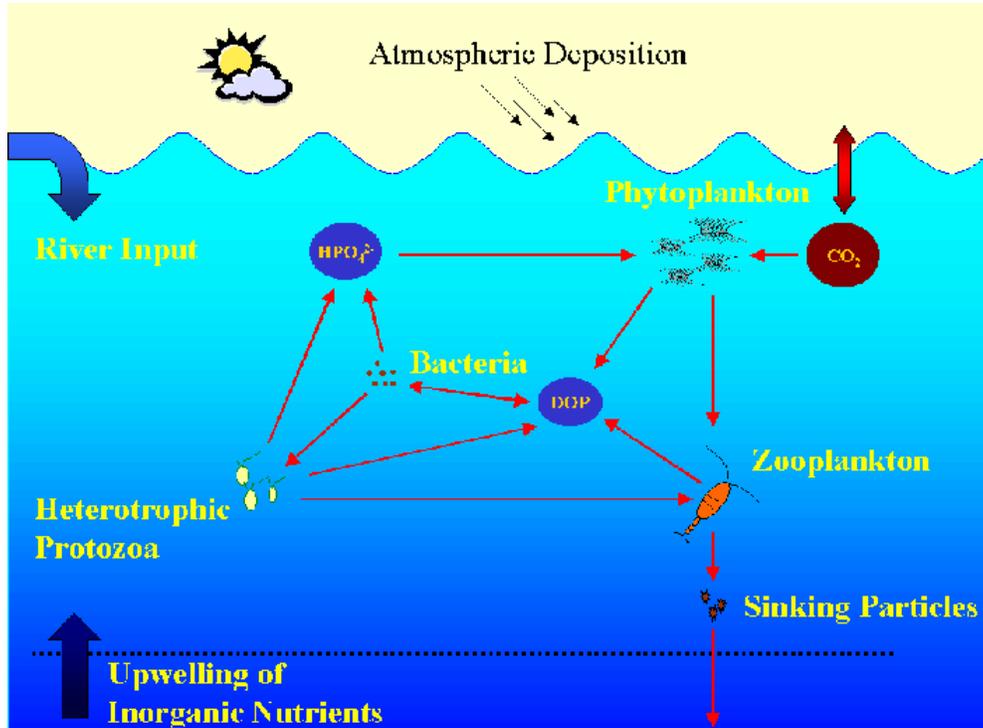
Carbon is not considered "sequestered" unless it settles to the ocean floor where it may remain for millions of years. Most of the carbon that sinks beneath plankton blooms is dissolved and remineralized well above the seafloor and eventually (days to centuries) returns to the atmosphere, negating the original benefit (Gregg et al, 2002).

Advocates argue that modern climate scientists and Kyoto Protocol policy makers define sequestration over much shorter time frames. For example, trees and grasslands are viewed as important carbon sinks. Forest biomass sequesters carbon for decades, but carbon that sinks below the marine thermocline (100–200 meters) is removed from the atmosphere for hundreds of years, whether it is remineralized or not. Since deep ocean currents take so long to resurface, their carbon content is effectively sequestered by the criterion in use today.

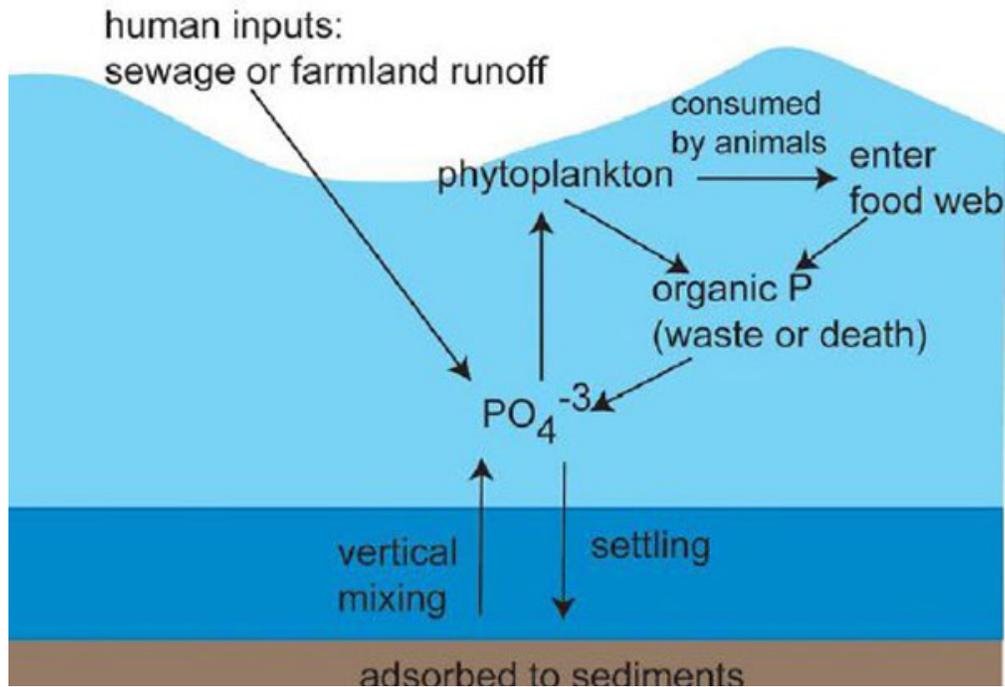
**Already enough iron?** Lauderdale et al, (2020) recently hypothesized that a global-scale selection for **microbial Fe ligand cycling** may have occurred to maintain "just enough" iron in the ocean.

### **Phosphorus Nourishment**

In the very long term, phosphorus "is often considered to be the ultimate limiting macronutrient in marine ecosystems" (Paytan and McLaughlin, 2007) and has a slow natural cycle. The following are two illustrations of the marine phosphorus cycle.



The upper ocean P cycle. © Claudia Benitez-Nelson, 2000



Marine phosphorus cycle

Where phosphate is the limiting nutrient in the photic zone, addition of phosphate is expected to increase primary phytoplankton production. This technique can give 0.83W/m<sup>2</sup> of globally averaged negative forcing (Lenton

and Vaughan, 2009) which is **sufficient to reverse the warming effect of about half the current levels of anthropogenic CO<sub>2</sub> emissions**. One water-soluble fertilizer is diammonium phosphate (DAP) (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, that as of 2008 had a market price of \$1,700/ton of phosphorus. Using that price and the C : P Redfield ratio of 106:1 produces a sequestration cost (excluding preparation and injection costs) of some \$45/ton of carbon, substantially less than the trading price for carbon emissions.

Biomass production inherently depletes all resources (save for sun and water). Either they must all be subject to fertilization or sequestration will eventually be limited by the one mostly slowly replenished (after some number of cycles) unless the ultimate limiting resource is sunlight and/or surface area. Generally, **phosphate is the ultimate limiting nutrient**. As oceanic phosphorus is depleted (via sequestration) it would have to be included in the fertilization cocktail supplied from terrestrial sources (Lampitt, et al, 2008).

"Ocean fertilization options are only worthwhile if sustained on a millennial timescale and phosphorus addition may have greater long-term potential than iron or nitrogen fertilization" (Lenton and Vaughan (2009). Phytoplankton require a variety of nutrients. These include macronutrients such as nitrate and phosphate (in relatively high concentrations) and micronutrients such as iron and zinc (in much smaller quantities). Nutrient requirements vary across phylogenetic groups (e.g., diatoms require silicon) but may not individually limit total biomass production. Co-limitation (among multiple nutrients) may also mean that one nutrient can partially compensate for a shortage of another. Silicon does not affect total production but can change the timing and community structure with follow-on effects on remineralization times and subsequent mesopelagic nutrient vertical distribution (Lampitt, et al, 2008).

**Low-nutrient low-chlorophyll (LNLC)** waters occupy the oceans' **subtropical gyre systems, approximately 40 per cent of the surface**, where wind-driven down welling and a strong thermocline impede nutrient resupply from deeper water. Nitrogen fixation by cyanobacteria provides a major source of N. In effect, it ultimately prevents the ocean from losing the N required for photosynthesis. **Phosphorus has no substantial supply route, making it the ultimate limiting macronutrient**. The sources that fuel primary production are deep water stocks and runoff or dust based. (Lampitt, et al, 2008)

### **Nitrogen Nourishment**

This technique, suggested by Ian Jones (1996) proposes to fertilize the ocean with **urea**, a nitrogen rich substance, to encourage phytoplankton growth. This has also been considered by others (Karl & Letelier, 2008; Paytan and McLaughlin, 2007).

An Australian company, Ocean Nourishment Corporation (ONC), (see below for details), planned to inject hundreds of tons of urea into the ocean, in order to boost the growth of CO<sub>2</sub>-absorbing phytoplankton, as a way to combat climate change. In 2007, the Sydney-based ONC completed an experiment involving one ton of nitrogen in the Sulu Sea off the Philippines. (Salleh, 2007).

Macronutrient nourishment can give 0.38W/m<sup>2</sup> of globally averaged negative forcing, (Lenton and Vaughn, 2009) which is sufficient to reverse the warming effect of current levels of around a quarter of anthropogenic CO<sub>2</sub> emissions.

The Ocean Nourishment Corporation claimed, "One Ocean Nourishment plant will remove approximately 5–8 million tons of CO<sub>2</sub> from the atmosphere for each year of operation, equivalent to offsetting annual emissions from a typical 1,200 MW coal-fired power station or the short-term sequestration from one million hectares of new growth forest". (ONC, 2012). The two dominant costs are manufacturing the nitrogen and nutrient delivery. Jones, (2014) estimated the total cost would be \$20 per ton of carbon dioxide emission avoided for 100 years.

**Debate – The following objections apply to all fertilization experiments. As one can see, there are a lot of them.**

**Precautionary principle** The precautionary principle (PP) states that if an action or policy has a suspected risk of causing harm, in the absence of scientific consensus, the burden of proof that it is not harmful falls on those who would take the action. The side effects of large-scale iron fertilization are not yet quantified. Creating phytoplankton blooms in iron-poor areas is like watering the desert: in effect it changes one type of ecosystem into another. The argument can be applied in reverse, by considering emissions to be the action and remediation an attempt to partially offset the damage.

Fertilization advocates respond that algal blooms have occurred naturally for millions of years with no observed ill effects. The Azolla event occurred around 49 million years ago and accomplished what fertilization is intended to achieve (but on a larger scale).

**20th-century phytoplankton decline?** While advocates argue that iron addition would help to reverse a supposed decline in phytoplankton, this decline is controversial (see above Are Phytoplankton Decreasing?)

**Cloud formation** Fertilization may create sulfate aerosols that reflect sunlight, modifying the Earth's albedo, creating a cooling effect that reduces some of the effects of climate change. Enhancing the natural sulfur cycle in the Southern Ocean by fertilizing with iron in order to enhance dimethyl

sulfide production and cloud reflectivity may achieve this (Coale, et al, 2002).

Many phytoplankton species release dimethyl sulfide (DMS), which escapes into the atmosphere where it forms sulfate aerosols and encourages cloud formation, which could reduce warming (Speer, 2017). However, substantial increases in DMS could reduce global rainfall, according to global climate model simulations, while halving temperature increases as of 2100 (Grandey and Wang, 2015).

**Harmful Algal blooms** Critics are concerned that fertilization will create harmful algal blooms (HAB). The species that respond most strongly to fertilization vary by location and other factors and could possibly include species that cause red tides and other toxic phenomena. These factors affect only nearshore waters, although they show that increased phytoplankton populations are not universally benign.

Advocates respond that most species of phytoplankton are harmless or beneficial, given that they constitute the base of the marine food chain. Fertilization increases phytoplankton only in the open oceans (far from shore) where iron deficiency is substantial. Most coastal waters are replete with iron and adding more has no useful effect.

According to Gnaedesikan and Marinou, (2008), beyond biological impacts, evidences suggests that plankton blooms can affect the physical properties of surface waters simply by absorbing light and heat from the sun. Watson added that if fertilization is done in shallow coastal waters, a dense layer of phytoplankton clouding the top 30 meters or so of the ocean could hinder corals, kelps or other deeper sea life from carrying out photosynthesis (Watson et al. 2008).

A 2010 study of iron fertilization in an oceanic high-nitrate, low-chlorophyll environment, found that fertilized *Pseudo-nitzschia* diatom spp., which are generally nontoxic in the open ocean, began producing toxic levels of domoic acid. Even short-lived blooms containing such toxins could have detrimental effects on marine food webs. (Tricka et al, 2010).

The majority of mesoscale experiments were undertaken in Antarctic waters where diatoms were the predominant phytoplankton, and, in fact, Boyd et al (2014) showed that this was the predominate responding organism. One could argue that since diatoms sink especially fast, this may not be a problem.

**Ecosystem effects** Depending upon the composition and timing of delivery, iron infusions could preferentially favor certain species and alter surface ecosystems to unknown effect. Population explosions of jellyfish, that disturb the food chain impacting whale populations or fisheries is unlikely as iron fertilization experiments that are conducted in high-nutrient, low-chlorophyll waters favor the growth of larger diatoms over small flagellates. This has been shown to lead to increased abundance of fish and whales over jellyfish (Parsons and Lalli, 2002). A 2010 study showed that

iron enrichment stimulates toxic diatom production in high-nitrate, low-chlorophyll areas (Trick et al, 2010) which, the authors argue, raises "serious concerns over the net benefit and sustainability of large-scale iron fertilizations". Nitrogen released by cetaceans and iron chelate are a significant benefit to the marine food chain in addition to sequestering carbon for long periods of time.

Many locations, such as the Tubbataha Reef in the Sulu Sea, support high marine biodiversity (Mission, 1999). Nitrogen or other nutrient loading in coral reef areas can lead to community shifts towards algal overgrowth of corals and ecosystem disruption, implying that fertilization must be restricted to areas in which vulnerable populations are not put at risk (Smith, et al (1981).

As the phytoplankton descend the water column, they decay, consuming oxygen and producing greenhouse gases methane and nitrous oxide. Plankton-rich surface waters could warm the surface layer, affecting circulation patterns (Speer, 2017).

**Efficiency** Algal cell chemical composition is often assumed to respect a ratio where atoms are 106 carbon: 16 nitrogen: 1 phosphorus: 0.0001 iron. In other words, each atom of iron helps capture 1,060,000 atoms of carbon, while one nitrogen atom only 6. (Gilbert et al, 2008). In large areas of the ocean, such organic growth (and hence nitrogen fixation) is thought to be limited by the lack of iron rather than nitrogen, although direct measures are hard (Falkows, 2000).

On the other hand, experimental iron fertilization in HNLC regions has been supplied with excess iron which cannot be utilized before it is scavenged. Thus, the organic material produced was much less than if the ratio of nutrients above were achieved. Only a fraction of the available nitrogen (because of iron scavenging) is drawn down. In culture bottle studies of oligotrophic water, adding nitrogen and phosphorus can draw down considerably more nitrogen per dosing. The export production is only a small percentage of the new primary production and in the case of iron fertilization, iron scavenging means that regenerative production is small. With macronutrient fertilization, regenerative production is expected to be large and supportive of larger total export. Other losses can also reduce efficiency (Lawrence, 2014). Harrison, D. P. (2012) examined the costs of Fe fertilization and concluded most evaluations have underestimated the total costs. He was also concerned that under the most pessimistic parameters Fe fertilization could have a negative effect on carbon sequestration, i.e. release more carbon than it consumed.

**Ocean acidification** A 2009 study tested the potential of iron fertilization to reduce both atmospheric CO<sub>2</sub> and ocean acidity using a global ocean carbon model. The study showed that an optimized regime of micronutrient introduction would reduce the predicted increase of atmospheric CO<sub>2</sub> by more than 20 percent. Unfortunately, the impact on

ocean acidification would be split, with a decrease in acidification in surface waters but an increase in acidification in the deep ocean. (Cao and Calderia, 2010).

**Impact on fisheries** Adding urea to the ocean can cause phytoplankton blooms that serve as a food source for zooplankton and in turn feed for fish. This may increase fish catches (Jones and Renilson, 2011). However, if cyanobacteria and dinoflagellates dominate phytoplankton assemblages that are considered poor quality food for fish then the increase in fish quantity may not be large. (Gilbert et al, 2008). Some evidence links iron fertilization from volcanic eruptions to increased fisheries production (Olgun et al, 2013). Other nutrients would be metabolized along with the added nutrient(s), reducing their presence in fertilized waters. (Speer, 2017).

