Lecture 8 - The Ocean's Biological Carbon Pump

What is it? The "carbon pump" refers to the biologically produced flux of carbon out of the euphotic zone of the ocean

> *Why do we (and many others) study this?*
> - It regulates to some extent the pCO_2 content of the atmosphere.
> - It determines the O_2 and nutrient content of the deep sea.
> - If it changes in response to global warming, we should know this.

Some terminology:
Gross and Net primary production refer to the activity of plants:
(a) *Gross primary production (GPP)* – is the rate of organic carbon fixed by plant photosynthesis.
(b) *Net primary production (NPP)* – is the rate of organic carbon fixed by plant photosynthesis after accounting for respiration.
(c) *Net community production (NCP)* – is the net organic carbon fixed by plant photosynthesis after accounting for both plant and animal respiration.

^{14}C primary production is measured by addition of ^{14}C labeled DIC to a flask of the water to be studied and incubating the flasks at the depth it was taken form the ocean. Most biological oceanographers believe that ^{14}C primary production is something between *Gross* and *Net primary production*

The term **New Production (NP)** was coined by scientists who study nitrogen cycling in the ocean (Dugdale and Goering, 1967) and refers to that nitrogen fixation into organic matter that originates from nitrogen outside the euphotic zone (mostly NO_3^- but also N_2). At steady state NP is equal to the flux out of the euphotic zone.

Methods for Measuring the Net Carbon Pump and New Production.

New Production
NP is measured by incubating seawater samples with $^{15}NO_3^-$ and then measuring the amount that ends up in organic matter. Eppley and Peterson (1979) were the first to recognize the relationship between new production and the biological pump. New production was shown to be a fraction of ^{14}C primary production.
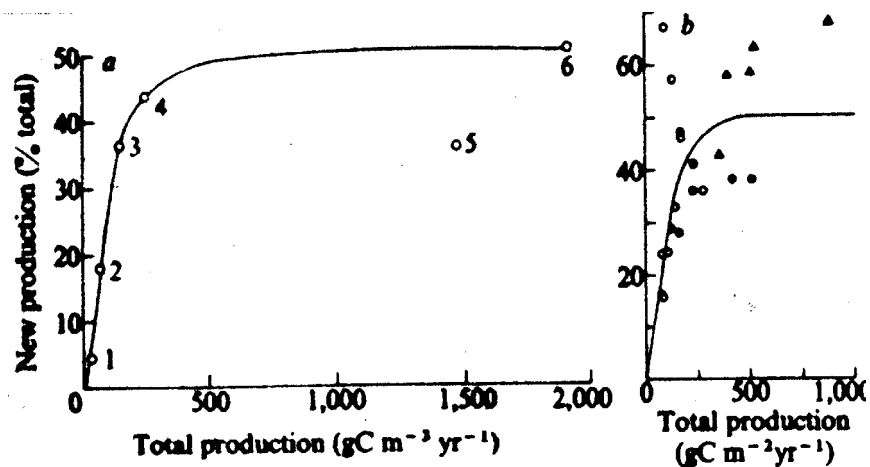
Fig. 2 *a*, New production as % of the total primary production versus total production for various ocean areas: (1) Central North pacific, (2) eastern Mediterranean Sea, (3) Southern California Bight, (4) eastern Tropical Pacific, (5) Costa Rica Dome, and (6) Peru upwelling. Total production was measured by the ^{14}C

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This fraction would depend on the presence of NO_3 in the euphotic zone. Eppley and Peterson (1979) established an empirical relationship between primary production and new production (see figure above). If one knows the global production, one can calculate the global new production from this relationship.

Sediment Traps
Sediment traps are used to determine the particulate fraction of the biological carbon pump. There are two problems with this estimate of the carbon pump:
- There is also a dissolved organic carbon component that "mixes" out of the upper ocean (recent estimates are that this is about 30 % of the flux.)
- There are questions about the accuracy of the particle fluxes determined this way in the upper ocean. In particular traps may under or over collect particles depending on horizontal advection.
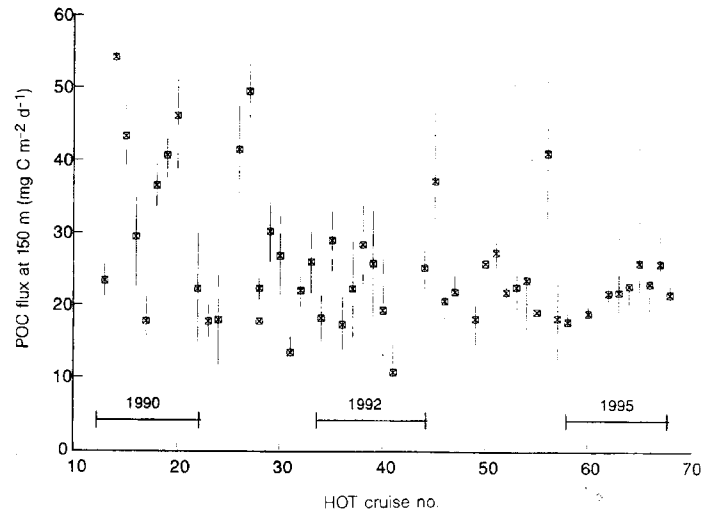

