detector to provide an absolute calibration. However, further development of this technology will eventually provide extremely versatile instrumentation for the investigation of fine-scale sea surface emission.

## Future Direction and Conclusions

In the last 10 years, considerable progress has been made in the development and application of IR sensors to study the air–sea interface. The continued development and use of FTIR sensors will provide the capability to accurately investigate the spectral characteristics of the sea surface in order to optimize the spectral intervals used by space sensors to determine SSST. It can be expected that in the near future, new algorithms will emerge for the direct measurement of the air–sea heat flux using multispectral sounding techniques and the accurate *in situ* determination of sea surface emissivity. Although still in their infancy, the development and use of thermal cameras will provide valuable insight into the fine-resolution two-dimensional spatial and temporal variability of the ocean surface. These data will be useful in developing and understanding the sampling limitations of large footprint satellite sensors and in the refinement of validation protocols. Finally, as satellite radiometers are now providing consistent and accurate observations of the SSST (e.g., ATSR), there is a need for autonomous operational *in situ* radiometer systems for ongoing validation of their data. Such intelligent systems that are extremely robust against the harsh realities of the marine environment are currently being developed.

## See also

**Air–Sea Gas Exchange. Heat and Momentum Fluxes at the Sea Surface. Radiative Transfer in the Ocean. Satellite Remote Sensing of Sea Surface Temperatures. Thermohaline Circulation.**

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# IRON FERTILIZATION

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## Introduction

The trace element iron has been shown to play a critical role in nutrient utilization and phytoplankton growth and therefore in the uptake of carbon dioxide from the surface waters of the global ocean. Carbon fixation in the surface waters, via phytoplankton growth, shifts the ocean–atmosphere exchange equilibrium for carbon dioxide. As a result, levels of atmospheric carbon dioxide (a greenhouse gas) and iron flux to the oceans have been linked to climate change (glacial to interglacial transitions). These recent findings have led some to suggest that large-scale iron fertilization of the world's oceans might therefore be a feasible strategy for controlling climate. Others speculate that such a strategy could deleteriously alter the ocean ecosystem, and still others have calculated that such a strategy would be ineffective in removing sufficient carbon dioxide to produce a sizable and rapid result. This article focuses on carbon and the major plant nutrients, nitrate, phosphate, and silicate, and describes how our recent discovery of the role of iron in the oceans has increased our understanding of phytoplankton growth, nutrient cycling, and the flux of carbon from the atmosphere to the deep sea.

## Major Nutrients

Phytoplankton growth in the oceans requires many physical, chemical, and biological factors that are distributed inhomogenously in space and time. Because carbon, primarily in the form of the bicarbonate ion, and sulfur, as sulfate, are abundant throughout the water column, the major plant nutrients in the ocean commonly thought to be critical for phytoplankton growth are those that exist at the micromolar level such as nitrate, phosphate, and silicate. These, together with carbon and sulfur, form the major building blocks for biomass in the sea. As fundamental cellular constituents, they are generally thought to be taken up and remineralized in constant ratio to one another. This is known as the Redfield ratio (Redfield, 1934, 1958) and can be expressed on a molar basis relative to carbon as 106C : 16N : 1P.

Significant local variations in this uptake/regeneration relationship can be found and are a function of the phytoplankton community and growth conditions, yet this ratio can serve as a conceptual model for nutrient uptake and export.

The vertical distribution of the major nutrients typically shows surface water depletion and increasing concentrations with depth. The schematic profile in **Figure 1** reflects the processes of phytoplankton uptake within the euphotic zone and remineralization of sinking planktonic debris via microbial degradation, leading to increased concentrations in the deep sea. Given favorable growth conditions, the nutrients at the surface may be depleted to zero. The rate of phytoplankton production of new biomass, and therefore the rate of carbon uptake, is controlled by the resupply of nutrients to the surface waters, usually via the upwelling of deep waters. Upwelling occurs over the entire ocean basin at the rate of approximately 4 m per year but increases in coastal and regions of divergent surface water flow, reaching average values of 15 to 30 or greater. Thus, those regions of high nutrient supply or persistent high nutrient concentrations are thought to be most important in terms of carbon removal.

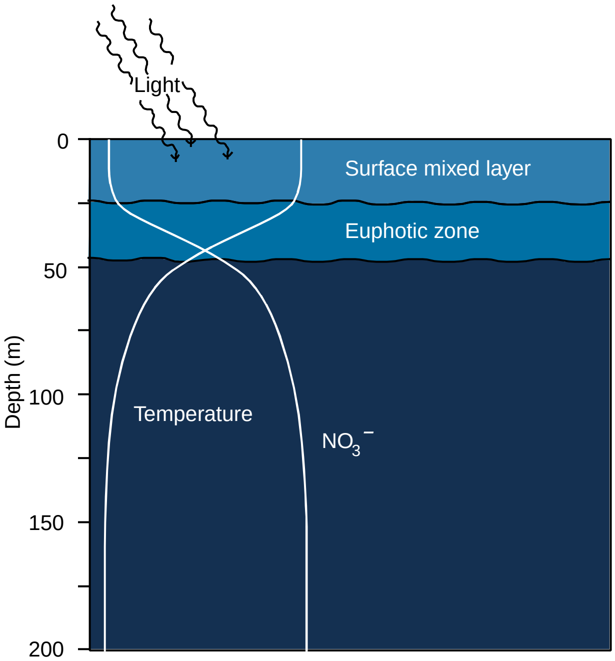

**Figure 1** A schematic profile indicating the regions of the upper water column where phytoplankton grow. The surface mixed layer is that region that is actively mixed by wind and wave energy, which is typically depleted in major nutrients. Below this mixed layer temperatures decrease and nutrients increase as material sinking from the mixed layer is regenerated by microbial decomposition.

## Nitrogen versus Phosphorus Limitation

Although both nitrogen and phosphorus are required at nearly constant ratios characteristic of deep water, nitrogen has generally been thought to be the limiting nutrient in sea water rather than phosphorus. This idea has been based on two observations: selective enrichment experiments and surface water distributions. When ammonia and phosphate are added to sea water in grow-out experiments, phytoplankton growth increases with the ammonia addition and not with the phosphate addition, thus indicating that reduced nitrogen and not phosphorus is limiting. Also, when surface water concentration of nitrate and phosphate are plotted together (**Figure 2**), it appears that there is still residual phosphate after the nitrate has gone to zero.