Krill populations have declined dramatically since whaling began. Sperm whales transport iron from the deep ocean to the surface during prey consumption and defecation. Sperm whales have been shown to increase the levels of primary production and carbon export to the deep ocean by depositing iron-rich feces into surface waters of the Southern Ocean. The feces cause phytoplankton to grow and take up carbon. The phytoplankton nourish krill. Reducing the abundance of sperm whales in the Southern Ocean, whaling resulted in an extra 2 million tons of carbon remaining in the atmosphere each year. (Lavery, 2010).

**Non-research projects** Many of the most vociferous objections to iron fertilization are aimed at commercial projects whose aim is to increase fish stocks and to make a profit selling carbon credits (Fountain, 2012; Tollefson, 2012). The Comings Foundation has the advantage that it is a non-profit for which research is a critical element.

**International Law** International law presents some dilemmas for ocean fertilization. The United Nations Framework Convention on Climate Change (UNFCCC 1992) has accepted mitigation actions. However, the UNFCCC and its revisions recognize only forestation and reforestation projects as carbon sinks.

**Law of the sea** According to United Nations Convention on the Law of the Sea (LOSC 1982), all states are obliged to take all measures necessary to prevent, reduce and control pollution of the marine environment, to prohibit the transfer of damage or hazards from one area to another and to prohibit the transformation of one type pollution to another. How this relates to fertilization is undetermined.

**Outright opposition** According to Lisa Speer of the Natural Resources Defense Council, "There is a limited amount of money, of time, that we have to deal with this problem....The worst possible thing we could do for climate

change technologies would be to invest in something that doesn't work and that has big impacts that we don't anticipate." (Speer, 2017).

In 2009 Strong et al. opined in Nature "...fertilizing the oceans with iron to stimulate phytoplankton blooms, absorb carbon dioxide from the atmosphere and export carbon to the deep sea — should be abandoned."

In response, it is likely that the **damage resulting from climate change is greater by far, than some of these concerns**, especially if we pay attention to the concerns and work to avoid them.

### **Assessment by GESAMP (2019)**

The purpose of the extensive above review of oceanography was to provide the background necessary to evaluate the possible support by the Comings Foundation of Ocean Fertilization or Ocean Nourishment approaches to combating climate change. Some of the major question were: Which is better to use - iron, nitrogen, or phosphorus, or combinations? What parts of the ocean should be nourished? What is the appropriate methodology? What are the negative aspects of these approaches? There are two ways to answer these questions. The first is what I have done above – provide a large amount of background information so we can answer these questions ourselves. The second is to take advantage of large working group of experts who have evaluated these approaches to geoengineering and see what they conclude. I have done both. The following are the results of this second approach. There will naturally be some overlap in the two.

**GESAMP (2019) is an advisory body** consisting of specialized experts nominated by the Sponsoring Agencies (IMO, FAO, UNESCO-IOC, UNIDO, WMO, IAEA, UN, and UN Environment, UNDP). Its principal task was to provide scientific advice concerning the prevention, reduction and control of the degradation of the marine environment to the Sponsoring Agencies. It provided a coordinated framework for proposing marine geoengineering activities, submitting supporting evidence, and integrating independent expert assessment. The findings of the GESAMP (2019) working group (WG) evaluation provide a streamlined, robust framework for scientific assessment that engages proposers of individual techniques and provides the opportunity for effective, transparent scientific review. In addition, this framework is essential to promote a transition towards a more holistic assessment that includes social, political, economic, ecological, ethical and other societal dimensions. Marine geoengineering approaches must be grounded in strong underpinning science, and then explored, and potentially developed, in a manner that is useful and acceptable to society.

Reviewing the effect of global warming on the oceans, the WG stated that carbon dioxide and other greenhouse gas emissions are giving rise to changes in the ocean including:

1. Temperature rise – effects include polar ice melting, coral bleaching and fish migration;

2. Ocean acidification – Ocean acidification reduces the ability of marine organisms, such as corals, plankton and shellfish, to build their shells and skeletal structures. It also exacerbates existing physiological stresses and reduces growth and survival rates during the early life stages of some species;

3. Sea level rise – effects include drowning wetlands and increased coastal erosion/flooding; and

4. Expanding of oxygen minimum zones as an indirect effect of increased stratification.

In evaluating the suitability of the ocean for geoengineering the WG stated:

“The unprecedented scale and rapidity of climate change (IPCC, 2013) means that climate intervention approaches must be correspondingly large and rapid if offsetting these changes is a desirable. The ocean covers three quarters of Earth’s surface area, and hence this areal coverage offers some potential for Albedo Modification (AM) for example using foams. The ocean is also characterized by diverse biogeochemical cycles such as for carbon and trace elements, and ocean circulation has much longer timescales than the atmosphere, meaning that additional anthropogenic carbon could be potentially stored, in the deep ocean or on the sea floor. The productivity of the ocean is limited in large areas of the ocean by iron, nitrogen or phosphorus. So, there is some potential in attempting to boost productivity through intentional nutrient enrichment, as a means to enhance the ocean’s biological pump. Geoengineering has been suggested as a potential tool for addressing climate change.”

Subsequent to the publication of the 2009 Royal Society report, the terms Negative Emissions Technologies (NETs) and Greenhouse Gas Removal (GGR) technologies have come into common use. An additional term is CRD or Carbon Dioxide Removal.

### **Why Remove CO<sub>2</sub>?**

The United Nations Environment Program 2017 Emissions Gap Report (UNEP, 2017) stated that

“In order to achieve the goals of the Paris Agreement, carbon dioxide removal is likely a necessary step.”

The National Academy of Sciences CDR report (National Research Council, 2015) comments in the ‘Way Forward’ chapter that CDR deployment would be necessary to achieve climatic stability for IPCC goals. A large number of reports agree with these conclusions (GESAMP, 2019).

### **Marine geoengineering**

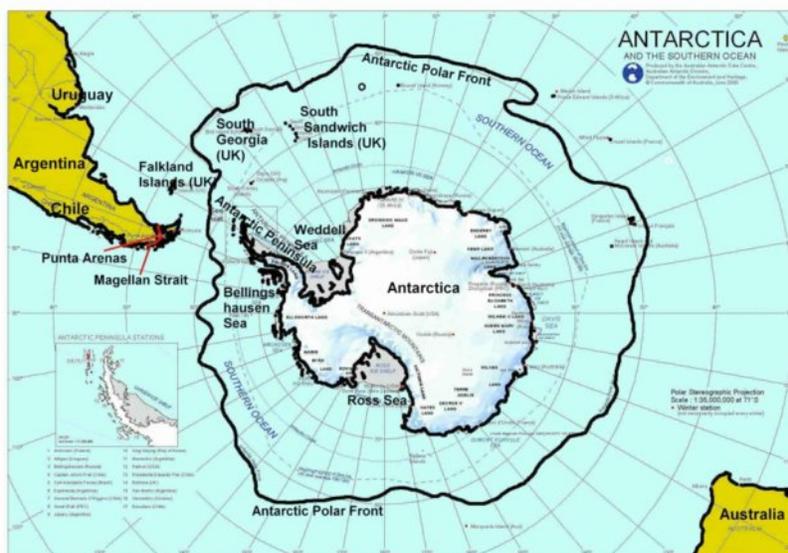
Most agree approaches such as ocean fertilization can proceed if accompanied by scientific research and oversight.

We emphasize one of the GESAMP (2019) conclusions: “We need to consider the potential detrimental effects of these marine geoengineering measures, and any potential benefits of such interventions, against the potential harms from ‘climate change’ that will come from greenhouse gas emissions in the absence of marine geoengineering.” In other words, **we need to assess the potential local problems of ocean enrichment against the well-known and devastating world-wide effects of doing nothing.**

### **Evaluation of Ocean Fertilization**

The best rated and documented approach to date was Ocean Iron Fertilization for Carbon Sequestration. However, information was insufficient to enable a scientific assessment of its global consequences as observations to date are on areas of ocean < 1000 km<sup>2</sup> (Boyd et al., 2007). Even less can be said about other criteria such as environmental benefits and consequences, and less again about socio-political risks. However, on other criteria, such as scale (geographical and temporal) there is more certainty based on modelling projections that indicate that the Southern Ocean is the only region in which enhanced carbon sequestration might occur but requiring sustained iron fertilization for at least 100 years. Recent modelling initiatives such as CDR-MIP have been useful in providing estimates of the potential efficacy of approaches such as ocean iron fertilization, which at most could contribute the removal of 1 Gt C each year (10% of current emissions). There is inadequate information to evaluate other issues such as subsurface acidification (Cao and Caldeira, 2010), deoxygenation (Keller et al., 2014), and ‘robbing’ nutrients destined for lower latitude waters (Gnanadesikan et al., 2003). Information is limited about the total costs both direct financial and indirect of via carbon dioxide expended, and other issues such as social-political consequences.

Maps of the upper ocean macronutrient inventory for either Phosphorus (P) or Nitrogen (N) compounds reveal three conspicuous regions in which there is a perennial surplus of nutrients (termed HNLC High Nutrient Low Chlorophyll) (Boyd et al., 2007; Cullen, 1991). It is now established that the paradox of HNLC regions is due to **iron limitation of primary producers in the Southern Ocean**, subarctic North Pacific and Eastern Equatorial Pacific (Boyd et al., 2007).



Southern Ocean around Antarctica

The rationale for ocean iron fertilization is based on the purposeful addition of iron (Fe) to the ocean, such that it drives blooms in HNLC regions which can utilize the unused stocks of macronutrients which in turn results in enhanced carbon sequestration via the biological pump, and hence carbon dioxide removal. The biological pump is the ocean's biologically driven sequestration of carbon from the atmosphere to the deep ocean and underlying sediments. It is the part of the oceanic carbon cycle responsible for the cycling of organic matter formed mainly by phytoplankton during photosynthesis. The biological pump removes 4-10 Gt C from surface waters annually, however,  $\approx 90\%$  of this C is released back into the atmosphere within a year. An example of a pronounced effect (200-300%) is the polar Southern Ocean experiment EIFEX (Smetacek et al., 2012).

Proposed deployment zone(s) and potential scale of use. Proposed zone includes the 3 main HNLC regions (subarctic Northern Pacific, Eastern Equatorial Pacific, Southern Ocean), with modelling studies suggesting that the latter is the most promising for net carbon sequestration (Bopp et al., 2013; Keller et al., 2014; Robinson et al., 2014; Sarmiento and Orr, 1991). Modelling also reveals that the scale of use would require the entire Southern Ocean to obtain a large enough enhancement of export flux (Oschlies et al., 2010a). Duration of deployment Based on modelling studies multiple years of fertilization would be required (Oschlies et al., 2010a).

Appraisal of the potential impacts of the techniques on the marine environment (and the atmosphere where appropriate). Several potential side-effects have emerged from mesoscale scientific iron enrichment experiments, including the emergence of stocks of potential toxic species of diatoms during the development of several of the mesoscale iron enrichment experiments (Silver et al., 2010; Trick et al., 2010). There is also limited

evidence of increased concentrations of other GHG's such as methane and nitrous oxide during the subsurface decomposition of the sinking particles from iron stimulated blooms (Law, 2008). These GHG's are more potent than CO<sub>2</sub> and hence the release of even small amounts of them into the atmosphere could have a disproportionately large effect in offsetting any additional drawdown of CO<sub>2</sub> into the ocean that was mediated by ocean iron fertilization.

### **Other ocean fertilization macro-nutrients – nitrogen and phosphorus**

**Approach/rationale** Much of the global ocean in the low latitudes, comprising the tropics and sub-tropics, is characterized by nutrient-impooverished waters where either N or P limit primary productivity and hence the export of carbon to the ocean's interior (Moore et al., 2013). It has been proposed that these so-called LNLC (Low Nutrient Low Chlorophyll) waters could be fertilized with N and/or P (Jones and Young, 1997) to boost fisheries productivity and sequester carbon.

Underlying principles with citation and extent of knowledge The oceans biological pump is projected, across a suite of Earth system models, to export 4-10 Gt C out of the surface layer each year (Bopp et al., 2013), resulting in the removal to vanishingly low levels of N and/or P in the surface ocean (Martinez-Garcia et al., 2014). Hence, fertilization of these LNLC waters with N and/or P would likely result in a further enhancement of the oceans' biological pump. However, **≈ 90% of the 4-10 Gt C is re-released into the atmosphere within a year.**

**Evidence of concept from the natural world** Evidence comes from the role of the oceans' biological pump discussed above, and the resulting low inventories of N and P in the upper ocean. Further evidence comes from a number of shipboard experiments that show that N and/or P addition causes an increase in phytoplankton productivity and biomass (Moore et al., 2013).

**Direct/indirect sequestration** The sequestration of carbon would be direct via an enhanced biological pump. However, if such a nutrient enrichment approach was also used concurrently to boost fisheries productivity this could offset the magnitude of the carbon sequestration, as the carbon flowing through enhanced fisheries would ultimately be released into the atmosphere (Young, 2007).

**Proposed deployment zones and potential scale of use** Three options have been proposed by Harrison (2017): addition of N to waters with excess P (relative to N, termed P\* (see Deutsch et al., 2007, for the conceptual background for P\*)) which are mainly located in the low latitude oceans; continuous fertilization with only N; and continuous enrichment with both N and P (both of the latter options would avoid low iron HNLC waters) and hence would not be global deployments. Duration of deployment Both

one-off (in regions with positive P\*) and continuous deployments have been discussed (Harrison, 2017).

**Evidence of feasibility and efficacy** of the techniques for climate mitigation or other purposes - modelling, lab, pilot experiments The evidence is based on both modelling studies (Harrison, 2017; Lawrence, 2014; Matear and Elliott, 2004) and mesoscale P addition field experiments (Dixon, 2008; Thingstad et al., 2005). However, there is no acknowledgement of the findings from the research on mesoscale P addition by researchers examining modelling simulations e.g. Harrison (2017).

Lawrence (2014) reported a 75% sequestration efficiency of global N enrichment, with some variation evident dependent on the chemical form in which the N was added. His study took into consideration additional costs such as manufacture of the chemicals and their transport and distribution by vessels on the ocean. He defined this efficiency as the percentage of additional C fixed photosynthetically, following N enrichment (i.e. sequestered carbon per atom of added nutrient), that could potentially be transported into the ocean's interior - i.e. long-term sequestration. Lawrence speculated that N enrichment is potentially a more efficient means of sequestration than that projected for iron fertilization. Estimates from Harrison (2017) and Matear and Elliott (2004) were 78% and 80% efficiencies, respectively.

Thingstad et al. (2005) added phosphate during the CYCLOPS study to a mesoscale (sulphur hexafluoride labelled) patch of LNLC ocean in the Eastern Mediterranean Sea using a scientific research approach successfully used for mesoscale iron enrichment studies (Law et al., 2005). Half of the added phosphate was taken up biologically, and the remainder was 'lost' laterally from the P-enriched path as the added P was diluted by mixing with the surrounding low P waters (Law et al., 2005). Thingstad et al. (2005) reported a decrease in chlorophyll stocks following P enrichment and provided a putative explanation that much of the added P was taken up by heterotrophic bacteria and removed into the upper food web via 'ecological tunnelling'. An increase of 50% in nitrogen fixation (relative to the surrounding 'control' waters) was reported from this P-enrichment in the Eastern Mediterranean Sea (Rees et al., 2006).

In a further P mesoscale enrichment experiment called FeeP - in May 2004, in the subtropical N Atlantic, 20 tons of anhydrous monosodium phosphate was added at 10 metres depth over  $\sim 25 \text{ km}^2$ , and in a further patch experiment a similar amount of P was added over the same area but with the addition of 5 tons of an acidified iron salt (Dixon, 2008). These additions raised phosphate from  $9.6 \pm 4.9 \text{ nM}$  to  $163 \pm 18 \text{ nM}$  (for P patch) and  $200 \pm 13 \text{ nM}$  (for P + Fe patch) within  $\sim 12\text{-}16 \text{ h}$  after enrichment(s) (Dixon, 2008).

Neither community primary production or chlorophyll concentrations exhibited any increases in situ during either P or P/Fe enrichment, relative to

the natural variability for rates and stocks of phytoplankton at all control sites samples outside of the P and P/Fe enriched mesoscale patches (Dixon, 2008). There appears to be a disjoint between global model projections (see above) and the outcomes of these two mesoscale scientific research P enrichment studies.