Figure 3 The particulate carbon flux at the depth of 150 m as a function of the Hawaii Ocean Time series (HOT) cruise number, with the 1990, 1992 and 1995 intervals indicated. Vertical error bars indicate the standard deviation of fluxes determined in 2-4 separate sediment-trap collector tubes at the 150-m reference depth deployed for 2-3 days on a free-drifting trap array. Methods are described in ref. 3.

Regardless of these limitations a lot can be learned about relative changes in particle flux over time from sediment traps.

The ^{234}Th method
The particulate thorium flux determined by the integrated deficiency of this isotope relative to its parent ^{238}U is a measure of the particulate carbon flux if one determines the organic C/ ^{234}Th ratio in the particles. Again, this method determines only the particulate portion of the carbon flux. Buessler (1999) compared the organic C flux determined by this method with ^{14}C primary production and showed that the ratio (analogous to the f ratio in Eppley and Peterson's study) is 2-10 % in most of the ocean. Exceptions are high latitudes (where NO_3^- concentrations are high in surface waters) and large "bloom" events in the ocean.

Oxygen Mass Balance
A simplistic view of the oxygen mass balance approach is that the flux of O_2 produced in the euphotic zone by photosynthesis must balance the carbon flux into the ocean interior.

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Accordingly, one can assume that at steady state the flux of O_2 from the ocean to the atmosphere should equate with new production. If this were the case then one could calculate the global new production rate by determining the flux of oxygen to the atmosphere. The figure of the relationship between measured oxygen concentrations in surface waters sampled during the GEOSECS program and the saturation value illustrates that surface waters are on average 3% supersaturated.
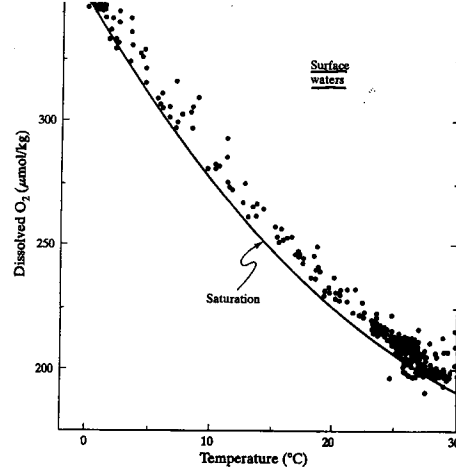
At steady state:

$$F_{O2} = (106 / 138)\ F_C\ \text{ and }\ F_{O2} = G_{O2}\ \{[O_2]_{s.w.} - pO_2\ K_H\}$$

$(pO_2)\ K_H = 220 \times 10^{-3}$ mol m^{-3} (@25° C)
G_{O2} is the mean piston velocity for oxygen, $G_{O2} = 5$ m d^{-1}
Surface waters are on average 3% supersaturated

$$F_{O2} = 5 \times 220 \times 10^{-3} \times 0.03 = .033 \text{ mol m}^{-2} \text{ d}^{-1}\ O_2 = 12 \text{ mol m}^{-2} \text{ yr}^{-1}$$
$$\text{This corresponds to:} \qquad\qquad => 9 \text{ mol C m}^{-2} \text{ yr}^{-1}$$

This value is much larger than estimated from other carbon pump measurements because biological activity is not the only processes causing oxygen super-saturation. The main other mechanisms — warming and bubbles can be subtracted out by comparing the mass balance of oxygen with the other inert gases like Ar and N_2. Emerson et al. (1997) showed that about half of the oxygen super-saturation in ocean surface waters is caused by biological processes.