The notion of nitrogen limitation seems counterintuitive when one considers the abundant supply of dinitrogen ($N_2$) in the atmosphere. Yet this nitrogen gas is kinetically unavailable to most phytoplankton

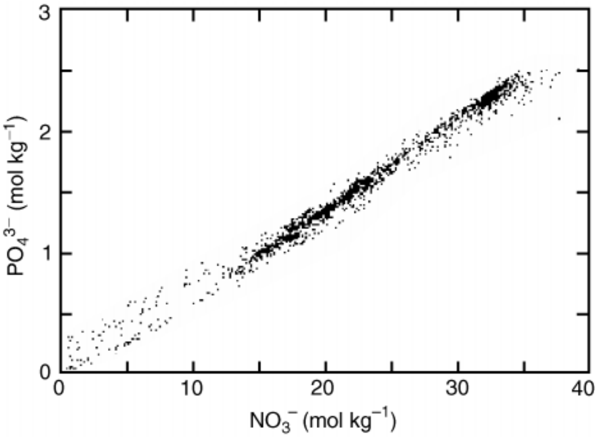

**Figure 2** A plot of the global surface water concentrations of phosphate versus nitrate indicating a general positive intercept for phosphorus when nitrate has gone to zero. This is one of the imperical observations favoring the notion of nitrate limitation over phosphate limitation.

because of the large amount of energy required to break the triple bond that binds the dinitrogen molecule. Only those organisms capable of nitrogen fixation can take advantage of this form of nitrogen and reduce atmospheric $N_2$ to biologically available nitrogen in the form of urea and ammonia. This is, energetically, a very expensive process requiring specialized enzymes (nitrogenase), an anaerobic microenvironment, and large amounts of reducing power in the form of electrons generated by photosynthesis. Although there is currently the suggestion that nitrogen fixation may have been underestimated as an important geochemical process, the major mode of nitrogen assimilation, giving rise to new plant production in surface waters, is thought to be nitrate uptake.

The uptake of nitrate and subsequent conversion to reduced nitrogen in cells requires a change of five in the oxidation state and proceeds in a stepwise fashion. The initial reduction takes place via the nitrate/nitrite reductase enzyme present in phytoplankton and requires large amounts of the reduced nicotinamide–adenine dinucleotide phosphate (NADPH) and of adenosine triphosphate (ATP) and thus of harvested light energy from photosystem II. Both the nitrogenase enzyme and the nitrate reductase enzyme require iron as a cofactor and are thus sensitive to iron availability.

## Ocean Regions

From a nutrient and biotic perspective, the oceans can be generally divided into biogeochemical provinces that reflect differences in the abundance of macronutrients and the standing stocks of phytoplankton. These are the high-nitrate, high-chlorophyll (HNHC); high-nitrate, low-chlorophyll (HNLC); low-nitrate, high-chlorophyll (LNHC); and low-nitrate, low-chlorophyll (LNLC) regimes (**Table 1**). Only the HNLC and LNLC regimes are relatively stable, because the high phytoplankton growth rates in the other two systems will deplete any residual nitrate and sink out of the system. The processes that give rise to these regimes have been the subject of some debate over the last few years and are of fundamental importance relative to carbon export (**Figure 3**).

### HNLC Regions

The HNLC regions are thought to represent about 20% of the areal extent of the world's oceans. These are generally regions characterized by more than 2 μmol l$^{-1}$ nitrate and less than 0.5 μg l$^{-1}$ chlorophyll-*a*, a proxy for plant biomass. The major HNLC regions are shown in **Figure 4** and represent the Subarctic Pacific, large regions of the eastern equatorial Pacific and the Southern Ocean. These HNLC regions persist in areas that have high macronutrient concentrations, adequate light, and physical characteristics required for phytoplankton growth but have very low plant biomass. Two explanations have been given to describe the persistence of this condition. (1) The rates of zooplankton grazing of the phytoplankton community may balance or exceed phytoplankton growth rates in these areas, thus cropping plant biomass to very low levels and recycling reduced nitrogen from the

**Table 1** The relationship between biomass and nitrate as a function of biogeochemical province and the approximate ocean area represented by these regimes

| | *High-chlorophyll* | *Low-chlorophyll* |
|---|---|---|
| High-nitrate | Unstable/coastal (5%) | Stable/Subarctic/Antarctic/ equatorial Pacific (20%) |
| Low-nitrate | Unstable/coastal (5%) | Oligotrophic gyres (70%) |