Appraisal of the potential impacts of the techniques on the marine environment (and the atmosphere where appropriate) There is indirect evidence of detrimental side effects of N and/or P enrichment via agricultural runoff, resulting in both dead-zones (Diaz and Rosenberg, 2008) and in increased incidents of harmful algal blooms in the coastal zone (Glibert et al., 2008; Glibert et al., 2014). However, the magnitude of nutrient enrichment that results in either dead-zones or harmful algal blooms, may differ from that employed using this approach.

### **Artificial Upwelling (GESAMP, 2019)**

**Approach/rationale** Over vast areas of the mid- and low-latitude oceans, nutrients are depleted in the surface waters, limiting biological production (Cullen, 1995; Karl et al., 1997; Moore et al., 2013). Artificial upwelling has been suggested as a fertilization measure by bringing deeper, nutrient-rich waters to the sunlit surface ocean, where they can stimulate phytoplankton growth and subsequently export of organic carbon to depth.

Artificial upwelling has also been discussed for enhancing fish production or cooling coral reefs (Kirke, 2003). Deeper waters are generally enriched in nutrients relative to surface waters due to the remineralization of organic matter exported from the surface to the ocean interior. For the same reason, deeper waters generally hold more dissolved inorganic carbon. In contrast to iron fertilization, artificial upwelling does not introduce new nutrients, but merely redistributes nutrients within the ocean. A second effect of artificial upwelling is that upwelled deeper waters are generally colder than ambient surface waters, thereby cooling the ocean's surface and, eventually, the overlying air, thus helping counter global warming at least at local/regional scales.

**Underlying principles** Lovelock and Rapley (2007) suggested in a short note that artificial upwelling could "...stimulate the Earth's capacity to cure itself...". Oschlies et al., (2010b) and Yool et al. (2009) essentially refuted the concept that fertilization by artificial upwelling could lead to a significant drawdown of CO<sub>2</sub> because upwelled nutrients are accompanied by a stoichiometric equivalent of respired carbon, i.e. CO<sub>2</sub>. Artificial upwelling can, however, induce some net marine CO<sub>2</sub> uptake in regions where upwelled waters have a particularly low CO<sub>2</sub> content. Integrated until year 2100 in a business as usual emission scenario, the oceanic uptake is estimated as less than 20 Gt C (Oschlies et al. (2010). That is equivalent to a 10-ppm atmospheric drawdown, which is appreciable compared to capacity some of the other techniques mentioned.

Colder upwelling waters lead to lower sea surface temperatures and a number of dominant effects:

(i) surface air temperatures are reduced, which if conducted at a large enough scale cools the land. In the models, this reduces respiration and thereby enhances terrestrial carbon sequestration (up to 100 Gt C in the model experiments of Oschlies et al. (2010). The cooling also helps counter, at least at some spatial and temporal scale, ongoing GHG-driven surface warming.

(ii) Lower sea surface temperatures reduce outgoing long-wave radiation of the planet. As a result, Earth accumulated more energy during the operation of artificial upwelling. The additional energy is stored as heat in the subsurface waters that are displaced downward by the overlying upwelled waters. This disturbs the thermocline and, on centennial timescales, leads to higher global mean temperatures (Kwiatkowski et al., 2015).

(iii) Artificial upwelling can have substantial termination effect. Once artificial upwelling stops, the additional heat can make it back to the surface and lead to surface temperatures that exceed those of a planet that had never experienced artificial upwelling (Keller et al., 2014; Oschlies et al., 2010).

**Evidence of concept from the natural world** Because of the enhanced supply of nutrients from a few hundred meters depth to the sea surface, regions of natural upwelling, in particular eastern boundary upwelling regions off Namibia, California and Peru, but open-ocean upwelling regions along the equator and in the Arabian Sea, are the most productive regions in the World Ocean (Chavez and Messié, 2009). Temperatures of the surface waters are lower than ambient temperatures by several degrees. However, because of the high amounts of respiratory carbon in the nutrient-rich upwelled waters, upwelling regions are usually areas where CO<sub>2</sub> outgasses from the ocean to the atmosphere (Takahashi et al., 2009). From the natural world, there is thus strong evidence that upwelling enhances biological production, phytoplankton growth and export. There is also strong evidence that upwelling cools the ocean surface and overlying atmosphere. However, there is no evidence that upwelling leads to local [net] uptake of CO<sub>2</sub> from the atmosphere.

**Direct/indirect sequestration** Direct sequestration is thought to be small (< 20 Gt C until year 2100). Indirect sequestration is estimated several times larger and related to reduced soil respiration at lower atmospheric temperatures that follow colder sea surface temperatures.

**Proposed deployment zones and potential scale of use** Deployment zones are the vast areas of the mid- and low-latitude oceans where nutrients are depleted in the surface waters, limiting biological production. Since, the power of hurricanes/cyclones are strongly affected by the sea surface temperature (Murakami et al. 2018;), artificial upwelling has

also been **proposed as a measure to weaken hurricanes by bringing cooler water to the surface**, with model studies showing some potential for artificial upwelling reducing hurricane-induced damages on land (Klima et al., 2012; Launder, 2017).

A sobering aspect of artificial upwelling is the statement that it would **require 4.32 million pipes** with pumps, (Lenton & Vaughan, 2009) to allow 1.3 Tmol carbon per year to be sequestered.

**Duration of deployment** Different durations of deployment are discussed for different applications. Ocean carbon sequestration is discussed in terms multi-decadal operation of artificial upwelling, possibly with seasonal modulation to maximize CO<sub>2</sub> drawdown (Pan et al., 2016). Deployment would be much shorter (days) for a potential mitigation of hurricanes.

**Evidence of feasibility and efficacy** of the techniques for climate mitigation or other purposes - modelling, lab, pilot experiments A number of modelling studies have shown that **there is limited potential in artificial upwelling drawing down carbon from the atmosphere** (Oschlies et al., 2010). Artificial upwelling devices have been tested in the field (White et al., 2010). A number of short-term field trials focused mainly on the technical feasibility of generating upward transport and on the supply of nutrients (Pan et al., 2016). Casareto et al. (2017) described enhanced phytoplankton production in a small-scale upwelling field experiment. They did not report measurements on carbon sequestration.

Appraisal of the potential impacts of the techniques on the marine environment (and the atmosphere where appropriate) Giraud et al. (2016) studied the potential impact of artificial upwelling on plankton ecosystems and found substantial changes in species composition. Enhanced biological production at the scale required for climatic benefits is likely to lead to enhanced remineralization of organic material in the water column and thus significantly deplete mid-water oxygen levels and increase methane and nitrous oxide release (Williamson et al., 2012a and 2012b) .

## **After GESAMP**

In addition to the GESAM evaluations, there are two recent developments that need to be discussed – Biogenic Iron Dust and KIFES.

**Biogenic Iron** In a recent paper by Emerson (2019) entitled - Biogenic Iron Dust: A Novel Approach to Ocean Iron Fertilization as a Means of Large Scale Removal of Carbon Dioxide From the Atmosphere, proposed the use of biogenic iron for iron fertilization projects. His idea was to take advantage of nanoparticulate, poorly crystalline Fe-oxides produced by chemosynthetic iron-oxidizing bacteria, as an iron source to the ocean. Upon drying these oxides produce a fine powder that could be dispersed at altitude **by aircraft** to augment wind-driven Aeolian dust that is a primary

iron source to the open ocean. Based on Fe-oxidation rates for natural populations of iron-oxidizing bacteria it was estimated 1,500 hectares of production ponds ( $1 \times 100 \times 100$  m) would be required to produce sufficient iron dust to supply the 30% of the global ocean that is iron-limited. Addition of biogenic iron to meso-scale eddies could provide an effective means of testing this process. Nonetheless, there are many unknowns, thus any such effort will require research and development integrated across oceanographic and Earth science disciplines to determine its long term efficacy. Given the remarkable ability of aeolian dust to stimulate phytoplankton growth (see above) this is a particularly intriguing proposal.

**KIFES** Korean Iron Fertilization Experiment in the Southern Ocean Yoon et al (2018) reviewed the entire artificial ocean iron fertilization (aOIF) field. They concluded that:

“to maximize the effectiveness of aOIF experiments under international aOIF regulations in the future, we therefore suggest a design that incorporates several components.

(1) Experiments be conducted in the **center of an eddy structure** when grazing pressure is low and silicate levels are high (e.g., in the SO south of the polar front during early summer).

(2) Shipboard observations extending over **a minimum of ~ 40 days**, with **multiple iron injections** (at least two or three iron infusions of ~ 2000 kg with an interval of ~ 10–15 days to fertilize a patch of 300 km<sup>2</sup> and obtain a ~ 2 nM concentration).

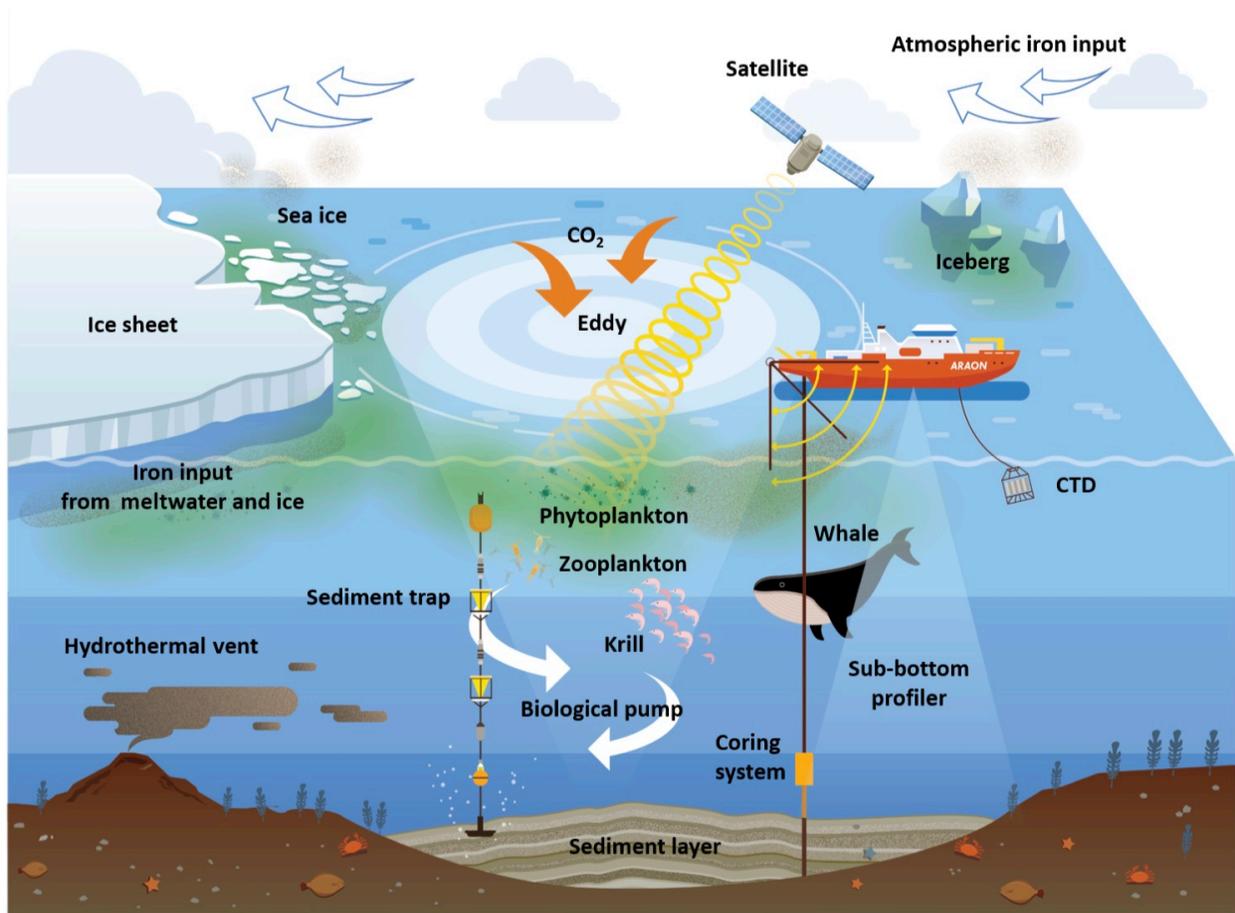
(3) Tracing of the iron-fertilized patch using both physical (e.g., a **drifting buoy**) and **biogeochemical** (e.g., sulfur hexafluoride, photosynthetic quantum efficiency, and partial pressure of CO<sub>2</sub> tracers).

(4) Employment of **neutrally buoyant sediment traps (NBST)** and application of the water-column-derived **thorium-234** (<sup>234</sup>Th) method at two depths (i.e., just below the *in situ* MLD (mixed layer depth) and at the winter MLD, with autonomous profilers equipped with an **underwater video profiler (UVP) and a transmissometer**.

(5) Monitoring of side effects on marine/ocean ecosystems, including production of **climate-relevant gases** (e.g., nitrous oxide, N<sub>2</sub>O; dimethyl sulfide, DMS; and halogenated volatile organic compounds, HVOCs), decline in oxygen inventory, and development of toxic algae blooms, with optical-sensor equipped autonomous moored profilers and/or autonomous benthic vehicles.

(6) Lastly, we introduce the scientific aOIF experimental design **guidelines** for a future Korean Iron Fertilization Experiment in the Southern Ocean (KIFES).”

The elements of KIFES are shown in the following figure.



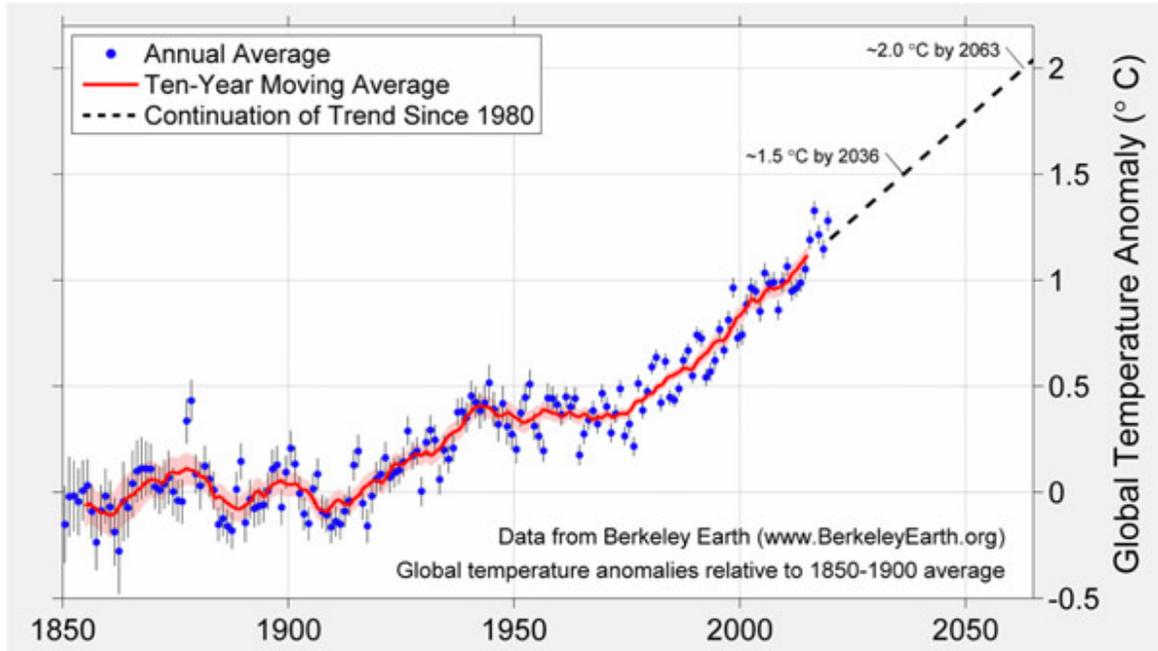
Schematic diagram of the Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) representing the experiment target site (eddy structure) and survey methods (underway sampling systems, multiple sediment traps, sub-bottom profilers, sediment coring systems, and satellite observations).

This is obviously a large project far beyond the financial capabilities of the Comings Foundation. We propose to leave such well-regulated studies to national resources such as the KIFES. We will continue to monitor the progress of this five-year project.