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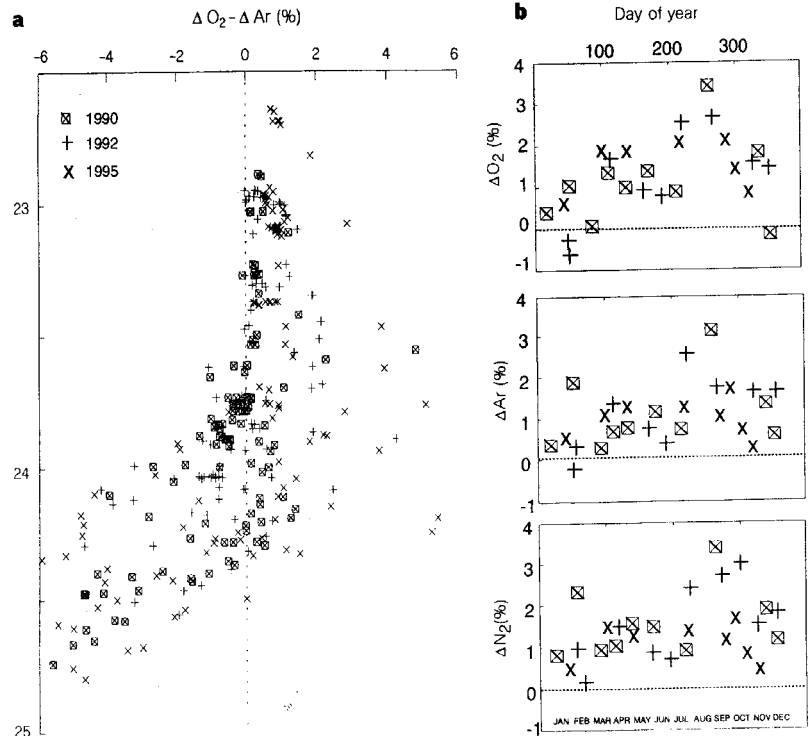
NET ANNUAL OXYGEN OR ORGANIC CARBON EXPORT
IN THE SURFACE OCEAN

Location	Net O_2 production	Other Methods
	(moles C m^{-2} yr^{-1})	
Subtropical Pacific (HOT)	2.3±1.4	2.1 ± 1.0[a]
Subarctic Pacific (Stn. P)	2.0 ± 1.1	2.8 ± ?[b]
Subtropical Atlantic (Bermuda)	3.3 ± 1.1	1.8 ± 1.0[c]
Equatorial Divergence		4.2 ± 2.3[d]

(a) The mean result from O_2 and DIC - δ^{13}C DIC mass balances, and organic C fluxes
(b) Calculated from productivity and ^{15}N-f ratio measurements of Harrison et al. (1999) and Varela and Harrison (1999)
(c) Based on particulate C and DOC fluxes at the Bermuda time-series station
(d) Based on δ^{13}C-DIC and DIC mass balance. Assumes fall equatorial Pacific sampling is representative of annual non-ENSO period

Biological carbon fluxes determined by the oxygen mass balance method in three locations of the ocean where time-series have been measured indicate that the biological carbon pump is 2 – 3 moles m^{-2} yr^{-1}

Comparison of the O_2 method with a ^{13}C mass balance and sediment trap POC + independent DOC fluxes at the Hawaii Time series indicated reasonable agreement.

Comparison of the O_2 method with ^{15}N-determined "f "ratios and ^{14}C productivity at Station P indicated good agreement

However, comparison of the O_2 method with sediment trap POC + DOC fluxes at Bermuda indicate that the O_2 method is about twice the value determined by measuring POC and DOC. Each of these methods has inherent errors and complications.

Oxygen Utilization Rates Below the Euphotic Zone
The idea here is that if waters on isopycnal (or neutral) surfaces can be dated using this "age", the rate of O_2 consumption can be determined and this should be proportional to the rate of organic flux input the deep ocean from the euphotic zone. This has been done in the Atlantic by Jenkins (1982). Tritium was used to calculate water ages. Tritium (^{3}H) has an atmospheric source. The natural source of ^{3}H is very small but it was greatly enhanced by atmospheric nuclear bomb testing in the early 1960's. The source of the ^{3}H is neutrons escaping from the bomb test. Tritium is incorporated into water as H^{3}HO and has a half-life of 12.5 years. When tritium beta decays, it turns into a helium isotope (^{3}He). Using the ratio of ^{3}He/^{3}H and the known half-life of ^{3}H one can calculate the water mass "age", or time since it was in contact with the atmosphere.

$$^3H \quad \rightarrow \quad ^3He \qquad t_{1/2} = 12.5 \text{ yrs}$$

(1) $d[^3He] / dt = - d[^3H] / dt = \lambda_{3H}[^3H]$
(2) $[^3H](t) = [^3H](t=0) \exp^{(-\lambda_{3H}t)}$
(3) $[^3He](t) = [^3H](t=0) – [^3H](t)$ (if $[^3He]$ at the sea surface is zero)
(4) $[^3H](t) / \{[^3He](t) + [^3H](t)\} = \exp^{(-\lambda_{3H}t)}$
(5) $t = (1 / \lambda_{3H}) \ln\{1 + [^3He] / [^3H]\}$