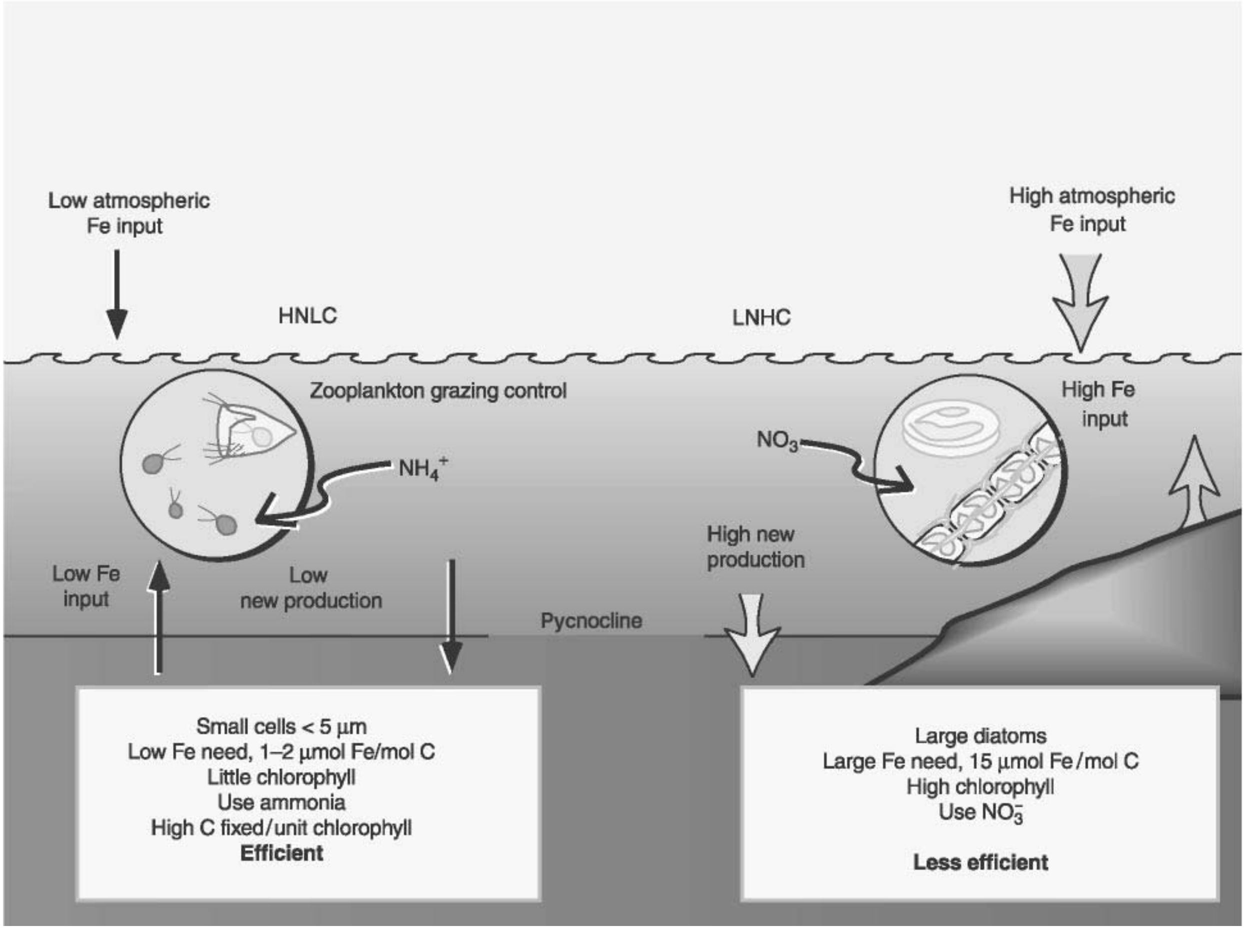

**Figure 3** A schematic representation of the 'iron theory' as it functions in offshore HNLC regions and coastal transient LNHC regions. It has been suggested that iron added to the HNLC regions would induce them to function as LNHC regions and promote carbon export.

plant community, thereby decreasing the uptake of nitrate. (2) Some other micronutrient (possibly iron) physiologically limits the rate of phytoplankton growth. These are known as top-down and bottom-up control, respectively.

Several studies of zooplankton grazing and phytoplankton growth in these HNLC regions, particularly the Subarctic Pacific, confirm the hypothesis that grazers control production in these waters. Recent physiological studies, however, indicate that phytoplankton growth rates in these regions are suboptimal, as is the efficiency with which phytoplankton harvest light energy. These observations indicate that phytoplankton growth may be limited by something other than (or in addition to) grazing. Specifically, these studies implicate the lack of sufficient electron transport proteins and the cell's ability to transfer reducing power from the photocenter. These have been shown to be symptomatic of iron deficiency.

## The Role of Iron

Iron is a required micronutrient for all living systems. Because of its d-electron configuration, iron readily undergoes redox transitions between Fe(II) and Fe(III) at physiological redox potentials. For this reason, iron is particularly well suited to many enzyme and electron carrier proteins. The genetic sequences coding for many iron-containing electron carriers and enzymes are highly conserved, indicating iron and iron-containing proteins were key features of early biosynthesis. When life evolved, the atmosphere and waters of the planet were reducing and iron was abundant in the form of soluble Fe(II). Readily available and at high concentration, iron was not likely to have been limiting in the primordial biosphere. As photosynthesis evolved, oxygen was produced as a by-product. As the biosphere became more oxidizing, iron precipitated from aquatic systems in vast quantities, leaving

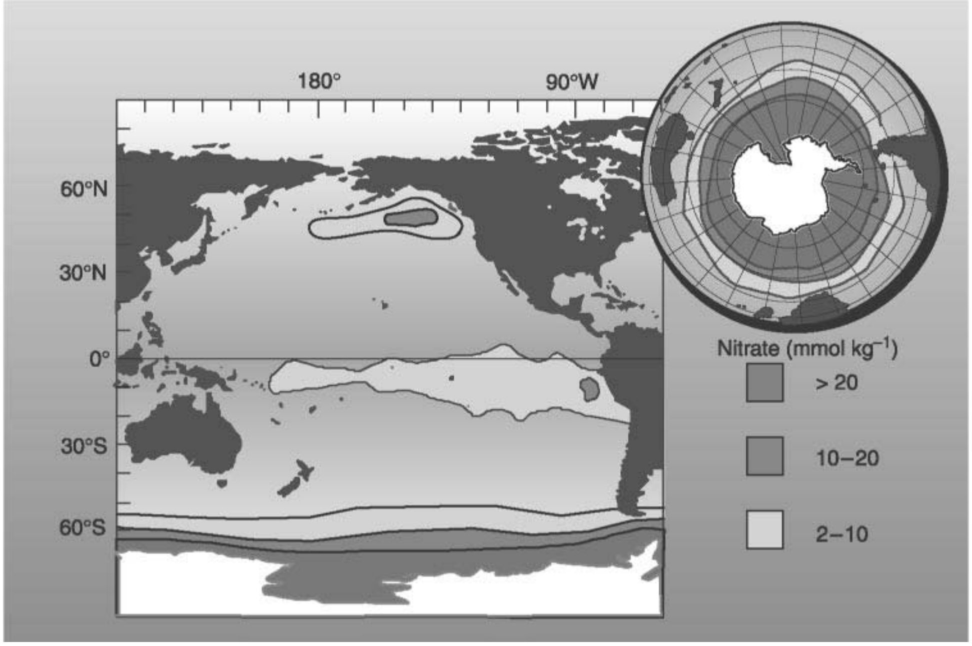

**Figure 4** Current HNLC regions of the world's oceans covering an extimated 20% of the ocean surface. These regions include the Subarctic Pacific, equatorial Pacific and Southern Ocean.

phytoplankton and other aquatic life forms in a vastly changed and newly deficient chemical milieu. Evidence of this mass Fe(III) precipitation event is captured in the ancient banded iron formations in many parts of the world. Many primitive aquatic and terrestrial organisms have subsequently evolved the ability to sequester iron through the elaboration of specific Fe(II)-binding ligands, known as siderophores. Evidence for siderophore production has been found in several marine dinoflagellates and bacteria and some researchers have detected similar compounds in sea water.