**Is the use of trees to sequester CO<sub>2</sub> doomed?** In a recent study, Sullivan et al (2020) reported that measurements of carbon storage and growing conditions for some 500,000 trees around the world suggest some tropical forests, particularly in Africa and Asia, will—if left intact – continue to sequester large amounts of carbon even as global temperatures rise. But only up to a point. As the temperature rises the respiration rate of trees begins to exceed the photosynthesis rate and they produce more CO<sub>2</sub> than they sequester. If warming reaches 2°C above preindustrial levels, the study finds that huge swaths of the world’s tropical forests will begin to lose more

CO<sub>2</sub> than they accumulate. Already, the hottest forests in South America have reached that point (Pemmosi, 2020).

If we continue business as usual how long will it take to reach this 2°C mark? The following graph suggests an answer – 2063!!



Uggh!

## Aeolian Iron

First a definition of a term often used. **Primary production** is the rate at which atmospheric or aqueous carbon dioxide is converted by autotrophs (primary producers) to organic material. Primary production via photosynthesis is a key process within the ecosystem, as the producers form the base of the entire food web, both on land and in the oceans.

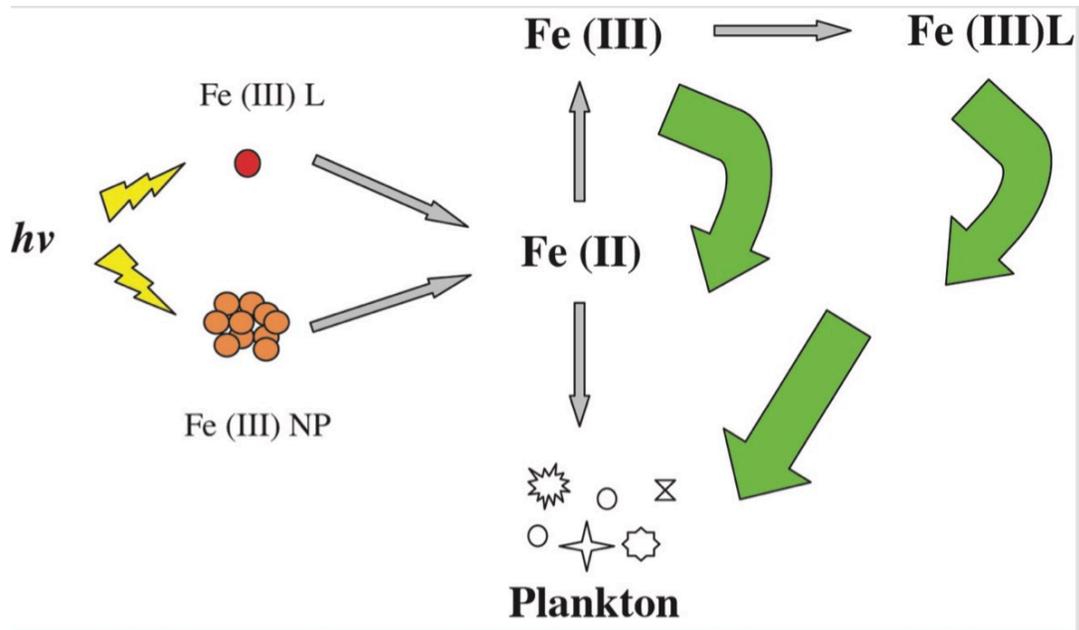
The iron supply is a limiting factor on phytoplankton growth over 30 percent of the modern ocean. The dominant external input of iron to the surface of the open ocean is aeolian (wind-blown) dust transport, mainly from the great deserts of the world. Desert dust aerosol is dominated by particles of diameter 0.1 to 10 μm, with the mean size being around 2 μm. Such aerosols have a lifetime of hours to weeks, allowing long-range transport over scales of thousands of kilometers. Much of the transport of dust occurs at altitudes of several kilometers.

**Iron Chemistry** All the main redox states of iron are Fe(0), Fe(II) and Fe(III). Iron II refers to the element iron in its <sup>+2</sup> state and Fe (III) in its <sup>+3</sup> state. Only the Fe(III) state is thermodynamically stable and predominates in oxygen rich surface seawater where Fe(II) gets oxidized to Fe(III). The main inorganic Fe(III) compound in seawater at pH 8 is the Fe(OH)<sub>3</sub> complex, which constitutes 92% of the aqueous iron pool (Raiswell and

Canfield, 2012). The controls on aerosol iron solubility include the photoreduction of Fe(III) to Fe(II) and acidity, particularly during aerosol cloud processing (Jickells et al, 2005). Fe(II) can also be transiently present in seawater as a result of photochemical reactions. Although it is kinetically labile, it is the highly **bioavailable** form (Raiswell and Canfield (2012).

The complexation of iron to organic ligands could explain some of the mysterious aspects of ocean iron (Johnson et al, 1997). These include the fact that the amount of iron in much of the subsurface ocean exceeds the solubility of iron. Two distinct classes of iron-binding ligands, with different affinities for complexing iron, have been identified (Rue & Bruland, 1995). A 'strong' iron-binding ligand class (L1) is confined to the upper ocean, whereas the 'weak' iron-binding ligand class (L2) is generally observed throughout the water column (Rue & Bruland, 1995). Current evidence suggests that L1 is produced by heterotrophic and autotrophic bacteria to aid iron acquisition, and on the basis of comparable conditional stability constants, the L1 class may be composed largely of siderophores.

Degradation products released during the decomposition of organic matter may constitute the L2 class. A significant portion of iron and iron-binding ligands can reside in both the soluble (<0.02 μm) and colloidal (0.02–0.4 μm) size ranges (Boyd & Elwood, 2020).



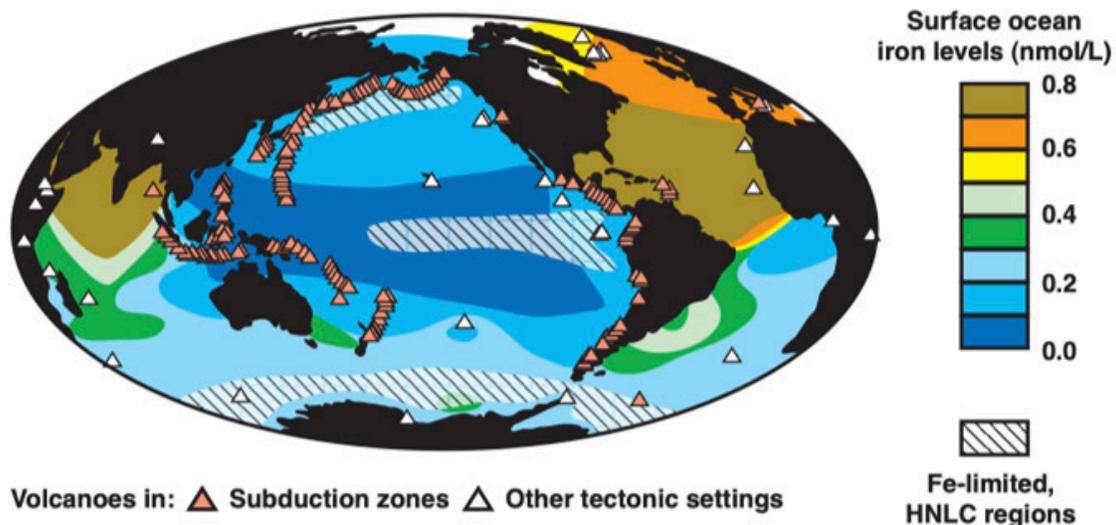
A schematic model for the formation of bioavailable Fe(II) by photochemical reduction of ligand complexed (L) and nanoparticulate (NP) Fe(III); photons represented as  $h\nu$  (after Barbeau, 2006).

Iron supply also helps to regulate **nitrogen fixation** by diazotrophs in nutrient-poor low-latitude waters, according to some modelling studies (Moore J.K. et al, 2009) and field surveys (Moore C.M. 2009). Nitrogen fixation and cycling by other marine organisms are also found to depend on the concentration of dissolved Fe (Falkowski, 1997).

In iron-replete waters, diatoms and copepods make a much greater contribution to the biogenic particulate iron pool than in low-iron waters, where the microbial community of small cells makes the largest contribution (Boyd & Elwood, 2010)

Fan et al (2006) suggested that increasing SO<sub>2</sub> emission alone could have caused significant Fe fertilization in the modern northern hemisphere oceans.

**Global Distribution of Iron** Knowledge of the areas of the ocean that are deficient in iron is critical if we plan to augment ocean iron. No sense seeding iron in places where it is already abundant. The following map of global ocean iron levels was published by Duggen et al (2010).



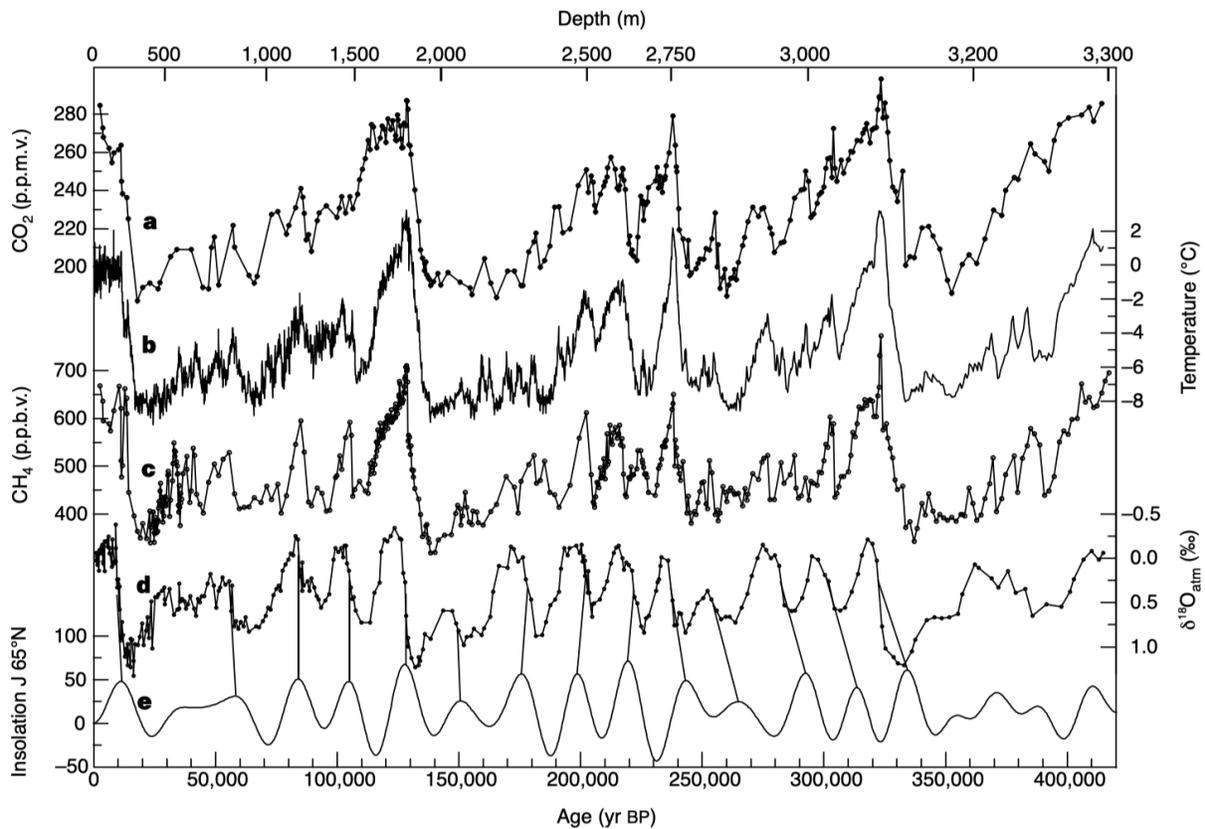
World map showing surface ocean iron-concentrations, locations of iron-limited (HNLC) regions and subaerially active volcanoes in subduction zones and other tectonic settings. Data sources are: Surface ocean iron-concentrations (Parekh et al., 2005)

This is an important map because the most widely publicized HNLC area with iron deficiency is the Southern Ocean around Antarctica. This map shows that there are also iron deficient HNLC areas in the Pacific equatorial and Northern Pacific regions.

**Volcanic ash** may be transported up to several tens of kilometers high into the atmosphere during large-scale eruptions and fine ash may stay aloft for days to weeks, thereby reaching even the remotest and most iron-starved oceanic regions.

Large amounts of iron containing dust from Africa and South America are blown onto the oceans of the world every year, some years more than others. In addition, iron containing volcanic ash periodically seeds the ocean. Understanding how much iron is deposited in this fashion and into which oceans is important if we are to ask whether artificial Ocean Iron Fertilization (OIF) is a good idea or if it is too dangerous. For example, if the amount of iron seeded into the oceans by these natural means far exceeds any planned amounts for OIF, then concerns about OIF are probably over-blown. What is the evidence?

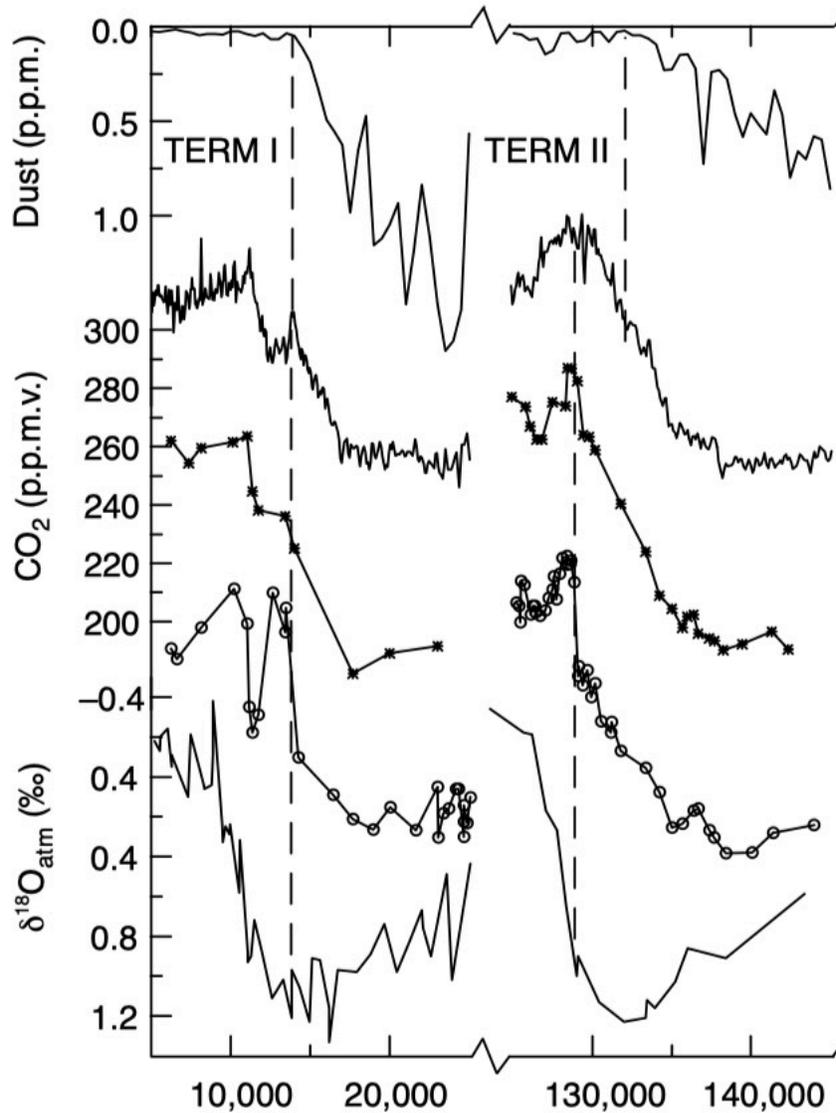
**Ice cores** A great deal can be learned from studying ice cores. Information about temperature, atmospheric CO<sub>2</sub> and methane, oxygen levels, and the amount of dust deposited can be obtained from these cores and this information can reach back for over 400,000 years.



Vostok time series. **a.** CO<sub>2</sub>; **b.** temperature of the atmosphere; **c.** CH<sub>4</sub>; **d.** a measure of O<sub>2</sub>; and **e.** mid-June insolation (see original paper).