The tritium-helium age, t, assumes no mixing with surrounding waters

Jenkins (1982) used the tritium-helium method to date water on different isopycnal surfaces in the North Atlantic around Bermuda. He then plotted AOU versus age on individual density surfaces (e.g. $\sigma_o = 26.80$ which is at about 400m, see figure below). The slope gives the oxygen utilization rate (OUR) on a given isopycnal surface. He then plotted OUR versus depth. OUR decreases exponentially with depth below the euphotic zone (Z in m) according to the relation:

$$\ln OUR = -(0.68+0.17) - (0.00295+0.00027)\ Z.$$

When Jenkins integrated the OUR from 100m to the bottom of the sea he obtained the total deep water O_2 consumption of:

$$\int_{z=0}^{z=1000m} OUR\,dz = 5.7\,mol\,O_2\,m^2\,yr^{-1}$$

The implication is that the flux of organic carbon required to produce this integrated OUR is

$$F_C = (106/138)F_{O2} = 4.4 \text{ mol C m}^{-2} \text{ yr}^{-1}$$

The paradox with this data set was that this organic carbon consumption rate at depth was about double the accepted primary production for this region. The expected new production would be about 10% of this. Jenkins suggested that the historical primary production rates were low because they were based on small bottle, long incubation time technique.

mol m^{-3} ml l^{-1}
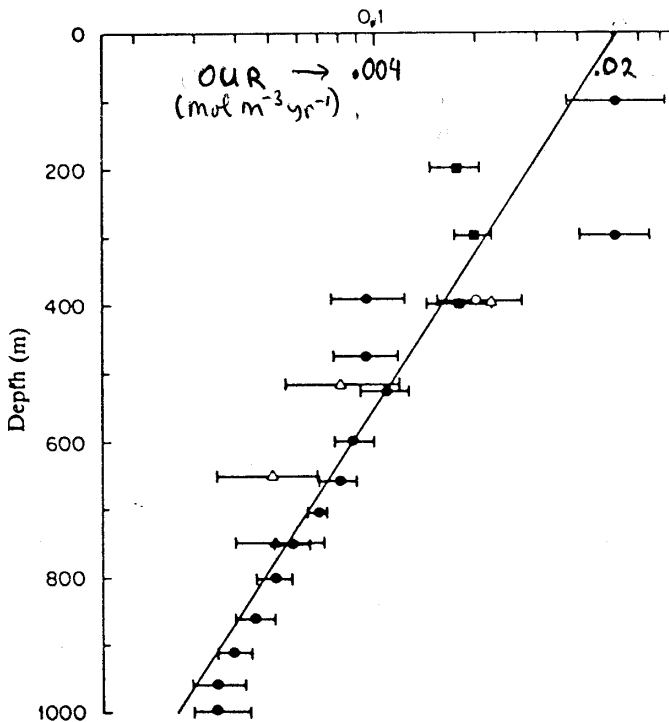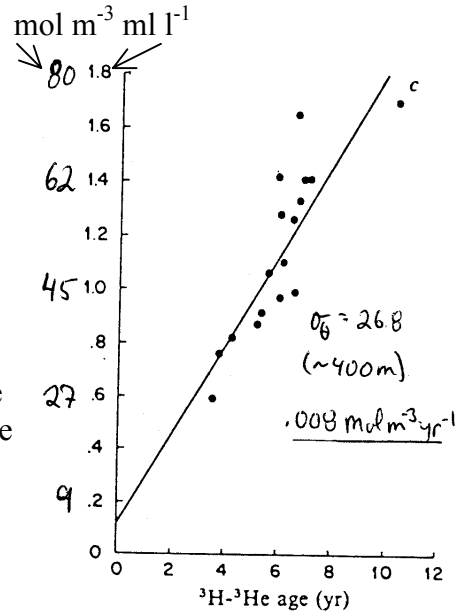
A summary of OUR measurements as a function of depth from the N. Atlantic subtropical ocean yields a measure of the oxygen consumption rate depth dependence.

OUR (mol m^{-3} yr^{-1})

Large dots are from the Sargasso Sea Squares and open circles are from the beta triangle in the western subtropical N. Atlantic Triangles are data from Riley (1951)

Summary of Carbon Pump Estimates

The table indicates that estimates of the carbon pump have been growing since Eppley and Peterson, (1967) made the first calculation. It seems to be converging at about 15 Gt yr^{-1}, which is equivalent to a Flux of 3.5 mol C m^{-2} yr^{-1} if spread evenly over the ocean surface.

GLOBAL MARINE ORGANIC CARBON EXPORT FROM THE EUPHOTIC ZONE

FLUX		METHOD	SOURCE
Gt yr^{-1}	(mol m^{-2} yr^{-1})		
3.4-4.7	0.8-1.1	Sediment Traps	Eppley and Peterson (1974)
6	1.4	Sediment Traps	Martin et al.(1987)
5	1.2	Sediment Traps	Karl (1996)
10	2.3	Global Model	Sarmiento and Siegen. (1992)
19	4.4	Atm. O_2 / N_2	Keeling et al. (1992)
10-15	2.3-3.5	Marine O_2 balance	Emerson (1996)
16	3.7	Satellite color	Falkowski et al. (1998)

What are the Sinking Particles Made Off?