Today, iron exists in sea water at vanishingly small concentrations. Owing to both inorganic precipitation and biological uptake, typical surface water values are on the order of $20\,\mathrm{pmol\,l^{-1}}$, perhaps a billion times less than during the prehistoric past. Iron concentrations in the oceans increase with depth, in much the same manner as the major plant nutrients (**Figure 5**).

The discovery that iron concentrations in surface waters is so low and shows a nutrient-like profile led some to speculate that iron availability limits plant growth in the oceans. This notion has been tested in bottle enrichment experiments throughout the major HNLC regions of the world's oceans. These experiments have demonstrated dramatic phytoplankton growth and nutrient uptake upon the addition of iron relative to control experiments in which no iron was added.

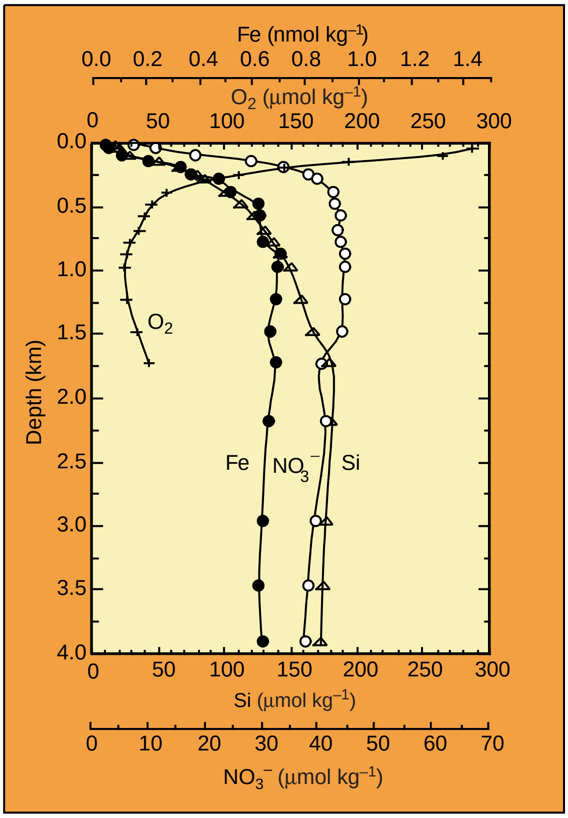

**Figure 5** The vertical distributions of iron, nitrate, silicate, and oxygen in sea water. This figure shows how iron is depleted to picomolar levels in surface waters and has a profile that mimics other plant nutrients.

Criticism that such small-scale, enclosed experiments may not accurately reflect the response of the HNLC system at the level of the community has led to several large-scale iron fertilization experiments in the equatorial Pacific and Southern Ocean. These have been some of the most dramatic oceanographic experiments of our times and have led to a profound and new understanding of ocean systems.

## Open Ocean Iron Enrichment

The question of iron limitation was brought into sharp scientific focus with a series of public lectures, reports by the US National Research Council, papers, special publications, and popular articles between 1988 and 1991. What was resolved was the need to perform an open ocean enrichment experiment in order to definitively test the hypothesis that iron limits phytoplankton growth and nutrient and carbon dioxide uptake in HNLC regions. Such an experiment posed severe logistical challenges and had never been conducted.

## Experimental Strategy

The mechanics of producing an iron-enriched experimental patch and following it over time was developed in four release experiments in the equatorial Pacific (IronEx I and II) and more recently in the Southern Ocean (SOIREE). At this writing, a similar strategy is being employed in the Caruso experiments now underway in the Atlantic sector of the Southern Ocean. All of these strategies were developed to address certain scientific questions and were not designed as preliminary to any geoengineering effort.

### Form of Iron

All experiments to date have involved the injection of an iron sulfate solution into the ship's wake to achieve rapid dilution and dispersion throughout the mixed layer (**Figure 6**). The rationale for using ferrous sulfate involved the following considerations: (1) ferrous sulfate is the most likely form of iron to enter the oceans via atmospheric deposition; (2) it is readily soluble (initially); (3) it is available in a relatively pure form so as to reduce the introduction of other potentially bioactive trace metals; and (4) its counterion (sulfate) is ubiquitous in sea water and not likely to produce confounding effects. Although mixing models indicate that Fe(II) carbonate may reach insoluble levels in the ship's wake, rapid dilution reduces this possibility.

New forms of iron are now being considered by those who would seek to reduce the need for subsequent infusions. Such forms could include iron lignosite, which would increase the solubility and residence time of iron in the surface waters. Since

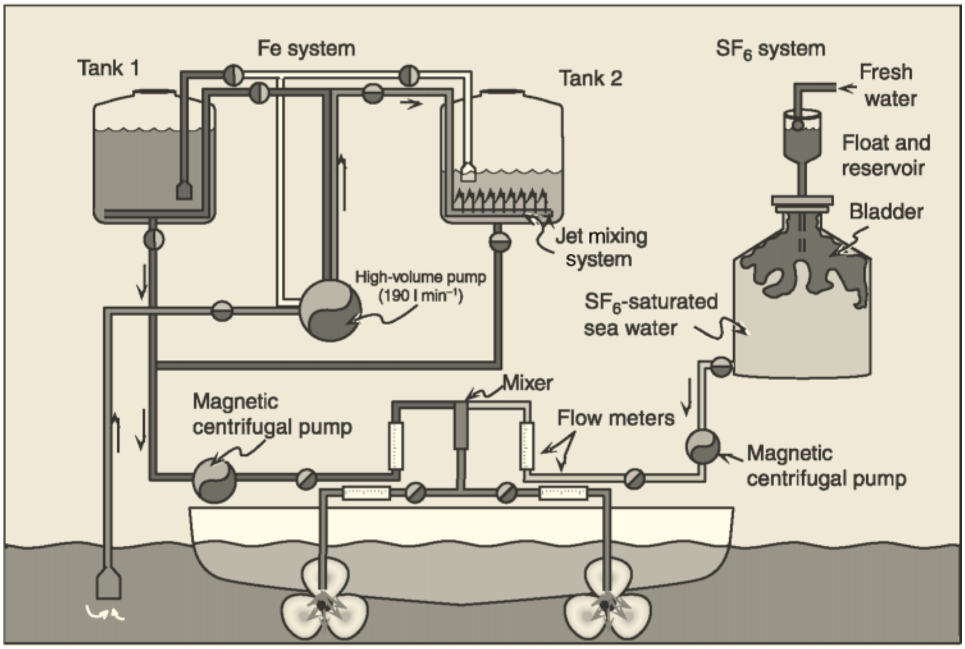

**Figure 6** The iron injection system used during the IronEx experiments utilized two polyethylene tanks that could be sequentially filled with sea water and iron sulfate solution while the other was being injected behind the ship's propellers. A steel tank of sea water saturated with 40 g of sulfur hexafluoride ($SF_6$) was simultaneously mixed with the iron sulfate solution to provide a conservative tracer of mixing.

this is a chelated form of iron, problems of rapid precipitation are reduced. In addition, iron lignosulfonate is about 15% Fe by weight, making it a space-efficient form of iron to transport. As yet untested is the extent to which such a compound would reduce the need for re-infusion.