In 1999, Petit, et al, published the results of the East Antarctica Vostok Station ice cores dating back 420,000 years, covering all four glacial periods (**above figure**). Their data was relevant to both the role of CO<sub>2</sub> on temperatures, and the effect of dust on CO<sub>2</sub> levels (see below). For example, they showed that atmospheric concentrations of CO<sub>2</sub> (**a** in ppm) and methane (**c** in ppb) correlated well with each other and with Antarctic air-temperature, **b**.

The following figure from that study shows that the presence of substantial dust is associated with a significant decrease in atmospheric CO<sub>2</sub>. Martin, (1990) proposed this was a manifestation of his 'iron hypothesis' stimulating phytoplankton growth.



Vostok time series during glacial terminations. Variations with respect to time (years from present). **top**, dust (inverted scale); **2nd**, temperature; **3rd**, CO<sub>2</sub>; **2<sup>nd</sup> from bottom** CH<sub>4</sub>; and **bottom**, a measure of O<sub>2</sub>. **Term I** = termination of the last ice age, **Term II** = termination of the next to last ice age. Term III and IV not shown (see original paper).

In this regard the authors pointed out that **the termination of dust deposition correlated with a rise in temperature and the termination of ice ages** (Ridgwell & Watson, (2002) In terms of the iron hypothesis this suggests that the termination of dust led to decreases in phytoplankton with a resulting increase in CO<sub>2</sub> levels and temperature.

Such findings lend support to the suggestion that oceanic iron accounted for up to 25% of the decrease in atmospheric carbon dioxide concentrations during glacial maxima in the geological past (Sigman and Boyle, 2000) .

**Aeolian Iron in Modern times.** In modern times, the seeding of the oceans by aeolian iron occurs every year. The following table shows the seasonal amount of such iron falling onto the oceans every year in many different ocean regions (Gao, et al. 2001).

**Table 1.** Seasonal and Annual Deposition of the Total Atmospheric Iron to the Major Ocean Basins.

Ocean Basin	Seasonal Fe Deposition (10 <sup>12</sup> g mon <sup>-1</sup> )				Annual Fe Deposition (10 <sup>12</sup> g yr <sup>-1</sup> )		
	Spring	Summer	Fall	Winter	This work (% of the total)	Duce and Tindale <sup>a</sup>	Jickells and Spokes <sup>b</sup>
North Pacific	0.28	0.17	0.34	0.20	3.0 (22%)	17	7.3
South Pacific	0.023	0.024	0.035	0.022	0.31 (2.3%)	1.4	0.67
North Atlantic	0.43	0.78	0.72	0.26	6.6 (48%)	7.7	6.0
South Atlantic	0.046	0.063	0.051	0.035	0.59 (4.3%)	0.84	0.46
Indian	0.21	0.15	0.26	0.18	2.4 (18%)	5.1	2.2
Antarctic	0.0062	0.0043	0.0078	0.0054	0.071 (0.52%)		
Arctic	0.0078	0.0099	0.018	0.0066	0.13 (0.93%)		
Mediterranean	0.068	0.043	0.048	0.022	0.54 (4.0%)		
Global Total					14	32	17

<sup>a</sup> Estimates of Fe deposition of Duce and Tindale (1991), scavenging ratio = 200 for North Atlantic and 1000 for all others.

<sup>b</sup> Based on dust estimates of Jickells and Spokes (2000), scavenging ratio = 200 for all ocean basins.

For example, in the North Pacific, during the fall peak season, 0.34 x 10<sup>12</sup> grams of iron were deposited. This equals 3.5 x 10<sup>5</sup> metric tons/mo. The total was 14 x 10<sup>6</sup> or 14 million metric tons. There is not only no evidence this has any negative effects it is actually critical for the health of the oceans and their phytoplankton. Some have suggested if the deserts were covered with vegetation the loss of dust would result in a significant increase in temperature. By contrast to most of the oceans, the Antarctic, the location of the Southern Ocean which is a HNLC (High Nutrient, Low chlorophyll) area, received only 0.0078 x 10<sup>12</sup> g/mo. It is no wonder this is a low iron part of the ocean.

**Southern Ocean.** There is compelling evidence that iron supply from a number of sources, such as coastal sediments, aerosols, upwelling, ice melting, affects the gross production of phytoplankton and carbon export by Southern Ocean ecosystems. Ocean color data show that biomass is elevated downwind of aeolian iron sources. Cassar et al, (2017) specifically examined aeolian iron and the Southern Ocean. Their results showed that photoautotrophs (autotrophs utilizing photosynthesis) may rely on aeolian input of Fe over a broad area of the Southern Ocean. Net community

production **was proportional to modeled input of soluble iron in aerosols**. These results strengthen the evidence that the addition of aerosol iron fertilizes export production in the Southern Ocean. The data also show that aerosol iron input particularly enhances gross primary production over the large area of the Southern Ocean downwind of dry continental areas.

They note there are five sources of bioavailable iron to surface waters of the Southern Ocean.

**First**, melting of sea ice can release accumulated iron that contributes locally to springtime blooms along the ice edge. Iron accumulates in sea ice with concentrations one to two orders of magnitude higher than the underlying seawater. Dense phytoplankton blooms have been observed in combination with the receding ice edge or in coastal shelf areas (Holm-Hansen et al., 1989).

**Second**, the release of dissolved iron or resuspension of sediments can supply iron to waters overlying shallow sea floor, accounting for high productivity in continental shelf environments (along the Antarctic coast, for example).

**Third**, upwelling supplies iron and accounts for elevated productivity in some areas of the Southern Ocean (de Baar, et al, 1995, see below) and along the continental slope.

**Fourth**, vertical mixing, induced by rough bottom topography, supplies iron to surface waters and enhances productivity in regions such as the Scotia Sea east of the Drake Passage, and the Kerguelen Plateau in the center of the Indian Antarctic sector

**Fifth**, As the authors discuss, there is delivery of soluble iron by **aerosol deposition** to the Southern Ocean, particularly areas downwind of substantial dust sources, accounting for elevated chlorophyll and/or productivity to the east of Patagonia and to the south and southwest of Australia, New Zealand, and Africa.

In regard to the iron hypothesis, it should be noted that **each of these sources of iron is associated with an increase in growth of phytoplankton**.

Regions lacking all these sources are the least fertile in the Southern Ocean, despite their high burdens of  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{Si(OH)}_4$ . These include waters overlying the Enderby Abyssal Plain (western Indian sector), South Indian Basin (eastern Indian sector), and the Bellingshausen abyssal Plain (Pacific sector), all in the Antarctic Zone of the Southern Ocean. These would be the areas where iron fertilization would be most productive. Their work showed that delivery of airborne Fe increases production of sub Antarctic waters, **strengthening the link between enhanced Fe delivery and lower  $\text{CO}_2$  during the ice ages** (Cassar et al, 2017).

The largest HNLC region, the Southern Ocean, has the biggest potential to influence atmospheric  $\text{CO}_2$ . Here atmospheric dust supply is low, originating from small dust sources in Argentina, Australia, and South Africa.

Changes in these small and little studied desert regions may have a disproportionately large global impact (Jickells et al, 2005).

A surprising additional source of iron is by the meteorities. While it is difficult to assess due to the sporadic events, the amount of soluble (presumably bioavailable) iron input into the ocean from extraterrestrial dust is estimated to be  $7 \times 10^9$  g/year (Johnson, 2001).

### **Artificial vs Natural Iron**

All 12 artificial iron experiments have confirmed that iron supply limits primary production and has impact on phytoplankton species composition and bloom dynamics in tropical as well as in polar HNLC waters (Boyd et al., 2007).

de Baar et al (1995) tested the iron hypothesis by looking at natural levels of phytoplankton productivity in regions of the Southern Ocean with differing iron abundance. The southerly branch of the Antarctic Circumpolar Current (ACC) results in upwelling of deep waters and supplies sufficient iron to the surface to sustain moderate primary production but not to permit blooms to develop. In contrast, within the fast-flowing, iron-rich jet of the polar front (PF), spring blooms produced phytoplankton biomass an order of magnitude greater than that in southern ACC waters, leading to CO<sub>2</sub> undersaturation. The plankton-rich PF waters were sharply delineated from adjacent iron-poor waters, **indicating that iron availability was the critical factor in allowing blooms to occur.**

Between 2004 and 2005 the first planned natural iron fertilization experiment in the Southern Ocean, took place (Breitbart, E. et al (2010). It was termed CROZEX for the CROZet natural iron bloom and EXport experiment. The CROZet bloom which occurs annually north of the Crozet Islands and Plateau and is caused by upwelling, was surveyed by Pollard et al, (2007). This showed that the efficiency of natural fertilization was at least 10 to 20 times greater than that of a phytoplankton bloom induced artificially by adding iron.

Blain et al (2007) described a second similar study the KEOPS (Kerguelen ocean and plateau compared study) carried out between January 19 to February 13, 2005. They also reported observations of a phytoplankton bloom induced by natural iron fertilization due to upwelling. These studies offered an opportunity to overcome some of the limitations of short-term artificial Fe fertilization experiments. They found that a large phytoplankton bloom over the Kerguelen plateau in the Southern Ocean was sustained by the supply of iron and major nutrients to surface waters from iron-rich deep water below. The efficiency of fertilization, defined as the ratio of the carbon export to the amount of iron supplied, was **at least ten times higher** than previous estimates from short-term blooms induced by artificial iron-addition experiments. At the center of the bloom the partial pressure of CO<sub>2</sub> dropped from 390 to 310 uatm.

The specific results are as follows. The artificial experiments indicated an efficiency of biological carbon export into deeper water (100–250 m) ranging from 650 (SERIES, Boyd et al., 2004) to 3300 (mol C/mol Fe) (SOFEX – south, Buesseler et al., 2004). The seasonal sequestration efficiencies estimated for natural Fe fertilization are much higher, 8640 for CROZEX (Pollard et al., 2009) and 154 000 for KEOPS (Chever et al., 2010).

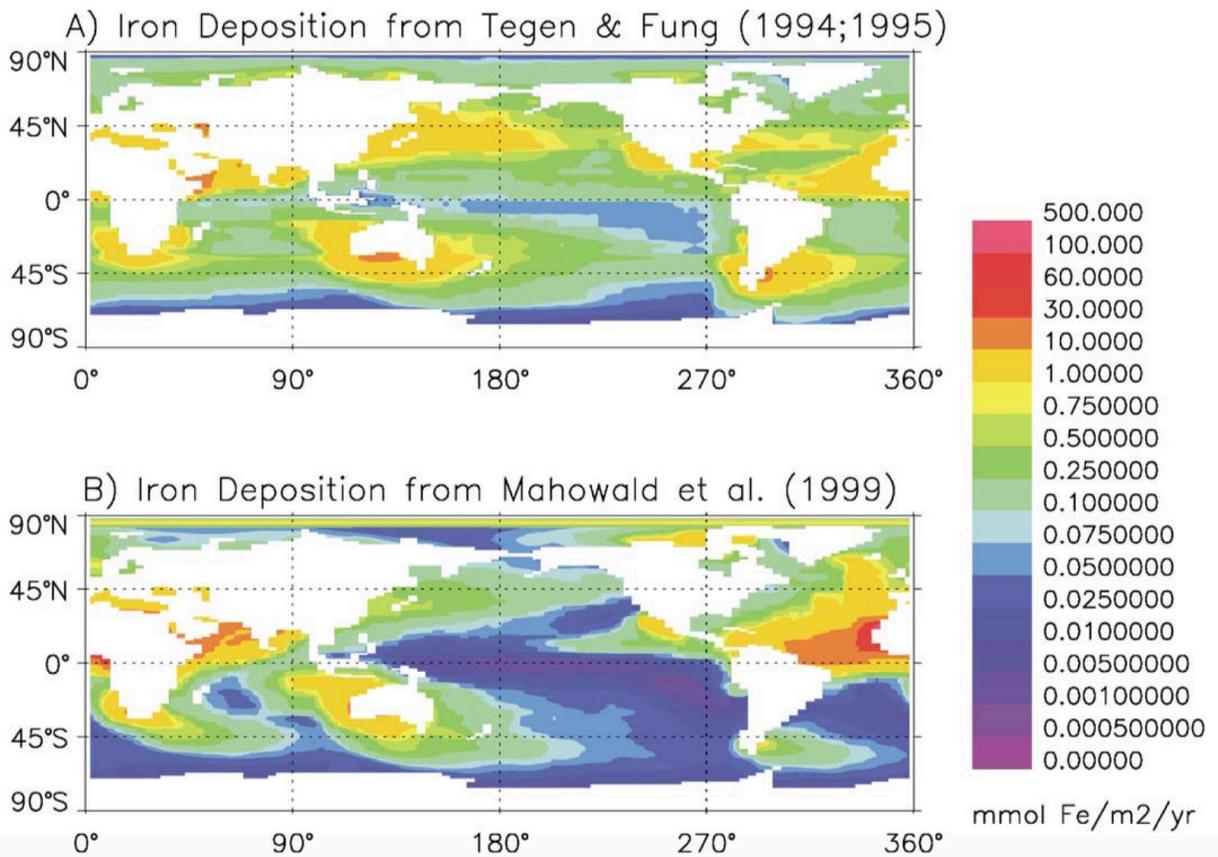
The discrepancies in effectiveness between natural and purposeful fertilizations might be partly due to the ~75% immediate loss of added Fe in artificial fertilizations (de Baar et al., 2008).

This superiority of natural iron sources over artificial one suggest **that simulation of natural fertilization by the use of airborne aerosols might also be more efficient than ship-based iron fertilization.**

### **World Ocean Maps of Nutrients**

If one of the potential goals of the Comings Foundation is to explore iron and other nutrient fertilization, a critical question is: Where to do it? Every once and awhile, when doing research, one runs across a paper that clarifies many things. That happened when I downloaded the paper by Moore, J.K. et al (2002), entitled **Iron cycling and nutrient-limitation patterns in surface waters of the World Ocean**. It contained many maps of the world's oceans showing the level of nutrients and primary production in different areas. The best way to illustrate this information is to show these maps.

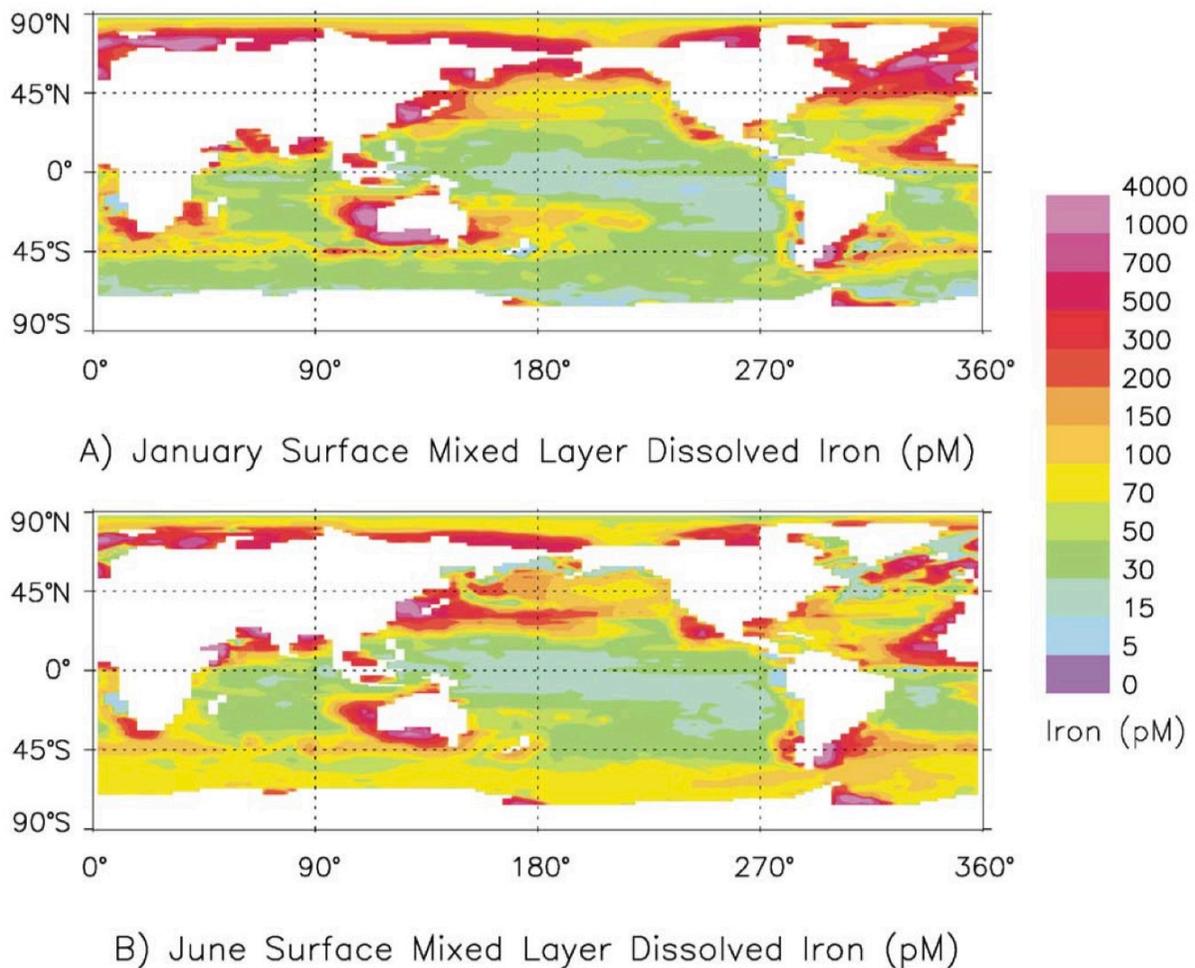
The first map showed the **iron deposition** across oceans using data from two different sources: Tegen & Fung, 1994; 1995 (TF95) and Mahowald et al, 1999 (MAH99).