McCave (1975) DSR, 22:491 showed that flux of material to deep sea should be dominated by **large, rare, fast** moving particles **>200μm**., especially: zooplankton fecal pellets and marine snow aggregates. Small, more frequent particles are insignificant in their mass flux to the bottom. This was confirmed by Bishop (1977) using in-situ filtration of large water volumes. Particles >50μm are responsible for 99% of POC flux out of euphotic zone.

The particles are composed of organic material, zooplankton fecal pellets, skeletal material, and detrital material aggregated together. These aggregates form mini-ecosystems that are different from the surrounding waters; within these particles, decomposition, photosynthesis, nutrient regeneration and other processes occur at much higher rates.
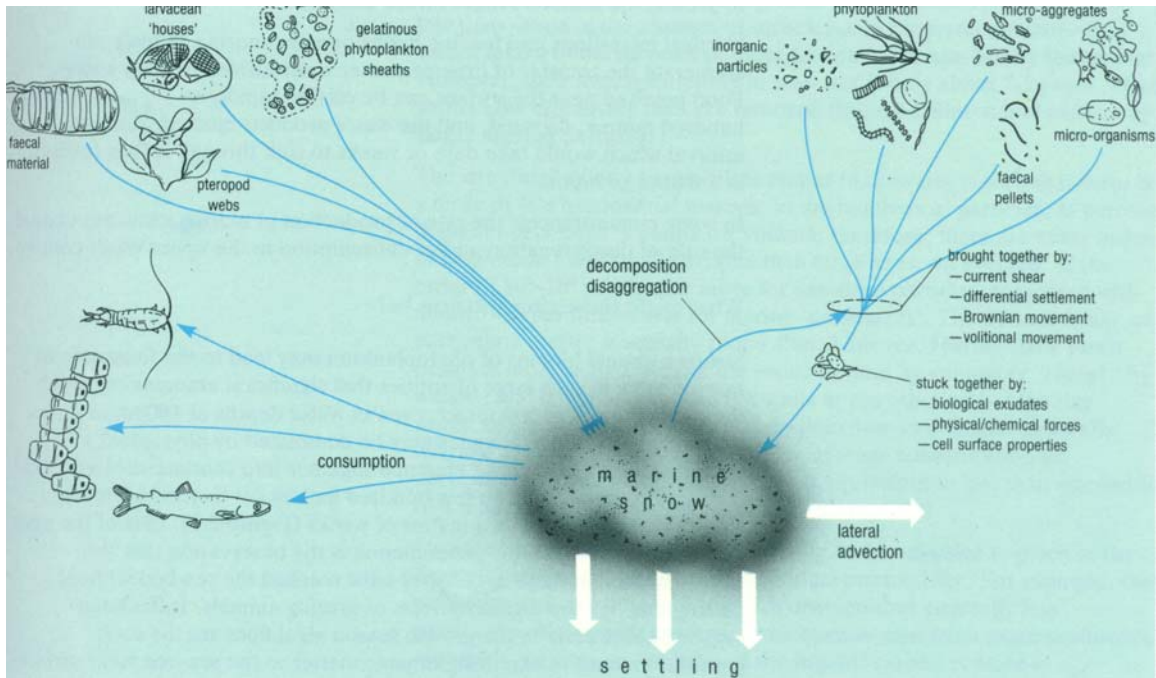
Settling rates for particles are estimated from **Stokes Law of Settling**.
This equation was derived assuming smooth, spherical particles

$$V = \frac{g}{18\eta}\Delta\rho d^2$$

mass flux: $= \Phi = mv$

v: velocity
η: water viscosity
g: gravitational acceleration
d: diameter of particle
$\Delta\rho$: density difference (between particle and seawater
m: particle mass

For water (at 20°C) the density of seawater is $\rho_w = 1.025$ g cm^{-3} and viscosity $\eta = 0.01$ g cm^{-1} sec^{-1}. There is always substantial uncertainty in assigning the equivalent spherical radius because natural particles are rarely spherical.

Particle Density:
The density of euphaussid fecal pellets was determined by Komar et al (1981) to be 1.23 g cm^{-3}. This is much larger than typical seawater density of about 1.025 g cm^{-3}. Pellets sink like little rocks. It was originally thought that fecal pellets were the main flux material but now it is believed that fecal pellets are relatively rare compared to marine snow (Pilskaln et al). Most recent work has suggested that the large marine snow particles are primarily responsible for the vertical transport of biogenic material (Alldredge and Gotschalk, 1988, Limnol. Oceanogr. 33, 339). These particles have a very small density difference from seawater, typically 1 x 10^{-2} g cm^{-3} to 1 x 10^{-5} g cm^{-3}. The density difference decreases with increasing particle size.

Finally, the most recent idea is that organic matter does not sink unless it is associated with mineral matter that can result in a large enough density difference to create sinking particles. This is the "ballast" hypothesis.