Although solid forms of iron have been proposed (slow-release iron pellets; finely milled magnetite or iron ores), the ability to trace the enriched area with an inert tracer has required that the form of iron added and the tracer both be in the dissolved form.

### Inert Tracer

Concurrent with the injection of iron is the injection of the inert chemical tracer sulfur hexafluoride ($SF_6$). By presaturating a tank of sea water with $SF_6$ and employing an expandable displacement bladder, a constant molar injection ratio of $Fe:SF_6$ can be achieved (**Figure 6**). In this way, both conservative and nonconservative removal of iron can be quantified. Sulfur hexafluoride traces the physical properties of the enriched patch; the relatively rapid shipboard detection of $SF_6$ can be used to track and map the enriched area. The addition of helium-3 to the injected tracer can provide useful information regarding gas transfer.

### Fluorometry

The biophysical response of the phytoplankton is rapid and readily detectable. Thus shipboard measurement of relative fluorescence ($F_v/F_m$) using fast repetition rate fluorometry has been shown to be a useful tactical tool and gives nearly instantaneous mapping and tracking feedback.

### Shipboard Iron Analysis

Because iron is rapidly lost from the system (at least initially), the shipboard determination of iron is necessary to determine the timing and amount of subsequent infusions. Several shipboard methods, using both chemiluminescent and catalytic colorimetric detection have proven useful in this regard.

### Lagrangian Drifters

A Lagrangian point of reference has proven to be very useful in every experiment to date. Depending upon the advective regime, this is the only practical way to achieve rapid and precise navigation and mapping about the enriched area.

### Remote Sensing

A variety of airborne and satellite-borne active and passive optical packages provide rapid, large-scale mapping and tracking of the enriched area. Although SeaWiffs was not operational during IronEx I and II, AVHRR was able to detect the IronEx II bloom and airborne optical LIDAR was very useful during IronEx I. SOIREE has made very good use of the more recent SeaWiffs images, which have markedly extended the observational period and led to new hypotheses regarding iron cycling in polar systems.

## Experimental Measurements

In addition to the tactical measurements and remote sensing techniques required to track and ascertain the development of the physical dynamics of the enriched patch, a number of measurements have been made to track the biogeochemical development of the experiment. These have typically involved a series of underway measurements made using the ship's flowing sea water system or towed fish. In addition, discrete measurements are made in the vertical dimension at every station occupied both inside and outside of the fertilized area. These measurements include temperature salinity, fluorescence (a measure of plant biomass), transmissivity (a measure of suspended particles), oxygen, nitrate, phosphate, silicate, carbon dioxide partial pressure, pH, alkalinity, total carbon dioxide, iron-binding ligands, $^{234}Th:{}^{238}U$ radioisotopic disequilibria (a proxy for particle removal), relative fluorescence (indicator of photosynthetic competence), primary production, phytoplankton and zooplankton enumeration, grazing rates, nitrate uptake, and particulate and dissolved organic carbon and nitrogen. These parameters allow for the general characterization of both the biological and geochemical response to added iron. From the results of the equatorial enrichment experiments (IronEx I and II) and the Southern Ocean Iron Enrichment Experiment (SOIREE), several general features have been identified.

## Findings to Date

### Biophysical Response

The experiments to date have focused on the high-nitrate, low-chlorophyll (HNLC) areas of the world's oceans, primarily in the Subarctic, equatorial Pacific and Southern Ocean. In general, when light is abundant many researchers find that HNLC systems are iron-limited. The nature of this limitation is similar between regions but manifests itself at different levels of the trophic structure in some characteristic ways. In general, all members of the HNLC photosynthetic community are physiologically limited by iron availability. This observation is based primarily on the examination of the efficiency of photosystem II, the light-harvesting reaction centers. At ambient levels of iron, light harvesting proceeds at suboptimal rates. This has been attributed to the lack of iron-dependent electron carrier proteins at low iron concentrations. When iron concentrations are increased by subnanomolar amounts, the efficiency of light harvesting rapidly increases to maximum levels. Using fast repetition rate fluorometry and non-heme iron proteins, researchers have described these observations in detail. What is notable about these results is that iron limitation seems to affect the photosynthetic energy conversion efficiency of even the smallest of phytoplankton. This has been a unique finding that stands in contrast to the hypothesis that, because of diffusion, smaller cells are not iron limited but larger cells are.

### Nitrate Uptake

As discussed above, iron is also required for the reduction (assimilation) of nitrate. In fact, a change of oxidation state of five is required between nitrate and the reduced forms of nitrogen found in amino acids and proteins. Such a large and energetically unfavorable redox process is only made possible by substantial reducing power (in the form of NADPH) made available through photosynthesis and active nitrate reductase, an iron-requiring enzyme. Without iron, plants cannot take up nitrate efficiently. This provided original evidence implicating iron deficiency as the cause of the HNLC condition. When phytoplankton communities are relieved from iron deficiency, specific rates of nitrate uptake increase. This has been observed in both the equatorial Pacific and the Southern Ocean using isotopic tracers of nitrate uptake and conversion. In addition, the accelerated uptake of nitrate has been observed in both the mesoscale iron enrichment experiments to date, IronEx and SOIREE.