Annual atmospheric iron input to the oceans estimated from two modeling studies of dust transport and deposition (A) iron deposition from Tegen and Fung (1994, 1995) and (B) Mahowald et al. (1999). Dust was assumed to be 3.5% iron by weight (see text for details).

According to the MAH99 data there was a huge area of decreased iron deposition in the Pacific stretching from the coast of Ecuador to Japan. By contrast, the TF95 model showed ten times the estimates in this area compared to MAH99. The MAH99 map showed significantly increased deposition on the west coast of Africa. These differences were thought to be due to differences in some of the variables used in the two models.

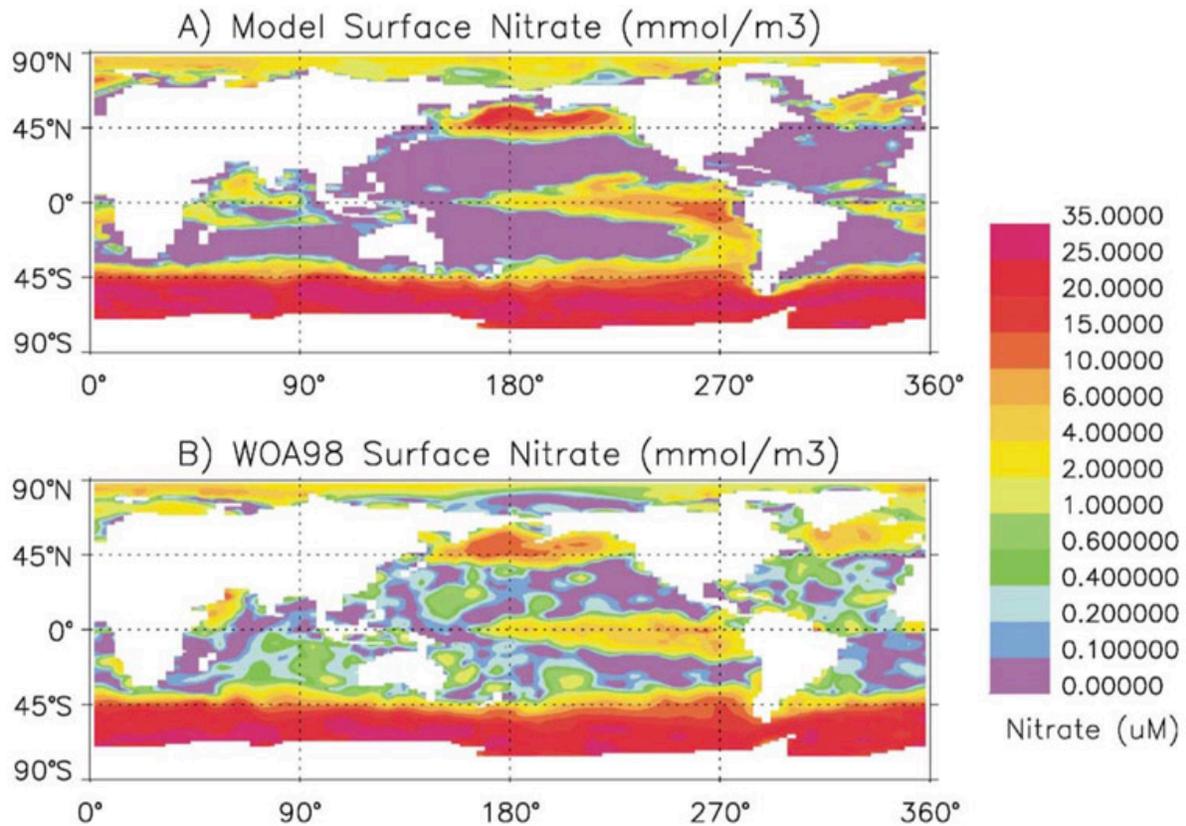
What the next map showed was quite interesting. It examined surface mixed-layer dissolved iron concentrations (pM).



Model estimates of surface mixed-layer dissolved iron concentrations (pM) for the months of (A) January and (B) July.

The coastal areas showed the highest dissolved iron concentrations. In the HNLC regions and parts of the North Atlantic concentrations are  $>30$  pM during summer, falling below 15 pM in the most iron-stressed regions. The highest dissolved Fe levels are seen in areas of high dust flux. It is only in these regions that iron gets much above 1.0 nM.

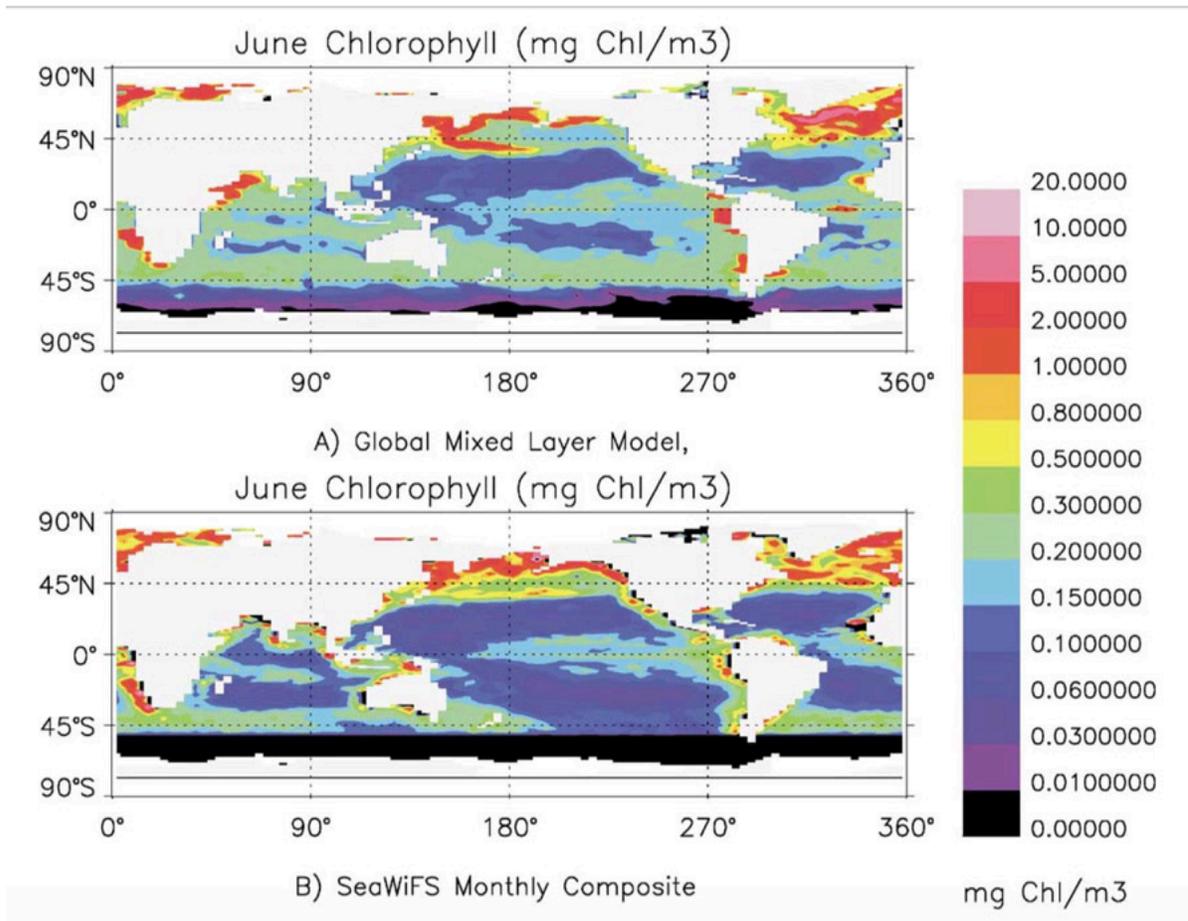
Next they compared mean nitrate concentrations in surface waters during summer months (December/February in the Southern Hemisphere and June–August in the Northern Hemisphere) with summer season surface values from WOA98. The model reproduces the generally high nitrate values in the Southern Ocean, the subarctic and equatorial Pacific, and in the North Atlantic, seen in the in-situ data. Nitrate is largely depleted in the North Atlantic by the end of the summer season in the model. The mid-ocean gyres have uniformly low nitrate concentrations.



Model estimates of surface mixed-layer nitrate concentrations during summer months (in each hemisphere) compared with the summer season nitrate data from the World Ocean Atlas 1998-WOA98 (Conkright et al., 1998). (A) Model surface nitrate (mmol/m<sup>3</sup>). (B) WOA98 surface nitrate (mmol/m<sup>3</sup>).

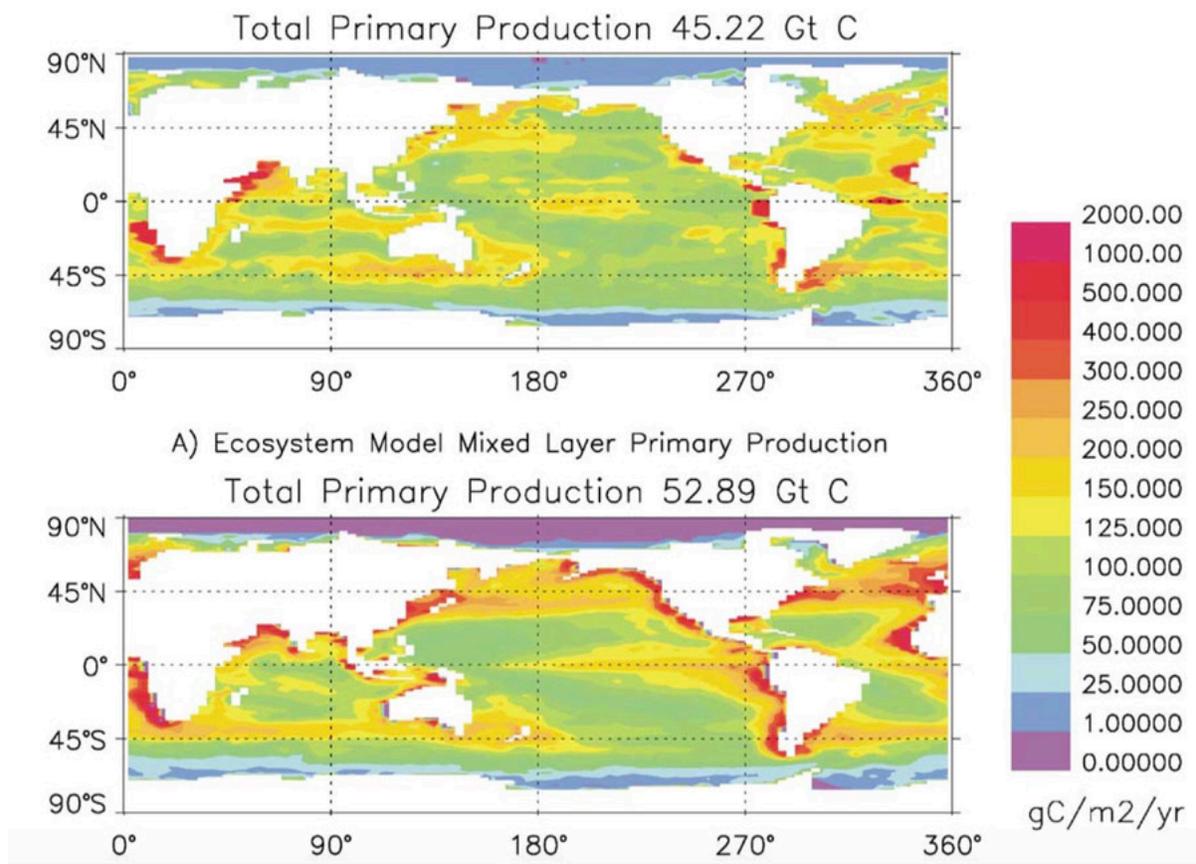
The difference in surface nitrate (A) between the Southern Ocean (red 20.00 μM) and the mid-ocean gyres (blue 0.00 μM) is striking.

The ocean maps of chlorophyll (below) show in dramatic fashion what is meant by the term HNLC (high nutrient or nitrate and low chlorophyll) in the region of the Southern Ocean. This area is intensely red (very high in nitrate) in the nitrate maps (see above) but totally black (zero chlorophyll) in the chlorophyll map (see below). It is even lower than in the oligotrophic gyres (blue).



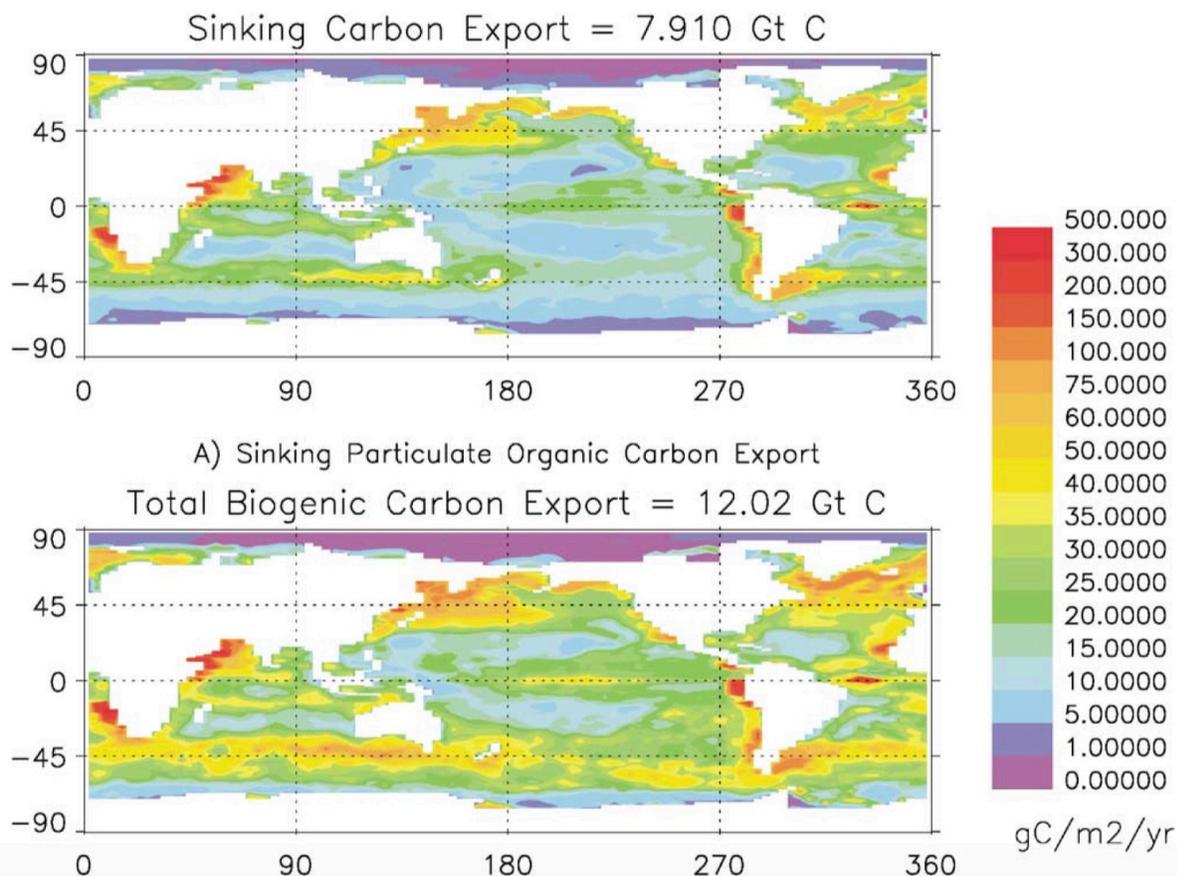
Surface chlorophyll concentrations (mg chl/m<sup>3</sup>) for the month of June from the ecosystem model (top panel) compared with satellite-derived estimates for June 1999 from SeaWiFS (bottom panel). (A) Global mixed-layer model. (B) SeaWiFS monthly composite.