Techniques for Determining Particle Flux
1. Sediment traps: bottom moored in deep water and drifting near the sea surface.
2. Radiotracer techniques: especially using the deficiency of ^{234}Th relative to its radioactive parent ^{238}U.
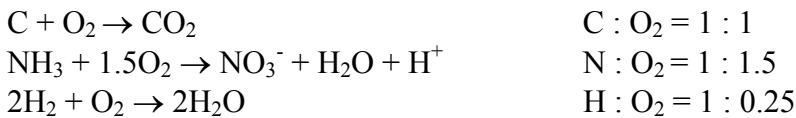3. Marine snow camera approach.

Flux Gradients and Respiration Rates
The decrease in flux with depth could be interpreted as respiration and modeled as:
$$\delta\phi C_{org} / dz = R$$
Where respiration equals the gradient in the flux. This probably represents an upper limit, as the model does not account for particle break up. The flux of particulate organic carbon for each depth is determined and a best-fit power function is obtained.
For example for the Vertex Particle Fluxes (stations in the NE Pacific; Martin et al., 1987), which was obtained from drifting sediment trap data the normalized power function was $F = 1.53 \, (z/100)^{-0.858}$ with units of mol C m^{-2} y^{-1}. They measured the C:H:N content of the sediment trap material and calculated O_2 utilization from the differences between sequential trap depths according to:

$C + O_2 \rightarrow CO_2$ $\qquad\qquad\qquad$ $C : O_2 = 1 : 1$
$NH_3 + 1.5O_2 \rightarrow NO_3^- + H_2O + H^+$ $\qquad$ $N : O_2 = 1 : 1.5$
$2H_2 + O_2 \rightarrow 2H_2O$ $\qquad\qquad\qquad$ $H : O_2 = 1 : 0.25$

The integrated respiration rate from 100m to 1000m was:
$\int R \, dz = 1.5$ mol O_2 m^{-2} y^{-1}

Deep Ocean Fluxes
There have been numerous studies of deep ocean fluxes using bottom-moored sediment traps. Sediment traps were developed in the late 70's (Honjo). There are many designs this includes bottom-moored traps in the deep sea and drifting traps near the sea surface. The sediment traps, which are designed to collect particles from a defined area at a certain depth, are deployed for a known period of time and they collect the particulate matter that sinks. The weight of the particulate matter is then determined to estimate the flux (g cm^{-2} day^{-1}). There is a lot of debate in the community with respect to the reliability of flux estimated determined by sediment traps some traps under collect (cone) and some over collect (jars) depending on design, but they have played a valuable role in our understanding of particle fluxes and degradation.

Different Styles of Sediment Traps
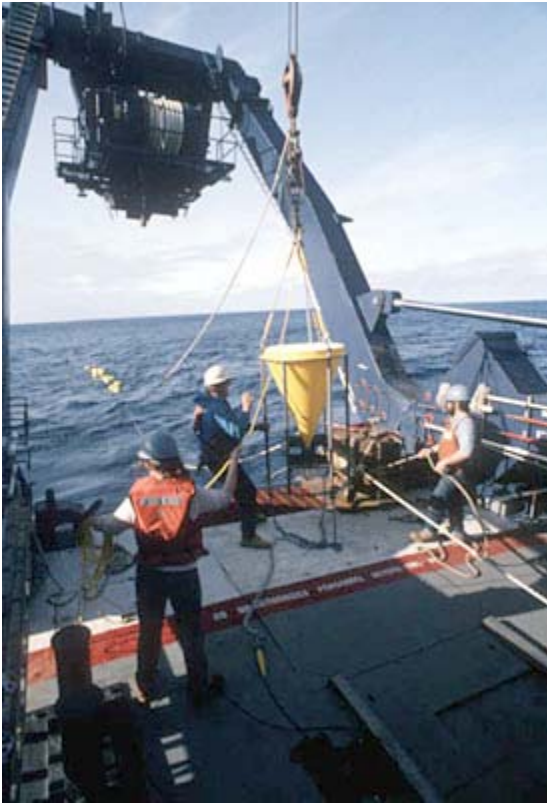
Bacterial degradation of the organic matter trapped can reduce org C content and result in underestimation of the flux. Poison is added to the traps to reduce this effect, but then "swimmers" get trapped which raises org C content. Another solution is to use concentrated NaCl as a poison or to use a rotating sphere to prevent simmers interference.

Changes of Flux With Depth

Typically the flux of particulate organic carbon decreases with depth and with distance from land (Suess (1980) Nature, 288:260-264). Synthesis of sediment trap deployment results show a relationship between C flux at depth and the C productivity in the overlying water column for numerous locations around the world ocean. Most org C degradation is occurring in upper water column. One empirical relationship based on best fit to sediment trap data is:

$$C_{flux} = \frac{C_{prod}}{0.0238z + 0.212}$$

C_{prod} = primary production rate at surface
C_{flux} = organic flux at depth of sediment trap

Thus, we can estimate C flux at any depth below 50 m if the overlying surface water production is known. Only about 10% of PP remains at 400m and only 1% below 5000m.