### Growth Response

When iron is present, phytoplankton growth rates increase dramatically. Experiments over widely differing oceanographic regimes have demonstrated that, when light and temperature are favorable, phytoplankton growth rates in HNLC environments increase to their maximum at dissolved iron concentrations generally below $0.5\,\mathrm{nmol\,l^{-1}}$. This observation is significant in that it indicates that phytoplankton are adapted to very low levels of iron and they do not grow faster if given iron at more than $0.5\,\mathrm{nmol\,l^{-1}}$. Given that there is still some disagreement within the scientific community about the validity of some iron measurements, this phytoplankton response provides a natural, environmental, and biogeochemical benchmark against which to compare results.

The iron-induced transient imbalance between phytoplankton growth and grazing in the equatorial Pacific during IronEx II resulted in a 30-fold increase in plant biomass (**Figure 7**). Similarly,

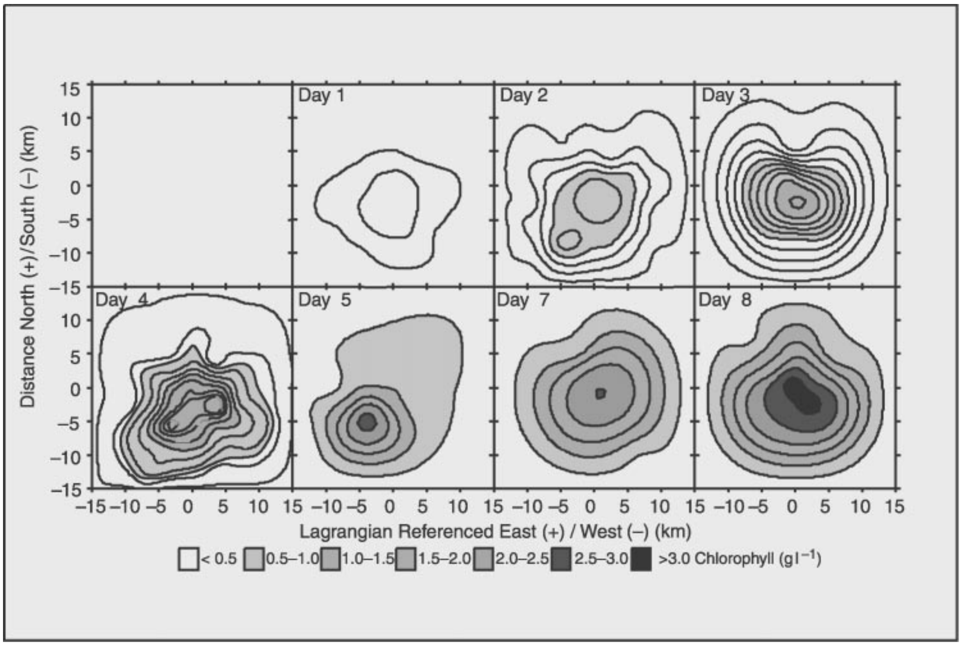

**Figure 7** Chlorophyll concentrations during IronEx II were mapped daily. This figure shows the progression of the phytoplankton bloom that reached over 30 times the background concentrations.

a 6-fold increase was observed during the SOIREE experiment in the Southern Ocean. These are perhaps the most dramatic demonstrations of iron limitation of nutrient cycling, and phytoplankton growth to date and has fortified the notion that iron fertilization may be a useful strategy to sequester carbon in the oceans.

## Heterotrophic Community

As the primary trophic levels increase in biomass, growth in the small microflagellate and heterotrophic bacterial communities increase in kind. It appears that these consumers of recently fixed carbon (both particulate and dissolved) respond to the food source and not necessarily the iron (although some have been found to be iron-limited). Because their division rates are fast, heterotrophic bacteria, ciliates, and flagellates can rapidly divide and respond to increasing food availability to the point where the growth rates of the smaller phytoplankton can be overwhelmed by grazing. Thus there is a much more rapid turnover of fixed carbon and nitrogen in iron replete systems. M. Landry and co-workers have documented this in dilution experiments conducted during IronEx II. These results appear to be consistent with the recent SOIREE experiments as well.

## Nutrient Uptake Ratios

An imbalance in production and consumption, however, can arise at the larger trophic levels. Because the reproduction rates of the larger micro- and mesozooplankton are long with respect to diatom division rates, iron-replete diatoms can escape the pressures of grazing on short timescales (weeks). This is thought to be the reason why, in every iron enrichment experiment, diatoms ultimately dominate in biomass. This result is important for a variety of reasons. It suggests that transient additions of iron would be most effective in producing net carbon uptake and it implicates an important role of silicate in carbon flux. The role of iron in silicate uptake has been studied extensively by Franck and colleagues. The results, together with those of Takeda and co-workers, show that iron alters the uptake ratio of nitrate and silicate at very low levels (**Figure 8**). This is thought to be brought about by the increase in nitrate uptake rates relative to silica.

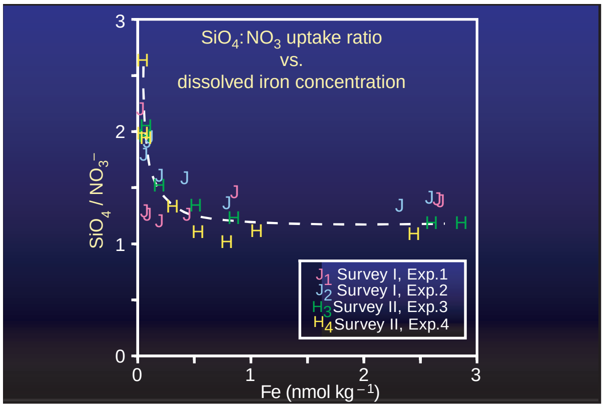

**Figure 8** Bottle enrichment experiments show that the silicate : nitrate uptake ratio changes as a function of the iron added. This is thought to be due to the increased rate of iron uptake relative to silicate in these experimental treatments.

## Organic Ligands

Consistent with the role of iron as a limiting nutrient in HNLC systems is the notion that organisms may have evolved competitive mechanisms to increase iron solubility and uptake. In terrestrial systems this is accomplished using extracellularly excreted or membrane-bound siderophores. Similar compounds have been shown to exist in sea water where the competition for iron may be as fierce as it is on land. In open ocean systems where it has been measured, iron-binding ligand production increases with the addition of iron. Whether this is a competitive response to added iron or a function of phytoplankton biomass and grazing is not yet well understood. However, this is an important natural mechanism for reducing the inorganic scavenging of iron from the surface waters and increasing iron availability to phytoplankton. More recent studies have considerably advanced our understanding of these ligands, their distribution and their role in ocean ecosystems.