Chlorophyll content is only part of the picture. A more complete picture is provided by total **primary output** and Vertically Generalized Production Model (**VGPM**). VGPM estimates total **euphotic zone** production. This is shown in the map below.



Annual primary production (Gt C) within the surface mixed layer estimated by the ecosystem model (top panel) (A) compared with satellite-based estimates of total water column primary production from the Vertically Generalized Production Model (VGPM) (bottom panel)(B) of Behrenfeld and Falkowski (1997).

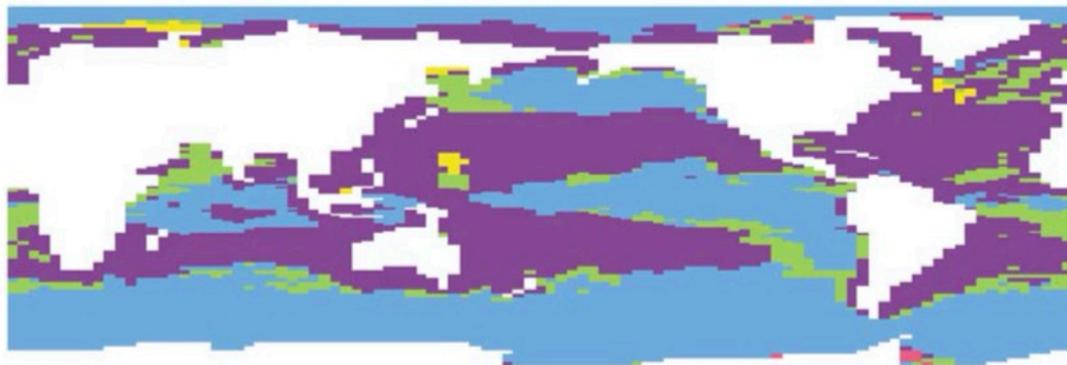
While the differences are not as striking, it is the chlorophyll that is important since it is a measure of CO<sub>2</sub> uptake by photosynthesis. An even more important measure is sinking carbon (see below).



The ecosystem model estimated annual export of biogenic carbon from the surface mixed layer (A, within the sinking detrital pool) and total biogenic carbon export (B). Total export is the sum of the sinking flux plus the export of biogenic carbon due to turbulent mixing at the base of the mixed layer and detrainment.

Highest export was in coastal areas and the North Atlantic, with **minimal export in mid-ocean gyres**. In the Southern Ocean there was elevated export at mid-latitudes in the South Atlantic and south of Africa but less so in the Pacific sector, similar to the pattern seen in the above figure. This model predicts higher export in the Southeast Indian sector of the Southern Ocean than that of Laws et al. (2000).

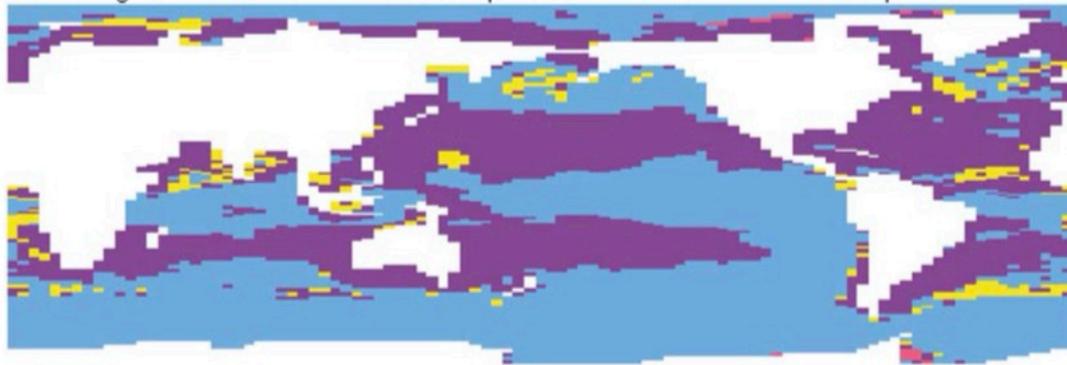
Before progressing to the next map, it is necessary to define the term **cell quota**. In 1998 Droop (Droop, M.R., 1998, 1973, 2003) observed that the growth rate of algae in chemostats did not depend directly on the concentration of the nutrient in the surrounding medium **but on the concentration of that nutrient inside the cells (cell quota)**. With that in mind Moore et al (2002) next examined **nutrient-limitation patterns**, which are a function of ambient nutrient concentrations relative to the half-saturation uptake constants for each phytoplankton class.



### A) Diatom Nutrient Limitation

Nitrogen 50.04%, Iron 38.75%, Silica 10.57%, Phosphorus 0.548%, Replete 0.0

■ Nitrogen ■ Iron ■ Phosphorus ■ Silica ■ Replete



### B) Small Phytoplankton Nutrient Limitation

Nitrogen 45.29%, Iron 50.20%, Phosphorus 4.405%, Replete 0.089%

■ Nitrogen ■ Iron ■ Phosphorus ■ Replete



### C) Diazotroph Nutrient Limitation

Nitrogen 0.000%, Iron 35.33%, Phosphorus 3.539%, Replete 61.12%

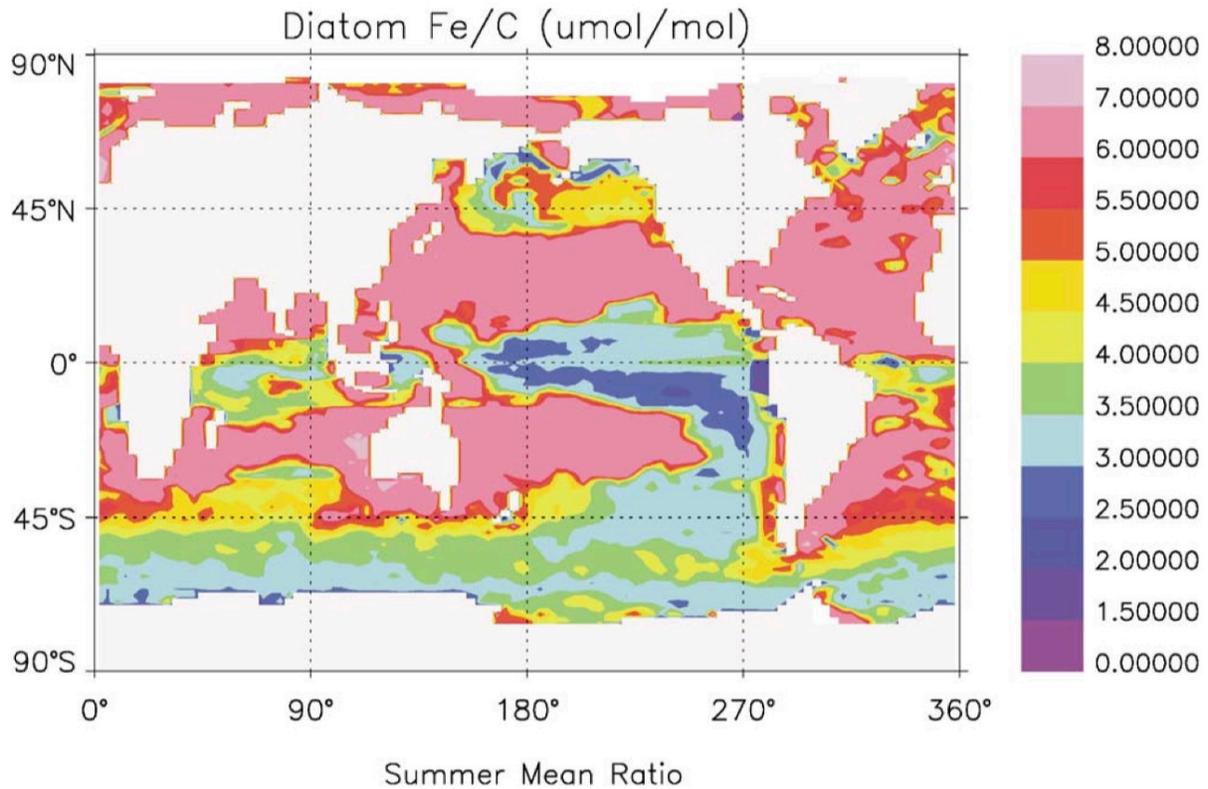
Nutrient-limitation patterns for the diatoms (A), the small phytoplankton (B), and the diazotrophs (C) during summer months. Areas where all nutrient cell quotas are >97% of the maximum cell quota values are arbitrarily defined as nutrient replete (adequate). Also shown is the **percentage of total ocean area where each nutrient is limiting growth.**

Bear in mind, when examining these maps the higher the percentages the more limiting the nutrient. Their focus was on summer months, which they defined as June–August for the Northern Hemisphere and December–February for the Southern Hemisphere. In the model the nutrient with the **lowest cell quota** relative to maximum quotas, limits carbon fixation or growth rate. We define phytoplankton as nutrient-replete (adequate) if all cell quotas are >97% of their maximum values.

The following is how I interpret these maps. In map A and B, in the purple areas, nitrogen was the limiting nutrient while in the blue areas iron was the limiting nutrient. Iron was limiting in 50 and 45 percent of the relevant ocean area. Silica was limiting in only small areas, phosphorous was virtually not limiting anywhere and there were virtually no areas where these compounds were adequate (replete). In map C, iron was limiting for diazotrophs in the equatorial regions. Nitrogen was not limiting anywhere else and in all other areas except blue, nutrient levels were adequate (replete).

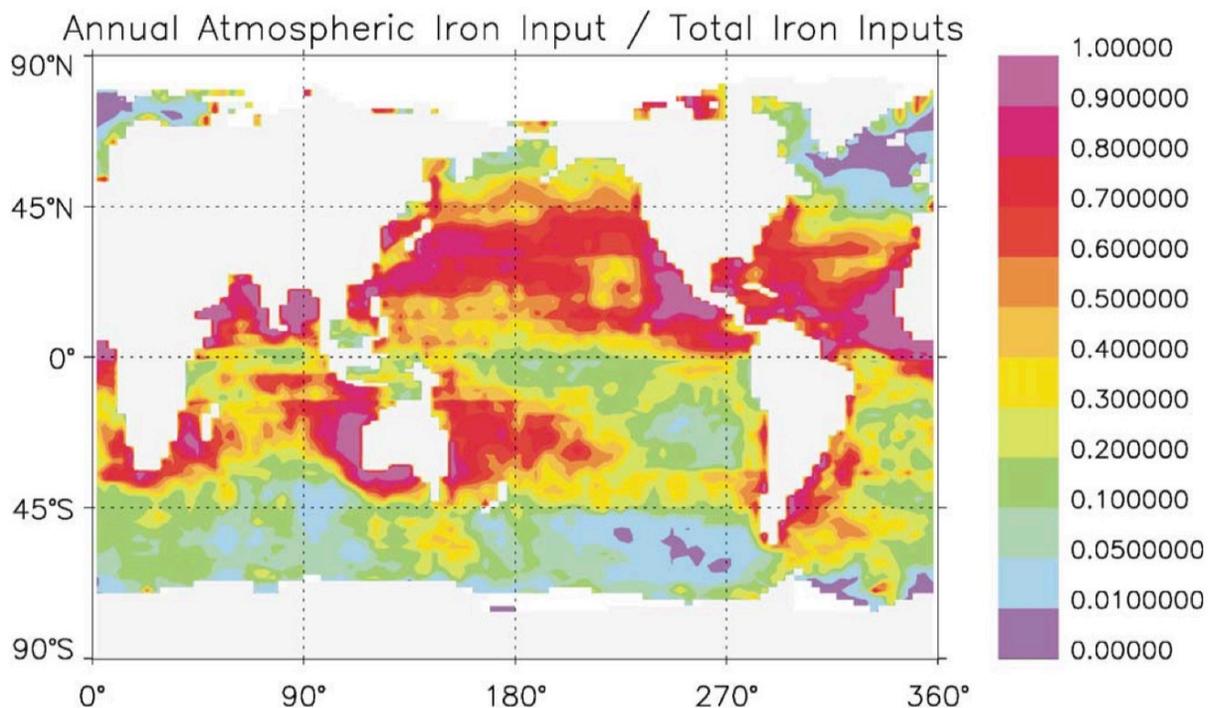
In essence, **the mid-ocean gyres are N-limited for the diatoms and small phytoplankton while the HNLC regions of the subarctic and equatorial Pacific, and the Southern Ocean are iron limited.** Nutrient-replete areas constitute <1% of the ocean area for the diatoms and the small phytoplankton.

Temperature is the dominant control on diazotroph growth at mid to high latitudes as we assume diazotroph production and biomass to be negligible when sea-surface temperature is <16°C. At the mid to low latitudes mixed-layer depth strongly influences both light and sea-surface temperatures, and the diazotrophs thrive only in areas where mixed layers remain shallow of an extended period. The diazotrophs are nutrient-limited over about 39% of the world ocean, with about 35% Fe-limited and about % P-limited. Cold sea-surface temperatures prevent diazotroph growth at high latitudes over about 29% of the world ocean.



Mean cellular Fe/C (mmol/mol) ratios for the diatoms during summer months.

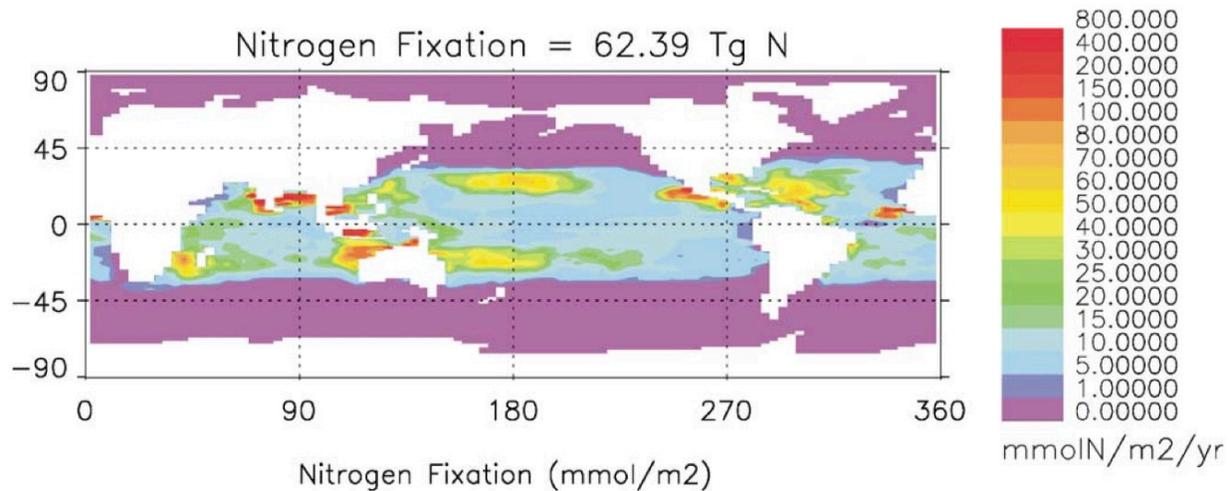
The cellular Fe/C ratio (mmol/mol) of the diatoms during summer months is shown in the above figure. In areas where iron is not strongly limiting, Fe/C ratios approach the maximum cell quota value of 7.0 mmol/mol. The lowest ratios ranging from 2–3.5 mmol/mol are seen in the most Fe limited regions of the equatorial Pacific and Southern Ocean and in some coastal regions where phytoplankton blooms have depleted iron. The Fe/C ratios for the small phytoplankton in the model display a very similar spatial pattern.