If depth can be converted to time by assuming an average settling rate (100m/day) we can calculated a degradation rate constant for organic C from the slope of the depth flux line.

$$\frac{1}{C_{flux(z)}\Big/C_{prod}} - 0.212 = 2.38t$$

U.S. JGOFS

Where: C_{prod} = production at t = 0

This is analogous to a 2nd order rate reaction in chemical kinetics: $1/C_t - 1/C_o = kt$ and gives an organic carbon decomposition constant of: $k = 2.38$ day^{-1}.

Seasonal Patterns in Deep Ocean Fluxes
Deuser (1986; Deep-Sea Res., 33, 225-246) maintained a time series of bottom-moored traps in the Sargasso Sea near Bermuda at 3200m. The data indicate that in some oceanic basins significant seasonal and inter-annual variability in the flux exists. The spring bloom in the Sargasso Sea is a classic example. Similarly large boom events were detected at the Ross Sea and other locations.
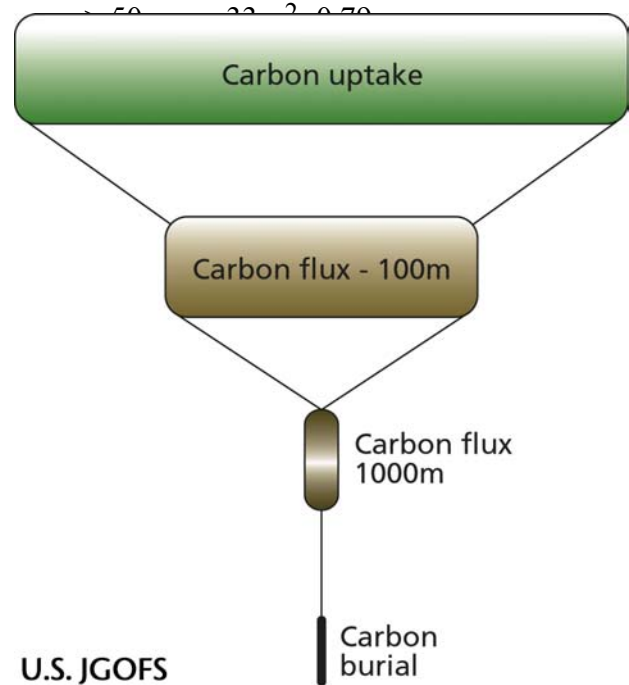
The Fe Hypothesis

What controls productivity in the ocean??

In much of the surface ocean nitrate and phosphate concentrations are low, often very close to zero, thus restricting productivity. These are <u>limiting nutrients</u>. However, about 20% of the world's open ocean is replete with light <u>AND</u> major nutrients (nitrate, phosphate, and silica) YET standing stocks of phytoplankton remain low. For example the Eastern Equatorial Pacific, the sub-arctic Pacific, and throughout the Southern Ocean (>35°S) phytoplankton do not exhaust nitrate and phosphate.

WHY? What is limiting growth in these High Nutrient Low Chlorophyll (HNLC) areas?? What is keeping the plankton biomass below the carrying capacity set by the nutrients?

Several hypotheses were suggested over the years:
1) Zooplankton grazing keeps standing stock of phytoplankton so <u>low</u> that they cannot deplete nutrient levels
2) Strong turbulence at high latitudes may mix phytoplankton down below euphotic zone causing light limitation.
3) Micronutrients, specifically - Fe - is limiting phytoplankton production. Fe is an important catalytic component in e- transport and enzymatic systems. John Martin first proposed the latter hypothesis in the late 1980s.

Early evidence for the latter:
- Open ocean [Fe] is about 10^{-12} M, very low!
- Fe has a nutrient - like profile
- Fe addition experiments (in bottles) show that Fe stimulates phytoplankton growth, especially large diatoms.

But...
- Extrapolation of lab and shipboard incubation experiments to "real life" is strongly criticized (Banse and Frost)
- Bottle experiments are not accurate representations of community response: scale and nature of response might be different.
- Possible Fe contamination could lead to faulty conclusions.

More recent evidence from natural systems (de Baar, 1995) is based on comparing natural levels of productivity in regions of the S. Ocean w/different levels of Fe. The Antarctic Circumpolar current (ACC) is characterized by very low levels of Fe ([Fe] = 0.2-0.6nM) while the polar-front waters are Fe rich ([Fe] = 2-4 nM). During spring bloom plankton biomass produced in the polar front zone was 10x greater than in Antarctic Circumpolar current (ACC) water.

Mesoscale enrichment experiments: (Martin and Coale et al 1994)
Fe was added to seawater to increase Fe concentrations from ambient 0.06 nM to about 4 nM over an oceanic patch of about $8x8$ km^2, an inert tracer of SF_6 was also added to mark the patch so it could be track for a relatively long period of time (10 days).