## Carbon Flux

It is the imbalance in the community structure that gives rise to the geochemical signal. Whereas iron stimulation of the smaller members of the community may result in chemical signatures such as an increased production of beta-dimethylsulfoniopropionate (DMSP), it is the stimulation of the larger producers that decouples the large cell producers from grazing and results in a net uptake and export of nitrate, carbon dioxide, and silicate.

The extent to which this imbalance results in carbon flux, however, has yet to be adequately described. The inability to quantify carbon export has primarily been a problem of experimental scale. Even though mesoscale experiments have, for the first time, given us the ability to address the effect of iron on communities, the products of surface water processes and the effects on the midwater column have been difficult to track. For instance, in the

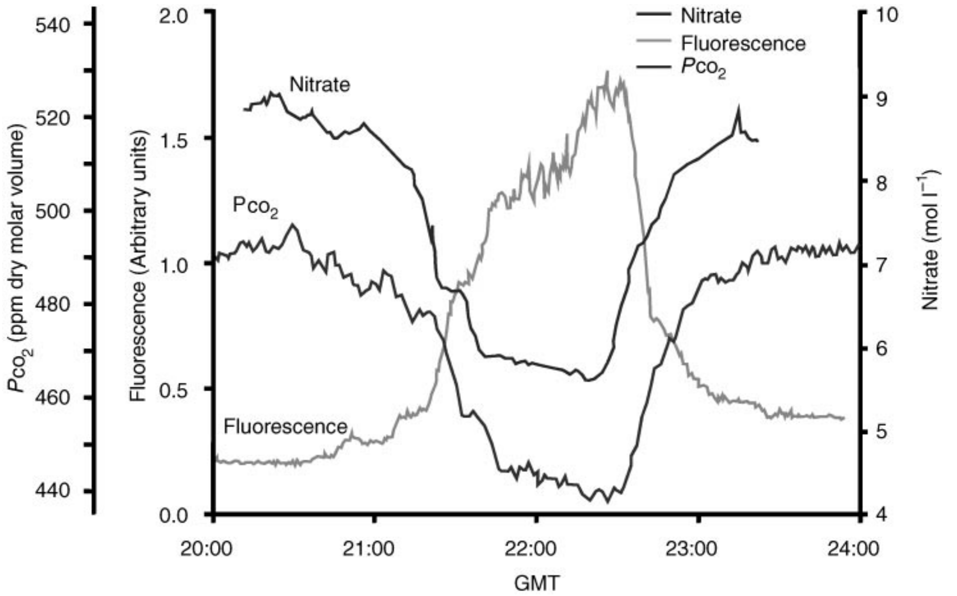

**Figure 9** A transect through the IronEx II patch. The *x*-axis shows GMT as the ship steams from east to west through the center of the patch. Simultaneously plotted are the iron-induced production of chlorophyll, the drawdown of carbon dioxide, and the uptake of nitrate in this bloom.

IronEx II experiment, a time-series of the enriched patch was diluted by 40% per day. The dilution was primarily in a lateral (horizontal/isopycnal) dimension. Although some correction for lateral dilution can be made, our ability to quantify carbon export is dependent upon the measurement of a signal in waters below the mixed layer or from an uneroded enriched patch. Current data from the equatorial Pacific showed that the IronEx II experiment advected over six patch diameters per day. This means that at no time during the experiment were the products of increased export reflected in the waters below the enriched area. A transect through the IronEx II patch is shown in **Figure 9**. This figure indicates the massive production of plant biomass with a concomitant decrease in both nitrate and carbon dioxide.

The results from the equatorial Pacific, when corrected for dilution, suggest that about 2500 t of carbon were exported from the mixed layer over a 7-day period. These results are preliminary and subject to more rigorous estimates of dilution and export production, but they do agree favorably with estimates based upon both carbon and nitrogen budgets. Similarly, thorium export was observed in this experiment, confirming some particle removal.

The results of the SOIREE experiment were similar in many ways but were not as definitive with respect to carbon flux. In this experiment biomass increased 6-fold, nitrate was depleted by 2 μmol $l^{-1}$ and carbon dioxide by 35–40 microatmospheres (3.5–4.0 Pa). This was a greatly attenuated signal relative to IronEx II. Colder water temperatures likely led to slower rates of production and bloom evolution and there was no observable carbon flux.

Original estimates of carbon export in the Southern Ocean based on the iron-induced efficient utilization of nitrate suggest that as much as $1.8 \times 10^9$ t of carbon could be removed annually (**Figure 10**). These estimates of carbon sequestration have been challenged by some modelers yet all models lack

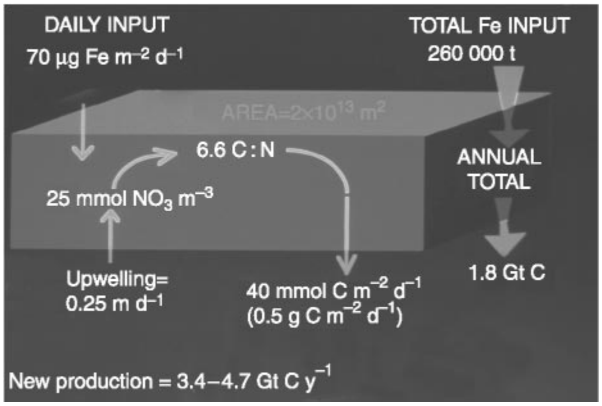

**Figure 10** Simple calculations of the potential for carbon export for the Southern Ocean. These calculations are based on the necessary amount of iron required to efficiently utilize the annual upwelled nitrate and the subsequent incorporation into sinking organic matter. An estimated $1.8 \times 10^9$ t (Gt) of carbon export could be realized in this simple model.

important experimental parameters which will be measured in upcoming experiments.

## Remaining Questions

A multitude of questions remain regarding the role of iron in shaping the nature of the pelagic community. The most pressing question is whether iron enrichment accelerates the downward transport of carbon from the surface waters to the deep sea? More specifically, how does iron affect the cycling of carbon in HNLC, LNLC, and coastal systems? Recent studies indicate that coastal systems may be iron-limited and the iron requirement for nitrogenase activity is quite large, suggesting that iron may limit nitrogen fixation, but there have been limited studies to test the former and none to test the latter. If iron does stimulate carbon uptake, what are the spatial scales over which this fixed carbon may be remineralized? This is crucial to predicting whether fertilization is an effective carbon sequestration mechanism.