The relative size of the **atmospheric dissolved iron source** relative to total dissolved iron inputs to the surface mixed layer. Total dissolved iron input is calculated as the sum of the atmospheric source plus dissolved iron inputs due to entrainment, upwelling and turbulent mixing.

This is an important map since it shows where **not to do Fe seeding**. The relative strength of the atmospheric iron source is compared with total inputs of dissolved iron to the surface mixed layer in above figure. Total dissolved iron input is calculated as the sum of atmospheric dissolved iron inputs plus the entrainment, upwelling, and turbulent mixing of dissolved iron into the surface mixed layer. This shows **a deficiency of aeolian iron in the Southern Ocean and far northern Atlantic**. In areas of deep winter mixing, such as the North Atlantic and the southeast Pacific sector of the Southern Ocean, large amounts of iron are entrained during winter months and then detrained unused by the biota in the spring.

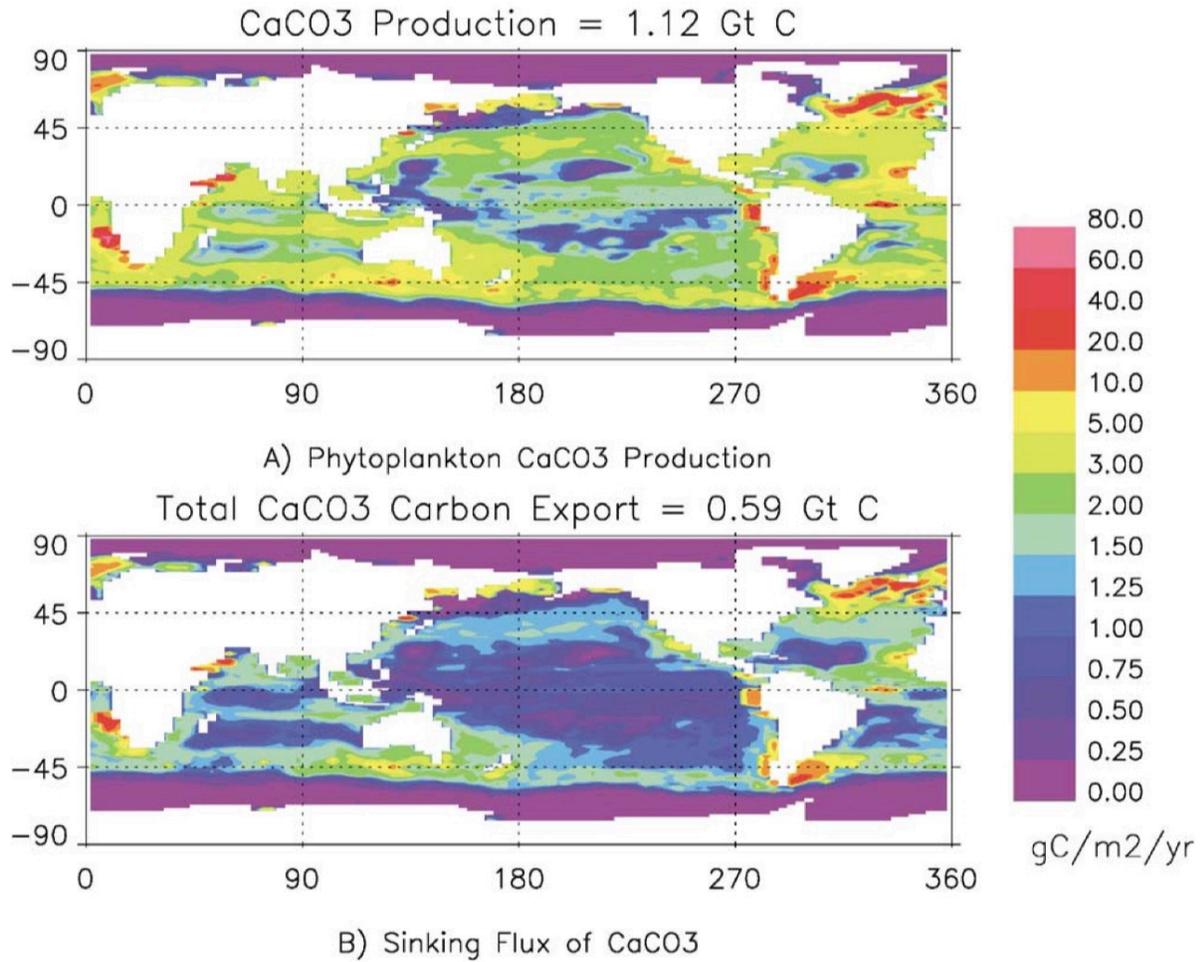
If this analysis is restricted to summer months (a time of maximum stratification and typically the strongest Fe limitation), the atmospheric source accounts for a significantly higher percentage of total iron inputs.



Model predicted surface mixed layer annual nitrogen fixation (Tg N) by the diazotrophs.

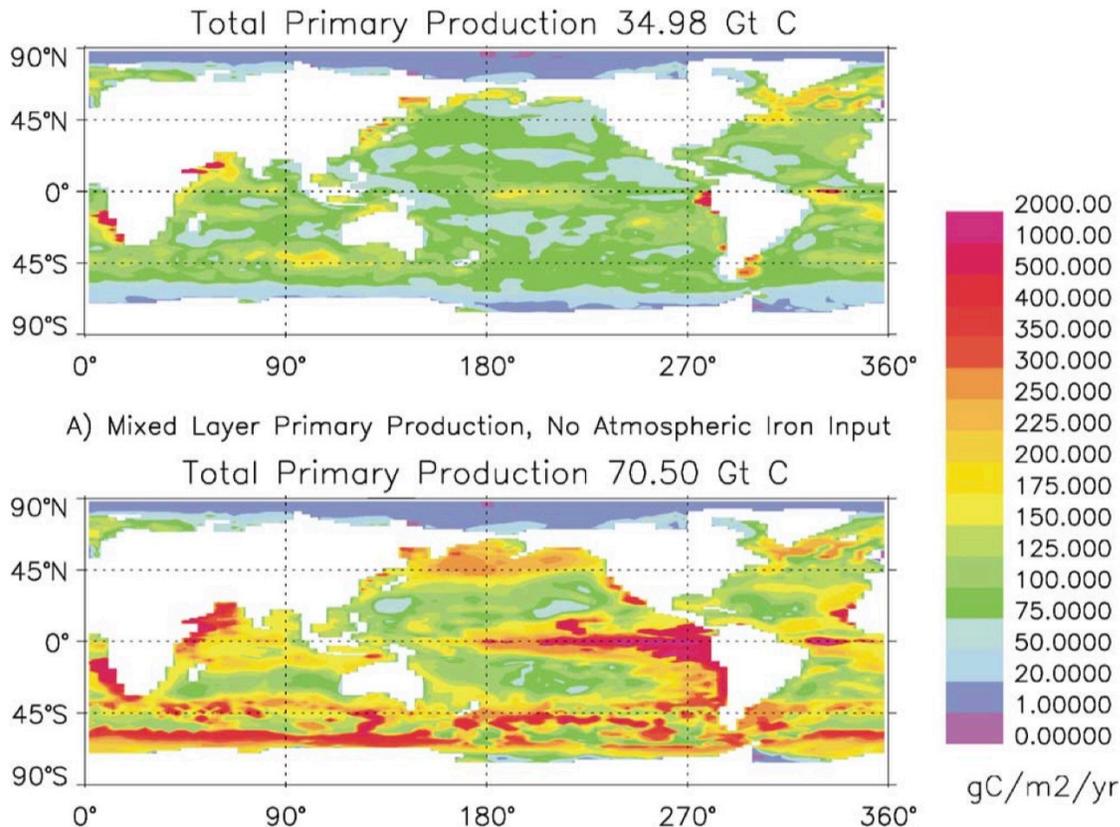
Annual surface mixed-layer nitrogen fixation predicted by the ecosystem model is displayed in the above figure. The relatively high rates for the central North Pacific gyre also been predicted by others. **Fe limitation is playing a key role in regulating nitrogen fixation at the global scale in this model, thus the low levels in the Southern Ocean.**

Hansell and Feely (2000) suggested that climate change, which leads to increased stratification, should increase nitrogen fixation. Our model results strongly support this hypothesis, and it may be that global scale nitrogen fixation will increase if surface waters warm and stratification increases as expected over the next century.



Annual calcium carbonate production (Gt C) by phytoplankton (A) and the sinking calcium carbonate export (B) predicted by the model.

The models predictions of the production and export of calcium carbonate by phytoplankton are shown above. The lowest fluxes were from the mid-ocean gyres and the highest latitudes (coldest waters) in each hemisphere. The high latitude North Atlantic is known to be a site of frequent coccolithophore blooms and high calcium carbonate export. In general, the spatial patterns of high calcium carbonate export are in good agreement with satellite estimates of coccolithophore bloom distributions.

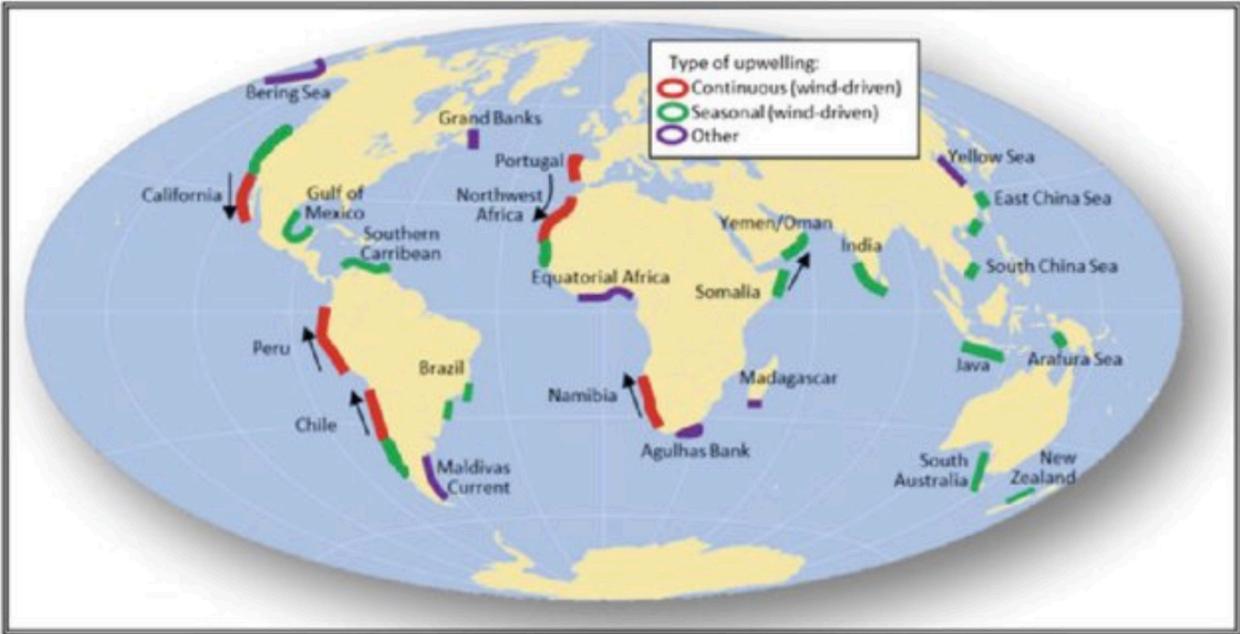


B) Mixed Layer Primary Production, Saturating Atmospheric Iron Input

Displayed is the annual mixed layer primary production from the ecosystem model with no atmospheric iron deposition (A) and with a saturating atmospheric iron deposition (B).

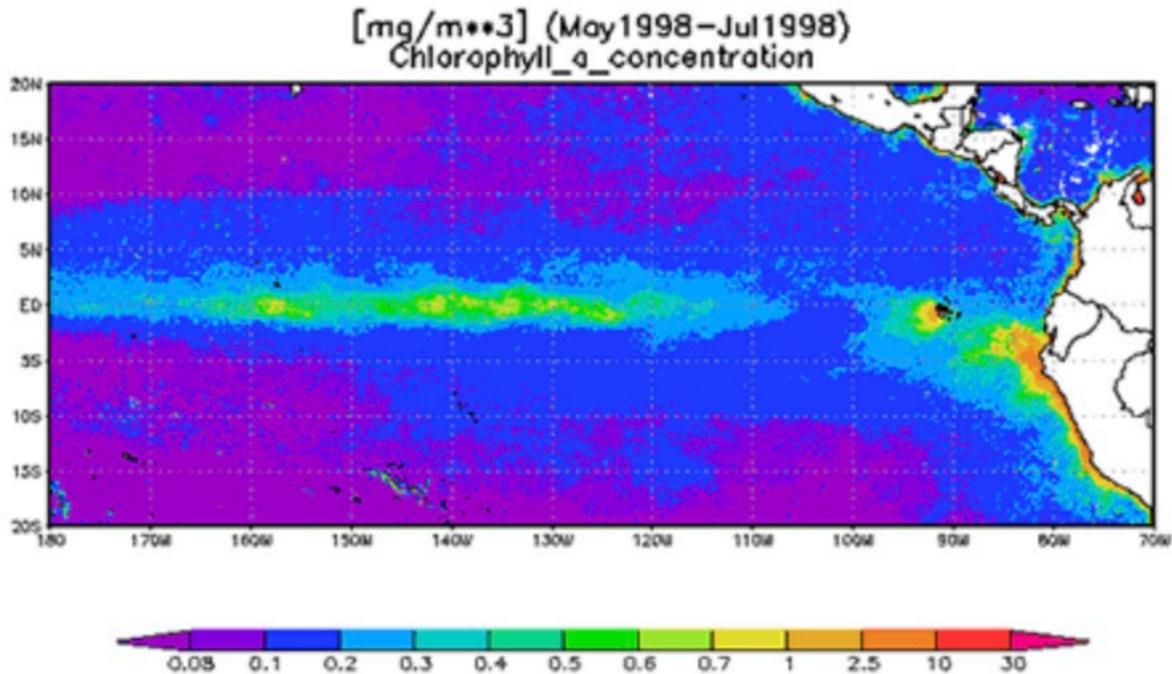
Next Moore et al (2002) examined the sensitivity of the marine ecosystem to variations in the atmospheric iron deposition (see above figure). In A, they examined the extreme cases of no atmospheric iron input versus B, a saturating iron input from the atmosphere. There was a drastic difference in primary production in the two model runs, from 35 Gt C with no atmospheric iron input to 70.5 Gt C with saturating input. **The increases at higher atmospheric iron flux are seen mainly in the HNLC regions of the Southern Ocean** and the subarctic North Pacific. In the Equatorial Pacific, there were large increases upwelling areas off the western coast of Peru (also see below).

Given how many times upwelling is mentioned it is informative to show a map of where the major upwelling regions of the ocean are located. The following is such a map.



The upwellings are of three types: continuous wind driven (**red**), seasonal wind driven (**green**) and other (**purple**).

Given the frequency with which the area off the western coast of Peru shows up in all the maps as a region of intense activity, the following map of the effects of this upwelling on chlorophyll in that area is shown below.



Effect of the western Peruvian upwelling on chlorophyll production.

The major conclusion from virtually all the above maps is that **Fe fertilization is most productively done in the Southern Ocean**. One could argue that a second suitable site is the equatorial area west of Peru. However, the above map and the map showing primary production with a saturating atmospheric iron deposition (B) (third map above) suggest that upwelling, but not aeolian iron, has adequately added iron to that region.

These maps and the above section on aeolian iron suggest that:

a) an iron fertilization technique that mimics natural iron sources, such as airborne spreading of biogenic iron (Emerson, 2005) might be more efficient than the usual dispersion of iron off of ships.

b) The amounts of iron delivered to various areas of the ocean by natural means, such as air borne or by upwellings, dwarf the amounts of iron that can be delivered artificially. This strongly suggests that most of the concerns about iron fertilization are unrealistic and overblown.