Results: "Dramatic and unequivocal" biological response to the addition of 450 kg Fe to a 64 km^2 patch in HNLC area.
- Plant biomass doubled!
- 3X increase in chlorophyll from 0.24 µg/l to 0.65 µg/l.
- 4 x increase in production! (from 10-15 µg C /l/day to 48 µg C /l/day)
- But nitrate concentrations fell only slightly.
- No change in the export production has been detected in the10 day time frame.
- relatively little CO_2 draw down (~10 ppm) was observed.
- Fe was rapidly removed with a half-life of 2 days.

Possible explanations to the smaller than expected changes:
- Grazing is more important than Fe. Increase in grazers quickly limited growth, so that Fe levels were no longer important.
- Limitation by another trace nutrient is important (Zn? Si?) that prevented growth.
- Rapid removal of Fe either by physical or chemical processes:
  e.g. flocculation, adsorption on to particles or precipitation.

Also, the Fe patch subducted after just five days to a depth of 30-35m and the experiment came to a crashing halt. Also, no zooplankton people were out there to measure grazing, and other problems with the experiment design were raised.

New Iron Ex II experiment summer 1996.
Again, an unenclosed patch 10x10 km was enriched with Fe in E. Equatorial Pacific. 3D survey of all nutrients, Fe, chlorophyll and SF_6 tracer was taken. In this experiment, 3 infusions of Fe as $FeSO_4$ were made with concentrations of: 2, 1, 1 nM over a period of 8 days. Like before, following each infusion, Fe was lost quickly from the patch but this time repeated re-supply appeared to stimulate a dramatic biological **and** geochemical response. Chl increased by a factor of 30 over the course of the experiment from 0.15 to 4µg/l. Nitrate got depleted by 5 µM. Plankton biomass increased by an order of magnitude. Also, a draw-down of pCO_2 of 60 - 100 ppm was observed. This translates to 100,000 kg of C that was fixed.

Similar observations were seen in an experiment off New Zealand (SOIREE http://www.whoi.edu/media/iron.html) and preliminary results from the SOFEX experiment (2002) are just getting published. Results prove that phytoplankton photosynthesis in HNLC areas is limited by Fe. It also confirmed what bottle (in vitro) incubation experiments showed, which is that larger phytoplankton cells (primarily pennate diatoms) respond when Fe is added. These cells are also responsible for the majority of export production since they are big, and sink quickly. Larger cells aggregate and fecal pellets will sink rapidly to interior of the ocean. Production of smaller cells tend to be based on recycled NH_4^+ rather than nitrate.

Interestingly, ice cores from Antarctica show large increases in dust input (rich in iron) during glacial periods. It has been suggested that this iron input increased new production in the Southern Ocean (HNLC area) during he last glacial period, resulting in increased sequestration of CO_2 and lowering of atmospheric pCO_2.

Recently, it has been suggested (Dugdale et al., 1998; Harrison, 2000) that in areas that get enough Fe (costal areas) the important nutrient that limits export production is silica. Availability of silica induces diatom blooms that modify the food web resulting in increased transfer of organic matter to the deep sea.
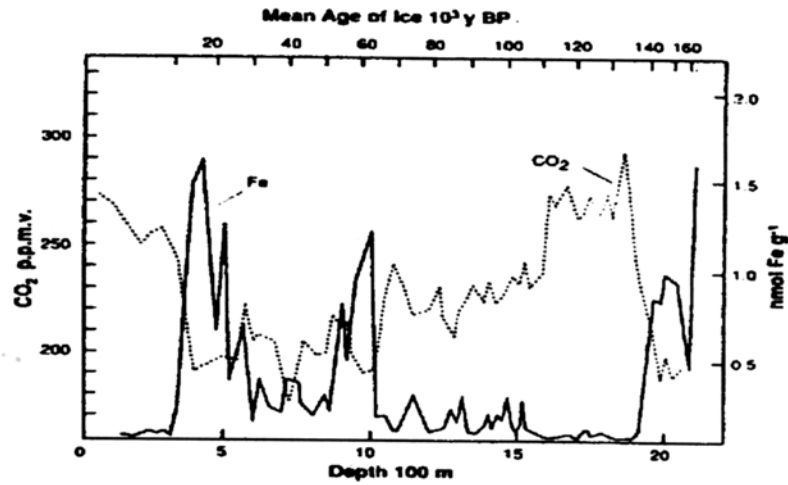
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Dugdale, R. and J. Goering (1967) Limnol. Oceanogr., 12, 196.
Emerson, S., et al. (1997) Experimental determination of the organic carbon flux from open-ocean surface waters, Nature, 389, 951-954.

Eppley, R. and B. Peterson (1967) Particulate organic matter flux and planktonic new production in the deep ocean, Nature, 182, 677-682.

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