Given these considerations, the most feasible way to understand and quantify carbon export from an enriched water mass is to increase the scale of the experiment such that both lateral dilution and sub-mixed-layer relative advection are small with respect to the size of the enriched patch. For areas such as the equatorial Pacific, this would be very large (hundreds of kilometers on a side). For other areas, it could be much smaller.

The focus of the IronEx and SOIREE experiments has been from the scientific perspective, but this focus is shifting toward the application of iron enrichment as a carbon sequestration strategy. We have come about rapidly from the perspective of trying to understand how the world works to one of trying to make the world work for us. Several basic questions remain regarding the role of natural or anthropogenic iron fertilization on carbon export. Some of the most pressing questions are: What are the best proxies for carbon export? How can carbon export best be verified? What are the long-term ecological consequences of iron enrichment on surface water community structure, midwater processes, and benthic processes? Even with answers to these, there are others that need to be addressed prior to any serious consideration of iron fertilization as an ocean carbon sequestration option.

Simple technology is sufficient to produce a massive bloom. The technology required either for a large-scale enrichment experiment or for purposeful attempts to sequester carbon is readily available. Ships, aircraft (tankers and research platforms), tracer technology, a broad range of new Autonomous Underwater Vehicles (AUVs) and instrument packages, Lagrangian buoy tracking systems, together with aircraft and satellite remote sensing systems and a new suite of chemical sensors/*in situ* detection technologies are all available, or are being developed. Industrial bulk handling equipment is available for large-scale implementation. The big questions, however, are larger than the technology.

With a slow start, the notion of both scientific experimentation through manipulative experiments, as well as the use of iron to purposefully sequester carbon, is gaining momentum. There are now national, international, industrial, and scientific concerns willing to support larger-scale experiments. The materials required for such an experiment are inexpensive and readily available, even as industrial by-products (of paper, mining, and steel processing).

Given the concern over climate change and the rapid modernization of large developing countries such as China and India, there is a pressing need to address the increased emission of greenhouse gases. Through the implementation of the Kyoto accords or other international agreements to curb emissions (Rio), financial incentives will reach into the multi-billion dollar level annually. Certainly there will soon be an overwhelming fiscal incentive to investigate, if not implement, purposeful open ocean carbon sequestration trials.

## A Societal Challenge

The question is not whether we have the capability of embarking upon such an engineering strategy but whether we have the collective wisdom to responsibly negotiate such a course of action. Posing the question another way: If we do not have the social, political and economic tools or motivation to control our own population and greenhouse gas emissions, what gives us the confidence that we have the wisdom and ability to responsibly manipulate and control large ocean ecosystems without propagating yet another massive environmental calamity? Have we as an international community first tackled the difficult but obvious problem of overpopulation and implemented alternative energy technologies for transportation, industry, and domestic use?

Other social questions arise as well. Is it appropriate to use the ocean commons for such a purpose? What individuals, companies, or countries would derive monetary compensation for such an effort and how would this be decided?

It is clear that there are major scientific investigations and findings that can only benefit from large-scale open ocean enrichment experiments, but certainly a large-scale carbon sequestration effort should not proceed without a clear understanding of both the science and the answers to the questions above.

## Glossary

| | |
|---|---|
| ATP | Adenosine triphosphate |
| AVHRR | Advanced Very High Resolution Radiometer |
| HNHC | High-nitrate high-chlorophyll |
| HNLC | High-nitrate low-chlorophyll |
| IronEx | Iron Enrichment Experiment |
| LIDAR | Light detection and ranging |
| LNHC | Low-nitrate high-chlorophyll |
| LNLC | Low-nitrate low-chlorophyll |
| NADPH | Reduced form of nicotinamide–adenine dinucleotide phosphate |
| SOIREE | Southern Ocean Iron Enrichment Experiment |

## See also

**Autonomous Underwater Vehicles (AUVs). Fluorometry for Biological Sensing. Fluorometry for Chemical Sensing. Nitrogen Cycle. Phosphorus Cycle. Primary Production Processes. Primary Production Distribution. Redfield Ratio. Satellite Remote Sensing SAR.**

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# ISLAND WAKES

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## Introduction

The 'island mass effect' has been documented for about half a century. This refers to a biological enrichment around oceanic islands in comparison to surrounding waters. Despite a relatively large body of evidence to support the existence of such an effect in the vicinity of islands, there have been few studies to investigate the underlying physical causes of this phenomenon. From a physical point of view the presence of an island in the background flow will disturb the flow regime to produce perturbations that ultimately must have biological consequences.

Two types of island disturbance have been investigated. The first takes place in shallow, stratified shelf seas with significant tidal regimes but no appreciable mean flow, where as the tide moves water back and forth the island acts as a stirring rod to enhance vertical mixing locally and break down the pycnocline. The second occurs in both shallow and deep water, where flow past an island generates eddies downstream and a wake of disturbed flow extends several island diameters away. This arises in the case of larger islands when a clear ambient flow dominates over tidal variability and also around islands small enough that the tidal stream itself can generate a similar effect. The scale of the eddies is typically close to the island diameter and their time scale will be several days for larger islands but only hours in the case of tidal flows. The nature of the wake and eddies may differ between the oceanic case where conditions can be considered quasi-geostrophic and the shallow case where they are frictionally dominated by bottom stress.

## Theory

### Nonrotating Case

The simplest case is where flow past isolated oceanic islands is considered to be analogous to that of channel flow past a circular cylinder. The work of Batchelor presented the case of nonrotating flow in a homogeneous fluid. The form of the downstream disturbance or wake is related to the value of the Reynolds number

$$R_e = \frac{Ud}{v} \qquad [1]$$

where $U$ is the free velocity upstream, $d$ is the diameter of the cylinder and $v$ is the molecular viscosity. Although this formula appears simple, there are certain practical difficulties in applying it to even a nonrotating ocean of homogeneous character. Few islands are isolated or cylindrical, the upstream velocity is generally not well known and finally the molecular viscosity must be replaced by the horizontal eddy viscosity in the ocean, which is in general poorly known. Studies of Aldabra, an Indian Ocean atoll, indicate that the same current speed impinging on the island from different directions produces a different wake because of the asymmetrical form of the island. It is frequently the case that the upstream current in the ocean varies on a range of time scales, or may be subject to horizontal shear, both of which complicate the